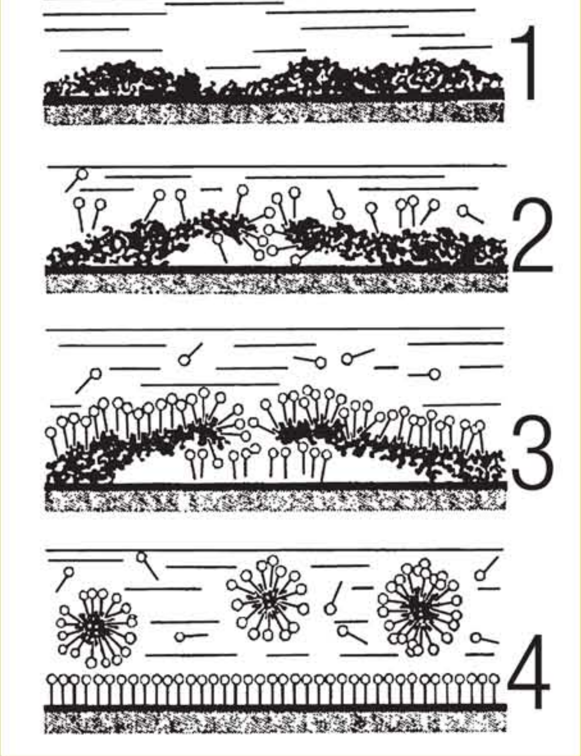
surfactant science series

volume **141**

HANDBOOK OF DETERGENTS

Part E: Applications



edited by

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HANDBOOK OF DETERGENTS

Part E: Applications

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HANDBOOK OF DETERGENTS

Editor-in-Chief

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Part E: Applications

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Contents

Handbook Introduction

The battle cry for sustainable development in our globalized world is persistent in all circles, gaining acceptance as the guiding rationale for activities and processes in the scientific, technological, environmental, economical, societal, and political interfaces, targeting improvement and growth. Such activities are expected to result in higher standards of living, leading eventually to a better quality of life for our increasingly technology-dependent modern society. Models of sustainable development and exemplary systems of sustainable management and applications are continually being developed or adapted and creatively applied, taking into consideration, more than before, human needs, rather than *wants* on the one hand, and long- versus short-term benefits and trade-offs on the other.

Detergents constitute a classic case study within this context: this is a multidimensional systemic enterprise, operating within complex sociopolitical/technoeconomical realities, locally and globally, reflecting in its development and contemporary "state-of-affairs," the changing dynamic equilibria and interrelationships between demands/needs, cost/benefits, gains/tradeoffs, and social preference–related policies. It is not surprising, therefore, that despite the overall maturity of the consumer market, detergents continue to advance, in the modern world and developing societies, more rapidly than population growth.

The soap and detergent industry has seen great changes in recent years and have been required to respond to shifts in consumer preferences, requests for sustainability, the availability and cost of raw materials and energy, demographic and social trends, as well as the overall economic and political situation worldwide. Currently, detergent product design is examined against the unifying focus of delivering performance and value to the consumer, given the constraints of the economy, technological advancements, and environmental imperatives. The annual 2–3% growth of the detergent industry, and the faster growth in personal care products, reflect impressive developments in formulation and application. The detergent industry is thus expected to continue its steady growth in the near future, in response to the ever-increasing demands from consumers for products that are more efficient, act faster and are easier to use.

For the detergent industry, the 1990s was an era of transformation, evolution, and consolidation. On both the supplier and consumer market sides (both remain intensely competitive), the detergent industry has undergone dramatic changes, with players expanding their offerings, restructuring divisions, or abandoning the markets altogether. This has resulted in changing hands and consolidation of the market, especially in the past several years. This trend appears to be gaining momentum. Yet, the key concepts have been and still are innovation, consumer preferences, needs, multipurpose products, cost/benefit, efficiency, emerging markets, partnership, cooperation, collaboration, merging (locally, regionally, and globally), and technological advancements. Although substantial gains and meaningful rapid changes with respect to the preceding concepts have been experienced by the surfactants/detergents markets, the same cannot be said for detergent/surfactant technology itself. The $9-billion-plus detergent ingredients market and the annual global consumption of ~13 million metric tons of surfactants in 2006 include many entrenched workhorse products. This may suggest that the supply of solutions to most cleaning problems confronted by consumers, in view of the increasing global demand for formulations having high performance and relatively low cost and the need for compliance with environmentally related regulation, is based on modifications of existing technologies.

What does all this mean for the future of the detergents enterprise? How will advances in research and development affect future development in detergent production, formulation, applications, marketing, consumption, and relevant human behavior as well as the short- and long-term impacts on the quality of life and the environment? Since new developments and emerging technologies are generating new issues and questions, not everything that can be done should be done; that is, there should be more response to real *needs* rather than *wants*.

Are all these questions that are discussed reflected in the available professional literature for those who are directly involved or interested, for example, engineers, scientists, technicians, developers, producers, formulators, managers, marketing people, regulators, and policymakers? Thorough examination of the literature, in this and related areas, suggests that a comprehensive series is needed to deal with the practical aspects relating to the detergent industry, thus providing perspective beyond knowledge, to all those involved and interested. The *Handbook of Detergents* is an up-to-date compilation of works written by experts, each of whom is heavily engaged in his/her area of expertise, emphasizing the practical, and guided by the system approach.

The aim of this six-volume handbook project (properties, environmental impact, analysis, formulation, application, and production) is to provide readers who are interested in any aspect of surfactants and detergents, a state-of-the-art comprehensive treatise, written by expert practitioners in the field. Thus, various aspects involved—properties, environmental impact, analysis/test methods, formulation application and production of detergents, marketing, environmental and related technological aspects, as well as research problems—are dealt with, emphasizing the practical. This constitutes a shift from the traditional, mostly theoretical focus, of most of the related literature currently available.

The philosophy and rationale of the *Handbook of Detergents* series are reflected in its title, its plan, and the order of volumes and flow of the chapters in each volume. The various chapters are not intended to be and should not, therefore, be considered to be mutually exclusive or conclusive. Some overlapping segments focus on the same issue(s) or topic(s) from different points of view, thus enriching and complementing various perspectives.

There are several persons involved whose help, capability, professionalism, and dedication made this project possible: the volume editors, contributors, and reviewers are in the front line in this respect. Others who deserve special thanks are my colleagues and friends in (or associated with) the detergent industry, whose timely help and involvement facilitated bringing this project to completion. I hope that the final product will justify the tremendous effort invested by all those who contributed. You, the reader, will be the ultimate judge.

Uri Zoller
Editor-in-Chief

Handbook of Detergents Series

Editor-in-Chief
Uri Zoller

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Handbook of Detergents Series Part E: Applications, edited by Uri Zoller
Handbook of Detergents Series Part F: Production, edited by Uri Zoller and Paul Sosis

Preface

As the annual global consumption of surface-active agents reaches about 13 × 10^6 metric tons and the detergent ingredients market more than $9 billion in sales, the cleaning products industry embraces sustainability. Recently, the environmental impact of consumer products has gone from being a fringe issue to a mainstream concern. Thus, regardless of the state of affairs in the detergent industry worldwide, with respect to scientific, technological, economics, safety, and “greening”-related regulation of detergent production and formulation, the basic modes of the latter’s *applications*, particularly domestically, will continue to be an issue of major concern. Yet, given our increasingly fast-moving world, customers’ demands are for products that are more effective and can help to save time for the customers. This means more demands for products that are faster acting, easier to use, more efficient, and environment-friendly. This is so in view of the operating global free-market economy, which is expected to ensure sustainable development, given the contemporary shifts in consumer preferences, availability and cost of raw materials and energy, demographic and social trends, and the overall economical/political situation, worldwide.

This fifth volume (Part E) of the six-volume series *Handbook of Detergents* deals with the various applications of detergent formulations—surfactants, builders, sequestering/chelating agents—as well as of other components of detergent formulations—in the entire spectrum of applications, including domestically, institutionally, and industrially.

This volume is a comprehensive treatise on the multidimensional issues involved, and represents an international industry that includes academia, and the collaborative effort of many experts and authorities worldwide, mainly from industry. As such, this Part E—Applications—represents the state of the art in this multidimensional cleaning practice.

All of the aforementioned are accompanied and supported by extensive relevant data, occasionally via a specific representative case study; the derived conclusions of which are transferable. Also, this resource contains several cited works, and is thus aimed to serve as a practical reference concerning the application aspect of surfactant–detergent formulations for engineers, technologists, scientists, technicians, regulators, and policymakers associated with the detergent industry.

I thank all the contributors, reviewers, publisher’s staff, and colleagues who made the realization of this volume possible.

Editor

URI ZOLLER is professor emeritus of chemistry and science education at Haifa University—Oranim, Kiryat Tivon, Israel. He has more than 220 published journal articles, one patent, and nine books to his name, including the thus-far published 5 parts and the shortly upcoming 6th part (Part F), of the *Handbook of Detergents*, for which he is the editor-in-chief. He is an active member of several professional organizations, including the American Chemical Society and the Royal Society of Chemistry (U.K.), and he is currently the chairman of the European Association for Chemical and Molecular Sciences (EuCHeMS) Committee on Education in Environmental Chemistry. His main areas of interest and research are synthetic organic chemistry, environmental chemistry, and science and environmental education and assessment. Following 10 years of research and development work in the detergent industry, Dr. Zoller received a BSc degree (summa cum laude) followed by an MSc in chemistry and industrial chemistry, respectively, from the Technion–Israel Institute of Technology, Haifa, Israel, an SM degree from the Massachusetts Institute of Technology in the United States, a DSc degree from the Technion–Israel Institute of Technology, Haifa, Israel, and an EdD in science education from Harvard University, Cambridge, Massachusetts. Currently, Dr. Zoller is the project coordinator of the Israeli Unified National Infrastructural Research Project (UNIRP).

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1 Detergents Application: Current Realities and Future Perspectives

Uri Zoller

CONTENTS

1.1 CURRENT REALITIES

The detergent industry has continuously changed in recent years in response to shifts in consumer preferences, the request for sustainability, the availability and cost of raw materials and energy, and demographic and social trends as well as the world's overall socioeconomic and political situations. Currently, detergent formulation design and product applications are examined against the unifying focus of delivering to the consumer performance and value given the constraints of the economy, technological advancements, and environmental imperatives. Yet the persistent annual growth of the detergent industry reflects impressive developments in formulation and application. This growth is expected to continue in the near future in response to the ever-increasing demands from consumers for products that are more efficient, act faster, are easier to apply and use safely, and comply with the cost–benefit criterion.

However, the golden days of consistent growth in production volume, high profit margins, and promising new emerging markets are unlikely to continue or persist, particularly as the various applications of detergent formulations are concerned—at home and institutions, as well as in industry and agriculture. The main determining factors in this respect are globalization, consolidation, regulatory legislation, and environmental concerns [1], the latter two being of particular pertinence to the *sustainable application* of detergents.

1.1.1 CLEANING PRODUCTS

Large volumes of laundry detergent formulations have produced components that ultimately are sent down drains and reach surface water and groundwater and thus require various kinds of wastewater treatment. For that reason, such formulations have become front and center topics in environmental discussions [2]. Accordingly, raw materials have been critically scrutinized, modified, or even phased out and consequently substituted by alternative *environmentally sound* ingredients.

TABLE 1.1
Development of Laundry Formulations, Their Performance, and Their Properties

		Particular Properties		
Detergent Formulation Ingredients	**Relative Performance**[a]	**Soil Anti-Redeposition**	**Deposition on Fabrics and Equipment**	**Fabric Yellowing**
Synthetic nonionic surfactants, sodium carbonate, sodium silicate	F–G	F	H	N
Synthetic surfactants: DDBS,[b] nonionics–dosium diphosphates–triphosphates	G	F–G/G	H/W	N
Synthetic surfactants: LABS, sodium tripolyphosphates, bleaching agents	G	G	W	N
Synthetic surfactant mixtures:[c] tripolyphosphates–zeolite 4A	G	G	W	N
Synthetic surfactants: zeolite 4A–polycarboxylates–sodium carbonate	G	G	W	N
Different formulations plus soil anti-redeposition agents, enzymes, FWAs,[d] foam regulators, soil repellents (or others)	VG	VG	VW	N

[a] F = fair; G = good; H = heavy; W = weak; VG = very good (as far as optimized, top-quality formulations are concerned)

[b] DDBS: dodecylbenzene sulfonate(s)

[c] Tricomponent mixtures; typically soaps, anionics, and nonionics

[d] FWAs: fluorescent whitening agents

The impact of these concomitant substitutions and modifications on detergent formulation and the modes of consumer applications of these newly emerging *greener* products on the ultimately resulting detergent performance is rather substantial. The historical environmentally related impact on the formulations and consequent results and performance of laundry processes and their applications by consumers are demonstrated in Table 1.1 [3,4].

Thus, the nonbiodegradability of the synthetic surfactants *dodecylbenzene sulfonates* (DDBSs) and nonylphenol ethoxylates, and the presence of polyphosphates—sodium tripolyphosphate and tetradosium pyrophosphate—resulted in the buildup of stable foam and algae eutrophication in rivers, lakes, and water reservoirs. These led to the substitution of DDBS by biodegradable straight-chain *linear alkylbenzene sulfonates* (LABS) and polyphosphates partially at first by zeolites and then by polycarboxylates. The substitution occurred as a result of *voluntary* agreements between industry and regulation agencies and governments and was followed later by rather strict *environmentally related* regulatory legislation.

The impact of the greening-sustainability trend on consumers' *washing behavior*—namely, how consumers *apply* detergent formulations—was recently investigated in Germany with respect to the usage of laundry detergents and washing machines. The limitations in scope and content of the findings and results obtained by way of an Internet-based questionnaire provide a rough overview of consumer *application behavior*. The essence of that behaviour is summarized in Table 1.2 [4].

However important the above raw results and findings may be, more important and relevant to the application of detergents is their appropriate interpretation in different contexts in

TABLE 1.2
"Application/Laundry Behavior" of Consumers

Results and Findings	Percentage	Related Comments
Overall degree of satisfaction with wash results	60	Reasons for dissatisfaction: insufficient stain removal; white (detergent) residues (although residues in the laundry after washing do not promote people to change their detergent formulation)
Dissatisfaction with wash results decreases in older generations	25	
The younger the consumer, the more reasons provided for dissatisfaction		
Most common reasons: the need to rewash items	37	
Change the detergent	26	
Using only one kind of laundry detergents	18	… "because that is enough"
Using *less* detergent formulation than recommended	33	
Most respondents use the average wash temperature in the *sustainable* range		

relation to agreed-on *sustainability* imperatives and their *translation* into relevant *application behavior.*

1.2 FUTURE PERSPECTIVES: THE CHALLENGE

A dramatic, synergistic, and systemic impact on the *application* modes of detergent formulations can be expected although not easily predicted given the following conditions and events:

1. The traditional segmentation of the chemical industry into commodities, fine chemicals, and chemical specialties according to the products manufactured, their volumes, prices, performance properties, and *applications*
2. The ever-increasing competition in the marketplace
3. The need to keep creating *sustainable* competitive advantage through differentiation on the one hand and *generication* on the other hand
4. The continuous change of the market dynamics concerning petrochemically derived versus oleochemically derived surfactants used in laundry detergents
5. The fast evolution of safety data sheets in the regulatory legislation of countries and the continents (for example, Ref. 5) as well as environmental ecotoxicology and the regulation of potential health risks
6. The recent skyrocketing increase in crude oil prices
7. The current realities and future perspectives of surfactant production [6]

All of the above, particularly those parameters or factors that affect surfactant properties, which make up 10–30% of detergent formulations, as well as sustainability and environment-related properties of the formulation components [7,8], are expected to play a key role in their application. Consequently, the challenge ahead is not only to formulate concentrated cleaners and surfactant-based detergents but also to ensure the providing of environmentally friendly technologies that deliver the benefits customers have come to expect at a cost they are willing to pay while in compliance with sustainability.

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2 All-Purpose Cleaners and Their Formulation

Karen Wisniewski

CONTENTS

2.1 INTRODUCTION

The most fundamental use of surfactants in cleaning formulations is probably personal cleansing, closely followed by laundry applications. However, the general cleaning of the surfaces of the home is represented by *all-purpose* cleaners. These are the topic of this chapter: formulations devoted to general household cleaning. They are referred to as either *all-purpose cleaners* (APCs) or in some cases *bucket dilutable cleaners* (BDCs). Although, as we shall see, the cleaners do not target any particular soil by name, the overall target is greasy soils.

In the beginning there was soap, the documented formula for which goes back to before 2500 BCE [1], although it was probably used more for cosmetic and medicinal purposes rather than for cleaning. Soap making had become a regular industry in the Middle Ages [2], and with the invention of *soap flakes* in 1899 [3] became the first household cleaner not in the bar form used for personal cleansing. With the synthesis of sodium lauryl sulfate in 1916 [4,5] the detergent industry was off and running. Despite the plethora of surfactants available today, there is a relatively small subset used routinely in household cleaner formulation. Some of the factors that influence this are

- Commercial availability
- Cost
- Relative effectiveness in the cleaning task
- Environmental impact (a more recent consideration for formulators)
- Safety

Commercial availability and cost are very important factors. These two factors are inextricably linked. For instance, easily made surfactants are less expensive because of the ease of processing. Even if a surfactant is difficult to synthesize, if it has extremely good performance qualities it can become in demand and then the price may be lowered by efficiencies of scale. There are many surfactants that may be effective in the cleaning task, but unless they are available for a reasonable cost, they are not worthwhile to the formulator.

2.1.1 Scope of the Discussion

Hard-surface cleaners are those products that are formulated to be used for household cleaning by consumers. For the purposes of this discussion, products used only in industrial and institutional cleaning of hard surfaces will not be included. (The topic of institutional and industrial cleaners is covered in a separate chapter of this book.) These I&I cleaners can be quite similar to household cleaners as they are often used on the same soil/surface combinations (e.g., soap scum on tile in a hotel shower), but the I&I field is also larger than household cleaners, as it can also include dish sanitizers, metal cleaners, and malodor treatments.

Household cleaners are used on every hard surface in the home except for dishes. (Cleaners formulated specifically for hand and automatic dishwashing are also covered in an other chapter.) The formulation of dishwashing products is significantly different from that of other hard-surface cleaners, which have other considerations and delivery forms. However, it must be acknowledged that the creativity of consumers in their use of cleaners is not limited by the manufacturers' definition of the product. Certain hard-surface cleaners, such as cleansers or cream cleansers, are also used on things like badly burned pans. Of course, the products are not formulated for this purpose, and this chapter will largely ignore these inventive uses of the products and concentrate on discussing the uses for which they are meant.

Most of the evolution in the field over the past 40 years has taken place in product form and delivery rather than in product ingredients, particularly the surfactants. Since the major change from the use of soap to the use of detergents in the middle of the past century, the array of surfactants used in the APCs has changed much less. However, the ways cleaning formulas are delivered have changed tremendously. The delivery of cleaners in plastic bottles, and then spray bottles followed by the rise and subsequent market importance of the wipes form, shows the trajectory of delivery systems, especially in developed markets.

The other major development in this field is the increase of the importance of specific adjunct ingredients. Cleaners are now being marketed to the consumers based on the inclusion of *orange* ingredients or Teflon®, to cite two examples. There is also an increase in the number of products formulated as *Oxy* variants as well. These also manifest the lack of development or significant change in the surfactant component of cleaners, but are differentiated mostly by the addition of these other ingredients. Formulators prefer to include ingredients that have *name recognition* with the consumers, rather than working with new and different surfactants. Of course, the names and advantages of surfactants are considered too *technical* to communicate easily to the average consumer, so the appeal of the more easily communicated additives like *orange oil* for the commercial formulator is understood.

In this discussion, "natural" will usually be used in quotes to designate an understanding of the word as seems to be found currently in various websites and advertising. To a working chemist no chemical is *unnatural*; all chemicals go back ultimately to compounds found in nature, and therefore all chemicals are naturally derived. For example, petroleum is a naturally occurring substance in the environment, and therefore is natural from a chemist's point of view. However, some groups of people generally associate "natural" with substances that not only occur in nature but also are derived from renewable (e.g., plant) sources. In one sense soap, often touted in advertising literature as "natural," is not natural in that to convert the naturally occurring fats and oils into soap the chemical process of saponification is needed. Therefore, the word "natural" occurs in quotes to designate this general understanding of the word rather than the technical meaning.

Additionally, there needs to be a word about surfactant terminology. The categorization of amine oxide surfactants in various sources can be as nonionic, cationic, or even amphoteric, depending on the author. In this discussion amine oxide surfactants are classed as nonionic surfactants. Also, the *amine oxide surfactants* and similarly *alkyl betaines* are simply referred to here as *amine oxides* and *betaines.*

2.1.2 Outline of the Discussion

This topic is divided into two parts. In the first part, Chapter 2, a discussion of basic formulation and types of APCs will be covered. The use of types of surfactants will be covered, including evolution of formulation, along with certain adjunct ingredients. Some formulation details will be covered, especially with respect to producing a commercial formulation. Details of formulation, with coverage of all the various components and their interactions, are covered in a chapter in another book of this series [6]. The second section in Chapter 5 is a description of specialty cleaners, those devoted to particular cleaning purposes largely targeting specific soils.

However, before these topics can be covered, some other conventions of the field must be discussed. These are the purposes for which the cleaners are intended and the general types regarding their forms and packaging.

TABLE 2.1
A Listing of Some Household Surface Types and Soils

Household Surfaces	Household Soils
Aluminum	Allergens
Brass	Crayon
Cement	Dirt
Ceramic	Dust
Chrome	Cosmetic residue
Corian®	Fingerprints
Fabric	Food residues
Formica®	Food stains
Glass	Germs
Granite	Grease
Lacquer	Hair
Marble	Ink
Paint	Lime scale
Plexiglas®	Mold/mildew
Polyurethane	Pet residues
Porcelain	Rust
Stainless steel	Scuffs
Terra-cotta	Soap scum
Vinyl	Toiletry residues
Wood	Water spotting

2.1.3 GOALS OF FORMULATION

Household cleaners can be divided into a few broad categories according to the use of product. However, even within these broad categories there is high fragmentation and a diversity of chemistries practiced. The oldest and broadest of the categories is that of the (APCs). This is the name manufacturers give to this group of products, although consumers will deny that there is a product that is truly *all-purpose*. This is understandable, as there is a wide variety of both surfaces and soils within a home, with myriad combinations possible (see Table 2.1). Naturally, not every soil occurs on every surface. Some soils, like soap scum, are largely limited to a single class of surface (like sinks and tubs). Other soils, like crayon marks or fingerprints, can occur anywhere. To have a single product that would be very effective at removing every soil and completely nondamaging to every surface would be a challenge indeed!

These are the main concerns of the product developer—that the product clean but that the cleaned surface be undamaged by the removal of the soil. Of course, the primary concern is that the cleaning chemistry first of all not be hazardous to the consumer using it. Generally, no one with current knowledge of toxicology would propose a cleaner largely based on carbon tetrachloride, despite the fact that this solvent is a very good grease cutter. This is one of the best attributes of surfactants: they are very good cleaning compounds, whose biggest risk to a consumer is usually skin irritation/drying. (This is more of a concern in dishwashing, where a consumer's hands might be in more intimate contact with the detergents for longer periods of time than in household cleaning.)

In household cleaning the consumer has several options of avoiding skin contact such as

- Using spray convenience products, where the only skin contact tends to be with cleaner soaked into the cleaning implement
- Minimizing contact with cleaner, for example, limiting contact to occasions such as wringing out a mop or
- Wearing gloves

This is not to say that surfactants or surfactant-like compounds are absolutely risk-free. However, the risk, in some cases, is from the contaminants that may accompany the surfactants, rather than from the surfactants themselves. An example of this was seen a few years ago in the concern over nitrosamine contamination of amine oxide surfactants, either from their manufacture or from the circumstances of their formulation. For example:

> Nitrosamines are formed as minor by-products in the conventional preparation of tert-amine oxides using aqueous hydrogen peroxide. Although the amount of nitrosamine is very small, on the order of parts per billion (ppb), this small amount renders the amine oxide unsuitable in many applications that involve human contact. This is because nitrosamines are reported to be carcinogenic and/or mutagenic. Amine oxides have properties that would make them very useful in shampoo, hair conditioners, dish and laundry detergent, fabric softeners and the like. Hence a need exists for a method for making tert-amine oxides in high conversion and yield and at a fast reaction rate and at the same time producing a tert-amine oxide product that is substantially free of nitrosamines … [7]

This was a serious concern that was approached by processing technology.

The more minor concern of skin irritation is usually approached by clever combinations of surfactants, in which the irritating effect of the usual main cleaning ingredient, anionic surfactant, is mitigated through the addition of nonionic surfactants, although the claim of increasing skin mildness is seen more often in dishwashing liquids than hard-surface cleaners. This can be one of the goals of formulation—to minimize the irritancy of the cleaner—although basic safety to the user is always assumed as an (unspoken) goal of the formulator. So, beyond the primary stated goals of cleaning and safety to the surface, other formulation goals in addition to decreased irritation can also be enumerated:

- Increasing the perceived *shine* of the surface
- Decreasing the effort of cleaning
- Shortening the time of the cleaning task
- Making the task more pleasant
- Eliminating the need for cleaning
- Long-lasting clean surface

The choice of surfactant(s) for the formula often has a very direct effect on cleaning, skin irritation, shine, and effort. Surfactant choice has a more indirect effect on surface safety, time, task pleasantness, and surface *conditioning*. These aspects are more often controlled by other formula ingredients or even packaging. However, surfactants can also contribute to these as well, as shall be seen.

2.1.4 PRODUCT FORMS AND TYPES

Another consideration of formulators is that consumers, as stated above, do not view products as being as neatly compartmentalized as manufacturers do. When a consumer wishes to clean a dirty bathtub, for example, they may have tried a cleanser, a dilutable APC, and a specialty spray soap scum remover to do the job. All of these products are competing for the same job—cleaning soap scum from the bathtub surface. The consumer may use any or all of them to get the job done, according to their own personal standard of cleanliness, desire to apply *elbow grease*, and evaluation of the surface condition (new or worn, sensitive or impervious, etc.).

The consumer trends in developed countries reflect the obvious implications of women (who still do the majority of the housework [8]) increasing the value of their time. Many more women work outside the home and have children with more activities to attend. If they work outside the home, they can put an exact dollar amount on what their time is worth. Few these days choose to spend those precious hours scrubbing their household surfaces. Therefore, the products tend to have

- More *ready-to-use* forms (less preparation time, more time actually spent cleaning)
- More 2 in 1 action (cleans and shines, or cleans soap scum and mildew stain)
- More preventative action (spray on regularly, no need to scrub later)
- More pleasant forms (brighter colors, better smells) [9]

Developing nations tend to use more *traditional* forms (powders or concentrated products that one dilutes). As countries become more affluent, or have an affluent neighbor on their border, more of the newer forms of cleaners are moving into the developing nations. Contrary to this usual trend of trickle of products from developed to developing markets, it could be argued that the trend for more *aesthetic* cleaning products began in Latin America and spread from there to Europe and North America. (This is seen, for example, in the launch of light-duty cleaners such as Fabuloso® in Mexico and other Latin American countries in the 1970s and the more recent launches in the mid-1980s and 1990s in the United States and France of more brightly colored, highly fragranced products.) Indeed, it can be argued that formulators have made products that clean so efficiently that only the added benefits—disinfectancy, less residue/better shine, etc.—serve to signal *improvements* in the products to consumers. Better aesthetics for the product itself or a more pleasant cleaning experience has emerged as a *raison d'être* for a product segment and attention to the aesthetics a major focus for the formulator, as will be seen in the aesthetic cleaner discussion.

Thus the largest trend in formulation has been in the direction of liquid products for developed countries, away from the more traditional form of powders [10]. Powder products are easier to package, usually in plastic bags or cardboard boxes or cylinders, which makes them an attractive option for developing nations or value-oriented market segments. However, hard-surface cleaners are seldom used unmixed with water, except perhaps for the initial application of a scouring cleaner. Therefore, when a powder product is used, it is mixed with water and necessarily requires time to dissolve. This can be messy and time-consuming with powders. Liquid cleaners are quick, easy, and convenient to use. (This parallels a similar shift in laundry detergents in developed countries.) Liquid cleaners are usually packaged in plastic bottles. The packaging for these products can become quite specialized, depending on their niche, as will be discussed. Packaging innovations still continue in this category.

Liquid products can be preferable for the manufacturer as well. To make powders, the surfactant mixtures must be dried somehow, usually by spray drying [11]. Spray drying requires large amounts of energy and can be *messy* as a process, with blow-off from the tower and dusting. By contrast, the manufacture of liquid products may require only the vigorous mixing of the ingredients. The liquid form therefore has advantages to the manufacturer in terms of equipment, environmental impact, and energy consumption.

The most important change in packaging has been the invention of the trigger sprayer in the 1970s [12]. Spray products are immensely popular in North America and to some extent in Europe. They can be viewed as the ultimate convenience product—already at appropriate use concentration, easily spread over the entirety of the soiled surface, and usually not requiring rinsing of the surface after use. Of course, the consumer pays a premium for these advantages, mostly for the packaging elements. Aerosol sprays were gaining prominence at the same time, but suffered during the chlorofluorocarbon controversy. In developed markets, where these expensive packages are common, spray triggers dominate some products (like glass or window cleaner), and aerosol sprays are limited. Although the aerosols are still popular for noncleaning products like polishing and dusting products or air fresheners, among cleaners they are largely limited to bathroom cleaners.

An even higher premium is paid when the cleaning product comes packaged already loaded onto the cleaning implement. This is the essence of the *wipes* form, where the product is loaded onto a nonwoven substrate and is usually disposed after one use. In this case, the premium is paid for the substrate rather than packaging or formulation.

As will be seen, APCs come in several types distinguished by variations in concentration and relative proportion of ingredients. These types are described in more detail in the next section.

2.2 ALL-PURPOSE CLEANERS

2.2.1 Types of All-Purpose Cleaners

APCs are supposed to be just what the name says—a cleaner for all household purposes. For this reason manufacturers try to make the cleaning potential as powerful as possible, while trying to keep in check any possibility of harming the surface to be cleaned. After all, cleaning by removing a top layer of the surface is not satisfactory.

APCs are usually formulas to be used either straight out of the package (for tough jobs) or in various dilutions. The label copy usually indicates that they are formulated against greasy soils and *tough dirt*. In the developed world, they are usually packaged in simple plastic bottles with either screw top or flip top caps. In the developing world, APCs may still be in powder form (a version largely abandoned in the developed world) and be packaged in plastic bags or cardboard boxes.

These products can also be called BDCs because that is one of their main uses. The product comes in concentrated form that allows it to be diluted to different levels for different tasks. The highest dilution, ~0.5 to 1.5% (or 0.6–2 oz. gal. or 5–15mL/L) is used for cleaning floors. Table 2.2 gives a list of typical dilutions and their uses. They are largely used in kitchens and sometimes bathrooms, and very occasionally general cleaning throughout the home.

A second group of APCs is that provided as spray cleaners. Trigger spray formulations are *ready-to-use* concentrations and therefore can be much weaker than the bucket dilutables, because they are provided less concentrated. These products are used all over the house for cleaning essentially every surface. These can vary in strength from the high-efficacy tough grease-cleaning *all-purpose* sprays down to window cleaners. Many consusmers consider window cleaners the only true APCs because they can be used on almost any surface, although they do not provide a high level of soil removal.

A third type of APC is that packaged as wipes. These also come in *ready-to-use* concentrations, with which nonwoven substrates are impregnated. The nonwoven substrates are carefully chosen both to carry the cleaning formulation and to contribute to the cleaning of the surface. These are usually used only once and then disposed.

Adding abrasive produce two other kinds of APCs. *Cleanser*, in the category of household cleaners, usually denotes a dry powder cleaner that contains an abrasive. *Cream cleansers* are

TABLE 2.2
All-Purpose Cleaner Dilutions for Different Purposes

Purpose	Form of Use	Dilution (Approximate) (w/w%)	Characteristics
Floor cleaning and spot cleaning	Diluted in bucket or pan	0.1–2	Dust, dirt, food spills cleaning with minimal rinsing, fingerprint cleaning, greasy spots
Heavier-duty spot cleaning	Diluted in sponge	10–30	Food spills, germ removal, grease residue by rinsing with sponge
Stove-top cleaning	Poured on surface	Full strength (undiluted)	Cooked-on grease, food residues by rinsing

liquid formulations with suspended abrasive. Despite the emergence of more (plastic) surfaces that are easily scratched, cleansers remain in the market, although their share of the market has not grown in many years, generally decreasing ~2 to 5% every year (dollar sales). They are still used for cleaning very tough soils, especially if the soil occurs on a scratch-resistant or older surface. These are also concentrated cleaners, but they are usually used full strength on the tough soils, which means they are often difficult to rinse.

These are all hard-surface cleaners. There are two types included in the general household cleaners that are, however, used on *soft* (fabric) surfaces. These are carpet and upholstery cleaners. Although these are not technically *hard-surface* cleaners, they are covered briefly.

2.2.2 Scourers: Cleansers and Cream Cleaners

As previously stated, cleansers are distinguished from other APCs by the inclusion of abrasive. In these types, abrasion is expected to contribute to the cleaning action. As household surfaces become softer and easier to scratch, these cleansers become more difficult to use without damaging the surface. However, they maintain popularity for cleaning resilient surfaces like ceramics and concrete and especially on soils that respond well to abrading such as cooked-on grease or soap scum.

2.2.2.1 Cleanser Formulation

As one of the last remaining powder products in the developed markets, cleansers hark back to the days when all cleaners were (soap) bars and powders. Likewise the formulation of these products has not changed very much for many years. There are several key ingredients that the surfactant works with to make an effective cleanser. However, the surfactant used in the typical cleanser formula has not changed in many years, usually an alkylbenzene sulfonate (ABS), usually spray dried. Spray drying is a technique developed to make powder cleaners of many types, especially for powder APCs and laundry detergents. For many years, branched ABSs were used, but when the biodegradability of these was called into question [13], the conversion was made essentially throughout the world to linear alkylbenzene sulfonate (LAS). The most common variant is sodium LAS. LASs are very effective cleaners and grease-cutting surfactants, and are relatively inexpensive to produce. (They are made entirely from petroleum feed stocks, however, and therefore their price can vary with oil prices [14,15].) In a reasonably inexpensive product with high-performance expectations, this makes LAS an ideal choice for the surfactant in cleanser.

The list of other ingredients in the cleanser is short. The actual main ingredient in cleanser is its abrasive component. It is the main cleaning ingredient by virtue of its mechanical action on the surface (depending on the amount of *elbow grease* supplied by the consumer), even above that of the surfactant. However, the surfactant helps to solubilize and lift greasy soils that the pure mechanical action of the abrasive might leave behind. The abrasive also makes up the bulk of the physical formula, usually comprising 60–90% by weight. The abrasive has evolved while the LAS component has remained essentially static. As mentioned before, many of the newer household surfaces are soft and therefore pose a challenge to the use of abrasives. Therefore, the main change in the abrasives is that the abrasives have become softer. Abrasiveness actually depends on three factors: the hardness of the material, its particle size, and the shape of the particles. These last two factors have remained similar over time, the main change being in hardness. Forty years ago silica was the preferred abrasive. Silica, basically being sand, is inexpensive, plentiful, and highly effective as an abrasive. However, in addition to the surface damage concerns of using silica as a cleaning abrasive, the plant handling and processing steps using silica require safeguards because of the dangers of silica dust. The preferred abrasive now, used in the largest brands, is calcite (calcium carbonate). This is still much harder than most soils that need to be abraded, but is significantly softer than silica, rating a 7 on the Mohs scale of mineral hardness, whereas calcite rates only a 3.

The other major active ingredient in cleanser is usually some form of bleach. Hypochlorite (*chlorine bleach* to use its colloquial name) is the usual choice, but is put into the formula in nascent form. Usually a powder chemical like trichlorocyanuric acid or dichloroisocyanurates is used. When these compounds become wet, they break down into hypochlorite, which is then available to do bleaching. This also makes compatibility with the surfactant a little easier, because all the components are present as powders, which thus minimizes the chemical interactions, unlike the strong interactions that would take place in the liquid product. The main problem of stability then is making sure that the product does not absorb and hold water, which would cause breakdown of the bleach-producing ingredient and product dumping of the powder for. To accomplish this, water-absorbing compounds like magnesium oxide or calcium sulfate are added.

Powder cleansers also cling to another adjunct of classic cleaning in that they are what are called *built* cleaners. Builders are compounds that serve three functions: they chelate hard water ions to increase the effectiveness of surfactants, they give the product a high pH, and they buffer this pH. These are usually carbonates, silicates, or, more rarely these days, phosphates. (Phosphates are seldom used because of the environmental restrictions against them legislated in the late 1970s and early 1980s [16].)

These are the main building blocks of cleanser formulation: bleaching ingredient (which is optional), abrasive, builder, and a simple surfactant system, often a single surfactant. As with most household cleaners, fragrance is usually added to cover the base odor of the detergent and to make the process of cleaning more pleasant. Dyes cannot be added to bleaching cleansers because of their sensitivity to bleach, but pigments (which are reportedly more stable in the presence of bleach) are sometimes added to give color effects, such as a color change from white to blue or green [17].

2.2.2.2 Cream Cleansers or Scouring Creams

One major innovation to the cleanser arena was the marketing of *cream cleansers*, with the patent art dating back to 1964 [18]. These products are fundamentally a liquid APC with suspended abrasive. These are packaged in plastic bottles for the most part, and are most popular in European markets. Cream cleansers or scouring creams (as they are called in Europe) are used similarly as powder cleansers. It is interesting that consumers view them as less abrasive than the powder cleansers, although for the most part they use the same abrasives used in modern powder cleansers.

Cream cleansers were created to address some of the shortcomings of powder cleaners, being easier to apply and eliminating dust. However, they still suffer from one of the difficulties of powder cleaners, which is difficulty of rinsing. The abrasive in both products tend not to be easy to rinse down the drain and builders, being powder ingredients, can be left behind as a film when dry. Both of these can contribute to a dulling residue if they are not ultimately rinsed or wiped away.

The key cleaning ingredients in cream cleansers echo those of the powder cleaners: highly efficacious surfactant system, abrasive, builder, and, optionally, a bleaching compound. However, because this is a liquid form, there are other ingredients and considerations. Other ingredients that become easier to formulate include surfactants available only as liquids such as some nonionics, and cleaning solvents such as glycol ethers or limonene. The main nonperformance consideration of the formulation is stabilizing the suspension of abrasive in the liquid.

Suspension takes place when the solid particles spread throughout the liquid matrix neither sink nor float. The usual way of accomplishing this is to set up the rheology of the system so there is an appreciable yield point so that the formula tends not to shear and thin under normal transport and storage conditions. This is reported to have been done generally by thickening the system with polymers [19,20], clay [21,22], colloidal alumina [23,24] or combinations [25]. This is especially difficult if the product is to include hypochlorite or peroxide bleaches, because bleach tends to be aggressive toward so many thickening agents and surfactants, and the liquid form allows them to interact. For this reason, the most usual polymer thickeners are acrylates that have good bleach stability. Hydrotropes are short chain anionic or amphoteric solubilizers that are used to help the solubilization of the system, keeping all the surfactant, solvent, and polymer ingredients in solution or break-up gel phases [26,27].

As mentioned above, being in a liquid form, cream cleansers can contain a wider variety of surfactants. Generally cleaning systems are more efficient and versatile when they are mixtures of surfactants and take advantage of the synergistic tendencies of surfactants. LASs tend to be the mainstay of the surfactant system, as in the powder cleansers, but may be mixed with nonionics such as ethoxylated alcohols or amine oxides. Ethoxylated alcohols are not used in the bleach products, but amine oxide is largely stable to bleach attack and therefore is widely used in hypochlorite-containing cleaning products. Amine oxide and soaps can form complexes that thicken the formulation and therefore can serve as both the cleaning surfactant and the thickening system. The combination of surfactants tends to give faster or greater grease solubilization.

The other change from powder cleansers is the variation in abrasive. Some cream cleansers have been commercialized with *soluble* abrasive. This is intended to circumvent the rinsing difficulties of standard abrasives, which consumers speak about having to *chase down the drain.* A soluble salt such as sodium carbonate or borax may be added to the formula in excess of its solubility limit, so that some of it is in the form of suspended particles. When the cleanser is rinsed the product is further diluted and reportedly the expected result is dissolution of the particulate salt [28–30].

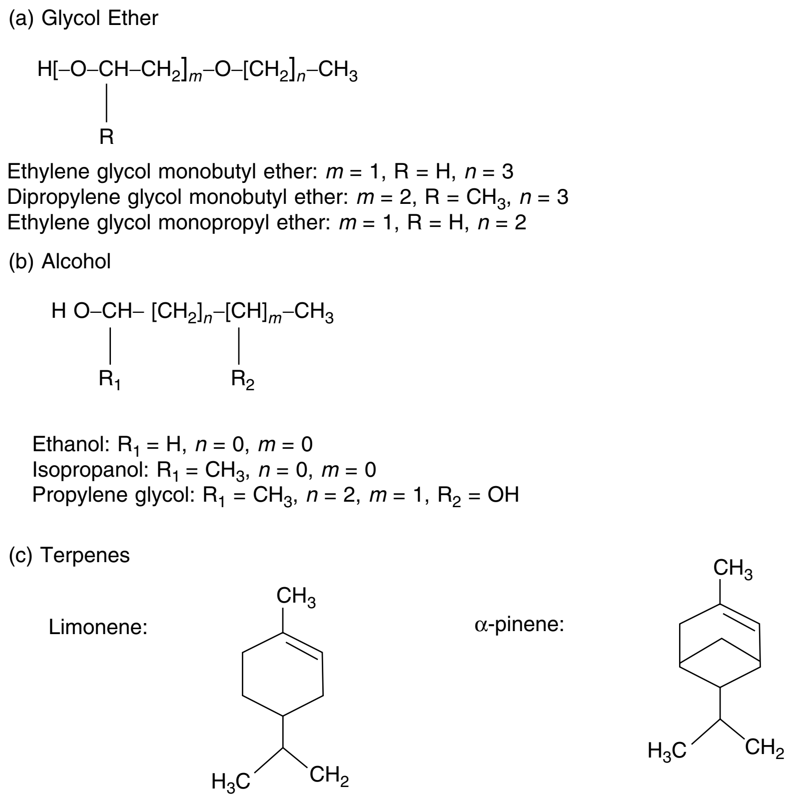
2.2.3 DILUTABLE CLEANERS

2.2.3.1 Liquid Dilutable Cleaners

Bucket dilutable or dilutable APCs have the highest concentrations of surfactant of products within this category—usually 8–25%. These depend more on the chemical action than the cleansers. *Bucket dilutable* is a term derived from the usual practice of using a bucket to make a dilution of product to do routine household cleaning tasks like washing floors. The product may be labeled as a *floor cleaner* or as an APC. The floor cleaners and APCs are sold in higher concentrations than spray or wipe products with the intention of allowing the consumer to adjust the dilution of the product to fit the cleaning task—full strength for small area/high soil tasks, down to a 90% dilution of the product for large area/light soil tasks. Emblematic of the first cleaning problem would be grease splatters around a stove, and representative of the second would be low-traffic dust/dirt on a regularly cleaned floor.

These types of cleaners are almost always mixtures of surfactants, usually combinations of anionic with nonionic surfactants. ABCs again lead the list of anionic surfactants commonly used in these cleaners, although ethoxylated alcohol sulfates are also popular. While some foam is desirable (as a signal to the consumer of the surfactant action), it is also desirable that the foam collapse quickly as well. Consumers tend to try to rinse a cleaned surface as long as they see foam. If foam persists then the consumer can be rinsing a long time. These products are often used on difficult to rinse surfaces (countertops, floors, walls), which makes the rinsing process even more laborious. If the surfactant system is designed to collapse quickly (usually on dilution), then the consumer ends the rinsing process sooner, resulting in a perceived increase in convenience. One of the interesting ways to encourage the foam to collapse usually reported is to include a small amount of soap in the surfactants [31]. Soap reportedly tends to destabilize the mixed surfactant foam films. High amounts of surfactant (>15% by weight) may require hydrotropes to maintain a single-phase product, but lower levels of surfactant are usually single phase without this help.

Solvents tend to make a much larger contribution to the cleaning in these products than in cleanser-type products. The most popular choices for solvents tend to be either glycol ethers or terpenes. Examples of structures are shown in Figure 2.1. Pine oil is a traditional choice for APCs. These terpenes are excellent grease cutters and grease solubilizers, with the main formulation challenge being solubilizing this very hydrophobic ingredient in the formulation, while minimizing the surfactant concentration. For this reason, pine oil cleaners tend to have 20% or less pine oil [32]. Recently, limonene has been more popular. Limonene is also a very good grease cutter and, to some



(a) Glycol Ether

$H[-O-CH(R)-CH_2]_m-O-[CH_2]_n-CH_3$

Ethylene glycol monobutyl ether: $m = 1$, R = H, $n = 3$
Dipropylene glycol monobutyl ether: $m = 2$, R = CH_3, $n = 3$
Ethylene glycol monopropyl ether: $m = 1$, R = H, $n = 2$

(b) Alcohol

$H\ O-CH(R_1)-[CH_2]_n-[CH(R_2)]_m-CH_3$

Ethanol: R_1 = H, $n = 0$, $m = 0$
Isopropanol: R_1 = CH_3, $n = 0$, $m = 0$
Propylene glycol: R_1 = CH_3, $n = 2$, $m = 1$, R_2 = OH

(c) Terpenes

FIGURE 2.1 Molecular structures of some common hard-surface cleaning solvents.

people, has a more attractive odor than pine oil. Glycol ethers, by contrast with the terpenes, are significantly more water soluble, although they are also very good grease cutters. They also do not have the strong distinctive odors of the terpenes. Glycol ethers, and to some extent alcohols, tend to be the most prevalent ingredients in the household cleaner patent literature after the surfactants themselves.

APCs or BDCs can also be built systems like the cleansers are. However, the builders, being powder ingredients, can leave behind residue as they do in the cleansers. The alkalinity supplied by the builders is an important adjunct to the surfactant and solvent action of these cleaners, although the amount used is usually minimized. Formulas that are microemulsions are made completely without builders and should have less rinsing or residue problems.

Microemulsions are a relatively recent form of APC formulation. Microemulsions are designated as liquid systems that are thermodynamically stable and macroscopically uniform, but microscopically made of emulsion droplets. These systems are well known for their very low interfacial tensions. They tend to maintain their phase only within fairly narrow ranges of concentration. Nonionics form microemulsions more easily, and when they are made from a mixture of anionic and nonionic surfactants, they usually need cosurfactants to form. The glycol ether solvents are often reported to make good cosurfactants [33,34], the chemical reasoning being that they closely associate with the surfactant micelles on the water side rather than being solubilized within the micelle as more hydrophobic solvents, such as pine oil, would be. Indeed, a microemulsion can be formed around the insoluble solvents, using them as the oil which is necessary for an emulsion. For example, it has been reported that microemulsions are able to deliver relatively high concentrations of water-insoluble solvents that would otherwise be cloudy or two-phase systems [35]. Some pine oil cleaners with over 10% pine oil appear as uniform clear liquids, which might indicate that they are in microemulsion form. These microemulsion systems are examples of the advancement of understanding of surfactant chemistry.

2.2.3.2 Powder Dilutable Cleaners

In developing markets, APCs are more often in powder form. This was also the original form of dilutable APCs in developed markets. Markets tend to move away from powder cleaners because of some drawbacks of the dry form. First, they take time to dissolve in water, being much slower than the quickly dispersing liquids. This lengthens the time needed to set up the task. Second, they tend to produce dust, which makes them messy to dispense and store. However, an overwhelming counterbalance to these disadvantages is cost. Powder detergents are less-expensive formulations than liquids, making use of usually relatively inexpensive single surfactants like LAS or soap, and being packaged in inexpensive cardboard boxes or thin plastic bags. Although spray drying may be a more expensive process than liquid mixing, the cost-effectiveness of the packaging evidently makes up for this. In this form, the dilutable cleaner finds more *all-purpose* uses than the liquid form in more affluent markets. The dilutable liquid cleaners in the United States, for example, are used largely for floor cleaning or, undiluted, for extremely greasy messes, which are kitchen cleaning jobs. In a less-affluent market like Colombia or Malaysia, a powder dilutable cleaner will be the detergent for cleaning not only the floor but also the dishes and the laundry. This maximizes the consumer's investment in a cleaning product by using it for a wide variety of cleaning tasks.

Powder dilutable cleaners use LAS or soap as the surfactant and builders to maximize their cleaning ability. The builder component may well be of higher concentration than the surfactant, with the surfactant ranging up to 15% and the builder ranging up to 50%. As with the abrasive in cleansers, the builder in powder dilutable cleaners is a less-expensive ingredient than the surfactant. These cleaners also contain a bulking or flow agent in the form of sodium sulfate, which is also used in powder laundry detergents. Unlike cleansers, where the bulk of the formula is in the form of abrasive, or liquid cleaners, where the bulk is water, powder cleaners have as the bulk of the formula sodium sulfate or similar salt, at levels of 30–50% by weight. Using this compound makes processing the product easier, makes an effective amount of surfactant available for an appropriate price, and delivers the surfactant at an appropriate concentration for use even at full strength.

2.2.3.3 Disinfectant Cleaners

One very important subset of the dilutable cleaners is disinfectant cleaners. The original household disinfectants were simply that—disinfecting compounds that were meant to be applied to clean surfaces. Disinfecting household surfaces was therefore a two-step process with two separate products—clean the surface thoroughly and then disinfect it. Beginning in the 1940s [36], single products claimed to be able to do both functions were commercialized. Various chemistries are used in disinfection. One of the oldest is pine oil, which can kill Gram-negative bacteria. However, this is rather narrow spectrum biocidal activity, so in modern formulation the usual disinfectant compounds are quaternary ammonium surfactants or *quats*. Quats are useful because they have broader spectrum activity and are also effective at low concentrations. Usually they are only formulated into a product at concentrations of 3–5%, and these concentrations are effective when the product is diluted according to the label directions. However, where the pine oil is broadly compatible with many types of surfactants, quats are inactivated by anionic surfactants. Therefore, formulations using quats are formulated with only nonionic or amphoteric surfactants. This is a large constraint on formulation, as many of the best cleaning surfactants are anionics. Nonionic-only formulations are still effective cleaners, but they depend more on their surfactant synergy for cleaning than, for instance, a cleaner based solely on LAS.

Two other approaches to disinfectancy are less commonly used. Contrary to the usual alkaline pH of household cleaners, some products are at acid pH, because their formula is said to depend on carboxylic acid in the disinfectant system [37,38]. Alternately, riding the consumer's interest in "naturals," some botanical oils are occasionally claimed as integral to the disinfectant formula [39,40]. Related to this may be a renewed interest in using that venerable "natural" ingredient, pine oil, as a disinfectant [41]. Pine oil has long been known as a disinfectant (although of limited spectrum), but the current attention to "natural" products may increase interest in this approach to disinfectancy.

2.2.3.4 Bleach Cleaners

Another subset of dilutable cleaners is bleach-containing cleaners. These are formulated with bleach to facilitate stain removal during the cleaning process. It is dangerous for the consumer to make *home brew* cleaners with bleach, because so many other cleaning ingredients are unstable in the presence of bleach. Many of these reactions would simply inactivate the bleach, because it would be consumed reacting with the other ingredients, but, as in the case of ammonia, dangerous compounds can be formed [42]. Manufacturers combining cleaning ingredients with bleach is a safer way of bringing the bleach advantages to the consumer than consumers making mixtures themselves. These can also be considered disinfecting cleaners (depending on the use dilution of the product), because hypochlorite bleach is a very effective, very broad spectrum biocide if used at high enough concentration (usually between 1 and 5%). The surfactant restrictions on this type of cleaner are even more severe than for quat-containing cleaners, because of the high chemical activity of the bleach. Essentially, many ethoxylated surfactants are eliminated from consideration as well as many anionic surfactants. The most prominent example of a bleach-stable surfactant, and the one used most often in *chlorine bleach* formulations, is amine oxide, usually in concentrations of 3–15%. Anionics such as soap or disulfonates such as the Dowfaxes® are also bleach stable and are used, but amine oxide is somewhat more common. Almost any commercial bleach-containing cleaner will contain amine oxide as the main surfactant. This also allows for the formulation of thickened or *gel* bleach cleaners, because there is reported to be a thickening interaction between amine oxide and soap [43].

One may argue with the designation of a bleach cleaner as an APC. Many household surfaces can potentially be damaged by bleach, some due to attack by the bleach itself, some by the high pH necessary to stabilize bleach in the formula. These include painted surfaces, aluminum, some ceramics, and wood. However, bleach formulas serve an important purpose in that they not only clean but also decolorize stains. If a stain cannot be cleaned off a surface it can be made less noticeable by decreasing its color, which the oxidizing action of the bleach does very well.

Cleaners containing *oxygen bleach* or peroxides are gaining in popularity. Contrary to the usual trend in developed nations, these products are often in powder form rather than liquid to facilitate delivery of the peroxide (usually in the form of percarbonate), which is very difficult to stabilize in liquid formulation [44]. They are usually aimed at laundry problems, but directions on the label give dilution instructions for use as a cleaner on a variety of hard surfaces as well. Surfactants used in these cleaners are usually anionic or nonionic at low concentrations (<5%). Oxygen bleach formulas are touted for their greater surface safety, but with the greater safety comes a decreased spectrum of stains that can be bleached.

2.2.3.5 Ready-to-Use Floor Cleaners

There is also an emerging segment within all-purpose/floor cleaners: the *ready-to-use* floor cleaners. These cleaners are essentially APCs already diluted to the concentration used for floor cleaning. This is a high dilution, because low surfactant concentrations are needed to avoid copious rinsing or sticky residue (due to inefficient rinsing). They are usually packaged in bottles with push/pull caps, although some are also packaged in spray triggers to facilitate even distribution. They are intended to be used straight from the bottle, squirting the product directly on the floor and mopping it out. This eliminates the step for the consumer of making a bucketful of diluted cleaner. These cleaners do not really signal a difference in formulation, but are another example of packaging being used to give ever more instantly *ready-to-use* products. Their ingredients do not differ significantly from regular APCs, the only important difference being the very low concentrations. Surfactant concentrations in these products are usually $< 1\%$.

It should be noted here that this is an important principle of formulation—avoiding overformulation. A product is not necessarily better because it contains more or higher concentrations of ingredients. If the properties of the cleaner are not well matched to tasks for which the consumer uses it, this results in consumer dissatisfaction. Products meant to be *ready-to-use* must be at lower concentrations, so that rinsing and cleaner residue can be minimized. Products that are used habitually, for example, products used for daily cleaning and wipe-ups, can also be at lower concentrations, because the daily cleaning regime usually does not allow for heavy soil buildup. Without heavy loading or particularly adhesive soils (such as baked-on food on stove tops), high surfactant concentrations in a cleaner serve no constructive purpose, only adding labor (in the form of laborious rinsing) and waste (in water and product) to the task.

2.2.3.6 Aesthetically Oriented Cleaners

Within the past 30 years, a growing segment of APCs has specialized in appealing to the consumers' senses. Fragrances in APCs, at their inception, were more about communicating the functional benefit of the cleaner rather than being *pretty*. Pine oil, of course, imparts its own odor to a cleaner. Many early APCs were lemon scented because of the common belief that lemon juice or lemon oil can be used as a cleaner on its own. Others had nondescript scents meant mainly to cover the base odor of the formulation due to the surfactant and solvent ingredients. Formulators are now interested in a wider pallet of scents, accommodating the increased fragrance appreciation of consumers in both developed and developing markets [45,46]. Popular household fragrances now include lavender, green apple, berry, vanilla, and herbaceous.

Cleaners focused on aesthetics were first introduced in the Latin American countries in 1975. These were formulated with daily cleaning in mind and so had surfactant concentrations at 1–3% level. The surfactants in these formulations were the typical choices of LAS, alcohol ether sulfates (ethoxylated alcohol sulfates), and ethoxylated alcohols used in synergistic combinations. The main difference between these and the more powerful APCs were their more impactful fragrances in a greater variety of scents—lavender, varieties of florals from gardenia to rose, orange citrus (instead of lemon), and many others. With daily cleaning—the light mopping of the floor to remove dust and light dirt, countertop and stove wiping—the fragrance of the cleaner is released into the room and lingers after cleaning is done. These effects are not necessarily due to higher concentrations of fragrance, but can also be accomplished by the use of more impactful fragrances—those formulated to evaporate easily from the surface. This interest has spread to other light-duty cleaner forms such as glass cleaners [47] and wipes [48]. It has turned to the fragrance impact of heavier-duty cleaners as well [49].

2.2.3.7 All-Purpose Cleaner Summary

APCs come in a wide variety of concentrations and adjunct ingredients depending on their intended use and flexibility. The choice of surfactants has not changed significantly in the past 30 years, although there is greater use of amine oxide and ethoxylated alcohols. Use of adjunct ingredients such as bleach, abrasives, and the like both simultaneously broaden the efficacy of the product and decrease the *all purposes* the product can be used for due to surface damage potential. These pros and cons of the various APCs and their typical uses are shown in Table 2.3.

2.2.4 SPRAY ALL-PURPOSE CLEANERS

A variation on APCs, popular in North America and some other parts of the developed world, are spray cleaners. These were some of the original convenience *ready-to-use* products. Sixty years

TABLE 2.3
Comparison of All-Purpose Cleaners

Type	Usual pH	Surfactant Concentration (By Weight) (%)	Key Ingredients	Advantages	Disadvantages
Powder cleanser	>8	<5	Abrasive, surfactant (bleach)	• Cleans tough soils, stains • Inexpensive	• Damages softer surfaces • Hard to rinse
Cream cleanser	>8	10–20	Abrasive, surfactant, thickener (bleach)	• Cleans tough soils, stains • Easier to spread • Less messy than powder	• Damages softer surfaces • Hard to rinse
Dilutable (liquid)	6–9	15–30	Surfactant, solvent (builder)	• Customized strength through dilution • Especially good grease cutting	• Requires dilution for most jobs
Dilutable (powder)	>8	5–10	Builder, surfactant	• Can be used on variety of surfaces and tasks • Works well in any water hardness • Inexpensive	• Damages alkaline sensitive surfaces • Slow dissolving
Disinfectant	>7	5–20	Surfactant, solvent, disinfectant	• Good general cleaning • Disinfection of surfaces available in same product	• Must be used exactly as per directions for effective disinfection • Surfactant choice limited by disinfection choice
Bleach	>10	<10	Surfactant, bleach	• Stain decolorizing combined with grease cutting • Safe combination of hypochlorite with other ingredients	• Potential surface damage due to bleach sensitivity • Surfactant choice severely limited by presence of bleach
Ready-to-use floor cleaner	>7	<2	Surfactant, solvent	• Ready to use, no bucket needed • Safe for many surfaces	• Limited to floor cleaning, light-duty jobs
Aesthetic	6–10	<10	Surfactant, solvent, fragrance	• Room freshening fragrance released during cleaning • Good general cleaning	• Limited cleaning strength—light-duty jobs

ago, a consumer had to dilute an APC to a very high extent and then lug that container to all their small cleaning jobs. This included window cleaning, which, considering the number of windows in a house, could be a very onerous task. The advent of cleaners in first pump bottles in the 1950s and aerosol cans, and then the significant improvement of the more ergonomic spray trigger in the late 1960s, greatly increased the convenience of doing these jobs. This packaging type actually dominates certain task areas in North America, such as bathtub/shower, window, and spot cleaning.

Spray cleaners come in several types. The usual classifications are APCs *glass-and-surface*, or *glass* cleaners. These products change along a continuum of surfactant-to-solvent ratio, with the highest amount of surfactant in *all-purpose* sprays, and the highest amount of solvent in the glass or window cleaners. They can be considered as optimizations of the more concentrated bottled

APC for quick cleaning. Dilutable cleaners can be used straight from the bottle, but this is rarer compared to the more usual use of diluting the cleaner in a container. These spray cleaners make their reputation on convenience; they are ready to use straight from the bottle, with the spray form facilitating the application of the product to any size soiled area. The other difference is the choice of implement used with them. Dilutable APCs are more often used with sponges, but the general purpose spray cleaners are more often used with a cleaning cloth, rag, or paper towel. They are also intended to not need rinsing to leave a shiny, streak-free surface. This also helps to make the cleaning task faster.

2.2.4.1 Spray All-Purpose Cleaners

The most concentrated of this type of cleaners are the *all-purpose* sprays. These sprays are diluted versions of the bucket dilutable APCs, with essentially the same selection of surfactants, solvents, and (sometimes) builders. However, although these cleaners depend on a blend of surfactants and solvents like the bucket dilutables, the ratio of solvent to surfactant is much greater. In some cases the amount of solvent approaches the amount of surfactant in the product. One can see an arc going from cleanser to dilutable cleaner to spray cleaners, where the surfactant, usually an anionic or anionic/nonionic blend, goes from playing a supporting role to the abrasive in cleanser, to being the main cleaning agent in the dilutable, to having a shared role with the solvent in the spray cleaner.

The spray cleaners are used for jobs that used to be done by either low dilutions or direct application of the dilutable cleaners. The spray cleaners have many advantages over using the dilutable cleaners this way. First and foremost, the spray format makes it easy to spread a small amount of cleaner over a wide area or to apply to a small spot. Second, the higher solvent content makes these cleaners more effective at penetrating greasy soils. Third, the relatively lower level of surfactant produces less foam and makes them easier to rinse or wipe up.

The most commonly used ingredients in these cleaners are ethoxylated alcohol sulfates with ethoxylated alcohols or amine oxide combined with glycol ether solvents. The surfactants are generally at the 5–20% level, with a similar level of solvent. In addition, builder or other alkaline compounds such as sodium hydroxide are added to raise the pH of the system to over 7. However, in the interests of surface safety, the pH is usually kept under 9. However, heavy-duty degreasers and high-efficacy sprays that have recently appeared on the U.S. and European markets [9] often have higher pHs to make the alkaline degradation of oily compounds a more important part of the cleaning mechanism, increasing the pH to the 9–10 range, but are otherwise very similar to the other all-purpose sprays.

2.2.4.2 Disinfectant Spray Cleaners

Similar to the disinfectant dilutable cleaners, disinfectant spray cleaners are intended to both clean and disinfect. Although they are very popular with consumers, they are not used without controversy in microbiological circles [50,51]. The usual disinfectant ingredient used in these cleaners is quats (quaternary ammonium surfactants), which were discussed with the dilutable cleaners. As previously mentioned, these disinfectants are inactivated by anionic surfactants, so these formulas are usually formulated with only nonionic surfactants.

Disinfectant sprays can also be made with hypochlorite bleach being the disinfectant ingredient. In this case, as with the dilutable bleach cleaners, the constraint on formulation is to have bleach stable surfactants. In practice, this usually means that the cleaner is formulated with amine oxide as the main cleaning surfactant. Amine oxides not only have the virtue of being resistant to bleach attack but also combine good grease-cutting ability with relative skin mildness. Solvents, because of their vulnerability to bleach attack, are generally not used in these cleaners.

One advantage of this form is that the disinfectant is used at the concentration intended by the formulator. When the disinfectant cleaner is a dilutable, effective disinfection depends on the consumer making the dilution or using the product at the dilution recommended by the formulator. Consumers are not always diligent about following label instructions, and so it can be debated whether the consumer is effectively disinfecting surfaces. However, this uncertainty is eliminated with the spray form, as the consumer uses it *as is*, which increases the chances that effective disinfection is taking place.

Another use instruction often on the label is the stipulation that the surface be clean when the product is applied for the purpose of disinfection. Many labels actually carry directions to go over the surface twice with the product—once to clean and then again to disinfect. This indicates that effective disinfection of the surface cannot take place through a soil layer. It is doubtful whether a consumer is *cleaning* a surface twice to achieve careful disinfection.

2.2.4.3 Window Cleaners

Window cleaners are the oldest of the spray cleaners, and the first to be put into pump packaging. The difficulty of spreading a cleaner over the (often) large vertical surfaces of windows made the spray application of the cleaner very attractive. Window cleaners were packaged in tapering glass bottles with thumb push type pumps. Such was the attractiveness of this delivery form that the first example was in a breakable glass bottle with a less than ergonomic pump. With the development of blow molding of plastic bottles in the early 1950s, the development of the polyethylene terephthalate, and the invention of the spray trigger, the way was paved for light-weight plastic bottles mated to a less fatiguing form of delivery, which was launched in the late 1970s and became well established in the 1980s in developed markets [52]. Distributing the cleaner as small droplets also encourages the cling of these droplets to the vertical surface, spreading the cleaner finely over the entire surface. The utility of this form for glass cleaners is testified by its being essentially the only delivery form for this product in North America (whereas Europe tends to use wipes).

Consumers sometimes describe window cleaners as the only truly APCs. This is because window cleaners can be used safely on almost any surface, the major exceptions being those surfaces (such as aluminum) that are very sensitive to alkalinity. Part of the surface safety of window cleaner is due to the fact that they are largely water—over 90% in many brands. For this reason, window cleaners are very light-duty cleaners, depending on their small solvent concentration (generally <5%) and alkalinity for their cleaning ability. The advantage of depending on the solvent, usually a short-chain alcohol like isopropyl alcohol, is that the solvent is *fugitive*—it easily evaporates leaving no residue. The most important dual characteristics of a glass cleaner is that it clean light soils without leaving streaks or residue. The ingredients of the cleaner, therefore, need to be easily absorbable back into the wiping implement, or be highly volatile so that they do not remain on the cleaned surface.

For this reason, ammonia was often used in early and some modern glass cleaners—it is a powerful source of alkalinity while also being highly volatile. However, most commercialized glass cleaners use more exotic surfactants than the dilutable cleaners or all-purpose sprayer, showing more use of amido nonionics, betaines, or amine oxide, although traditional anionics can also be used. The betaines and nonionics in the patent literature are often touted for their low streaking qualities [53]. These are used at very low concentrations, taught in patent literature up to 5%, but practically in commercial formulas at <1%. Builders are generally avoided in glass cleaners (because of possible residue), but strong bases, like sodium hydroxide, can be added in very small amounts and still achieve a pH in the range of 8–9.

Less frequently, glass cleaners can have a low pH in the range of 3–5. This is unique among the general purpose spray cleaners, which are almost always alkaline to help with grease cutting. Partly these cleaners are based on the popularity of vinegar in *home brew* window cleaners. There are evidently some soils that have good response to these low pH cleaners, and low pH has sometimes been related to shine benefits. The usual surfactants, like LAS or ethoxylated alcohol sulfates or ethoxylated alcohols, are equally good in acid or basic formulas.

Owing to the importance of streak-free cleaning, these formulas can contain ingredients that are said in the patent literature to contribute to a decrease in the tendency to streak, such as glycols

[54] or particular surfactant combinations, especially sulphosuccinates [55]. An added benefit that is often touted for glass cleaners is antifogging. This is especially desirable when cleaning mirrors or other surfaces in bathrooms or kitchens that tend to collect steam or mist. Polymers like silanes or silicone glycols [56] are often quoted for this use. Although antistreak polymers are sometimes claimed for all-purpose sprays, antifog claims are largely made only for glass cleaners.

2.2.4.4 Hybrid Spray Cleaners

The glass-and-surface cleaners are hybrids of the all-purpose sprays and the glass cleaners. Most consumers would probably not recognize them as being different from other all-purpose sprays. However, these cleaners were invented to answer a particular consumer behavior. Consumers would clean soiled surfaces with all-purpose sprays, but find that those sprays left streaks and residue (probably from builders and higher surfactant concentrations) after cleaning was done. Many consumers would then go back over the same location again with a glass cleaner that, being a streak-free light-duty cleaner, would remove the residue from the APC without leaving any streaks itself. The intention of the glass-and-surface cleaners was that they would clean nearly as well as the all-purpose sprays but leave significantly less residue, like a glass cleaner. These cleaners use essentially the same surfactants as the all-purpose sprays but at a lower concentration, although at a higher concentration than glass cleaners. The solvent level stays about the same as the spray APCs, so proportionately the cleaner depends more on solvent than the all-purpose sprays. The cleaning ability and the residue potential of these cleaners therefore fall between all-purpose sprays and glass cleaners.

There are also other multisurface cleaners that can be considered descendants of the glass-and-surface cleaners. There are cleaners that are claimed to be used on both glass and wood surfaces. This is interesting because wood is usually polished with an oil-containing cleaner, which would leave a dulling streaky film on glass. It is interesting that one of the companies that makes a product with this claim owns a patent directed to a low organic solvent cleaner [57]. A cleaner of this type could be used on finished wood surfaces without harming the common wood finishes of varnish or shellac. This kind of cleaner would be popular with people who have furniture that combines glass panels with wood frames. Being a cleaner, this would not polish the wood, but would tend to remove polish that was on the surface.

2.2.4.5 Summary of Spray Cleaners

Spray cleaners are used for a variety of surfaces in the household, on everything from baked-on grease on stove tops to fingerprints on windows. From all-purpose sprays, to glass-and-surface cleaners, to glass cleaners there is a decreasing amount of surfactant and larger amounts of solvent (compared to the amount of surfactant). All of these cleaners depend more on their solvent content for cleaning efficacy than the (bucket) dilutable cleaners. Because they are in the spray form, consumers expect them to clean quickly, and the penetrating action of the solvent helps to achieve this expectation. Table 2.4 gives a compilation of the different kinds of spray cleaners.

2.2.5 GENERAL CLEANING WIPES

Recently, wipes have become popular in developed countries for quick *touch up* cleaning occasions. Wipes are the ultimate step in convenience cleaning, because they not only supply the cleaner at the use concentration but also supply the cleaning implement as well. They are usually intended for a single use, after which they are disposed. The implement is a nonwoven material, which, as the name suggests, is a fabric that does not have a woven structure. Instead, fibers used to construct the fabric are pressed, entangled, or stuck together with resins. They can be made of a variety of fibers with respect to the length and the diameter of fibers, and the type of fiber. Fibers can be a variety of materials, from cotton and rayon to polypropylene and polyethylene terphthalate, or combinations

TABLE 2.4
General Purpose Spray Cleaners Comparison

Type	Usual pH	Surfactant Concentration (By Weight) (%)	Key Ingredients	Advantages	Disadvantages
Heavy duty (degreaser)	8–10	<5	Surfactant, solvent, alkalinity	• Cleans tough greasy soils • No need to rinse	• Damages alkaline-sensitive surfaces • Harsh to hands
All-purpose	8–9	5–20	Surfactant, solvent	• Cleans greasy soils • Safer to surfaces • No need to rinse	• Damages some alkaline-sensitive surfaces
Glass and surface	8–9	2–8	Surfactant, solvent	• Lighter-duty cleaning • Safer to surfaces	• Not for tough cleaning jobs • Can still leave streaks on some surfaces
Glass	8–9 (Occasionally 3–5)	<1	Solvent, surfactant (alkalinity)	• Safe for nearly any surface • Essentially streak and residue free	• Not for tough cleaning jobs
Bleach	>10	2–5	Surfactant, bleach	• Stain decolorizing combined with grease cutting	• Potential surface damage due to bleach sensitivity • Surfactant choice severely limited by presence of bleach
Disinfectant	>8	<10	Surfactant, disinfectant	• Cleaning and disinfection in one product • Effective disinfectant concentration delivery *as is*	• Disinfection requires a clean surface • Surfactant choice limited by disinfectant choice

of hydrophilic and hydrophobic fibers. A discussion of nonwoven technology and the different types and properties of nonwoven materials can be a chapter in itself [58,59]. As formulation is the focus of this discussion, not implements, this will not be discussed further. It suffices to say that the absorbent characteristics of the nonwovens allow them to be coated with these cleaning formulations simply by spraying or wiping the liquid onto the fabric. They are usually packaged in resealable pouches or envelopes.

Cleaning wipes come in the same varieties as the all-purpose sprays—largely all-purpose, glass, and disinfectant. In addition, there are wipes intended to be attached to specially shaped mops to do floor cleaning. These are similar to the formulation for *ready-to-use* floor-cleaning liquids. Cleaning wipes were largely unsuccessful when they were originally launched in the 1980s [60], but were the fastest growing segment of household cleaners for a decade at the end of the twentieth century. See Figure 2.2 for sales volume figures for various household cleaner forms. In general, the cleaning formulas on the wipes are similar to those on their spray or ready-to-use counterparts, although it is desirable that anionic or nonionic component is low foaming. They also tend to have relatively high solvent content, either alcohol (for window cleaners) or glycol ethers (all-purpose or floor cleaning). The *lotion* (as it is called in the industry) is generally added to the wipe in a mass ratio or 1:4–1:2 to the weight of the nonwoven substrate.

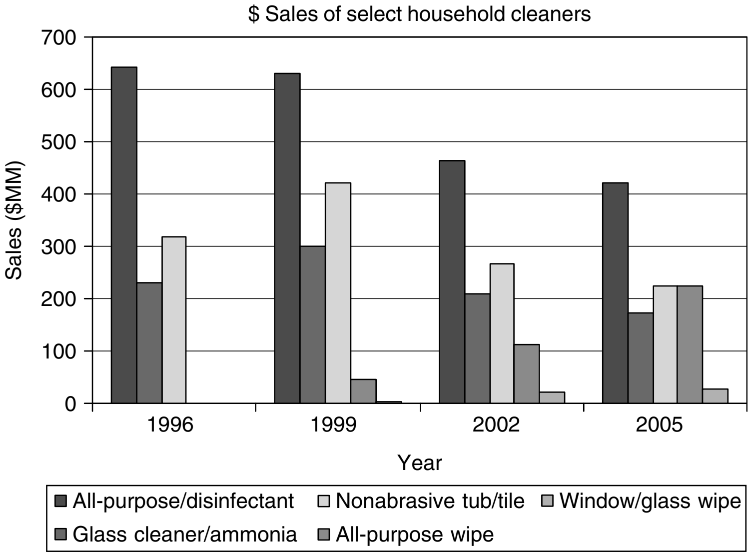


FIGURE 2.2 U.S. sales figures for some household cleaning types. Volumes after 1999 do not include Wal-Mart data. Sales data from Household and Personal Products Industry (HAPPI), Issues Dec. 1996, Dec. 1999, Nov. 2002, Nov. 2005, and Private Label Buyer Issues June 1, 2002 and July 1, 2006.

2.2.6 CLEANERS FOR FABRIC HOUSEHOLD SURFACES

As mentioned before, this field can also include cleaners for *soft* surfaces, such as upholstery and carpet cleaners. The focus here is not on cleaners that are used in commercial apparatuses for the mechanical washing of carpets, but on the ready-to-use cleaners (also used as *spot* cleaners) used in households. They are usually liquid formulations, but there are also a small number of powders. The packaging of these cleaners is often integral to their use. They may come in aerosol cans or plastic bottles, with scrubbers attached to the top or brushes cowrapped with the bottle. There are also a large number of upholstery cleaners which come in trigger spray bottles. These are formulated mainly against common spots and stains (dirt, food and drink spills, pet urine, etc.) that are encountered on furniture and in carpets. In both cases the packaging, whether aerosol or trigger spray, is intended to give quick, targeted delivery of the cleaner to the surface.

Unlike hard surfaces, these household soft surfaces pose a special problem to the formulator, because of the difficulty of rinsing the cleaner out of the surface. Hard surfaces are readily rinsed with the water running off the surface, and other cloth items in the home such as curtains are often washed in the laundry, where thorough rinsing is possible. Neither of these two statements is true of a large-area rug, wall-to-wall carpeting, or a sofa. Therefore, the need for rinsing has to be minimized or eliminated in these cleaners. Partly this is done with low surfactant concentrations. In many cases the cleaner is allowed to dry—and forms a powder that can be vacuumed up—a mechanism of cleaning unique to this area. Some formulas reportedly are made as powders containing absorbents such as powdered cellulose or zeolite to be sprinkled on the surface, left to absorb the soil, and then vacuumed up [61,62], In other cases, it is recounted that the cleaner is used in conjunction with a steam cleaner, which injects hot detergent solution into the carpet and then immediately sucks it back out again [63]. For spot cleaners, the direction is given that the cleaner is blotted up from the surface as thoroughly as may be done [64–66]. Care needs to be exercised, because if the surfactants that are used to clean the surface are left as a residue in the fibers, this can actually work to attract and hold soil to the surface. This makes the cleaned area more visibly resoiled. Avoiding this effect is a recent development in carpet and upholstery cleaning and involves the use of special surfactants.

The liquid cleaners are formulated mainly with anionic and nonionic surfactants (like ethoxylated alcohol sulfates, alcohol sulfates, and ethoxylated alcohols) and a solvent. This is also the only area in which fluorosurfactants are mentioned significantly in the patent literature. Fluorocarbons are well known for surface treatments that repel water and help keep surfaces soil-free. The total surfactant system is usually in the range of 0.01–2% and the solvent in the range of 3–10%. Various polymers are often incorporated as well, as part of the cleaning and soil consolidating system. The cleaners also tend to be in the slightly alkaline range of 7–9 so typical of APCs, although some examples are reported at acid pHs [67]. Alkaline agents include ethanolamines, builders, and ammonium forms of the surfactants themselves. Some contain special ingredients like bleach to help remove stains and odors that are reported not to be adequately removed by surfactants/solvents alone [68]. Powder formulas usually contain 30–50% of the absorbent, 0–3% surfactant, and 0–5% solvent. Keeping the powder from clumping and free flowing is a concern usually addressed by adding sodium sulfate or silica as a flow agent.

2.3 INGREDIENTS AND GENERIC FORMULATION

2.3.1 NONSURFACTANT INGREDIENTS

2.3.1.1 pH Effects

Most APCs, including the cleansers, are formulated in the pH range from ~6.5 to 11. Cleaners whose main ingredient is soap in particular must be formulated above pH 8 to avoid conversion of the soap back to its corresponding fatty acid. If the pH is in the upper end of this range, then of course product use on surfaces such as aluminum would be discouraged. APCs are seldom formulated at acid pHs, as the usual target of APCs are greasy soils and alkalinity helps to cut grease. Alkalinity also helps to stabilize hypochlorite in formulations and encourage the effectiveness of quat disinfectants. If a cleaner does, however, have an acid pH (for cleaning of specific soils such as hard water spots), then it would not be safe to use on acid-sensitive surfaces like marble or grout. Generally the usual pH-adjusting compounds are used, such as sodium or potassium hydroxide for alkaline systems and sulfuric or hydrochloric acid for acid systems. Amines such as triethanol amine have had some popularity as alkaline agents. However, when there is a need for buffering, then it is not unusual to encounter carbonates or bicarbonates (or other builders) for alkaline systems, and various carboxylic acids such as citric or glutaric acid for low pHs.

2.3.1.2 Bleaches

Starting in the 1970s, hypochlorite bleach has become a popular addition to APCs. This presumably reflects a behavior of consumers mixing household bleach into commercial APCs at home, or alternately using household bleach to clean a surface before or after using another cleaner, to disinfect or remove stains. The attendant potential dangers of this household *chemistry* are evident, as consumers are very seldom aware of the chemical identity of the APC's ingredients and whether these can be safely mixed with such a powerful oxidizing agent. Therefore, it is certainly a service of the manufacturers to provide ready-made combinations of detergent-based cleaner and hypochlorite bleach, where the chemical interactions are screened during the product development. However, this also becomes a two-edged sword: the oxidizing power of the bleach makes it a potent cleaning tool, but the same power also makes it a potential surface damager. The higher pHs needed to stabilize the bleach also bring the concerns mentioned above with regard to pH-sensitive surfaces.

Peroxide or *oxygen bleach* is increasing in popularity as an ingredient in household cleaners in developed markets. Peroxides are generally less damaging to surfaces but are also slower acting than hypochlorites or *chlorine bleach*. However, peroxides are stabilized by low pHs, and so peroxide-containing formulas lose the advantages that are gained by making the formula alkaline (see Section 2.3.1.1).

2.3.1.3 Solvents

As was mentioned several times, typical solvents used in modern formulation are usually of the so-called *glycol ether* group, for example, diethylene glycol monobutyl ether (see Figure 2.1). Various alcohols are sometimes used, but as glycols have better grease-cutting ability, they are more widely used. Glycol ethers are interesting in that they are both largely water soluble and good grease cutters—unique among organic solvents. Alcohols are more water soluble, but are not particularly good solvents for grease. Terpenes are somewhat better oil solubilizers, but are essentially water insoluble. Glycol ethers occupy the unique territory in between these extremes and share some structural similarities with the surfactants they blend with so well. Glycol ethers can also be adjusted by increasing or decreasing either of the ends of the structure, like some of the nonionic surfactants. Shorter-length glycol ethers tend to be better grease solubilizers, but also have significantly more health concerns. Longer-length glycol ethers have less water solubility, lower grease solubilization, and less health risks [69]. Generally, propylene and butyl groups are the lowest molecular units used in constructing these molecules.

Alcohols, although classed as solvents, tend not to be the grease solubilizers in the formulas they are found in, particularly the lower molecular weights (less than butanol). In formulations, the alcohol content usually serves other purposes; only in glass cleaners and their light-duty occupations does alcohol supply the *solvent* function. In most household cleaners, alcohol is more likely to be employed as a solubilizer for the surfactants themselves, to preserve the clarity and stability of the formula. Even higher-molecular weight glycols, such as polyethylene glycol, may, as stated in the literature, perform these hydrotroping-type roles or perhaps serve a purpose in preventing streaking and residue [70–72], rather than serving as straightforward grease solvents.

Terpenes remain popular in cleaners, particularly in dilutable cleaners or those intended for heavily soiled surfaces. Pine oil, that venerable choice of cleaning solvent, is also very much in evidence in the marketplace, particularly in the Americas. This is still the most effective grease solubilizer, although that very strength can also make it most damaging to a surface finish such as some paints [73], varnish, lacquer, or shellac. (For this reason they are generally not recommended for cleaning wood, which is often finished with these.) Limonene has become a very popular solvent in recent times. Both *d*-limonene and α-pinene, the major component of pine oil, are classed as terpenes, and their structural similarity can be seen in Figure 2.1. Part of the popularity of limonene is that it is often used in cleaners with claims to be "natural" or "naturally derived." (The main source of limonene is orange peel.) Depending on the amount and type of the solvent, restrictions are sometimes placed on their use on surfaces, such as wicker, brass, or wood, finished with lacquers or varnishes. They can also be damaging to painted surfaces, depending on the type of paint.

2.3.1.4 Abrasives

The abrasives in a formula can vary over the range from silica (Mohs hardness of 7) to calcite (Mohs hardness of 3). Most modern formulations of powder cleansers and nearly all the cream cleansers are formulated with calcite. However, the abrasiveness is not solely dependent on the abrasive hardness. Other significant characteristics include particle size and roughness of individual particles. The combination of hard, large particles with rough surfaces would result in the maximum visible surface damage. However, if the particles become too small, too smooth, or too soft, they would not contribute significantly to cleaning. Contrary to this is the characteristic of smaller particles being easier to suspend. Therefore, the usual particle size is in the range of 20–100 μm, large enough to abrade but small enough to suspend [74]. Usually not much is described about the shape of the abrasive.

2.3.1.5 Builders: The Pros and Cons

Builders, inorganic buffering salts, are an excellent source of alkalinity for a formulation. They are water soluble, so they can be added to liquid formulations, or dissolve reliably from powder formulations in use. They improve the performance of anionic surfactants by controlling hard water ions and contribute to cleaning by supplying and maintaining an alkaline pH. Anionic surfactants are subject, to greater or lesser extents, to precipitation by hard water ions, calcium, and magnesium. The most sensitive surfactant is soap, but even surfactants like LAS can have their cleaning ability enhanced in hard water by the addition of a builder that prevents hard water ion interaction with the surfactants. Furthermore, the alkalinity itself can have effects on household soils that encourage cleaning, like saponification of oily soils, swelling of proteins, and effects on surface zeta potential [75]. Phosphate salts are, of course, under restriction in many parts of the world, due to their contribution to waterway eutrophication, so that other salts such as carbonates or silicates are widely used. (Recently phosphates are even under pressure in automatic dishwashing products, where they were usually allowed in limited use.) More rarely salts such as citrates may be used. However, where regulatory restrictions are not a factor, phosphates are the first choice in builders.

The difficulty with builders is that they are crystalline solids. If a cleaned surface is not thoroughly rinsed, a thin layer of cleaner will remain on the surface. The builder content will return to its dry crystalline state and significantly contribute to the appearance of a dulling white residue on the hard surface. For this reason, the use of builders has become less and less as formulation has progressed and knowledge of surfactant synergies have increased the cleaning potential of a formula based on its surfactant ingredients alone.

However, there are still products where builders fill an important function. For instance, they are still used in powder and cream cleansers. In these cases, the product type itself, with high amounts of abrasive particles, requires extensive rinsing. The contribution of the builder to the overall rinsing requirements of the product is relatively minor. Also, surfactant concentrations in these products also tend to be minimized, for two reasons. First, the surfactant is an adjunct to the main cleaning done by the abrasive component, so judicious amounts are used. Second, cleansers tend to be *value* products, sold at low prices, and the price of the ingredients must be minimized. Excluding any perfume used in the cleanser, its surfactant portion is probably one of its costliest components. Any (less costly) ingredient that boosts the effectiveness of the surfactant, and of the overall formulation (alkalinity effect), is wise. The surfactants used in these formulations also tend to be anionics, the class that responds most to the water-softening effect of the builders. For these reasons, builders continue to be used in cleanser formulations, and in powder dilutable cleaners, where the builder substitutes completely for the abrasive as the mainstay of the cleaning. Builders also serve an important adjunct role in liquid dilutable cleaners, but at a lower level than in the powder forms.

2.3.1.6 Minor Ingredients and Aesthetics

By and large, the other nonsurfactant ingredients in an all-purpose formulation affect aesthetic qualities or foster stability of the cleaner. Occasionally the fragrance components are reported to have utilitarian uses in the formula [76]. Although they are not always considered this way, thickeners can also be considered esthetic components. Rheology not only serves practical functions, such as product cling on a surface or particle suspension in cream cleansers, but can also give aesthetic impressions. Consumers often assume that greater thickness means that a product is more highly concentrated or *stronger*. The texture of the product imparted by the thickener can also give a certain preferable *feel* in use.

Stability is fostered by ingredients such as preservatives, hydrotropes, or chelants. Preservatives prevent microbes from growing in the product after it has been contaminated in use by the consumer. Hydrotropes help to keep the formula, especially high surfactant concentrations, from separating or creaming out with extreme swings of temperature. Chelants, such as ethylene diamine tetraacetic acid, can be used to enhance the effectiveness of the surfactants in use by capturing hardness ions, but they can also be used to moderate hardness in the process water used to make the product. These ingredients all perform functions that are invisible to the consumer, unlike the functional ingredients like solvent, surfactant, or abrasive, whose role in the obvious effects of cleaning are recognized. Although these *invisible* ingredients all are usually regarded as purely *functional* components, they can also be considered as contributing in important ways to the aesthetics of the products. Bacterial or fungal growth in the product, prevented by the addition of preservatives, could produce unwanted changes of color, odor, or consistency, or even actual visible colonies. Hydrotropes and chelants prevent separations or precipitations in the products, which may be unsightly and certainly would communicate low quality of product to the consumer.

To be sure, an unprecipitated surfactant is a more effective cleaning agent. A product in which bacterial growth is minimized is also more effective and pleasant to use. However, one could argue that these negative effects, unless they started to affect the majority of the surfactant in the formula, are relatively minor with regard to the overall cleaning effectiveness. That is not to say that the choice of these ingredients is unimportant. Sometimes good aesthetics and quality appearance (or the failure of these) have more to do with a product's marketability than its actual cleaning ability. As such, they are vitally important in a successful formulation. However, the biggest difference in the cleaning performance of a product have more to do with the choice and relative amount of surfactant(s), the type and amount of solvents, the pH, and whether abrasive is present than with these other ingredients.

2.3.2 SURFACTANT USE IN HARD-SURFACE CLEANERS

The prevalent surfactants among commercialized hard-surface cleaners are still anionics. Anionics are well known for their effectiveness in penetrating and emulsifying oily soil, and it is their effectiveness in cleaning this type of soil that makes them so appreciated by formulators. Many other soils, such as dried-on food residues, are responsive to a great degree to cleaning by water. (Their cleaning is, however, facilitated by the addition of surfactant.) Particulate soils are also well removed by anionic surfactant [77]. Anionics also foam well, which is the signal to the consumer that there is detergent present, and that it is working.

After anionics, nonionics are the next biggest category of surfactant in APCs. These are used to a very limited extent in powder cleaning formulas. However, they are used in cream cleansers, which tend to be more complex formulations. Nonionics are extensively used now in liquid APCs and floor cleaners and the spray cleaners. There are even some few cases reported of APCs formulated entirely from nonionics, with no anionics at all [78,79]. Nonionics are well known for their ability to adsorb to greasy/oily surfaces, although they tend not to emulsify the oils in solution as well as the anionics. The properties of the two classes of surfactants would seem therefore to be complementary, and many modern formulation patents and publications describe these types of combinations [80–82].

Other classes of surfactants are now more often used in APCs. Various zwitterionics and amphoterics are now used, which would have been considered *exotic* only 15 years ago, and unusual 10 years ago. They are generally not used by themselves, but as part of a mixed surfactant system. They are cited as alternatives for amine oxide surfactants in bleach-containing cleaners. The examples in the patent literature tend to include cleaning wipe lotions [83,84], spray cleaners [85], carpet cleaners [86], and occasionally a dilutable cleaner [87]. Betaines (alkyl betaines) are popular zwitterionics, and they have found most use in the spray APCs and glass cleaners, often touted as good cleaners that have fewer tendencies to streak. This is especially important with the number of shiny surfaces in the home—stainless steel or black appliances, metal or ceramic sinks, chrome plumbing fixtures, polished stone countertops, and glass panels in cabinets.

Cationics are seldom used in household cleaners except for the quaternary ammonium surfactants (quats), which function as disinfectant agents, especially the ones with a benzyl group attached to the nitrogen. (See Figure 2.3 for structures of commonly used quats.) Cationics are generally inferior to anionics and nonionics in their grease-penetrating and emulsifying abilities, and so their main purpose in household cleaning formulations is for specified benefits like disinfection.

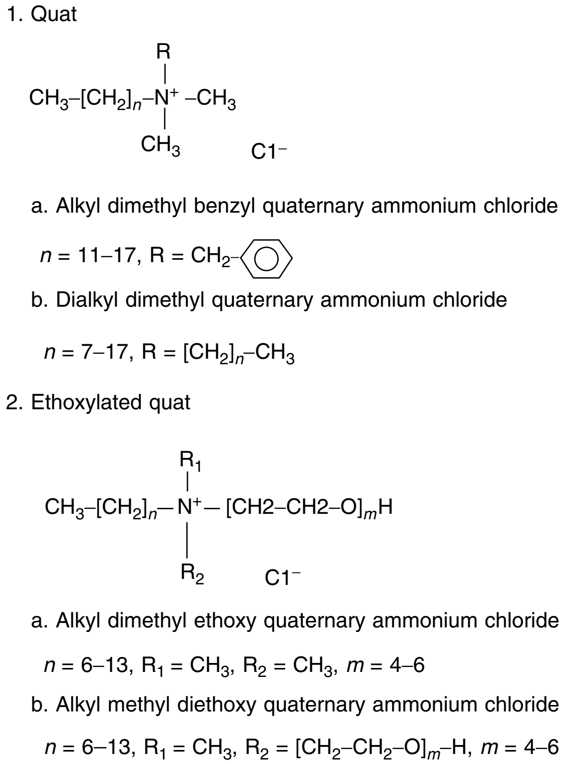


FIGURE 2.3 Structures of common disinfectant quats. 1a, the benzyl quat, is most commonly found in commercial products. Usually a combination of alkyl chain lengths are used in one product.

Quats are the most common disinfectant ingredient. These have the virtues of being effective at relatively low concentrations (0.2–3%), having broad disinfectant action, and having disinfectant action throughout the pH range (although they are less effective at neutral pH). The biggest problem with quats is that they are inactivated by anionic surfactants by forming an insoluble complex. Although this complex can be solubilized by excess anionic surfactant, the disinfectant action is essentially eliminated. As anionic surfactants are the most popular surfactants for household cleaners, this imposes great limitations on the formulator. Although some sources place amine oxides in the cationic category, here they are classed as nonionics.

2.3.3 GENERIC FORMULATION AND TESTING

Formulation always starts with the surfactant system. Considering carefully the target soils and surfaces, one picks the (usually anionic) surfactant appropriate to the cost and efficacy targets. Experimentation with surfactant blends usually yields greater efficacy and greater stability than with a single surfactant. At the current time, it is somewhat unusual (at least in developed-market cleaners) to encounter a formulation based on a single surfactant. Being highly synergistic compounds by their very nature, it is usually better to work with at least two surfactants in a formulation. Degree of synergy often cannot be predicted, and so the importance of experimental design in exploring the performance of the surfactant combinations cannot be underestimated.

One of the most important effects of surfactant synergy in liquid hard-surface cleaners is that the overall concentration of active ingredients can be reduced. More importantly, the amount of adjunct materials—builders, solvents, and the like—that must be added are decreased as the surfactant efficiency and effectiveness is increased due to synergy. While this has the effect of increasing the overall profitability of a formulation for the manufacturer, it also has positive effects for the consumers: less organic compounds in the waste stream, possible greater degrees of biodegradability, and less residue (more shine) on surfaces cleaned. This also has implications for sustainability in the environmental sense, because it makes better use of smaller amounts of petroleum-based surfactants, making greater use of nonpetroleum-based surfactants and reducing the amount of water used for both cleaning and rinsing.

As the surfactant system is being optimized, it is usually combined with whatever adjunct cleaning ingredients are deemed necessary—such as bleaches, solvents, builders, and pH conditioners. These can have influences on the stability and phase behavior of the surfactant mixture, so the formula must be tested not only for cleaning efficacy but also for robustness. At this point, it may be deemed necessary to add the ingredients that encourage various types of stability—such as hydrotropes or solvents (phase stability), preservatives (microbial contamination stability), and chelants (hard water or processing stability). Traditionally aesthetic properties were one of the last concerns of the formulator, and for some products still may be. However, with the increasing performance of formulations across the board, aesthetics become one easy way to differentiate the product for consumers. Dyes and fragrance ingredients are often chemically sensitive, being highly conjugated or unsaturated compounds (in the case of dyes) or aldehydes, ketones, and esters (in the case of fragrances). Stability testing should always include the aesthetic ingredients, as these are often some of the first portions of the formulation to change.

Efficacy testing of APCs often includes a reciprocating motion scrubbing machine. This is cited in many published cleaning methods and patent literature. Greasy soils, which occur regularly throughout the household, are water-resistant, since they are hydrophobic and therefore the *sine qua non* for judging the effectiveness of the surfactant in a cleaner. A search of the patent literature will show that greasy soils are a benchmark soil by which all-purpose cleaning formulations are judged [87–89]. Confirmation of this is found in the methods of the ASTM International [90], where no less than four [91] different grease-containing soils are specified for the testing of floor cleaners. Independent testing laboratories such as those run by Consumer's Union [73,92–94] often use their own soils to do their comparisons of various cleaners. One may quibble with the exact composition of such soils, but the importance of grease or oil as a major component cannot be denied. Tests may also be done of the foaming capacity of the cleaner and, inversely, its ease of rinsing. An *inverted cylinder* test is well known as a way of testing foaming, whereby a solution is introduced into a graduate cylinder, which is inverted a number of times, and the foam amount is generated by this mechanical action noted. Rinsing tests are more various, but generally center around the volume of water needed to completely collapse the foam. Streaking and filming, of the utmost concern in these days of shiny surfaces, can also be tested. The product is applied to a clean surface in a representative manner and then left to dry either with or without rinsing. The result is generally judged by a panel of observers [95,96]. Products can also be tested for their ability to clean a surface without marring it. Usually these tests are simply accomplished by applying the appropriate dose (neat or diluted) of the product to a clean sample of the target surface and observing over time if the surface is changed by this contact. Stability tests are usually run at higher than room temperatures, to try to speed up any reactions that might cause changes in the product [97].

2.4 SURFACTANT EVOLUTION IN HOUSEHOLD CLEANER FORMULATION

2.4.1 The Original All-Purpose Surfactant

Household hard-surface cleaner formulation begins where all cleaning technology begins: with soap. Since the advent of soap making in the ancient kingdoms of the Middle East, soap in its various forms was the single surfactant used for cleaning products. Indeed, the basic principles of making soap and using it have not changed significantly in all that time, although refinements have been introduced. It is convenient that soaps are most stable in alkaline solution, as alkalinity is a contributor to greasy soil removal. However, soap is far from perfect as a detergent.

One difficulty is that soaps are incompatible with neutral or low pH, which causes them to revert to the fatty acids from which they were made. The fatty acid creams out of the aqueous solution and makes little contribution as a surfactant for conventional cleaning. This makes them inappropriate for cleaning surfaces sensitive to higher pHs, where the soaps are stable. In other cases, the soil, such as rust, responds most effectively to acid cleaning. For both of these situations a soap-based cleaner would be inappropriate.

However, the greatest difficulty with soap is its sensitivity to hard water. Hard water is water containing concentrations of salts of various di- and trivalent ions, notably calcium and magnesium [98]. It is usually given in units of either equivalent parts per million or grains per gallon of calcium carbonate. In the United States, *soft water* is usually defined to be <50 ppm $CaCO_3$, with various degrees of hardness then defined up to >250 ppm. Water hardness in Europe can range anywhere from 50 to 400 ppm $CaCO_3$. The relative scales of water hardnesses are shown in Table 2.5 [99–103]. It is instructive that the United States rating of what is *hard* water is significantly lower than the European ratings.

When soap, which is sodium or potassium salt of various fatty acids, comes in contact with hard water, the fatty acids can be precipitated by the multivalent ions, which in high concentration forms *soap scum*. Of course, when soap was the only surfactant available, repeated heavy use of soap-only formulas without proper rinsing made soap scum buildup in hard water areas inevitable. The usual way to mitigate this effect is to formulate soap cleaners with chelants or builders to avoid the interaction with hardness ions. However, in practical use high amounts of builders can also leave mineral deposit on surfaces, visible as a dulling powdery residue if the cleaner is not thoroughly rinsed from the surface.

Today, soap is usually an adjunct surfactant, used in smaller amounts with more hard-water–resistant surfactants as the main cleaning agent. The soap in a modern APC is usually cited in the patent literature as a foam-control agent [104,105], or as part of the thickening system in bleach products [106]. Interestingly, soap, a moderate foaming surfactant itself, can be used to control the foam collapse of other anionic surfactants or anionic/nonionic surfactant mixtures. The use of soap as the main surfactant ingredient is largely restricted to scouring pads [10] and some specialty cleaners, where there is a traditional use of soap. It is also used where extreme economy in

TABLE 2.5
Water Hardness Ratings

Rating	U.S. ppm $CaCO_3$	By French Degrees		By German Degrees		Australia
		°f	ppm $CaCO_3$	°dH	ppm $CaCO_3$	ppm $CaCO_3$
Very soft		0–7	0–70	<4	70	
Soft	<17	7–15	70–150	5–10	90–180	<50
Moderately soft						50–100
Slightly hard	17–60	15–25	150–250			100–150
Moderately hard	60–120	25–32	250–320	11–18	190–320	150–200
Hard	120–180	32–42	320–420	19–30	340–535	200–450
Very hard	>180	>42	>420	>30	>535	>450

Source: http://water.usgs.gov/owq/Explanation.html; http://www.cleanmywater.com/water-hardness-classification-table.html; http://www.globalw.com/support/hardness.html; http://www.unitedutilities.com/?OBH=4050; http://www.aqwest.wa.gov.au/about/faq.asp#9.

the formulation costs is paramount, or manufacturing resources are at a minimum (like the inability to spray dry formulations). Although soap is a manufactured commodity, there are many who consider it more "natural" than other detergents. With the increasing interest in "natural" cleaners and sustainability, it may be that soap-based cleaners may see a resurgence.

2.4.2 ANIONIC EVOLUTION BEYOND SOAP

One of the major motivations behind the invention of detergents was making surfactants that had higher resistance to hard water precipitation. However, the legacy of soap is not soon left behind. Even to this day, anionic surfactants, of which soap is the prime example, play the largest part in the formulation of hard-surface cleaners. Although paraffin sulfonate predominates in Europe, ABS is the workhorse of the APC category over the rest of the world. ABS was embraced for household cleaning almost as soon as it was invented. However, LAS is the surfactant of choice after the ecological imperatives of the 1960s [13] found the biodegradability of the branched varieties insufficient, and branched ABS was banned in most developed markets by 1965. LAS and paraffin sulfonates both show a combination of valuable traits such as soil emulsification effectiveness, low price per pound, chemical stability in a variety of environments, and availability in powder or liquid form. Indeed, in developing nations, a bag of powder product, its surfactant portion made entirely of LAS, is truly an APC: laundry detergent, floor and surface cleaner, and dishwashing product all in one. It also explains why powder abrasive cleaners (powder cleansers) usually use only one surfactant—LAS.

While alcohol sulfates, like sodium lauryl sulfate, are seldom used in household cleaning formulations, ethoxylated alcohol sulfates or alcohol ether sulfates are used more often. The ethoxylated alcohol sulfates like sodium alkyl ethoxylated sulfate have become extensively used in many types of cleaners, often in mixtures with LAS for heavy-duty cleaners, or as the main surfactants themselves in the lighter-duty spray cleaners. They are generally somewhat milder than LAS and paraffin sulfonates, and higher foaming but somewhat less effective at grease removal.

2.4.3 USE OF NONIONIC SURFACTANTS: SYNERGY MAKERS

Nonionic surfactants were invented later than the anionics, but were quickly adopted into household cleaners, where form and cost allow. Nonionics are generally more costly than the standard LAS or soap. In most cases, the properties of nonionics are complementary to those of anionic surfactants. A comparison of the properties of some surfactant types appears in Table 2.6. They are also highly synergistic compounds owing to their lack of a charged head group. Anionic surfactants, by their very nature, are less amenable to synergies (with other anionics) than nonionic surfactants. The characteristic shape of the anionic micelle, spherical, is enforced by the mutual repulsion of the anionic head groups. Nonionic surfactants, on the other hand, are not limited by such repulsion. This facilitates their mixing with other surfactants, particularly the anionics [107]. The addition of a nonionic to an anionic often results (compared to the anionic alone) in more stable foaming, reduced skin irritation, and lower interfacial tensions. Nonionics are also synergistic or complementary with each other. Nonionics of various Hydrophilic–Lipophilic Balances (HLBs) can be blended easily to give systems of a variety of emulsification strengths or compatibilities with various solvents.

Nonionics can function as cosurfactants in microemulsions. This cosurfactant role, which can also be performed by short-chain alcohols or glycol ethers, can make it possible to form microemulsions or other phases from anionic surfactant systems that would otherwise be unreachable in a pure anionic system. By one definition, a microemulsion system is one that achieves a zero or close-to-zero curvature [108]. This is easily achievable in nonionic systems, but very difficult in pure anionic surfactant systems due to the head group repulsions. Mixing the nonionic with the anionic makes these types of systems, which sometimes have greater cleaning ability, easily accomplished.

Nonionics are used extensively in APCs and various specific *grease cutting* cleaners, usually mixed with anionics. Nonionics are also used where low suds are important, such as with upholstery

TABLE 2.6
Comparison of Properties of Some Surfactants

	Anionic			Nonionic		Zwitterionic
Property	**Linear alkylbenzene sulfonate**	**Alcohol ether sulfate (ethoxylated alcohol sulfate)**	**Soap (sodium or potassium salt of fatty acid)**	**Alcohol ethoxylate**	**Alkyl polyglucoside**	**Alkyl betaine**
Cost	Low	Higher	Low	Low	High	High
Foaming	High	High	Moderate	Moderate	High	High
Hardness insensitivity	Moderate	Good	Poor	Good	Good	Good
Emulsification of oils	High	Moderate	Moderate	Moderate	Low	Moderate
Ease of forming nonmicelle phases (liquid crystals, microemulsions)	Low	Low	Moderate	High	Moderate	Low
Mildness to skin	Poor	Moderate	Poor	Moderate	Good	Good
Adjustability of properties	Low	Moderate	Low	High	High	Low

and rug cleaners. However, they are not used in glass or glass-and-surface cleaners because of their tendency to streak. The mechanism of this effect is not well explained in the literature, but is usually accepted as a rule of thumb.

Nonionic surfactants are more *adjustable* in their properties, in the sense that their synthesis allows three adjustable parameters compared to two for anionics. In an anionic surfactant, the head group type can be changed, and the length of the hydrophobic tail can be changed. In a nonionic surfactant, the type of head group can be changed (ethylene oxide, propylene oxide, sugar group, etc.), the length of the hydrophobic tail can be changed, and the length of the head group can also be changed. This means that the HLB of the surfactant can be *tuned* in a way that the HLB of an anionic surfactant cannot.

The most popular group of nonionic surfactants is the ethoxylated alcohols like Neodols®. Ethoxylated alcohols are available in a wide variety of chain lengths and degrees of ethoxylation. Until relatively recently, alkylphenol ethoxylates (APEs), especially the nonylphenols, were also popular choices for cleaners. Whereas branched ABSs caused problems because they did not biodegrade, the problem is exactly the opposite for APEs. The APEs break down into metabolites that display estrogenic properties that are suspected to cause problems with wildlife [109]. They were essentially outlawed in Europe and frowned on by the United State's Environmental Protection Agency. Consequently, formulators have been withdrawing from APEs and increasing turning to the ethoxylated alcohols and to some extent to polyoxyethylene/polyoxypropylene block copolymers, which also function as surfactants.

The largest trend lately in nonionics has been the increasing number of nonionic surfactants based on sugar head groups. This means that these surfactants depend on renewable resources and are also easily biodegraded. These sugar-derived nonionics can be unstable in acid formulations due to acid-catalyzed hydrolysis of the sugar linkages.

Amine oxide surfactants were invented in the 1960s and began to appear in the patent literature in the 1970s. At first there were controversies over widespread use of amine oxides in household and personal-care products because of the small amount of nitrosamines present as by-products of the amine oxide's production. However, better manufacturing processes were found that limited the amount of nitrosamines to the single part per billion range, and the use of amine oxide rapidly increased. Amine oxides are very important in the formulation of bleach-containing formulas, with their superior stability in the presence of hypochlorite putting them ahead of any other surfactant for this use. Amine oxides, however, have also appeared in the patent literature in nonbleach-containing APCs [110–112]. Many of these cleaners contain disinfectant quats or have other special ingredients with which the amine oxide is compatible. They also are reported in combinations with anionic surfactants, boosting grease-cleaning ability, while also increasing skin mildness [113].

2.4.4 Use of Amphoterics

Betaines are the most popular type of amphoterics in household cleaners. Betaines are used in formulations to decrease streaking, most especially glass or glass-and-surface cleaners. Betaines are also synergistic with other types of surfactants, such as anionics and nonionics. Betaines have excellent foaming qualities and skin mildness. So, although they often do not have the cleaning potential of the anionic surfactants, that level of cleaning is not needed for light-duty cleaners like window cleaners.

2.5 SUMMARY

As can be seen from this discussion, most APCs are similar in their composition, being largely based on anionic surfactants and varying amounts of solvent. Delivery systems have evolved more over the past 30 years than the packaging systems used to deliver them. Based on current world political situations and various organizations' emphasis on sustainability, it may be anticipated that the major advances in future formulation will be the use of surfactants less dependent on petroleum than LAS, the current leader in APC formulation [114], and swing in the direction of more "naturally" derived surfactants [115]. Benefits claimed for APCs have advanced from simple cleaning, to stain removal, to disinfection, to more subtle effects like *increased shine*. Health-related claims in the future are already moving beyond disinfection to allergy control. All-purpose claims will continue to evolve in their chemistry as new household surfaces are invented and brought to market (like Formica in the 1920s, Plexiglas in the 1930s, or Corian in the 1970s) or as fabrication methods make formerly luxury surfaces such as polished granite more affordable and therefore more widespread. It is likely that household soils—greasy soils, dusty particulates, food residues—will continue as the problems that frustrate householders in their cleaning efforts, so the basic cleaning chemistry will probably remain constant. The overall trend of APC formulation is to instead increase speed of cleaning, reduce consumer effort, and restore surfaces, as closely as possible, to their original condition, while addressing that newer concern—how to do all this with the greatest sensitivity to the environment.

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3 Dishwashing with Detergents

Joan Gambogi, Sharon Kennedy, and Edna Ambundo

CONTENTS

3.1 INTRODUCTION

The primary function of dishwashing detergents is to clean a wide range of tableware, including dishes, glasses, utensils, pots, and pans. Many consumers use both hand dishwashing and automatic dishwashing detergents depending on the situation. Hand dishwashing is common for homes without automatic machines, hard-to-clean items such as pots and pans, fine crystal and china, large items, and in situations where there are not enough items to fill a load. Automatic dishwashing is

TABLE 3.1
Market Size of Hand and Automatic Dishwashing Detergents (Retail Value in U.S. Dollars at Fixed Exchange Rates)

Dishwashing Detergent Market	Size (Millions $, 2005)	Growth (1997–2005) (%)
World hand	6,404.4	33.5
World automatic	3,045.2	71.0
United States hand	875.1	−3.3
United States automatic	727.7	25.6

Source: Euromonitor International, 2007.

considered to be more convenient, involves less labor, provides a higher level of sanitization, and potentially utilizes less water.

Dishwashing detergents are a large and growing market throughout the world. As shown in Table 3.1, combined hand and automatic dishwashing detergents total almost $10 billion in retail sales worldwide. Currently, the bulk of worldwide sales come from hand dishwashing detergents; however sales figures show that automatic dishwashing detergents are growing at a faster rate, globally and in the United States. In the United States, automatic detergents have nearly caught up to hand dishwashing detergents and given the growth rate will potentially surpass them in the near future.

Hand and automatic dishwashing formulations differ greatly in large part due to the mechanism of cleaning in each process. In the case of washing dishes by hand, surfactants play a primary role in cleaning. Premium dishwashing liquids typically contain >30% surfactants. The surfactants are typically anionic and nonionic or amphoteric, and are chosen so as to provide grease cleaning, stuck-on food removal, long-lasting foam, and mildness. In automatic dishwashing, the primary cleaning comes from hot water spraying through the rotating arms and the detergent ingredients such as builders, bleach, and enzymes. Nonionic surfactants are used to reduce the surface tension of water; however they must be very low foaming, so as not to impede or stop the rotation of the arms.

There are a number of reviews published recently describing dishwashing detergents formulation,[1] liquid automatic dishwasher detergents,[2] and light-duty liquid detergents (LDLDs).[3] Outside of these and other review articles, the bulk of the technical development of dishwashing detergents is found in the patent literature. Patent reviews are also given in two of the previously mentioned reviews.[2,3]

In this chapter, we provide an overview of both hand and automatic dishwashing detergents, highlighting in particular the important role that surfactants play. Some of the information presented here has been discussed in other literature, but we have also tried to highlight technologies that have been developed and reported in the literature over the past 3–5 years.

3.2 HAND DISHWASHING DETERGENTS

3.2.1 HISTORICAL PERSPECTIVE/EVOLUTION

In early history only limited numbers and types of dishes and cookware were used, and people had very limited access to water. Dirty items were carried to streams and ponds for cleaning, or alternatively the water was carried to the home. This changed with the advent of indoor plumbing, which was installed in most homes by the 1930s, vastly simplifying the cleaning process. The first liquid hand dishwashing detergents were developed in the 1940s, and this remains the predominant form today. A typical liquid hand dish formulation and the role of each ingredient is shown in Table 3.2.

TABLE 3.2
Typical Liquid Hand Dishwashing Formulation

Ingredient	Amount (wt%)	Purpose
Surfactants	1–50	Cleaning, foaming
Hydrotrope	0–10	Phase stability, solubility
Salts	<3	Viscosity control
Preservative	<0.5	Microbial stability
Fragrance	0.1–1	Aesthetics
Dye	<0.5	Aesthetics
Other additives (chelants, antibacterial agents, enzymes, divalent ions, UV stabilizers)	0–3	Specific benefits
Water	Balance	Carrier vehicle

TABLE 3.3
Examples of Liquid Hand Dishwashing Formulations (1974 and 2003)

Example Formulation Taught by U.S. Patent 3793233 (1974 P&G)		Example Formulation Taught by U.S. Patent 6506719 (2003 Colgate)	
Ingredient	**Amount (wt%)**	**Ingredient**	**Amount (wt%)**
Ammonium alkyl sulfate-EO6	18	Mg linear alkyl benzene sulfonate	9
Ammonium alkyl sulfate	4	Na linear alkyl benzene sulfonate	3
Sodium alkyl glyceryl ether sulfonate	4	Ethoxylated alkyl ether sulfate	11.5
Coconut alkyl dimethyl amine oxide	5	Zwitterionic (cocopropyldimethyl betaine or cocoamidopropyl amine oxide)	5
Miscellaneous and water	Balance	Polyalkylglucoside	9.5
		Miscellaneous and water	Balance

An early hand dishwashing detergent is compared to a more recent formulation in Table 3.3. From this comparison one can see that the basic components have not changed much over the years. It is clear that surfactants have been and continue to be the most important ingredients, responsible for cleaning and foaming.

3.2.2 HAND DISHWASHING SURFACTANTS

Surfactants are the primary component of hand dishwashing liquids and are responsible for all of the product performance attributes. Hand dishwashing liquids are referred to as LDLDs and are primarily mixtures of surfactants dispersed in water. As opposed to heavy-duty liquid detergents (HDLDs), they are free of builders or alkaline inorganic salts. LDLDs are used primarily for hand dishwashing of dishes, glasses, pots and pans, and other cooking utensils. They can also be used for washing of hands, cleaning of kitchen countertops, cutting boards, stove surfaces and, less often, for the washing of delicate fabrics and general household cleaning. LDLD consumers expect the hand dishwashing products to clean, foam, and be mild to their hands. In addition, many consumers have come to desire long-lasting foam, pleasant fragrance, appealing appearance, ease of rinsing, safety for dishes, safety for consumers and the environment, convenient packaging, and of course a good value.

Surfactants are generally classified according to the charge on the polar head group. For example, anionic surfactants, such as sodium dodecyl sulfate (SDS), have a negative charge. Nonionic surfactants, such as long-chain ethoxylated alcohols, have no charge on the head group. Zwitterionic surfactants carry both negative and positive charges, an example being betaine, whereas cationic surfactants have positively charged head groups. An example of a common cationic surfactant is cetyl trimethyl ammonium bromide (CTAB). The most common surfactants used in hand dishwashing are anionics, with lesser amounts of secondary nonionic and zwitterionic surfactants. For automatic dishwashing, nonionic surfactants are predominantly utilized.

There are several important physical and chemical parameters that characterize a surfactant and determine how it will perform in a dishwashing detergent. These parameters include its critical micelle concentration, ability to pack at an air, oil, or solid interface, and ability to lower interfacial tension. Yet another important parameter is the extent to which various surfactants interact with each other to provide synergistic benefits. These fundamental characteristics determine how well the surfactant or surfactant mixture will remove grease, how well it will foam, and even how irritating/mild it will be on hands.

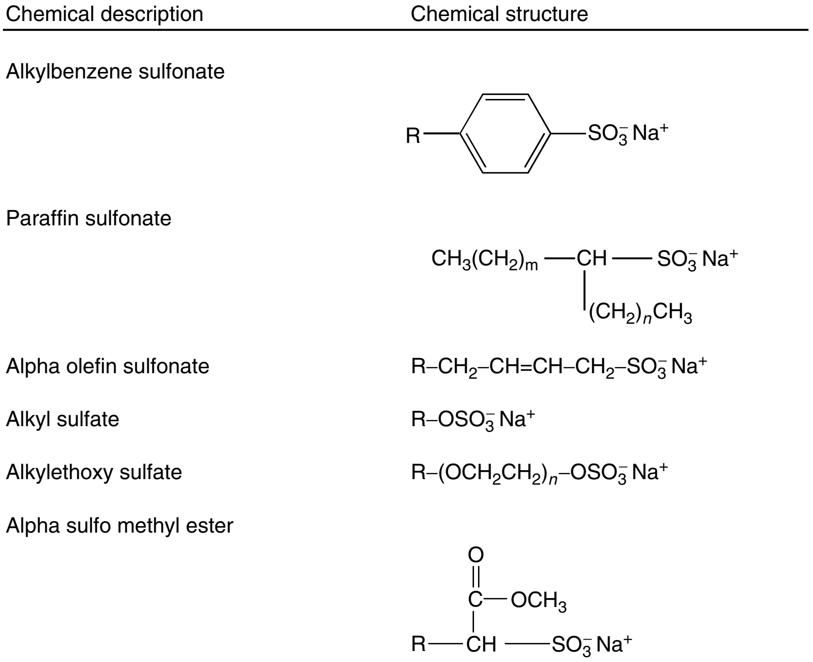
Hand dishwashing liquids are expected to clean all types of soils from dishware, have copious long-lasting foam, be mild to hands, and have a pleasant fragrance. These primary functional attributes are a result of the surfactant mixture used in the product. An excellent review of all types of surfactants used in detergents and their properties and applications is given in Ref. 4. The major surfactants utilized in hand dishwashing liquids are described here.

3.2.2.1 Cleaning and Grease Removal

The primary purpose of using a dishwashing detergent is to clean food remains off of dishware and cooking utensils. This soil removal process can occur via several mechanisms, including roll-up, emulsification, direct solubilization, and formation of microemulsion or liquid crystalline phases. It is hypothesized that solid inorganic soils are removed through a wetting and suspension mechanism, whereas solid organic soils, such as grease, are broken up and suspended in the water bath by the detergent.

There are numerous test methods described in the literature for evaluating the cleaning performance of a dishwashing detergent. Since greasy soils are the most common consumer complaint in this category, it should come as no surprise that the majority of dishwashing test methods are directed toward grease removal. Greasy soil removal can be measured in a static soak test such as, for example, described in the patent literature.[5,6] Grease removal is determined by the weight difference of a soiled surface before and after soaking in a product solution. Another test methodology for grease removal incorporates mechanical action.[7,8] In this test, greasy soil is spread onto glass slides or plastic tubes, which are subsequently dipped multiple times into diluted dishwashing detergent; grease removal is determined by the difference in weight. The Gardner washability apparatus, typically used to test cleaners, is sometimes used to evaluate hand dishwashing liquids. Performance tests with this apparatus are conducted under fixed time, soil, pressure, and sponge-stroke settings and the end point is quantified visually or by means of a turbidity reading[9] or glossmeter,[10] for example.

As mentioned previously, anionic surfactants make up the bulk of hand dishwashing liquid formulations because of their excellent cleaning and foaming properties, low cost, and availability. The anionic surfactants that are typically used have either a sulfonate (SO_3^-) or a sulfate (OSO_3^-)



where R is C_xH_{2x+1} and x is typically in the range of 12–18.

FIGURE 3.1 Structures of common anionic surfactants.

head group. In the case of the sulfonates, the sulfur atom is linked directly to the carbon chain, whereas the sulfates are connected via an oxygen atom. The C–O–S bond is more prone to hydrolysis, whereas the C–S bond is more stable and can be stored in a concentrated sulfonic acid form. Some common sulfonates are linear alkylbenzene sulfonate (LAS), alpha-olefin sulfonate (AOS), and paraffin sulfonate (PS, also referred to as secondary alkane sulfonate). Typical sulfate surfactants include alkyl sulfate and alkylethoxy sulfate (AEOS), which differ only by ethylene oxide groups. Alpha sulfo methyl ester (ASME) is an example of another anionic surfactant used on a limited scale. In U.S. hand dishwashing liquid products, LAS and AEOS are the most common anionic surfactants, whereas PS and AEOS are more prevalent in European formulations. The structure of these anionic surfactants that contribute to grease cleaning is illustrated in Figure 3.1 and described briefly.

3.2.2.1.1 Linear Alkylbenzene Sulfonates

LAS is the most widely used surfactant in the world. It is considered to be a workhorse for LDLDs because of its exceptional cost–performance profile, proven safety for humans, and environmental acceptability. LAS was first commercialized in the early 1960s as a replacement for branched alkylbenzene sulfonate, which was poorly biodegradable. LAS has a linear alkyl chain with the benzene ring randomly distributed in all positional isomers except 1-phenyl. In all cases, the sulfonate group is in the para position. This type of surfactant displays excellent cleansing/degreasing and foaming ability and is not greatly affected by water hardness, since its calcium and magnesium salts are water soluble. The primary disadvantage of LAS is its tendency to irritate the skin unless formulated with other ingredients designed to reduce skin irritation.

Some recent patents describe the use of modified alkylbenzene sulfonate surfactant mixtures.[11,12] The modified LAS is synthesized to contain some branching in the alkyl chain, while attempting to maintain the required biodegradability. It is claimed that using mixtures that contain branched

LAS results in products with better cold-water performance, and improved product stability and cleaning in hard water.[13,14]

3.2.2.1.2 Alpha Olefin Sulfonates

The primary commercial form of AOS is sodium C14-16 olefin sulfonate. AOSs have properties comparable to LAS and may be used in its place in many formulations, resulting in improvements in biodegradability, mildness to skin, foaming, and detergency. Additionally, AOSs also exhibit excellent foaming and detergency in hard water and are reasonably priced. They are primarily used in Asia for heavy- and light-duty laundry detergents and soap bars, and have also been used in the United States in several personal care products.

3.2.2.1.3 Secondary Alkyl Sulfonates

Paraffin sulfonates are highly water-soluble surfactants. These surfactants are good foamers and also act as excellent oil-in-water emulsifiers. They are primarily used in Europe in HDLDs and LDLDs, as well as in some all-purpose cleaners.

3.2.2.1.4 Alkyl Sulfates

Alkyl sulfates are produced commercially from either linear synthetic or natural alcohols. As mentioned before, the oleochemical fatty alcohols have even-numbered carbon chains, whereas the petrochemical-based fatty alcohols have both odd- and even-numbered carbon chain distributions. There are, however, no differences noted in the performance or physical properties of formulations made from oleochemical versus petrochemical sources.[15]

3.2.2.1.5 Ethoxylated Alkyl Sulfates

Ethoxylated alkyl sulfates are also called alkyl ether sulfates (AES) or AEOSs. After LAS, ethoxylated alkyl sulfates are the most important anionic surfactants in terms of production volume and product value.[16] There is usually, at least in commercial grade materials, a large distribution in ethoxylation degree. Ethoxylated alkyl sulfates have the advantage of greater water solubility and better foam stability in the presence of electrolytes, hard water, and protein as compared to alkyl sulfates.[14] They are milder to the skin than alkyl sulfates, and increasing the degree of ethoxylation has been found to reduce skin and eye irritation.

3.2.2.1.6 Alpha Sulfo Methyl Esters

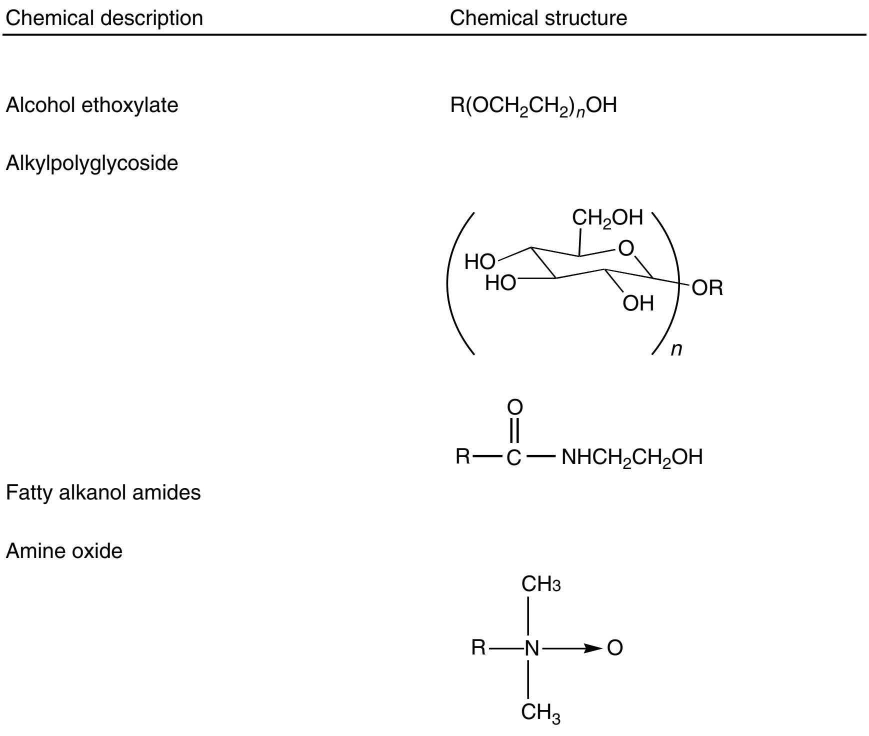
ASMEs have excellent detergency and are also potential substitutes for LAS.[13] These surfactants have not been used widely in hand dishwashing detergents thus far, presumably because of their cost and availability.

3.2.2.1.7 Nonionic Surfactants

The structures of some common nonionic surfactants are shown in Figure 3.2. Ethoxylated alcohols are produced from the reaction of fatty alcohols with ethylene oxide, which results in a broad distribution in the number of EO units per molecules. These surfactants are generally excellent detergents, very mild, and less sensitive to water hardness ions, and also act as solubilizers. A typical ethoxylated alcohol used in LDLDs has approximately 9 EO units and a carbon chain length distribution centered around C11.

In general, nonpolar (oily) soil is removed from hydrophobic substrates by polyethylene oxide nonionics better than by anionics. Also, nonionics are found to remove oily soils better than anionics at lower temperatures, due to lower CMC, and are generally better at preventing soil redeposition because of the greater surface area covered per molecule when adsorbed on substrate or soil.[14]

The correlation between the structure of a surfactant and its ability to clean and cut grease is complicated. This is due to the complex nature of hand dishwashing detergents and the huge variability in cleaning methods, water temperature and hardness, product use concentrations, and types of substrates and soils. The detergency or cleaning power of the dishwashing liquid is accomplished



where R is C_xH_{2x+1} and x is typically in the range of 12–18.

FIGURE 3.2 Structures of common nonionic surfactants.

by having the right combination of surfactants. The liquid must adsorb at interfaces, lower interfacial tension, solubilize and emulsify grease, and prevent redeposition. Some general comments on choosing the right type of surfactant or surfactant structural features are listed as follows:

- Detergency generally increases with an increase in length of the hydrophobic group, until solubility limits are reached.
- The presence of electrolytes enhances the performance of ionic surfactants by lowering the CMC. The lower the CMC the better the performance.
- An increased temperature often helps ionic surfactants.
- Anionics have very good detergency with respect to particulate soil, but nonionics can be superior at grease removal.
- An aromatic group can cause an increase in adsorption on polar surfaces but also loosens packing at interfaces.
- For optimum surfactant adsorption at solid/liquid interfaces, mixed micelles have more efficient packing, which in turn contributes to better detergency by lowering the CMC and interfacial tension.

3.2.2.2 Foam Performance

Foam is not in itself necessary for hand dishwashing efficacy. Instead, it is an attribute that consumers have come to expect and often equate with a product's cleaning ability. Dishwashing detergents need to provide foam in great amounts (foam volume) that is stable and long-lasting in the presence of food soils (foam longevity). Often the surfactant that provides the most foam volume is not the same as that which contributes to longevity.

The standard test for measuring foam volume has long been the Ross-Miles foam test (ASTM D1173-53).[17] In this test, foam is generated under low agitation and controlled conditions, and both foam formation and foam collapse are assessed. Modifications of the principles of this test allow for quicker or simpler test procedures. For example, foam volume can be measured simply by inverting a graduated cylinder containing the diluted product.[8]

Foam longevity has been measured by manual plate washing.[18] Dishes of equal size are soiled with an artificial soil, for example, beef tallow, a mixture of fat, starch, and protein, and then washed in detergent solution under fixed conditions until the foam collapses. A miniature version of plate washing has also been established; it utilizes small watch glasses.[19] The Shell test is yet another method that is used to evaluate the foam performance of light-duty dishwashing liquid in the presence of soil.[20] In this test, foam is generated in a vessel by stirring a diluted solution of the test product. Foamicidal soil is then titrated into the vessel, under constant-rate stirring, until a point where foam is no longer observed.

Many anionic surfactants listed above have excellent foaming characteristics, for example, ethoxylated alkyl sulfates, LAS, and PS. In addition, certain nonionics are often added to increase the foaming performance. Several of those nonionic surfactants are described in the following sections.

3.2.2.2.1 Amides

Mono ethanol amides, in particular lauryl myristyl mono ethanol amide (LMMEA), have found use in dishwashing formulations as foam boosters (structure shown in Figure 3.2). Alone, they have very poor water solubility at room temperature, but when used in small amounts in combination with anionic surfactants, they contribute to the stabilization of foam that would otherwise collapse in the presence of grease or oils. Mono ethanol amides are also excellent viscosity builders.

3.2.2.2.2 Amine Oxide

Amine oxides constitute another important class of nonionic surfactants. Examples of these surfactants include dimethyl dodecyl amine oxide (DMDAO) and cocoamidopropyl dimethyl amine oxide (CAPAO). This type of surfactant is nonionic at pHs above its pK_a and cationic below that point. When functioning as a nonionic, amine oxides have many useful properties. They interact strongly with anionics, which can result in performance benefits.[21] Amine oxides help to mitigate anionic surfactant irritation, act as foam stabilizers, and can also function to improve grease removal.

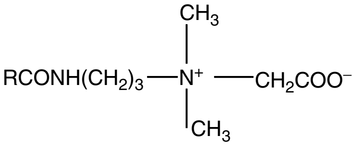
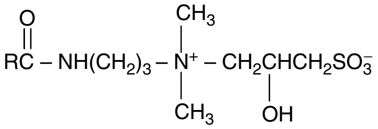
Amphoteric surfactants are surfactants that, depending on the pH, can have either anionic or cationic properties. They also have an isoelectric point at which they possess zwitterionic character. These surfactants are typically compatible with anionic, nonionic, or cationic surfactants. The structure and properties of two amphoteric surfactants used in hand dishwashing formulations are shown in Figure 3.3.

3.2.2.2.3 Betaines

Betaines are zwitterionic at neutral and alkaline pHs. At acidic pHs, below the isoelectric point, they are strictly cationic. They are generally compatible with both anionic and cationic surfactants except at low pHs, where they are incompatible with anionic surfactants. The most interesting properties of betaines are derived from their strong interactions with other surfactants, in particular anionics. Studies on reported synergistic properties of betaines and anionics have been published by Rosen and coworkers.[22,23] When betaines are used as a secondary surfactant with anionic surfactants, the mildness, foaming, and viscosity properties of the formulation are all improved.

3.2.2.2.4 Hydroxysultaines (Sulfobetaines)

Sulfobetaines function similarly to betaines. They differ structurally in that the anionic site is a sulfate group in place of a carboxylate. They also differ in performance in that they are zwitterionic at all pHs and are known to be extremely mild and provide a rich, creamy foam.

Chemical description	Chemical structure
Cocoamidopropyl betaine	 $RCONH(CH_2)_3-N^+(CH_3)_2-CH_2COO^-$
Hydroxysultaines (sulfobetaines)	 $RC(=O)-NH(CH_2)_3-N^+(CH_3)_2-CH_2CH(OH)CH_2SO_3^-$

where R is C_xH_{2x+1} and x is typically in the range of 12–18.

FIGURE 3.3 Structures of two amphoteric surfactants for hand dishwashing formulations.

Choosing the right surfactant or surfactant combination that can deliver a desired foam profile is often done on a trial-and-error basis. As mentioned previously, often the surfactant structure that improves foam volume is not the same as that which contributes to foam stability. Some general guidelines about surfactant structure and optimum foam performance are listed as follows:

- Foaming performance goes through a maximum as chain length increases (C12 peak) for a homologous series. Longer chain length leads to a lower surface tension and lower CMC; however, a chain that is too long has reduced solubility, slow diffusion, and limited adsorption.
- Branched chains generally can have higher initial foam height but reduced foam stability. This is due to a more rapid lowering of surface tension, but the reduced packing ability at the interface leads to reduced film elasticity.
- Ionic surfactants help film formation and stabilization due to disjoining pressure.
- Added electrolyte is important for ionic surfactants and has an optimum level. Adding electrolyte reduces the CMC and increases packing of the surfactants, which is good for foaming, but high levels of electrolyte reduce disjoining pressure, which leads to less film/foam stability.
- Nonionic surfactants generally have less initial foam and less stability. The large surface area/molecule leads to lower interfacial elasticity, and the big bulky head groups are slow to diffuse to new interfaces.
- For nonionic surfactants near their cloud point, foaming is diminished.

3.2.2.3 Mildness

The third important performance property of a hand dishwashing liquid is mildness. The hands spend a lot of time in contact with the surfactant system either neat or diluted in a warm solution. Negative signals to the consumer include dryness, inflammation, redness (erythema), or swelling (edema).

Mildness or lack thereof of dishwashing products can be assessed by both *in vitro* and *in vivo* methods. *In vitro* methods are useful to prescreen formulations, since they are easy to perform and inexpensive, and give an indication of how the formulation will perform in an *in vivo* test. The most common *in vitro* methods are based on protein denaturation[24,25] or—as is the case in the zein test[26]—solubilization of zein (Indian corn protein). There is yet another *in vitro* test that is based on swelling of a collagen film.[27] In contrast, *in vivo* testing includes hand immersion. Panelists immerse their hands in products under various controlled conditions. The condition of the hands is then evaluated either by the panelists themselves, by trained clinicians, or via instrumental measurements. The Frosch–Kligman soap chamber test is an example of an *in vivo* test that is used to evaluate the mildness of surfactant-based products.[28] In this and similar patch tests, multiple products are usually patched onto panelists' forearms for a set treatment time, after which the sites are evaluated for redness and dryness.

Surfactants interact with skin, specifically the stratum corneum, in many ways. They have been reported to bind to proteins in the stratum corneum membrane, inducing swelling in the process.[29] Binding of surfactant sodium lauryl sulfate (SLS) to skin has been studied, and the results of such investigations are similar to a Langmuir isotherm, leveling off near the CMC.[30] Data collected supports the hypothesis that it is the surfactant monomers, and not micelles, that bind to the skin. Therefore, surfactants with lower CMC are likely to induce less surfactant binding. Another response of the skin is membrane swelling.[29] Again, the data suggests that monomers, not micelles, are responsible for swelling. Studies have reported that maximum swelling is induced by C12 or C14 alkyl chain length in a homologous series.[31] It has been postulated that this is due to a balance between an increase in hydrophobicity with increasing carbon chain lengths and a decrease in penetration ability. Ethoxylation of alkyl sulfates reduces swelling, as does the presence of divalent cations. In general, nonionic surfactants exhibit little substantivity to skin.

There are several approaches utilized to develop skin-friendly dishwashing formulations. The first approach is to select mild surfactants. Some examples of mild surfactants are the ethoxylated alcohols, alkyl polyglucosides, and although not commonly used in dishwashing detergents, sulfosuccinate esters and isethionates.

The second approach used to develop mild formulations is to mitigate irritation caused by harsher anionics by taking advantage of surfactant interactions. Mixing a mild surfactant with a harsh one can significantly lower the irritation beyond what is expected by simple additive rules. This reduction in irritation can be explained by synergistic lowering of the CMC of the mixed micelles, resulting in lower monomer concentrations. Alternatively the mild surfactant may compete with the more irritating surfactant for binding sites on the strateum corneum.

Another approach to incorporating mildness is to add special ingredients that are designed to improve skin feel or combat dryness and irritation. This approach is not widely used because of cost constraints; however, some examples of ingredients that might be used include aloe, polyquaternium-7, protein, or enzymes. It should be noted with this approach that though the actual or clinical irritation maybe unchanged, the consumer perception or sensory experience is usually altered.

In summary, some ways to increase mildness of a hand dishwashing detergent are to

- Select mild surfactants
- Recognize that C12 or C14 carbon chain lengths are typically most irritating
- Lower the CMC of the surfactant mixture
- Drive milder surfactants to interfaces while keeping more irritating surfactants in micelles
- Add special skin-enhancing ingredients

3.2.2.4 Safety and Environmental Considerations

It is required that dishwashing detergents be safe in the consumers' hands and not damaging to the environment. Safety encompasses nonsensitizing and nonirritating formulations as well as important environmental parameters such as biodegradability, aquatic toxicity, and bioaccumulation. Since most surfactants used in households end up in the sewage, the rate of biodegradability at the sewage plant determines the amount of surfactant that reaches the environment. Bioaccumulation is usually not a critical issue for the vast majority of surfactants.

Biodegradability is carried out by bacteria through enzymatic reactions. The surfactant molecule is reduced to CO_2, H_2O, and oxides. The rate of biodegradation depends on the surfactant's structure. Some important surfactant requirements for adequate biodegradation include reasonable water solubility of the surfactant and its decomposition intermediates. It is desired that the surfactant contain some bonds that can easily be broken down by enzymatic catalysis, so-called cleavable surfactants.[32] A weak bond can actually be built into the structure to ensure fast degradation and is typically placed between the head and tail group. A third important structural aspect for consideration in biodegradation is branching. It is known that extensive branching in the hydrocarbon chain is not good for biodegradation, and this may be due to steric hindrance as well as other factors.

The biodegradability and safety of LAS have been studied, and the data have been compiled by the Council for LAB/LAS Environmental Research.[33] The database they have established for LAS is more extensive than on any other surfactant. The studies have shown that LAS is rapidly biodegradable under aerobic conditions and can degrade under oxygen-limited conditions. Anaerobic conditions are much more difficult for biodegradation of many surfactants.

3.2.3 Typical Applications

The main application of hand dishwashing detergents is to wash dishes by hand. Liquid products can also be used for washing cars, fine laundry, kitchen countertops, and hands. Consumer habits and typical washing procedures vary widely with hand dishwashing. Some of the variables are amount of product used, water temperature, water hardness, use of implements, type of soil, dish surface properties, and time.

3.2.3.1 Washing Methods

Dishwashing habits are very diverse and can vary greatly according to the individual, geography, local culture, lifestyle, size of household, and nature of the food prepared. Methods of dishwashing are typically divided into two categories: neat (i.e., concentrated) and dilute. Neat dishwashing refers to the practice of placing the dishwashing liquid directly on the item to be washed or directly on the washing implement (sponge, brush, dishcloths, etc.). Dilute dishwashing is the practice of filling a tub, sink, or pot with water and adding the dishwashing liquid to make a solution. The dishes are either submerged in the bath all at once or submerged one at a time and then washed. For hard-to-clean and baked-on grease soils, dishes can also be soaked. One or two squirts of the product are added directly to the cookware, filled with hot water, and left to soak for a period of time. After soaking, the items are cleaned with much less effort, since the soils have been loosened. The reality is far less simple, with many consumers using a combination of these methods to wash, depending on the situation.

3.2.3.2 Multifunctional Benefits

As in section I, the primary purpose of hand dishwashing liquids is to clean the dishes, specifically to remove food and grease soils. Secondary critical benefits are foaming, mildness, and safety. Different products have been launched throughout the world with other added benefits. Some examples are shown in Table 3.4.

The first liquid hand soap and hand dishwashing liquid product that offered long-lasting antibacterial protection on hands was introduced in 1994 by Colgate-Palmolive. The antibacterial ingredient was triclosan, and the product delivered the advertised efficacy as documented in clinical and laboratory testing. This type of product quickly became an important segment of the U.S. dish market.

TABLE 3.4
Claimed Benefits of Hand Dishwashing Liquids

Product	Claimed Benefit
Palmolive Spring Sensations, Dawn Botanicals	Fragrance and pleasant experience
Palmolive Sensitive Skin, Palmolive Dry Skin with Aloe	Skin mildness, gentle on dry and sensitive skin
Dawn Complete, Dawn Plus Hand Care	Improves hands
Palmolive Dish Liquid & AB Liquid Hand Soap; Dawn Dishwashing Liquid and AB Liquid Hand Soap	Antibacterial on hands
Palmolive Oxy Plus Odor Eliminator, Dawn Odor Eraser	Eliminates unwanted cooking odors
Dawn Oxi	The power of active oxides
Dawn with Bleach Alternative	Powers away unseen food residue
Axion Trichloro	Eliminates stains, odors, and bacteria
Palmolive Scrub Buster with Microbeads	Busts away stuck-on food

In 2000 and 2001 sensorial dishwashing liquids were launched in the United States. Colgate-Palmolive introduced the Spring Sensations line in the spring of 2000 and Procter & Gamble followed with Joy Invigorating Splash and Tropical Calm and Dawn Fresh Escapes. Following the lead from personal care products, aromatherapy dishwashing liquids were launched next. This type of dishwashing liquid offers the consumer a pleasant dishwashing experience, in addition to the cleaning. A step beyond pleasant fragrance are the products that claim to eliminate unwanted cooking odors (Palmolive Plus Oxy Odor Eliminator).

Future lifestyle and consumer product trends may influence the direction of new hand dishwashing liquids. Some important trends prevalent now are environmentalism, health and wellness, and convenience, as well as the growing number of aging consumers in certain geographies. A new benefit or product claim that seems to be gaining some momentum and appeals to the trend of environmentalism is the advent of natural or naturally derived products. Some examples of these include: Seventh Generation Natural Dish Liquid, Earth Friendly Products Ultra Dishmate, Mrs. Meyers Liquid Dish Soap, and Sun and Earth Ultra Dishwashing Liquid. This segment is rapidly growing across all household cleaners, as well as personal care products. For hand dishwashing liquids, the claims and benefits center on naturally derived cleaning agents (nonpetroleum-based) and ingredients safe for the environment. Other product claims are being biodegradable, hypo-allergenic, and not tested on animals in the case of Seventh Generation.[34] For Earth Friendly Products, similar claims are made such as being nonpolluting, nontoxic, and made of replenishable/sustainable ingredients, and having an easy-to-recycle container.[35]

3.2.4 FORMS AND SPECIALTY PRODUCTS

3.2.4.1 Product Forms

Liquids are the predominant form of hand dishwashing products in developed countries. Recently a product form was introduced by Proctor & Gamble (P&G) in the United Kingdom in 2005 with the launch of Fairy Active Foam. This launch was followed by U.S. launches of Dawn Direct Foam and Palmolive Oxy Plus Foam. Most foaming dishwashing products utilize a pump dispenser that incorporates air into the product as the pump is depressed. The foam form offers advantages to the consumers such as an easy-to-use pump that saves time and reduces messiness around the cap.

3.2.4.2 Specialty Products for Hand Dishwashing

Through the years different specialty products have been sold to be used either in conjunction with a normal hand dishwashing liquid or as stand-alone products. Some of the specialty products that have been sold in the United States include

- Palmolive Dish Wipes (Colgate-Palmolive)
- Dawn Wash & Toss (P&G)
- Dawn Power Dissolver (P&G)
- Palmolive Super Scrub Gel Paste (Colgate-Palmolive)
- Dawn Power Dish Brush (P&G)

For the most part, these specialty products have not gained a large market share and consumers predominantly continue to wash their dishes by hand using traditional liquid products.

Specialty products, however, have the potential to add an element of convenience to the dishwashing process, which may be desirable to the busy consumer. Some interesting product ideas have appeared in the patent literature. One pending patent application is directed to a method of cleaning cookware by applying a composition that forms a film on the soil.[36] The film is then removed, leaving a clean surface. An issued patent is directed to an in-sink dishwasher.[37] Small, portable devices like this may appeal to the consumer who does not have enough dishes to fill a full size machine or cannot afford one. Another patent describes cleaning products that use ultrasonic waves.[38] This patent alleges that the combination of ultrasonic waves with cleaning agents such as enzymes and bleach catalysts leads to superior cleaning. For many busy consumers, easing cleaning chores is welcomed.

3.3 AUTOMATIC DISHWASHING DETERGENTS

The automatic dishwashing segment is growing at a very rapid pace. In terms of market penetration, it has been reported that the number of American households with dishwashers is 56.5%, whereas those with refrigerators is 98% in spite of the fact that both appliances were introduced into the market about the same time.[39] This trend also holds true in established European markets like Germany and the Netherlands, where the estimate for dishwasher ownership is ~50% and only about 27% in the United Kingdom.[40] With continued improvements in dishwashers and the automatic dishwashing detergents (ADDs) they employ, it is easy to envision continued growth in this segment.

Automatic dishwashing can offer a number of benefits to the consumer, including convenience and sanitization. For instance, a study by the University of Louisville School of Medicine showed that the average bacteria count for all machine-washed dishes was <1 per plate, whereas bacteria count on dishes washed by hand during the same test averaged 390 per plate.[41] This result is presumably due to the fact that bacteria gets trapped in working surfaces, dishcloths, sponges, and dishtowels, and this increases the amount of bacteria found on dishes washed by hand. Machine-washed dishes typically meet the standard set by U.S. health authorities of <100 counts per plate, and therefore automatic dishwashing is the method required by law to clean dishes in hospitals and other service institutions in the United States.

In the past 10 years there have been a number of reviews that describe automatic dishwashing detergent formulations and their ingredients.[1,42–44] Shi et al.[1] provide a summary of ADD compositions, applications, and patent activity for the period from 1990 to 2004. In this section, some of the information presented already will be revisited, but the bulk of this review is dedicated to technologies that have been developed and reported in the patent literature over the past 3–5 years. The last part of the review will discuss the current environmental concerns and the future of automatic dishwashing detergents.

3.3.1 HISTORICAL PERSPECTIVE/EVOLUTION

The modern-day dishwasher descended from the 1886 hand-powered invention of Josephine Cochrane.[45] This invention was presented at the 1893 Chicago World Fair, and permanent models with plumbing began to be installed in homes in the 1920s. The first automatic dishwashing machines were not efficient enough to completely eliminate hand work; however, their lack of acceptance at that time was largely attributed to the unavailability of soaps tailored for these machines. In the 1950s, special dishwashing soaps had started to be developed. These products cleaned without excessive sudsing and were easily rinsed away. It was then that the dishwasher started to gain in popularity.

By 1953, sales of detergents in the United States had surpassed those of soap. Now detergents have all but replaced soap-based products for dishwashing and household cleaning. Since those early achievements in detergent and builder chemistry, new product activity has continued to focus on developing automatic dishwashing detergents that are efficient and easy to use, as well as safe for consumers and the environment. A timeline of evolution for automatic dishwashing detergents is provided in Table 3.5.

3.3.2 CLEANING WITH AUTOMATIC DISHWASHERS

When a consumer washes their dishes or tableware using an automatic dishwasher, their expectation is that their utensils will be clean in appearance once the process is complete. It is also expected that the machine-washed tableware will be completely free from food residues, spots, and white residues that result from hard water stains and other mineral salts. These consumer expectations are not always met because of various problems associated with automatic dishwashing. These are summarized in Table 3.6.

Since the introduction of the first dishwashers, formulators and detergent producers have been designing formulations and products aimed at addressing the issues described above. The next section of this review will summarize the chemistries and technologies that have been developed to resolve these issues and meet consumer expectations.

3.3.2.1 Cleaning Process in Automatic Dishwashing

Cleaning in automatic dishwashers occurs via a combination of mechanical, thermal, and chemical processes. Of these three processes, it has been suggested that mechanical energy is responsible for 85% of all soil removal.[46] Automatic dishwashers provide the necessary mechanical action to carry the detergent solution and rinse water over, under, and around the dishes to loosen and remove soil and the mechanical force/velocity at which the water is sprayed can significantly impact

TABLE 3.5
Evolution of Automatic Dishwashing Detergents

Period	Product
1950s	Automatic dishwasher powders
1960s	Detergents with enzymes
1980s	Automatic dishwasher liquids
1990s	Automatic dishwasher gels
2000s	Automatic dishwasher tablets and unit dose pouches

TABLE 3.6
Common Automatic Dishwashing Complaints

Spotting/filming	Black/gray marks
Dark spots	Dishes do not dry
Discoloration of aluminum	Glassware etching
Plastic distortion	Caking of detergent in the dispenser
Yellow/brown stains	Tarnishing of silverware
Residue on washed items	Chipping
Pitting	Dishwasher odor
Deposits on stainless steel	Discoloration of dishwasher interior

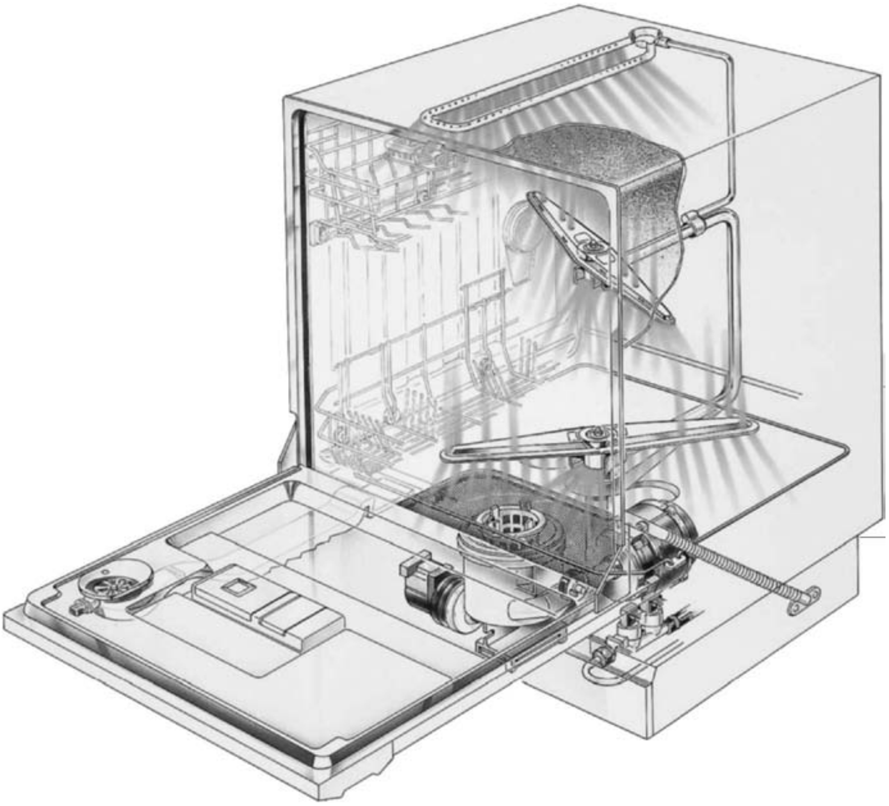


FIGURE 3.4 Schematic drawing of today's typical dishwasher. (From Asko Appliances, www.Askousa.com, 2006.)

cleaning. A schematic drawing of a dishwasher is shown in Figure 3.4 to better illustrate the cleaning process.[47]

Typically, domestic dishwashing machines have three cleaning stages: a prerinse cycle, a main wash cycle, and a final rinse cycle. In most machines, the prerinse cycle can be selected for heavily soiled loads, but usually consumers only select it in exceptional cases. During the main wash cycle and sometimes in the prerinse cycle, the detergent solution is sprayed over and around the dishes. The temperature of the solution used here is anywhere from 40 to 65°C and its pH is between 9 and 11. Temperature is important because thermal energy helps in increasing the solubility of some of the inorganic salts and removal of fatty soils, while at the same time making the mechanical and chemical processes more effective. Additionally, the activity of most oxidizing agents used in ADDs is enhanced with increasing temperature. A highly alkaline environment is also important because it maximizes soil decomposition and cleaning. High alkalinity does not pose any safety concerns, since the detergent solution is completely rinsed away before consumers handle the utensils. The rinse cycle is the final stage of cleaning, and during this step, rinse aids can be added to the dishwasher from a dosing tank.

Though both mechanical and thermal processes contribute to cleaning, detergent chemistries also play an important role. The function of detergents in an ADD is to swell food residues, detach them from the dishes, and disperse or emulsify them in the solution. Unlike hand dishwashing formulations, where foam is a desired attribute, it is critical that foam be inhibited in the dishwasher to increase the effectiveness of the machine and facilitate rinsing. Foam can be controlled with the right combination of surfactants, water hardness, inorganic builder salts, and chlorine-bleach stable-foam depressants or inhibitors. Surfactants, more specifically nonionic surfactants, are also present in rinse aids, and these will be described in more detail in the following section.

Surprisingly, the amount of water needed in a complete dish wash cycle is relatively small. This is because dishwashers employ several low-volume fills during a cycle to accomplish the washing and rinsing operations. The estimated variation in water consumptions for a complete cycle is from 6 to 10 gal., depending on the number of the wash and rinse cycles selected by the consumer.

3.3.2.2 Detergent Composition

The final result obtained when using a well-formulated automatic dishwashing detergent is clean, spot-free, shiny dishware. However, to obtain this desired result, the detergent must be formulated with a balanced combination of ingredients to target specific functions. These functions include

1. Emulsification of greasy and oily soils
2. Suppression of foam generated from surfactants and protein soils
3. Sequestering of water hardness minerals to improve detergent efficacy and decrease spotting
4. Reduction of the surface tension of water to penetrate soils and create a sheet effect for increased emulsification and reduction of spots
5. Protection of dishware from corrosion

To accomplish these functions, most automatic dishwashing detergents are complex mixtures composed of several active ingredients. Unlike hand dishwashing detergents, where surfactants are the key actives, builders in the form of complex phosphates make up the bulk of the formula, with levels as high as 30% of the overall composition in automatic dishwashing detergents. Surfactants are usually present in the formulation at levels of 2% or less. Typical powder ADD formula compositions are listed in Table 3.7. Comprehensive descriptions on the chemistries and functions of ADD ingredients have been described in previous reviews and are summarized in Table 3.8.

3.3.2.3 New Technologies and Applications

Although ADD formulations have been studied and developed for approximately half a century now, there has recently been a renewed focus on developing new technologies aimed at increased product performance. This is suggested by the number of patent publications that have been published in recent years. For example, a search revealed over 200 in the time period from 2002 to 2007. This section will highlight specific new technologies aimed at improved overall cleaning in automatic dishwashing.

TABLE 3.7
Typical Automatic Dishwashing Compositions

Ingredient	Amount (wt%)
Sodium tripolyphosphate (STPP)	25–45
Sodium silicate	15–60
Sodium carbonate	0–25
Chlorinated compounds	0–25
Surfactant	0–6
Sodium sulfate	0–40
Other additives	0–3
Water	Balance

Source: Gorlin, P.A., Dixit, N., and Lai, K. Y., Liquid Detergents, Surfactant Science Series, Vol. 67, 1997.

TABLE 3.8
Classification of Ingredients and Function in Automatic Dishwashing Detergents

Class/Type Ingredient	Primary Function	Typical Examples
Surfactants (typically nonionics)	Reduce the surface tension of water and help emulsify soils. Nonionic surfactants are used because they are low foaming. Additionally, because they do not ionize in solution, they are resistant to water hardness and clean most soils well.	Alcohol ethoxylates (e.g., Neodols)
Builders	Bind water hardness minerals (calcium and magnesium). Help maintain high alkalinity during washing to aid in soil removal.	Complex phosphates (e.g., sodium tripolyphosphate, sodium citrate, sodium carbonate, sodium silicate)
Corrosion inhibitors	Protect dishware, glassware, and machine components from corrosion by metals.	Sodium silicate, zinc salts, bismuth salts
Chlorine compounds	Aid in the emulsification of protein soils like egg and milk. Also help in sanitization, removal of stains such as coffee or tea, and reduction spotting.	Sodium hypochlorite
Alkalis	Aid in emulsification and removal of greasy soils. Alkalinity plays a role in removing acidic, fatty, and oily soils.	Sodium carbonate, sodium tripolyphosphate, caustic soda
Enzymes	Help break down enzymatic soils into smaller pieces that can be washed away.	Proteases, amylases, lipases
Special additives	Protect china patterns from over-glaze.	Sodium aluminate, boric oxide, aluminum phosphate
Thickening agents	Used mostly in gel forms. Ensure that products have the right viscoelastic properties for dispensing and dispersing.	High-molecular weight cross-linked polymers
Processing aids	Allow ingredients to be combined into a usable form.	Polymers, clays, solvents
Fragrance/color	Masks formula base odor and odor of stale food. Creates appealing product.	

TABLE 3.9
Common Surfactants Used for Automatic Dishwashing Compositions

Surfactant	Structure	Performance Characteristics
Alcohol ethoxylates	$R(OCH_2CH_2)_nOH$	Poor foaming compared to anionics, very mild, reasonable detergency.
EO/PO block copolymers	$RO(CH_2CH_2O)_n(CH_2CH[CH_3]O)_mH$	Very effective. Can be used to control cloud point and hydrophobicity by altering EO/PO ratio. Incompatible with chlorine bleach.

Note: EO/PO = ethylene oxide/propylene oxide.

3.3.2.3.1 Cleaning/Low-Foaming Surfactants

Automatic dishwashing detergents require low-foaming surfactants for optimal performance, and this unique limitation is an atypical characteristic for most surfactant systems. Therefore there is a constant need for surfactants that have good cleaning ability and that generate little foam. Typically, low-cloud point, low-foaming nonionics are chosen for ADD formulations. However, with these surfactants the cleaning benefit is limited due to their low solubility in the aqueous wash solution. Instead, they mainly provide spot/film prevention, sheeting action, and soil dispersion. More soluble, higher-cloud point nonionics produce too much foam. Table 3.9 summarizes some of the surfactants that have been used in ADDs.

It is important to note that although nonionics are important functional ingredients of the vast majority of powder and tablet ADDs, there is a need for such surfactants in liquid gel ADDs containing hypochlorite bleach. Commercially available nonionics developed for ADDs have limited bleach stability in aqueous gel formulations. For this reason all the liquid ADD gels marketed contain either no surfactants or bleach-stable surfactants.

In addition to low-cloud point nonionics, the patent literature describes the use of some additional surfactants in ADDs. The use of a mixture of high- and low-cloud point surfactants is reported to provide benefit in terms of greasy soil cleaning.[48] Low-cloud point nonionics are also used in combination with charged surfactants (anionic, zwitterionic) for removal of greasy soil such as lipstick. Examples include amine oxide, alkyl carboxy ethoxylate, or sulfobetaine.[49] For automatic dishwashing tablets, the use of disulfonated anionics such as Dowfax 3B-2 or 2A-1 manufactured by Dow Chemicals has been reported to decrease the solubility rate and the friability percentage loss.[50]

In recent patent literature, butoxy-capped nonionic surfactant compounds have also been reported to reduce spotting without high sudsing. These surfactants have the general formula

$$R^1(EO)_a(PO)_b(BO)_c$$

where R^1 is a linear or branched C6 to C20 alkyl chain.

For any given alkoxylated surfactant, “X” is defined as the sum of protons attached to carbon atoms that are adjacent to oxygen, whereas “Y” is the sum of all the protons attached to carbon atoms that are nonadjacent to oxygen. There is a specific X/Y ratio that describes a desired hydrophobic-to-hydrophilic ratio for nonionic surfactants, and the structure of these surfactants is represented in Figure 3.5.

3.3.2.3.2 Bleach Technology

ADD compositions are often composed of ingredients which improve the removal of hot beverage stains (e.g., tea, coffee, cocoa, etc.) from drinking utensils. These strong alkalis are used to increase soil removal from dishes, promote antiredeposition, and decrease spotting. Technologies that have been used include sodium hydroxide, hypochlorite, and hydrogen peroxide, alone and together with tetraacetylethylenediamine. It has been reported that these technologies can sometimes be too

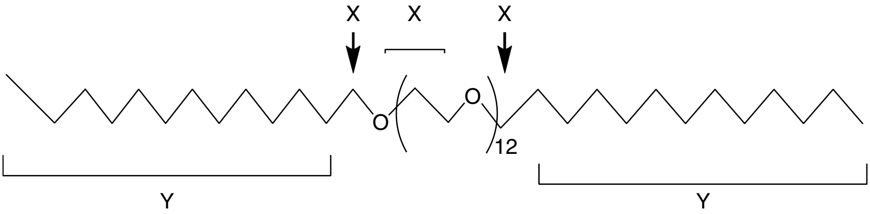


FIGURE 3.5 A typical example of an ethoxylated nonionic surfactant demonstrating the X/Y ratio for $C_{13}EO_{12}C_{13}$, X = 52 and Y = 50, X/Y = 1.04.

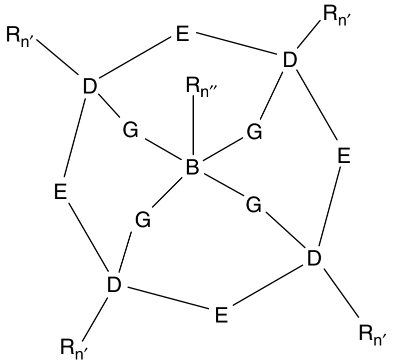


FIGURE 3.6 Structure of cross-bridged macropolycyclic ligand with a detenticity of 4 or 5.

damaging or may be limited in their ability to remove tea stains especially in hard water.[51] Attempts have been made to address these shortcomings by incorporating amylolytic and protease enzymes, manganese catalysts, and cobalt-containing small bleach particles.[52]

One reported development in ADD bleaching technology is the use of transition metal catalysts having specific cross-bridged macropolycyclic ligands.[53] These ligands reportedly exhibit kinetic stability, and an example of such cross-bridged macropolycyclic ligands is shown in Figure 3.6.

In this ligand structure "E" is the moiety $(CR_n)_a$-$X(CR_n)_{a'}$, where X is can be O, S, N, or P and *a*/*a*′ is an integer between 1 and 5, "G" is the moiety $(CR_n)_b$, R can be an H, such as alkyl, alkenyl, alkynyl, and D is a donor atom.

It is reported that the metal ions in these catalysts dissociate slowly under harsh conditions and therefore reportedly exhibit thermal stability. It is also reported that a major benefit of these catalysts includes beneficial effects with one or more primary oxidants such as hydrogen peroxide, preformed peracids, or monopersulfate. Additionally, unlike traditional catalyst containing Mn(II), these have little to no color and are reportedly well matched with ADD compositions. They may also work well with other ADD ingredients such as hydrophobic bleach activators.

An additional problem encountered during automatic dishwashing is the color staining of plastics by food soils. In general, bleaching chemistries promote soil and stain removal, but are limited in their ability to remove these stains from hydrophobic surfaces like plastics. Color stains usually arise from soils containing tomatoes (like lasagna), carotene or lycopene soils, curry sauces, and food mixtures containing these ingredients. The more soil that is present in the dishwasher, the more difficult it is to remove these stains. Researchers have reported that diacyl and tetraacyl peroxides are effective at the removal of these color stains;[54] however, the technology produces unsatisfactory results in the presence of high soil levels. Brooker et al.[55] have recently reported that this problem can be alleviated with the use of a cobleaching surfactant such as an ethoxylated alcohol. According to Brooker et al., the combination of the diacyl or tetraacyl peroxides and cosurfactant is expected to have improved efficacy for several reasons. First, there is an increase in the solubility of the bleaching species. Additionally, the cobleaching surfactant seems to preclude reaggregation of the bleaching species, thereby further increasing their solubilization. It is also suggested that the surfactant drives the bleaching species to the soiled substrate, as well as emulsifying greasy soils and preventing redeposition on the substrates. The bleaching species reportedly becomes more effective because it not only attacks soils on the substrate, but also attacks the emulsified soils. These factors combined give rise to improved color stain removal from plastics.

3.3.2.3.3 Corrosion Inhibitors—Metal Cookware Protection

Stainless steel is the most prevalent alloy used for consumer cookware and cooking utensils; however, it is also highly susceptible to corrosion under normal automatic dishwashing conditions. Such corrosive conditions include high electrolyte concentrations, high humidity, high pH, high temperature, and shear stress from the mechanical action of the dishwasher. This corrosion can be reduced significantly by using a corrosion inhibitor. A corrosion inhibitor is a chemical compound that stops or delays the corrosion of metals and alloys. Corrosion inhibitors formulated into ADD compositions provide protection to stainless steel cookware by forming an extremely thin film over the metal surfaces. This thin film of corrosion inhibitors is a passivation layer that inhibits either oxidation or reduction in a corrosive system and scavenges dissolved oxygen. Corrosion inhibitors in ADD compositions typically focus on glassware, but not stainless steel. Berger et al.[56] describe an ADD composition comprising specific corrosion inhibitors. Specific corrosion inhibitors are listed in Table 3.10 (taken from Ref. 58).

3.3.2.3.4 Glass Protection

Corrosion of glassware is detected by the appearance of clouding, streaking, scratching, or iridescence of the glass surfaces.[55,56] Glasses will become more opaque with repeated washing, and the process is irreversible. This same type of corrosion also occurs on china, porcelain, and ceramics. Corrosion happens for two reasons, the first being the escape of alkali metal and alkaline earth metal ions from the glass combined with hydrolysis of the silicate network and the second, the deposition and redeposition of silicate compounds on the surface of the glass.[58] ADD compositions, because of their high alkalinity and high levels of builders, are prone to attack and corrode glassware. There have been several approaches to mitigate this corrosive environment. These solutions for anticorrosion have included low-phosphate detergents, compositions containing disilicate, metasilicate, and alkali metal silicates partially substituted with calcium, magnesium, strontium, or cerium counterions, and the addition of crystalline layered silicate polycarboxylic acids. Bismuth, aluminum, zinc, and the salts thereof have also been described.[59]

Some of these technologies are not as effective because of the presence of hard water, where free calcium ions are available for precipitation. The calcium ions have a tendency to interact with many corrosion inhibitor actives, and they precipitate when combined. This creates a visible film that is sometimes described as corrosive, because the process is irreversible. In an automatic dishwasher, calcium also has a strong tendency to interact with aluminum ions to produce calcium

TABLE 3.10
Potential Corrosion Inhibitors for Metal Cookware Protection

Commercial Name	Active Ingredients
Cortec® S-69	Benzioc acid, ethanolamine, sebacic acid
Berol® 725	Phosphate ester
Maphos® 43T	Phosphate ester, triethanolamine
Phosphonics P-04-002a/b	Disodium ethyl, butyl phosphonate silica
Miral® A400	Phosphonate
Surfynol® 61	Alkyne nonionic surfactant, methyl butyrol

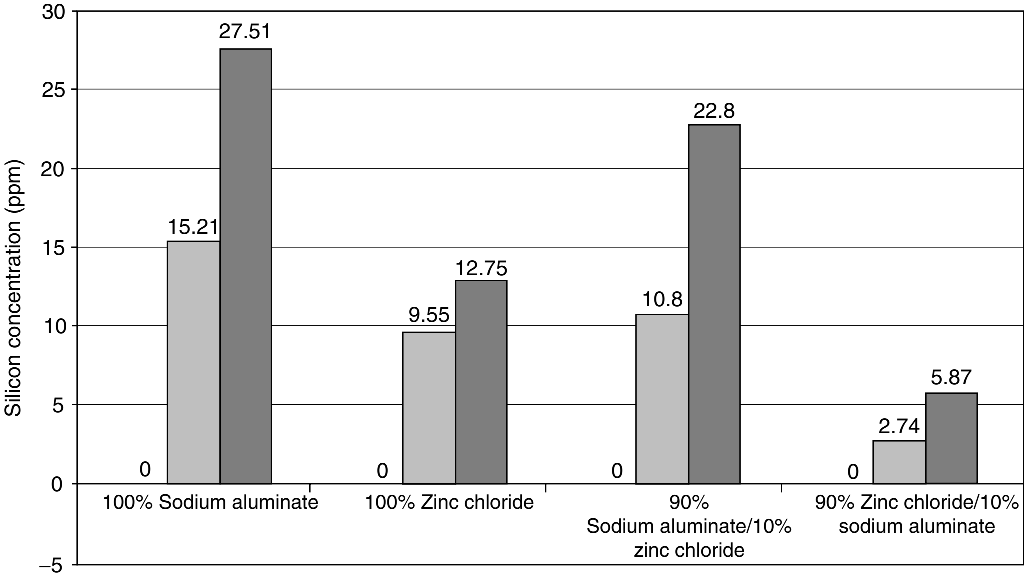


FIGURE 3.7 Graph showing silicon concentration in a detergent solution from washing drinking glasses at different exposure times in hours: t = 0, t = 48h (light gray), and t = 96h (dark gray). (From Smith, K.R., Olson, K.E., Kestell, H., Bartelme, M.J., Lentsch, S.E., Man, V.F., Baum, B.M., and Everson, T.P., U.S. Patent Publication No. 2006/0270580 A1, Ecolab Inc.)

aluminate, which precipitates quickly and is very difficult to remove. A method to decrease these types of precipitates and therefore corrosion uses the combination of aluminum and zinc and is described in detail by Smith et al.[60] The described mechanism for anticorrosion involves the interaction of aluminum and zinc ions to form zinc aluminate, which is insoluble in water. The zinc aluminate precipitates slowly during the wash to form a film on the glass surface that is reportedly less visible to the eye than the iridescent film that forms from silicate precipitates. According to Smith et al., zinc aluminate forms a protective layer over the glass, inhibiting corrosion. The ingredients in the ADD composition such as alkalis and builders attack the protective layer before attacking the glass. The reported efficiency in the reduction of etching of a glass surface using this technique is described graphically in Figure 3.7. The data in this graph were taken from an experiment, where glasses were washed using a dish detergent solution containing different amounts of sodium aluminate and zinc chloride. The level of silicon in the detergent solution was measured initially (t = 0) and after 48 and 96 h. The level of silicon is a measure of the amount of glass etching occurring during exposure to detergent solutions. The composition containing 100 and 90% sodium aluminate reportedly resulted in the largest increases in glass etching, whereas the composition with the mixture of 90% zinc chloride and 10% sodium aluminate reportedly provided the most etch protection.

Waits et al.[60] have reported a different method for preventing corrosion. Their approach to reducing glassware corrosion utilizes encapsulated glasscare active salts like aluminum sulfate to alleviate the aforementioned problems. They reported that good corrosion protection for glassware could be achieved by protecting certain glasscare active salts from dissolving in or reacting with the detergent composition. By encapsulating the salts, better product stability and performance were reported in a variety of forms including liquids, powders, and tablets. Encapsulation works by sequencing and delaying the release of the glasscare actives in the detergent, allowing time for the bleaching agents, like oxygen bleach, to remove tea stains before the active salts react. Several delayed-release methods have been reported for active ingredients that utilize a variety of trigger mechanisms including time, temperature, water hardness, interfacial tension, mechanical, and pH.

3.3.2.3.5 Sanitization—Electrochemical Cells

In recent years, researchers have explored electrochemical methods for use in automatic dishwashing for sanitization and stain removal.[61] In dishwashers, it has been observed that electrochemical cells operate by making use of the water electrolysis process, where OH^- present in the water from the electrolytic dissociation of water molecules donates an electron to the anode and is therefore oxidized to oxygen gas, which can be removed from the system. As a result, H^+ is enhanced at the anode–water interface, and enriched acidic water is produced. The advantage of this electrolyzed water is that it can provide improved cleaning, stain removal, and sterilization benefits in automatic dish care. Combined with ADD compositions, electrolyzed water can be effective at removing a number of soils and stains from dishware. Additionally, the combination of electrolyzed water with ADD combinations may alleviate the need to add additional bleach to the detergent.

While electrolyzed water does provide a source of alkalinity and bleach, there is a lack of ability of electrolysis and traditional ADD compositions to control water hardness, dispersantcy, and corrosion. Scheper et al.[62] contend that using electrolyzed water in conjunction with an ADD composition containing a halogenated salt provides complete cleaning and superior results. Halogenated salts or halogen dioxide salts having the formula $(M)_x(X)_y$ or $(M)_x(XO2)_y$, where X can be Cl, Br, or I and M can be a metal ion, were reportedly effective in the electrolysis process to produce oxidizing agents. For example, it was reported that free chloride ions can be electrolyzed to produce chlorine gas that can be converted to hypochlorous acid, chlorine dioxide, and other chloro-oxide molecules. Other products from the same electrolysis reaction could include ozone, hydrogen peroxide, and free radicals. Such halogenated mixed oxidants have been described to be very effective biocidal agents with short life spans.[57] These *in situ* generated agents can be very effective at use time with the other ADD actives and are then consumed without contact by the consumer.

3.3.3 FORMS AND SPECIALTY PRODUCTS

Today there is an array of automatic dishwashing detergents in various forms. These forms can be classified into four classes—powders, tablets, liquids, and gels.[63,64] The powders were the first form to be developed and are generally free-flowing granules. They are very stable due to the nature of the materials, but have a tendency to clump when placed in high-humidity areas. Tablets are formulated for effective cleaning and convenience. They eliminate measuring, waste, and mess. Unlike powders they are typically prewrapped, and this avoids issues with moisturization. However, tablets sometimes do not completely dissolve depending on the conditions. Liquid automatic dishwashing detergents gained more popularity over powder forms due to their convenience and performance benefits. However, liquid formulations have been shown to demonstrate physical instability and residues on the bottle. Gorlin et al.[65] were able to develop a formula that had shown increased stability, low levels of bottle residue, high cleaning performance, low spotting, and low filming. Gels are formulated for controlled dispensing. They dissolve easily and are less likely than powders to be spilled.

These many new forms have afforded researchers with vehicles to have improved chemistries and to offer multiple benefits. Additionally, for added convenience, many of the product types can be purchased in unit dose form. Unitized doses of dishwashing detergents are more attractive because they alleviate the need for precise dosing and avoid wasteful overdosing. Packaging materials have been developed such that one dose could have several layers or compartments that break down and dissolve over the wash or with specific triggers.[66–68] Sharma et al., for example, discuss a multicomponent pouch that can deliver a powder form on one side and liquid/gel form on the other side. Some of these newer product forms with their reported benefits can be seen in Figure 3.8.

3.3.4 RINSE AIDS

Consumers also use rinse aids in addition to their detergent formulation, to obtain the sheeting effect that gives the dishes that spotless shiny appearance. These aids are wetting agents that are introduced in the final rinse cycle, and they have the function of lowering the surface tension of the

Detergent/Form	Product Claim
Method Dish Cubes 	Method Dish Cubes are prepackaged gelpacs. One gelpac cleans a load of dishes without the need to measure, scoop, or open any packaging. The Method Dish Cubes cleans well and leaves dishes fresh and sparkling.
Palmolive Gel Dishwasher Detergent 	Palmolive’s Gel Dishwasher Detergent is easy to pour from the bottle without the need for excessive squeezing. Palmolive Dishwasher Detergent will clean and polish your dishes leaving a fresh scent.
Electrasol 3 in 1 Tabs with Jet-Dry Power Ball 	Electrasol’s 3 in 1 Dishwasher Detergent Tabs have a double layer of dishwasher detergent to break up tough grime and dissolve grease in the dishwasher. As an added benefit the Jet-Dry PowerBall helps keeping dishes from becoming cloudy and streaky during a wash.
Ecover Dishwasher Tablets 	Ecover’s Dishwasher Detergent comes in a convenient tablet form that is still environmental friendly. Ecover includes no artificial fragrances, phosphates, or chlorine bleach. Ecover's cleaners biodegrade well and cause no problems for marine and river life. These easy premeasured tabs do a great job at cleaning dishes without harming the environment.
Electrasol Dishwasher Detergent Powder 	For those hooked on a powder dishwasher detergent, Electrasol has a great one. Especially effective on greasy stains and grime, Electrasol’s Dishwasher Detergent Powder has the power you need to get even the toughest dishes clean.
Cascade 2 in 1 Action Pacs Pure Rinse 	Cascade’s 2 in 1 Action Dishwasher Detergent Pacs combine the power of Cascade with the grease fighting action of Dawn dishsoap. Each premeasured tab works to remove grease and stuck-on food from dishes preventing the necessity to rewash and rerinse dishes again and again.

FIGURE 3.8 Examples of current automatic dishwashing detergent product forms, pictures, and claims.

water so that it forms a closed film on the dish surface. This film becomes thinner during rinse-off and finally disappears to ensure that the dry dishes have a uniform shine.[69] They allow the water to drain effectively and quickly from the dishes so that the dishes are free from spots and residues. Rinse aids are particularly useful in geographical areas with hard water where the heating cycle is eliminated to conserve energy. Traditionally, rinse aids are composed of nonionic surfactants, hydrotropes, pH regulators, and bloom-inhibiting polymers. Rinse aids and their properties have also been summarized in detail in the past reviews[1,43]; however, there are new technologies that reportedly improve on the efficacy and benefits that rinse aids may offer.

3.3.4.1 Antimetal Corrosion

Traditionally, anticorrosion ingredients are added in the wash-cycle phase in automatic dishwashing, and these are usually targeted toward glass surfaces. Water-soluble metal salts have been used in the wash to target metals, but they are usually insoluble and therefore precipitate onto the metal surfaces. Song and Salem[70] have reported that by incorporating these metal salts into a rinse formula, the insoluble precipitation on all hard surfaces can be avoided. The key to this technology is the use of an organic or inorganic acid with a nonionic surfactant. The water-soluble salts could include magnesium acetylacetonate, magnesium ammonium phosphate, and magnesium. The rinse aid has a pH of less than ~5 in an aqueous solution. The acid reportedly enables the water metal salt to dissolve quickly in the rinse liquor to reduce the formation of the insoluble salts, thereby resisting both corrosion and rust.

3.3.4.2 Surface Coatings

Recently a different approach has been investigated for rinse aids. This approach involves leaving a surface coating on the dishware that reportedly provides multiuse benefits. Dispersive film-forming polymers [e.g., alkoxylated silicones, poly(*N*-vinyl-2-pyrrolidones, diblock copolymers of poly(ethylene oxide) and poly(lactide)] have been investigated.[71] The compositions containing these polymers reportedly give the treated surface run, spot, and the mark resistance; however, spot and residues on dishware returned after 1–2 rinse cycles. Aubay and Embleton[72] reported that amphoteric copolymers derived from diallyldimethylammonium chloride with an appropriate selection of charge ratio, could be used as soil antiredeposition agents in both two-in-one (washing and rinsing) compositions. Also, Ghosh et al.[73] sought to address the limitations of polymer technology by the use of nonphotoreactive nanoparticles. These nanomaterials reportedly imparted dish surface multiuse benefits that included durability and protection. The coatings were also reported to be long-lasting and semipermanent in the automatic dishwasher environment. Particularly, it was reported that a nanoclay (LAPONITE RD™) at 500 ppm in a formula could deliver a coating and eliminate spot formation.

3.3.4.3 Detergent/Rinse Combinations

In 1978 Henkel[69] reported the formulation of detergent that integrates the rinse agent into the dishwasher detergents. This development reportedly alleviated the need for the consumer to add a separate rinse agent. Today, with the increase in the unit dose forms in the marketplace, more manufacturers have combined the functionality of dishwashing detergent and rinse aid. Many of these type products are in tablet form, where the rinse aid is prevented from dissolving during the wash cycle. The dissolution is triggered in the rinse cycle by either loss of surfactants and builders, a reduction in pH, or change in temperature. The requirement is, however, that the solid rinse aid–containing portion survives the wash cycle and is also not pumped off between cycles. The limitation with this method is that particles must be big enough and therefore in solid tablet form. Wiedemann et al.[74] have proposed the use of floating-delayed soil release particles that could be formulated in any form. The particles have diameters of ≤1 cm and a bulk density of <1, and reportedly can even be formulated stably into a liquid form, with the pump off between cycles.

3.3.5 INDEPENDENT PERFORMANCE EVALUATION OF AUTOMATIC DISHWASHER DETERGENTS

In September of 2006, the Consumer's Union, which publishes *Consumer Reports*, published an independent study evaluating the performance of 27 ADD products from a variety of manufactures including familiar brands such as Electrasol, Cascade, and Palmolive, as well as store brands such as Trader Joe's and America's Choice.[75] The performance categories evaluated were *Cleaning*, *Prevents redeposits*, *Prevents water spots*, *Doesn't etch glass*, and *Doesn't damage silver.* From the 27 detergents, they reported a wide range of scores and found that the products that were judged very good or excellent overall contained enzymes. The enzymes reportedly made a difference between an outstanding detergent and a dull detergent. Additionally, powder and tablets compositions by far outperformed the gels that mostly scored only fair. The products that scored the highest ratings in the order of their ranking were Cascade 2 in 1 Action Pacs packets, American's Choice (A&P) powder, and Ecover Ecological tablets. The Consumer Reports best picks based on both price and performance were Kirkland Signature (Costco) powder, Target powder, Great Value (Wal-Mart) powder, and Everyday Living (Kroger) powder.

3.3.6 Specialty Products Machine Cleaning and Upkeep

The inside surface of the dishwasher becomes covered with residue over time. These residues include lime scale, soap scum, and food deposits. The removal of lime scale from the dishwasher has been the main concern of patent inventions, because lime scale residues deposit on the heating elements and reduce the overall heat exchange of the systems. However, soap scum and food deposits have also been seen as a problem because these can redeposit on the dishes as well as reduce the effectiveness of the detergent. In 2006, Binder obtained a patent that reportedly targets all three types of deposits left in the dishwasher.[76] The detergent tablet contains 10–75% of a limescale remover acid, 11–20% nonionic surfactant, and from 0 to ~5% of a detergency enzyme.

Additionally, conventional cleaning machine products are placed in the machine's dispenser and/or sprinkled on the base of the machine. Sometimes these formulations coagulate in the sieves at the bottom of the machines and can block the machine. Tomlinson et al.[77] discuss a cleaning formula that mitigates the problem of coagulation. The active ingredient in this formula is a fully hydrated organic acid.

3.3.7 Safety and Environmental Considerations

Soap and detergent manufacturers are committed to understanding the effect that their products have on the environment as well as making sure that they meet environmental regulations. Environmental considerations include the restriction of phosphate, the desire to provide ever-better cleaning results with fewer products, requiring less thermal energy, and using less water to assist the washing process. As has been described in the introduction, the use of the dishwasher minimizes the amount of water and energy as compared to traditional dishwashing. However, there are two major concerns with the usage of chlorine and phosphates in dishwashing products.

When excess chlorine enters the waterways, it often mixes with organic compounds and reacts to form chloro-organic compounds, such as chloroform, and other known carcinogens.[78] More so, the use of phosphates has caused the most concern and will potentially undergo stricter regulations in the future. The issue with phosphate is that once they are released into the environment, they promote massive algae growth in local waters. These algae trigger a process called eutrophication in which the water becomes starved of oxygen and devoid of life. With the exception of automatic dishwashing formulae, phosphates were banned from household cleaning products in the 1970s. Automatic dishwashing detergents were exempt, and now phosphates can still be found to make up as much as 30% of the formula.

Consumer product manufacturers are aware of the problems caused by phosphates and have been researching ways to minimize or even altogether eliminate phosphates from their formulations. There are now a number of automatic dishwashing detergents that are phosphate free or have low levels of phosphate.[79,80] Some of these are listed in Table 3.11.[81]

3.4 CONCLUSIONS

Both the hand and automatic dishwashing segments are important markets in the developed world. It is anticipated that as dishwashing technologies continue to improve, the end-use benefit

TABLE 3.11
List of Automatic Dishwashing Detergents with Little to No Phosphate

Automatic Dishwashing Detergents	Type	Phosphate Content (%)
Bi-O-Kleen	Powder	0
Citrus Magic	Gel	0
Ecover		
Seventh Generation	Tablet	0
Shaklee	Powder	0
Sun & Earth	Tablet	0
Trader Joe's Automatic Dishwashing Detergent		0
Palmolive Gel	Gel	1.6
Electra-Sol Gel	Gel	3.7
Wal-Mart Automatic Dishwashing Detergent	Gel	4.0
Pure Power Gel	Gel	4.0
Sunlight Liquid	Liquid	4.3
Electra-Sol Powder	Powder	4.5
Cascade Liquid	Liquid	5.0
Sunlight Powder	Powder	4.5
Cascade Complete	Liquid	5.0
Pure Power Powder	Powder	5.3
Hannaford Dishwasher Detergent	Powder	5.3
Shaws Automatic	Powder	6.0
Wal-Mart Automatic Dishwashing Detergent Powder	Powder	6.3
Cascade PureRinse	Powder	6.4
Cascade Action Pac	Tablet	8.0
Electra-Sol Tablets	Tablet	8.7
Electra-Sol GelPac	GelPac	8.7

Source: http://www.assabetriver.org/nutrient/detergents.html, Phosphate content in popular cleaners (accessed April 26, 2007).

to consumers will also advance. In addition to discussing existing dishwashing chemistries, this review has highlighted some of the key new detergent technologies that have been introduced to the market in the past 10 years. These new technologies have helped to increase the growth of dishwashing products globally. Other trends in the dishwashing segment were also noted. These include a shift toward sensorial and natural products that claim to offer consumers an ever more pleasant dishwashing experience in the hand dishwashing segment. In automatic dishwashing detergents, the trend is toward new and more convenient forms that offer multiple benefits to consumers. In hand and automatic dishwashing detergents, consumers, retailers, and manufacturers have placed an increased emphasis on environmentally friendly products. While this provides a challenge to formulators, it is not expected to hamper the growth in either segment.

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4 Applications of Detergent in Laundering

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and Gregory Bogush

CONTENTS

4.1 INTRODUCTION

One of the major uses of surfactant that the average person encounters in everyday life is in household products, particularly laundry detergent. This chapter will briefly summarize various ingredients and forms of detergents. The primary focus of this chapter will be on the application of various detergent formulations and product forms to specific laundering situations.

To understand how a detergent works, it is necessary to examine the ingredients found in such a product, and how they interact. Detergent ingredients and formulations have been discussed extensively in Part D [1] of this series, so this chapter will only include a brief summary.

4.2 DETERGENT INGREDIENTS

4.2.1 Surfactants

The major component of a laundry detergent is surfactant. Surfactants, alone and in combination with other ingredients, work to remove soils from the surface of the cloth through emulsification, roll-up, and electrostatic forces. A variety of different surfactants have been used in laundry detergents, and they can be classified as anionic, nonionic, and cationic.

4.2.1.1 Anionic Surfactants

Anionic surfactants comprise the bulk of the surfactants used in laundry detergents today. The anionic surfactants are derived from both oleochemical and petrochemical sources. The choice of feedstock depends on availability and cost.

At present linear alkylbenzene sulfonate (LAS) is the primary surfactant for most powdered and liquid detergents. Its low cost and high performance make it ideal for detergent applications. LAS is easily processable in both powders and liquid detergents. It provides excellent detergency on a variety of soils, and has high foaming characteristics that are desirable in laundry detergents, particularly in hand wash markets. LAS is relatively stable to oxidation, and is acid and alkali stable. Additionally, LAS can be manufactured consistently and cost-effectively. LAS does have some disadvantages, however. It is relatively sensitive to water hardness, which decreases performance in high-hardness areas. LAS is also not mild to the skin, which is a detriment in hand wash markets.

Although sulfonates are the major anionic surfactant in laundry detergents, other anionics are also used. Sulfates are often used in detergent products, either alone or more often as cosurfactants with LAS. The primary sulfonate in detergents is alcohol ether sulfate (AEOS). AEOS has increased hardness tolerance compared to LAS. It is also more effective than other surfactants at low temperature, and works particularly well on oily soils [2]. Although there are instances of AEOS as the primary surfactant, particularly in European formulations, in general AEOS is used as a cosurfactant with LAS. Beneficial effects on detergency have been reported for LAS/AEOS combinations [3]. Other anionic surfactants have also found usage in laundry detergents. Some examples are soap and alkyl sulfates and coco fatty acid sulfonate. However, their usage is relatively minor.

4.2.1.2 Nonionic Surfactants

The second major class of surfactants used in detergents currently is nonionic surfactants. Nonionic surfactants have a number of advantages over anionic surfactants. Nonionic surfactants tend to be more hardness tolerant than anionic surfactants, and to have increased oily soil detergency. Additionally, nonionic surfactants are more compatible with enzymes than are anionic surfactants.

Alcohol ethoxylates (AEs) are used extensively in both powders and liquids. AE in combination with anionic surfactants does provide synergistic cleaning benefits, particularly on oily soils [4]. Typically in detergents a C12–15:7 ethylene oxide (EO) AE provides acceptable performance. Depending on the particular need, the carbon chain and EO level can be varied.

4.2.1.3 Cationic Surfactants

In general, cationic surfactants are used in fabric softeners rather than in detergents. However, there are reports of addition of small amounts of cationic surfactants to anionic-based formulations resulting in the formation of a *pseudo-nonionic* surfactant, with a reported improvement in oily stain removal [5,6].

4.2.2 BUILDERS

The primary functions of builders in laundry detergent formulations is to remove hardness ions to protect the surfactant. Calcium and magnesium ions in wash water can react with surfactants to form insoluble or nonfunctional complexes. Builders reduce water hardness by three main mechanisms. Sequestration forms a soluble complex between builder and hardness ions. Precipitation forms an insoluble complex with hardness ions. Ion exchange removes calcium and magnesium ions by replacing them with soluble sodium ions.

In addition to hardness control, builders serve other functions in a laundry detergent, such as increasing wash water pH to help cleaning through emulsification of oily soils.

4.2.2.1 Phosphates

Phosphates are considered to be the most cost-effective detergent builder available, combining the properties of high efficacy (calcium sequestration, antiredeposition, buffering of pH), low toxicity, and relatively low cost. Phosphates are compatible with a wide variety of processing methods and product forms, which allows their use in powders, liquids, and bars. Although sodium tripolyphosphate (STPP) is the most common phosphate builder, sodium pyrophosphate is also used in some countries. In Asia, Latin America, and Africa, phosphates are the predominant detergent builders used.

Owing to environmental concerns over eutrophication, phosphate restrictions were implemented in 1970 in parts of the United States. Other areas with limitations now include Canada, Japan, and Western Europe.

4.2.2.2 Nonphosphate Builders

No single builder is capable of replacing STPP on a cost/performance basis. As a result, nonphosphate detergent formulations commonly employ combinations of builders, each having some specific benefits.

4.2.2.2.1 Zeolites

Zeolites are used as the primary builder in areas where phosphates cannot be used. Zeolite A is the most common type. This material is a synthetic aluminosilicate, made from alumina and alkaline sodium silicate. Zeolite A has a cage-like structure, which is of the right size to trap calcium ions from the wash water. Sodium ions are released from the cage in an ion exchange process.

Compared to STPP, zeolite is reported to be less effective due to a lower calcium-binding capacity and its inability to bind magnesium ions [7]. Zeolites also have some environmental disadvantages. They are not biodegradable, and they are insoluble, thus adding solid waste to the environment.

4.2.2.2.2 Carbonates

Whereas sodium carbonate is used as the primary builder in some economy brands, carbonates are more frequently used as a cobuilder along with zeolite. Carbonates are inexpensive and safe to the environment. Carbonates buffer wash water at an alkaline pH, which aids in stain removal but can be harsh to the skin in hand wash applications. Carbonates remove calcium ions by precipitating calcium carbonate. This precipitate can cause encrustation on fabrics, resulting in a harsh feel and a dingy appearance.

4.2.2.2.3 Silicates

Sodium silicates serve several purposes in a laundry detergent. Silicates can form a protective film on the surfaces of washing machine parts, helping to prevent corrosion over time. They are used as a processing aid in both phosphate and nonphosphate powder detergents, providing strength to the spray-dried detergent bead. Finally, silicates are a relatively inexpensive cobuilder. In zeolite-based detergents, silicates are used at low levels to minimize the formation of insoluble complexes with zeolite.

4.2.2.2.4 Polycarboxylates

Polycarboxylates are generally used as cobuilders in zeolite-based systems. In most cases, their relatively high cost generally precludes their use as a primary builder. Limited biodegradability and high cost are the main reasons that polymers are not used as primary builders.

Although surfactants and builders are the main ingredients in detergents, a variety of other minor ingredients also play a significant role in providing added benefits to the consumer. Such ingredients include enzymes, fluorescent whitening agents, antiredeposition agents, and fragrance.

4.3 DETERGENT FORMS

The ingredients discussed above can be delivered to the consumer in a variety of forms. Typically, there is an evolutionary trend in detergent forms based on economic status of the consumers from laundry bars to powders to liquids. All of these forms are discussed here briefly.

4.3.1 LAUNDRY BARS

Laundry bars can be divided into two main categories—soap bars and syndet bars. In some markets, combars are available, which contain both soap and synthetic detergent. Soap bars are generally more mild to the skin than syndet bars, but syndet bars are usually more efficacious, especially at high water hardness. Consumers will choose a laundry bar based on their habits and practices, desired level of efficacy, and their economic situation.

Soap bars are more basic, and consist largely of saponified animal tallow or vegetable oils. The choice of fats and oils is often dictated by local availability. In some soap bars, other ingredients are included, such as fragrance, pigments, clays, soda ash, and silicates. The quality of the final product is a function of the oil used. Formulation examples for both soap and syndet bars are shown in Table 4.1.

TABLE 4.1
Formulation Examples of Soap and Syndet Laundry Bars

Ingredients	Soap (wt%)	Syndet (wt%)
Soap	60–80	5–15
Surfactants	—	10–35
Antiredeposition agents	—	0–0.5
Filler (sodium sulfate)	—	20–60
Brighteners	—	0–1.0
Colorants/perfumes	0–1.0	0–0.2
Other ingredients	0–20	0–15
Water	20–30	5–15

TABLE 4.2
Formulation Examples of Conventional and Superconcentrated Powder Detergents

Ingredients	Conventional (wt%)	Superconcentrated (wt%)
Water	3–15	3–10
Surfactants	15–25	10–40
Builder	20–55	30–55
Filler (sodium sulfate)	20–45	0–20
Brighteners	0–0.8	0.–0.5
Bleach system	0–25	0–25
Polymers	0–6.0	0–5.0
Enzymes	0–1.0	0–2.0
Flow aids	0–1.0	0.–2.0
Density	0.2–0.5	0.5–1.0

Syndet bars consist of similar ingredients as powdered detergents. Surfactants, builders, brighteners, antiredeposition agents, and perfumes are some of the major components.

4.3.2 POWDERS

In most developed countries, laundry detergent powders comprise the bulk of the detergent market. Powders are used both for hand and machine washing, depending on the markets in which they serve. Powders basically fall into two categories, conventional and superconcentrates.

Conventional powders have a low bulk density (0.2–0.5 g/mL). They are typically produced via a spray tower process, in which the detergent ingredients are mixed in a concentrated viscous slurry and dried with hot gases, resulting in puffed, shell-like detergent beads.

In the early 1990s, superconcentrated detergent powders with a higher bulk density (0.5–1.0 g/mL) were introduced. Formulation examples for both conventional and superconcentrated powders are shown in Table 4.2.

4.3.3 LIQUIDS

Liquid detergents are the relative newcomer in product form, being first introduced in 1956 [8]. Liquid detergents also tend to be a more profitable form than either bars or powders, since the filler material for liquids is typically water versus other fillers for bars and powders.

Liquid detergents can be broken down into two types—unstructured and structured. Both types of heavy-duty liquids have varying levels of concentration, ranging up to superconcentrated products.

Unstructured liquid detergents are typically thin, clear single-phase liquids. They are called unstructured because the systems are homogeneous, with only small circular micelles being formed. The micelles are too small to affect the light scattering of the system, and so the product appears transparent. The viscosity of unstructured liquids ranges from waterlike (~50 cP) to a maximum of 1000 cP. Some formulation examples are given in Table 4.3. Unstructured liquid detergents are found primarily in the United States and Europe, and occasionally in various other parts of the world.

In contrast to unstructured liquids, structured liquids are typically thicker and opaque. Structured liquids are a heterogeneous system containing surfactants, builder, and other detergent components. In structured liquids, the surfactants combine to form lamellar droplets, which scatter incoming light resulting in an opaque appearance. The lamellar droplets interact, providing a structure to the product. Often the lamellar structure suspends particles, such as builder or brightener. Viscosities of structured liquids range from 1500 to 10,000 cP. Formulation examples are shown in Table 4.4.

TABLE 4.3
Formulation Examples for Unstructured Heavy-Duty Liquid Detergents

Ingredients	Conventional (wt%)	Superconcentrated (wt%)
Water	60–80	40–60
Surfactants	10–20	15–30
Builder	0–5	0–10
Antiredeposition agents	0–0.5	0–0.5
Brighteners	0–0.5	0–0.5
Colorants/perfumes	0–1	0–1
Buffers	0–5	0–5
Hydrotropes	0–5	0–5
Enzymes	0–1	0–1
Enzyme stabilization systems	0–10	0–10

TABLE 4.4
Formulation Examples for Structured Heavy-Duty Liquid Detergents

Ingredients	Conventional (wt%)	Superconcentrated (wt%)
Water	50–70	35–50
Surfactants	10–20	25–35
Builder	10–20	20–30
Deflocculating polymers	—	0.5–2
Antiredeposition agents	0–0.5	0–0.5
Brighteners	0–0.5	0–0.5
Colorants/perfumes	0–1	0–1
Enzymes	0–1	0–1
Enzyme stabilization systems	0–10	0–10

Structured liquids are found throughout the world, with the exception of the United States. They are particularly popular throughout Europe and in the Asia Pacific region.

Given the basics of detergent ingredients and forms, it is possible to determine the application of a particular detergent depending on the washing system and the desired benefit beyond basic cleaning. This is discussed extensively in the next section.

4.4 APPLICATIONS

From a scientific standpoint, the process of laundering involves the physical separation of a material from a substrate (typically in an aqueous medium) via chemical and physical processes. Both chemical and mechanical energies are put into the system to accomplish this task. The optimum formulation in a particular situation depends on the fundamental parameters of the system.

4.4.1 Source of Mechanical Energy

In the laundering process, mechanical energy is put into the system either via hand washing or the use of a washing machine. Washing machines vary in type from semiautomatic to top-loading with an agitator in the middle to front-loading, in which tumbling of the clothes against each other provides the mechanical energy. Each of these processes adds less mechanical energy to the system, thereby requiring increased levels of chemical action to clean the garments.

This balance is evident in the types of products often used in each process. Hand washing often involves significant mechanical action via scrubbing. Laundry bars (either soap or synthetic) or simple powder detergents typically provide the chemical action in this process. The simplicity of these systems is compensated for by: 1) the relatively high concentration of detergent in the hand-wash system (for powders typically ~5 to 7 g/L); and 2) letting the clothes soak once they have been saturated with detergent. Typically soaking times range from 30 min to overnight.

In the washing machine, the chemistry of the system becomes more important. The concentration of detergent is typically much lower (1–3 g/L), and often there is little to no soaking (although filling the machine and letting the garments soak for ~30 min prior to restarting the machine is not uncommon in developing markets). Therefore, to attain the same level of cleaning, more efficient technologies must be employed. In these instances, detergents containing enzymes, polymers, antiredeposition agents, and activated bleaches will be used. Owing to difficulty of dissolution, laundry bars are not typically used in washing machines. Powders and (in the developed world) liquids are the form of choice. Liquids are especially preferred due to the ease of dissolution.

In front-loading washing machines, the reduced mechanical action of the machine is compensated for by longer wash times and higher detergent concentrations (4 g/L). Again, powders and preferably liquids are the forms used in these conditions. The key issue in front-loaders is foam control. Although foam is very desirable in hand washing as a sign of efficacy, and acceptable in top-loading machines, excess foam actually decreases the impact of the mechanical action in the front-loader, and significant amounts of foam can cause the machine to stop (foam lock). Therefore, detergents designed for front-loading machines must either utilize non- or low-foaming surfactants (typically nonionics), or contain a foam-suppression agent. Typical foam suppression agents are silicones and (in high water hardness areas) soap [9–11].

4.4.2 PHYSICAL ASPECTS OF THE SYSTEM

4.4.2.1 Water Temperature

One of the critical parameters in laundering is water temperature. As a rule of thumb, a 10°C increase in temperature doubles the rate of most reactions (laundering included) [12]. This is especially true for hydrophobic soils (e.g., oily soils). Water temperatures for laundering vary significantly. Hand wash is typically done at ambient temperature (~70 to 80°F), whereas water temperatures in washing machines can vary from 4 (cold water in winter in Canada) to 90°C (hot wash in European front-loaders). In general, however, wash temperatures have decreased significantly over the past 20 years, and this trend is expected to continue. From a formula standpoint, lower wash temperatures can be compensated for by increasing the concentration of surfactants, using enzymes that are more efficient at lower temperature, increased use of water-soluble polymer for antiredeposition, and using more efficient low-temperature activators for oxygen bleaches. Owing to their superior solubility, liquids are the preferred form for low-temperature washing. In contrast, the low-temperature dissolution rate of powders decreases to the point that detergent residue becomes a concern during a typical washing machine cycle. Obviously in hand wash, the lower water temperature is compensated for by the mechanical action of the person washing. The person washing will agitate the mixture until all the powder is dissolved.

4.4.2.2 Detergent Concentration

Another critical parameter is detergent concentration. Typical concentrations of detergent are shown in Table 4.5. Again, higher concentrations drive the reaction forward. However, in all systems there

TABLE 4.5
Detergent Concentration in the Wash Water by Region

Region	Hand Wash Concentration (g/L)	Machine Wash Concentration (g/L)
North America	NA	1.5
Europe	6.0	3.0
Latin America	7.0	3.0
Asia	3.0	1.5
South Pacific	NA	1.5
Africa	6.0	3.0

is a leveling off, where continued increase in an ingredient (e.g., surfactant) has no additional benefit. Therefore, it is often advisable to use formulas with lower levels of basic surfactants and builders, but with enzymes, polymers, and bleaches. These materials interact with various types of stains to break them down into components that are easier to remove. Although increased concentration can increase cleaning power, it also has the disadvantages of increased color and fiber damage to the clothes, increased cost to the consumer, and a significant increase in the amount of rinsing required to remove all the detergent from the clothes.

4.4.2.3 Water Hardness

Water hardness also will dictate the types of detergent required for a particular application. Water hardness can vary both in level and composition, even in the same area. In areas with low to moderate hardness (150 ppm or less), detergents high in surfactant and lower in builder perform well. Unstructured liquids (which by their nature contain little if any builder) work well in these areas. In areas with high water hardness (200–400 ppm), high levels of builder are preferred. Sodium tripolyphosphate is the preferred builder, especially in areas with high concentrations of magnesium ions in water (zeolite is not effective against magnesium). Lower levels of surfactant are acceptable because the high builder levels allow the surfactant to be effective. In high-hardness areas, nonionics are the surfactant of choice (especially when no builder is present). Minimum levels of sodium carbonate and soap are to be used, to minimize the buildup of precipitate on the clothes. Interestingly, calcium and magnesium precipitates of soap on the clothes has a slight softening effect, whereas the calcium and magnesium carbonate salts result in encrustation of the clothes. In high-hardness areas, powder detergent is the most efficient form. Structured liquids are limited in the amount of builder that can be formulated stably. Unstructured liquids in a high-hardness environment must be nonionic surfactant–based to be effective.

4.4.2.4 Substrate Composition

The composition of the substrate (often in combination with the composition of the soil) drastically impacts the type of detergent chosen as well as the wash conditions. Clothing can be categorized by three types of fabrics: cellulosics (e.g., cotton, viscose), wool, and synthetics (polyesters, polyamines [e.g., nylon], acetates, etc.).

Cellulosics, particularly cotton, is a major fabric in garments. The cotton fiber is very hydrophilic and negatively charged. Therefore, although it attracts dirt, the dirt is easily removed by the detergent system. Cotton fibers have both crystalline and amorphous regions, due to glycosidic bonding as well as hydrogen bonding across fibers. The crystalline regions can form microfibrils on the fiber. The microfibrils tend to trap dirt and make the fabric look dull by diffuse scattering of light. The amorphous regions also tend to trap particulates in the fabric. Therefore, it may be beneficial to use a detergent containing cellulase enzymes when washing cotton fabrics [13–15,16]. Depending on the type of cellulase, it can break bonds in both amorphous and crystalline regions. This opens the fabric so that the trapped particulate can be more easily removed by the rest of the detergent system. Also by removing the microfibrils, the fabric reflects more light, and therefore the colors may appear brighter [13–15,16]. Cotton fabrics can withstand high-temperature washing, and are resistant to destructive oxidation due to bleaches. Another advantage of cotton fabrics is that typical fluorescent whitening agents deposit very efficiently.

Synthetic fabrics, particularly polyester and polyamine (nylon), are produced from polymerization of carbon- or nitrogen-based monomers. These materials are spun fibers [17] and are much smoother than comparable cotton fibers. The cross-linking due to hydrogen bonding does not occur in synthetic fibers. Also, because there is no amorphous structure in synthetics, the entrapment of particulates in the fiber does not occur as it does in cotton. Synthetics are much less tolerant of high wash temperatures, as the fibers can melt at high temperature. They are also much less tolerant of oxidation due to oxygen bleach or hypochlorite. There are also a limited number of fluorescent whitening agents that deposit on synthetic fabrics. Most notably, synthetic fibers are much more hydrophobic than cotton, which results in oily stains being more strongly bonded to synthetic fibers than to cotton. Therefore, a detergent technology with great applicability for synthetics is soil-release polymer. Soil-release polymers are typically copolymers of polyethylene–polyethylene terephthalate [18,19]. They bind to the polyester fiber during wash, and make the fiber more hydrophilic. When the fabric is then stained with oily stains, the stains are more easily removed in the subsequent wash. Multiple washes result in a buildup of the soil-release polymer, creating a thin film on the garment. Although there have been soil-release polymers patented for cotton fabrics, their use is extremely limited.

Wool is the third major fabric class. Wool requires very different detergents than either cellulosics or synthetics. Wool is spun from animal hair (typically sheep) and is composed of proteins with sulfide linkages. Given its composition, detergents for wool need to be neutral or slightly acidic pH, since alkaline pH may result in felting (an irreversible change in shape due to breaking of disulfide bonds between fibers) [16]. Therefore, builders such as phosphate, zeolite, and sodium carbonate must be avoided. Also, detergents containing protease are not advisable. Low water temperature is a must to prevent shrinking. There are a limited number of specific brighteners that deposit on wool.

4.4.2.5 Soil Composition

Finally, the composition of the soil to be removed can dictate the type of detergent used. Soils can be categorized in four major classes: particulate, oxidizable, enzyme, and oily.

Particulates include dirt, clay, and soot. These materials respond well to detergents containing LAS and tripolyphosphate. When there is a high particulate load in the wash, antiredeposition agents also provide added benefits by solubilizing the entrapped particulate, thereby preventing its redeposition on the clothing during the wash cycle.

Oxidizables consist of oxidizable stains, such as coffee, tea, grape juice, and tomatoes. Both LAS and phosphate are somewhat effective on these stain types. However, to achieve the next level of stain removal, bleach is required, whether hypochlorite or oxygen bleaches, such as perborate or percarbonate. In high-temperature water (90°C), perborate will dissociate to produce hydrogen peroxide in sufficient quantities to promote bleaching action. At lower temperatures, an activator is required, typically tetra-acetyl-ethylene-diamine or sodium nonaoyloxybenzene sulfonate. Activated bleaches are found in powder detergents. Activated bleach or hydrogen peroxide is typically incompatible with liquid detergents or laundry bars.

Enzyme-based stains are a very broad class of stains, depending on the enzyme in question. Protease-sensitive stains include blood, grass, and body soils [20]. Amylase-sensitive stains include bananas, potatoes, chocolate fudge pudding, and other food stains [21]. Lipase-sensitive stains include salad dressing, tomato sauce, and the like [22]. Although all of these stains can be removed to a great extent by standard detergent ingredients, in many cases complete removal is only achieved with enzyme-containing formulas. Enzymes can be present in either powder or liquid formulas; however, enzyme stability is much higher in powders, since the enzyme is granulated and therefore is isolated from surfactants and builders that can denature it.

Oil-based stains include sebum, salad oil, natural and synthetic lubricants, and liquid makeup. Oily stains respond well to nonionic surfactants and alkaline conditions. Particularly for triglyceride-based oils, the alkaline condition facilitates the cleavage of the ester linkage. The resultant di- or monoglyceride is more easily emulsified by the surfactants. Lipase also is effective on oily stains, for the same reasons [23]. Finally, high-temperature washing also improves oily soil detergency significantly. Oily stains on synthetics often require the use of formulations with soil-release polymers for complete stain removal.

4.4.3 End Benefit

Obviously, consumers wash their garments to remove soil and leave a fresh, clean finish. However, aside from the basic result of laundering, there are other dimensions of cleaning and fabric care that detergents can provide. These are discussed in detail in the following sections.

4.4.3.1 Whitening/Brightening

Basic cleaning can be broken down into two dimensions—whitening/brightening and stain removal. Whitening/brightening focuses on improving the overall appearance of a garment. There are a number of technologies that can be used to achieve a whitening/brightening effect. Three approaches are to remove soil from the surface (dinginess removal), to increase the emission of light from the surface (brightening), and to alter the hue of the surface (bluing/tinting).

Obviously, the first desired step in whitening is to thoroughly clean the surface of the fabric. Over time and usage, garments tend to lose their initial appearance, becoming grey and dingy [24,25]. This also happens to colors, except that they become dull and washed out. In analyzing dingy garments, it has been reported that the garments tend to contain high levels of metals, sebum, protein, and particulates [24,25]. Metals, from both wash water and antiperspirants, become embedded in fibers of the garment. They attract sebum from body soil. The sebum acts as a glue for dirt and proteins also from body soil. These materials become entrapped in the fibers. They are removed partially by conventional detergents (LAS and STPP), but not completely. Additional technologies are required to remove these materials. Cellulases can open the fibers, enabling access to the materials. Polymers can be used to remove the metals, proteases likewise to remove the proteins. Combinations of these technologies, in a detergent containing healthy levels of surfactant and builder, are very effective at both preventing dinginess and restoring dingy garments [26].

The second method of whitening is to increase the emission of light from the surface by the use of fluorescent whitening agents (FWAs). FWAs are aromatic compounds that deposit on the fabric. They absorb UV light and emit visible light, thereby increasing the emission from the fabric surface, making it appear whiter/brighter [27].

The third method of whitening is altering the hue of the fabric by tinting. This is done by adding a substantive colorant to the detergent at low levels. The material deposits evenly on the fabric and alters the shade of the fabric. Conceivably any color could be chosen, but the tint of choice is usually blue. Bluing is a well-known process that has been used for over a century. Studies have shown that whites tinted toward the blue hue are perceived as whiter by consumers [28–30]. Presumably the blue tint counteracts the yellow part of the light spectrum in the human eye. Potential downsides of tinting include buildup of multilayers of tint, resulting in staining of fabrics.

4.4.3.2 Stain Removal

In contrast to whitening, which is a total garment phenomena, stain removal tends to be a localized process. Stains can be characterized as a localized, high concentration of unwanted material on a garment. Types of stains and technologies designed for their removal were discussed earlier in the chapter.

There are other attributes from the laundering process that consumers desire beyond basic cleaning. In many cases, these attributes are mutually exclusive with maximum cleaning, and so there is an optimization of the detergent system to balance cleaning with other attributes. Some of these attributes include color protection, fabric softening, fiber restoration/protection, and antibacterial and antiallergenic action.

4.4.3.3 Color Protection

Color degradation can be broken down into three different processes: fabric degradation, dye removal from fabric, and dye transfer in the wash process. Color protection can be achieved by attacking any one of those processes. Typically color protection is documented over multiple washes, due to the levels of ingredients used and the sensitivity of the eye to slight changes in color [31].

Fabric degradation is particularly prevalent on cotton fabrics. On abrasion, multiple washes, or use of highly alkaline detergents, cotton fibers form microfibrils. Visually, the consumer sees pilling on the garment [13–15,16]. On a microscopic scale the microfibrils scatter the light more diffusely, making the color of the garment look duller. As discussed earlier, cellulase will break the glycosidic bonds of the microfibril, eliminating these fibrils and therefore making the color of the garment look brighter and newer.

Dye removal from fabric is the major culprit in color degradation. This tends to be an issue on cottons more so than synthetic fabrics. In synthetics, the color is typically spun into the fiber during synthesis. With cottons, the dye is applied to the surface of the finished cloth. Detergents are designed to removal materials from the fabric surface, and dyes are no exception. The degree of dye removal depends on a number of factors, such as the chemical composition of the dye, the dyeing process, additional fabric finishes and dye fixatives, and the type of detergent used.

Dye removal can be mitigated by using detergents with lower levels of sodium carbonate. The lower alkalinity of the wash liquor solubilizes less dye. Color protection polymers are also available. Many of these polymers are amine based, and act as dye fixatives, locking colors onto the surface [31–35]. One drawback of such materials is that they can lock dirt as well as colors onto the surface, and therefore compromise detergent cleaning performance. Color protection has also been reported via the addition of amphoteric cosurfactants to highly anionic detergent systems [36]. These materials behave similarly to color protection polymers, without impacting the cleaning performance of the detergent.

Dye transfer is the result of dye removal. In a mixed load, dye removed from garments is free in solution and then deposits on another garment, changing its color. An example is the addition of a red sock to a load of whites, resulting in pink garments. Dye transfer is particularly obvious on pastels and light colors, but can occur in all wash types. This can be counteracted by a class of polymers known as dye transfer inhibitors (DTI). Dye transfer inhibitors, such as polyvinylpyrrolidone and its derivatives, reportedly interact with dye molecules in the wash liquor and act as antiredeposition agents [37–39]. The effectiveness of DTIs is dye dependent and formula dependent.

All of the technologies listed above for color protection must be employed over multiple washes to see benefits, typically in a comparative setting. There are no commercially available detergents to date that provide consumer-perceivable color protection in the first wash.

4.4.3.4 Fabric Softening

Another attribute often desired in laundering is fabric softening. Detergents remove materials from the fabric surface, whereas standard softeners deposit lubricating materials on a surface, which is why softeners are usually added during the rinse cycle. However, for a variety of reasons, consumers are interested in products that both clean and soften in the wash cycle. Softergents, as these products were known, were common in the 1980s, but due to deficiencies in both cleaning and softening, eventually were discontinued. However, in the early 2000s, these products were reintroduced as detergents with a touch of softener. These products focus on cleaning, with a slight softening benefit. The softening benefit is reportedly greater than no softener but significantly less than rinse cycle fabric softener [40]. It has been reported that softening in these systems is form dependent. For powders, the softening ingredient is typically clay [41]. During the wash, clay adsorbs on the fabric surface, and the platelets expand in solution, providing a softer hand to the fabric. For liquids, a small amount of lauryl trimonium quaternary amine is often used, particularly in more nonionic surfactant systems [40]. Silicones can also be used as effective softening agents in detergents [42]. Detergents with softeners also contain lower levels of sodium carbonate and anionic surfactant, as both these materials tend to harshen the fabric surface. This formulation change also can reduce cleaning performance. Again the challenge is to provide softening benefits with minimal negative impact on cleaning.

4.4.3.5 Fiber Restoration/Protection

In this category of attributes are shape retention, fiber elasticity, and other care attributes not covered in the previous sections. Over multiple washes, fibers are distorted or compressed and lose their elasticity. This results in general wrinkling and loss of shape. Detergents focusing on this attribute contain silicone and silicone-based polymers, designed to act as lubricants to the fiber. The additional lubrication reportedly increases the elasticity of the fibers [32–35].

4.4.3.6 Antibacterial Action

In addition to removing dirt and stains, detergents also remove bacteria and various microbes from the surface of clothes very effectively. This effect is enhanced by hot water temperatures, high detergent concentration, and soaking. However, to claim an antibacterial action for detergent, in many countries (USA included) a set testing protocol must be followed that results in a 3 log reduction in the bacterial activity on the cloth [43]. Typically, this level of benefit is attained through the use of detergents containing activated bleach. In many cases, the claim is documented using the detergent at higher-than-normal concentration with a soaking regimen.

4.4.3.7 Antiallergenic Action

Antiallergenic action is also an attribute desired by many consumers. In many cases, these types of detergents contain no colorants or fragrances, and are marketed as *free* detergents. In addition, an antiallergenic claim may be made on a detergent when it is documented by a series of tests showing allergen removal and dust mite kill [44–46]. Again this effect is enhanced by hot water, high detergent concentration, and soaking. The effect is not necessarily due to an added unique technology, but to the laundering regimen used.

4.4.4 EXTERNAL FACTORS

In addition to the particulars of the laundering system, there are external factors influencing the detergent formulation that the consumer uses. In many countries there are regulations regarding various detergent ingredients which impact detergent manufacturers. Some examples are the local/regional regulations in the United States banning phosphate in detergents, which resulted in removal of sodium tripolyphosphate from all U.S. detergents [47]. In Europe, a similar result occurred due to the legislation requiring the E.U. to determine phosphate restrictions by April 2007 [48]. Additionally, in the Nordic countries there are strict regulations on what ingredients can be included in detergents at particular levels to achieve a Nordic Swan label, designating the product as environmentally acceptable [49]. Also, there is pressure to limit or eliminate the use of other ingredients due to environmental impact. This is emerging in Europe with the REACH initiative, which strives to have a complete safety/toxicology portfolio on all chemicals, including those in detergents, and to define acceptable chemicals from that list moving forward [50]. Finally, there are ongoing initiatives on sustainability that may drive products toward continued concentration and desulfation [51]. These initiatives are trade-driven and focus initially on North America and Europe, and will have a definite impact on products available to the consumer.

4.5 CONCLUSION

As can be seen, laundry detergents are a complex mixture of ingredients designed to provide the consumer with an efficient and cost-effective method of cleaning clothes. There are a variety of forms and technologies available to consumers. The application of which form and technology to use is highly dependent on the physical and chemical parameters of the system, and the desired product benefits go beyond basic cleaning.

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5 Specialty Cleaners

Karen Wisniewski

CONTENTS

5.1 INTRODUCTION

Household cleaners are generally classified as either *all-purpose* or specialty cleaners. The difference lies in how strongly focused the cleaner's action is against a specific soil. All-purpose cleaners are essentially what their name indicates—for all soils on all surfaces. In fact, all-purpose cleaners usually emphasize their ability to clean grease, demonstrating cleaning greasy messes in advertising or showing grease-cleaning tests in the patent or patent application. There are other household soils—dust, some particulates, dried-on food—that can be largely cleaned with water. Grease, being a hydrophobic soil, tends to be hard for water to remove and so is most affected by the addition of the surfactants and other cleaning ingredients. However, there are other household soils that are not grease based—hard water buildup (limescale), soap scum, baked-on food—that are also challenging to clean. Specialty cleaners are usually closely targeted at the chemistry of the specific soil. Specialty cleaners are therefore also somewhat limited in their scope of use, but should justify their worth by being powerful against their chosen soil.

5.1.1 DEFINITION AND SCOPE

Hard-surface cleaners are those products that are formulated to be used for household cleaning by consumers. For the purposes of this discussion, products used only in industrial and institutional cleaning of hard surfaces will not be included. (The topic of institutional and industrial cleaners is covered in a separate chapter of this book.) These "I&I" cleaners can be quite similar to household cleaners, as they are often used on the same soil/surface combinations (e.g., soap scum on tile in a hotel shower), but the I&I field is also larger than household cleaners, as it can also include dish sanitizers, metal cleaners, and malodor treatments.

Household cleaners are generally used on every hard surface in the home except for dishes. In this chapter, the discussion concentrates on specialty cleaners that are formulated for specific cleaning problems, whereas all-purpose cleaners and their variants are covered in Chapter 2. This means that most of this chapter will be spent discussing cleaners used in the bathroom—such as soap scum cleaners, mildew removers, and toilet bowl cleaners. Additionally, there are cleaners that are used for extremely narrow use, such as oven and drain cleaners. Disinfectant cleaners as variants of all-purpose cleaning were covered in the previous chapter, but will also be covered here with the emphasis on the disinfectant action rather than on the cleaning function.

This chapter will not discuss some products that are not cleaners *per se* but are often grouped with household cleaners in various business or economic reports. This includes products like air deodorizers in all their various forms and furniture polishes. These are not so much cleaners as *treatments* to either the air or a surface. Wood cleaners are also not covered here, as they can be considered as all-purpose cleaners with a specific recommended use and so were covered in Chapter 2.

Specialty cleaners tend not to appear in as many diverse forms as general all-purpose cleaners. All-purpose cleaners appear in powder, liquids in conventional bottles, sprays, wipes, pastes, gels, and suspensions. Specialty cleaners tend to be mostly liquid formulations delivered in packaging tailored to the specific use. (The biggest exceptions to this are powder drain cleaners and toilet cleaner blocks.) The specialty cleaners could be said to have benefited most from the packaging developments of the past 40 years compared to the all-purpose cleaners. The newer packaging forms serve to *short circuit* the cleaning process by eliminating cleaning solution preparation, easing application, and shortening the put-away process. In the case of wipes, the implement is even supplied in disposable form. There are all-purpose cleaners, aimed at spot cleaning or quick cleanups, that occur in these forms, but all-purpose cleaning is still dominated worldwide by the dilutable cleaners in simple bottles or bags. However, in developed markets, products like bathroom cleaners or toilet bowl cleaners are dominated by forms in specialty packaging—sprays, special dispensers, and aerosols—over bottles with conventional open/close closures. The advantages of these packages for these jobs seem to greatly augment the chemistry inside the package.

Specialty cleaners are also largely a phenomena of developed countries. Given the smaller disposable incomes among households in developing markets, income tends to be spent on the main all-purpose cleaners—dishwashing product, laundry detergent, and bucket dilutable cleaners. These cleaners give the largest *bang for the buck* in terms of the number of cleaning occasions per package, but the consumer also has to spend more time and more of her own energy cleaning because the cleaner is not as targeted against the soils. This is not to say that specialty cleaners do not exist in developing nations, but the products discussed in this chapter will concentrate on those sold in developed markets.

5.1.2 Outline of the Discussion

The kitchen and bathroom tend to be the two rooms of the house that have the most cleaning jobs—both high amounts of surface that need cleaning and relatively high amounts of soil on those surfaces. Countertops, floors, sinks, and cabinets have to be cleaned in both, and the kitchen has stovetops, appliances, and tables, and the bathroom has toilets, bath enclosures, and mirrors. Both have a characteristic dominant soil—grease in the kitchen and soap scum in the bathroom—but the number of subsidiary soils are different. Both rooms also have dust, dirt, and hard water spotting, which in the bathroom can become actual scale buildup. The other soil in the kitchen would be food spills and splatters. The bathroom's additional soils include toothpaste residue, cosmetic spills, hair spray films, hair, and, in the toilet, excrement. Grease-targeted and general-purpose cleaning were covered in a previous chapter, whereas this chapter covers these bathroom cleaning problems. Additionally there are the chemical digesting cleaners—oven and drain cleaning—which are very targeted cleaners. The chapter begins with a discussion of the general formulation, followed by details of performance and robustness testing. Surfactants are key to these cleaners, but their choice is subsidiary to the overall chemistry—acid, base, and bleach—necessary to attack these particular soils.

5.1.3 Goals of Formulation

The goals of formulation are reasonably straightforward:

- To use the most safe chemicals (to the person, surface, and the environment)
- To remove the soil effectively
- Not to damage the underlying surface
- To use the most convenient method
- To keep cost at a minimum

Surfactants are, of course, key to these objectives. However, with specialty cleaners, the choice and action of the surfactants in the formulation are subject to the chemistry, which is targeted at the soil removal. Unlike grease removal, which is largely facilitated by the surfactant content of a cleaner (due to the hydrophobic nature of greasy soils), other household soils can be attacked chemically, and it is this attack that has a significant effect on soil removal. Surfactants, however, are necessary to the formulation for two reasons. Because the formulations are water based, surfactants significantly decrease the surface tension of the cleaner, facilitating contact with the surface, which in turn is the key first step in the cleaning process. Secondly, surfactants also facilitate the removal of the loosened or altered soil from the surface and help prevent its redeposition.

In addition to the main objective of cleaning the surface, cleaners often have added benefits built in. Among these consumer desirable additions are maintenance or increase in surface shine, disinfection of surfaces, decreasing soil tenacity, and deodorization. Many of these are priorities in the bathroom, which contains many large shiny surfaces that are perceived to be *germy* (contaminated with germs) and covered with tough soils.

5.1.4 Product Forms

Specialty cleaners are largely a developed market phenomena. Less developed markets usually have consumers that are using all-purpose cleaners for truly all purposes. With more disposable income in developed markets, consumers can afford to have both all-purpose and specialty cleaners in their cabinets. The all-purpose cleaners are most used for greasy soil or *dirt* cleaning in the kitchen or household walls and floors, whereas the specialty cleaners are used for their target situations such as soap scum on bathroom surfaces.

Given that the specialty cleaners largely exist in the developed markets, they can also afford somewhat more expensive packaging that also gives the product greater convenience in application.

These forms would be spray trigger bottles, aerosols, squeeze bottles with specially shaped nozzles, and increasingly, wipes. These forms dominate many of the specialty product types, such as bathroom cleaners in the United States being available almost entirely as spray trigger cleaners. There are a few aerosol bathroom cleaning products, but virtually no bathroom cleaners as dilutable products in conventional bottles with simple closures such as flip caps. Although this is still a very popular form for all-purpose cleaners (and was an original form for bathroom cleaners) it has essentially died out in the United States in favor of the spray triggers.

Most specialty cleaners come as water-based liquid formulations, although there are exceptions. Drain cleaners now have liquid as well as powder forms. Automatic toilet bowl cleaners come both as liquids in elaborate dosing containers and as solid blocks or pucks. Oven cleaners tend to come as aerosols or liquid sprays. Most of the bathroom cleaners, shower treatments, toilet-bowl cleaners, mildew removers, and the like are liquids.

5.2 SPECIALTY CLEANERS

5.2.1 ALKALINE-BASED CLEANERS

First this discussion will turn to the simplest of the specialty cleaners, those based on very high pH: the oven and drain cleaners. Both are usually based on a high concentration of an alkaline ingredient such as sodium hydroxide. In both cases, the alkalinity of the formula is key to its ability to clean the soils encountered in these problems. The choice of surfactant is somewhat limited, as the surfactant needs to be stable at pHs of 11–14, but there is still reasonable choice. The main function of the surfactant in these products relates primarily to their foaming.

5.2.1.1 Drain Cleaners

One of the main requirements of drain cleaners is that they need to be able to reach the clog in the piping. This dictates the form, which must be something that can sink down the piping to where the clog is. This has brought a number of forms, such as powders, high-density liquids, thick gels, and even containers that are pressurized to send the product down the pipe.

Clogs are usually a conglomeration of greasy deposit mixed with food residues (kitchen) or hair (bathroom). Many drain cleaners contain a high amount of sodium hydroxide as the primary source of alkalinity that degrades the grease components. If the product is in solid form, the dissolution of the hydroxide in water also generates heat, which helps to melt the grease in the clog. The formula can also contain hypochlorite, which helps to degrade hair and other protein-type soils. In liquid form, this takes the form of the usual sodium hypochlorite, but in granular or solid form, the product usually contains compounds that break down into hypochlorite when dissolved. These bleach-generating compounds can react with the hydroxide, so the hydroxide particles must be coated or otherwise prevented from interacting.

Drain cleaners have also traditionally contained ingredients to generate a gas so that the area around the clog is agitated, increasing the interaction of the product with the clog ingredients. In earlier days, this was said to be done by combinations such as sodium nitrate, a hydroxide, and aluminum to generate ammonia gas [1]. However, they can also contain ingredients that are typically used to create effervescence, usually acid/base combinations like bicarbonate salt and citric acid. However, these are more common in the powder or granular forms than the liquids. If both a hypochlorite and a peroxide compound are included in a formula, then oxygen gas can be generated, which is assumed to agitate the clog area [2]. This can also be done in a liquid form, but directions are given that the two ingredients are kept separate until the time of use [3].

Surfactants therefore are a small part in the declogging process. Much more typical is that surfactants are used in the liquid products to form thickening systems, with examples in the literature such as quaternary ammonium surfactants (*quats*) [4], betaines [5], or the more typical amine oxide/soap combinations, which are said to be stable in bleach systems [6]. It is believed that thickened liquids are

TABLE 5.1
Examples of Drain Cleaner Compositions

Ingredients (with Some Typical Examples)	Purpose	Solid (Powder or Granular) (w/w%)	Liquid (w/w%)
Alkali metal hydroxide (usually NaOH)	Strong alkalinity	40–80	0.1–20
Chlorine bleach; solid example: chloroisocyanurates; liquid example: sodium hypochlorite	Oxidizing agent	5–40	1–15
Oxygen generator; solid example: sodium perborate or percarbonate; liquid example: hydrogen peroxide	Make O2 with chlorine bleach	5–10	0.01–5
pH adjustment base: silicate, carbonate, bicarbonate acid: sulfuric or citric acid	Stabilize bleach or peroxide, provide effervescence	0–30	0–10
Salt; example: sodium chloride	Increase ionic strength, *densify*	—	0–30
Surfactant: quaternary ammonium amine oxide/soap betaine/sodium xylene sulfonates	Thickening	—	0.1–15
Surfactant: ethoxylated alcohols, alkyl benzene sulfonates, fluorosurfactant	Foaming	0–5	
Solvent: methyl pyrrolidone, limonene, methyl soyate	Noncaustic/nonbleach formulas	—	5–90
Thickener: methyl cellulose	Noncaustic/nonbleach formulas	—	1–10
Water	Filler		q.s.

better able to penetrate standing water without becoming diluted and therefore have greater efficacy against the clog [7]. They are probably also helped by their high concentration of sodium hydroxide, which increases the density of the liquid as well. However, surfactants are sometimes also used simply to create a foam; as most drain cleaners generate a gas of some kind to agitate the liquid containing the product in the pipe, a surfactant present could result in a foam whose expansion is said to have both some physical effect on the clog and to encourage contact with all the soiled surfaces [8].

There have also been efforts to formulate drain cleaners that are claimed to be less toxic or less chemically aggressive and therefore safer for a consumer to use. They usually base their action on solvents. There are formulas for which these assertions are made based on a lack of the typical hydroxide/bleach ingredients [9] or on the basis of safer solvents [10].

There are some examples in the patent literature of acid drain cleaners, but these are either industrial applications or based on high concentrations of sulfuric acid. There seems to be a consensus that the acid versions are too dangerous for consumers to handle, and the commercial formulas are alkaline. Some examples of ingredients and their relative concentrations for drain cleaners are outlined in Table 5.1.

5.2.1.2 Oven Cleaners

Similar to the situation with drain cleaners, one of the main requirements of oven cleaners is their need to reach and maintain contact with the soiled surface. This poses a challenge in oven cleaning, because of the vertical surfaces in the oven. Therefore oven cleaners often tout their ability to cling to the surface and therefore work more effectively. The main soil in oven cleaning is baked-on grease and food residues that have been oxidized or polymerized on the oven surfaces. These are not easy to clean soils, and they usually require long contact time (*soaking*) with the

TABLE 5.2
Examples of Oven Cleaner Compositions

Ingredients (with Some Typical Examples)	Purpose	Concentration (w/w%)
Alkaline agent: sodium or potassium hydroxide, ethanolamines, carbonates, bicarbonate	Supply high pH for breakdown of soils	Hydroxides: 20–30; ethanolamines: 1–15; carbonates: 1–10; bicarbonates: 1–20
Solvent: glycol ethers	Soften soils	2–30
Chelator: EDTA, sodium gluconate	Control of hard water salts	0–1
Surfactant: alkyl sulfonates, ethoxylated alcohol sulfate, ethoxylated alcohols, betaines, amine oxide, sarcosinates	Foaming (cling), wetting	0–2
Thickener: usually clays	Cling	0–1
Fragrance and color	Aesthetics	<1
Propellant: alkanes such as isobutene	Only in aerosol products	2–10
Water		q.s.

cleaning product. There are two popular approaches to prolonging contact time on vertical surfaces: foaming and thickening. If the product has a high viscosity, it will tend to flow more slowly down the sides of the oven than a thinner product. Likewise, if the product is foamed, the foam form also tends to cling to the vertical surface. Also, thickening or foaming the product tends to produce less mist when the product is sprayed; given the very high alkalinity of these products, this mitigates the unpleasantness and increases safety to the consumer. Therefore, oven cleaners come in either spray triggers or aerosol cans, which help distribute the product evenly over the entire surface.

Also similar to the drain cleaners, the main ingredient in oven cleaners are alkaline agents such as sodium hydroxide or ethanolamines. Cleaners that do not use sodium or potassium hydroxide for the alkaline agent are usually referred to as *noncaustic*. The alkalinity has to be formulated so as to be compatible with today's modern oven surfaces, such as self-cleaning ovens that have catalyst imbedded in the finish of the surface. (Consumers do clean *self-cleaning* ovens with products between self-cleaning cycles—the cycles take extended time and very high temperatures that discourage consumers from using them often.) Again, the main form of cleaning is the attack of high pH on the baked-on soil. Therefore, the surfactant is adjunct to this action, facilitating surface contact (by lowering the surface tension) and, in foaming products, being the ingredient that provides the foam. This also uses surfactants such as alkyl sulfonates, amine oxides, and betaines. When the product is thickened to increase its cling, the thickeners shown in patent properties are those compatible with high pH, such as the polyacrylates, clays [11], and sometimes cellulosic thickeners [12]. Examples of ingredients and their relative concentrations are given in Table 5.2.

5.2.1.3 Testing Methods for Strong Alkaline Cleaners

The testing methods for efficacy of these products are different from other specialty cleaning products, consisting largely of static soaking tests. For oven cleaners, this means the application of a soil that is applied to either porcelain test plates or a section of oven wall material and baked on at high temperatures (205–232°C or 400–450°F). The soils can either be pure grease, mixed food and grease, or only food. However, key components seem to be fat/oil, sugar, and protein. After the soil has been baked onto the surface, the cleaner is applied. The soiled surface with cleaner is then maintained conditions similar to those of the oven walls—in a vertical position, at a specified temperature, and enclosed. The temperature may be either room temperature or moderately hot, depending on the condition contemplated for use. After a set dwell time, the cleaner is either wiped or rinsed from the surface, and the degree of cleaning is determined.

For drain cleaners there are also static tests. The main challenge seems to be the action of the declogger on hair, and so the decomposition of hair is often featured as a key test. There is a patented method, where there is a drain model with areas for placing clog components; clog ingredients are placed, treated, and then removed and weighed to determine the efficiency of the cleaner [13]. In both cases, the test not only gives an indication of how much soil can be removed in a given time but also whether or not the test surface is damaged during this soak time.

5.2.2 BATHROOM CLEANERS

Most of the specialty cleaners that are formulated for household use are intended for the bathroom. Although hard water scale can occur in any room with running water, soap scum and mildew tend to be concentrated in the bathroom. Bathroom cleaners mostly are claimed to have action against the *big three* of bathroom soils: soap scum, mildew (or mildew stain), and hard water buildup. These soils are best removed with specialized chemistry, and so the specialty cleaners are very successful in this area.

What will become evident in this discussion is that bathroom cleaners tend to one end of the pH range or the other. This is partially due to the chemistry involved in disinfecting surfaces—disinfecting cleaners are very popular for bathroom use. pHs below 5 and above 8 tend to facilitate disinfection chemistries such as those due to hydroxy organic acids, quats, and bleaches. Quats give effective disinfection throughout the pH range, but are usually formulated at higher concentrations between pH 5 and pH 8. Hydroxy acids work (of course) at lower pH, and peroxy bleaches are stabilized at very low pH, and become more active as the pH rises. Hypochlorite bleaches are stabilized at high pH and become more active as the pH drops, such as through dilution or use.

However, the pH also tends to the extremes because of the chemistry of the soil removal as well. Acid formulas tend to remove soap scum and water scale better, because the low pH tends to reverse the chemistry that made the soil, namely the formation of insoluble calcium salts. However, mildew is decolorized seemingly best with hypochlorite bleach, and so is better cleaned at high pH. Mildew and soap scum often occur together as bathroom soils, and so it would be desirable to have a cleaner that removes both. There are cleaners that are claimed to clean both, but they are usually formulated at one pH extreme or the other, and therefore tend to give weaker performance on the soil of the opposite pH. A cleaner that powers through soap scum/water scale while rapidly decolorizing mildew stain would be the *holy grail* of bathroom cleaning.

5.2.2.1 Toilet Bowl Cleaners

Toilet bowl cleaners are a good example of this dichotomy of pHs in bathroom cleaners. Manual toilet bowl cleaners are usually either acid cleaners or hypochlorite cleaners. Toilet bowl cleaners also come in two different forms. There are the in-bowl, manual cleaners that are the most effective, largely because they are applied in high concentration directly to the dirtiest area and the cleaning usually includes mechanical action with some kind of implement. The other product type is in-tank cleaners. These are products that are usually put into specialized packaging that parcels out a portion of the product with each flush. (There are also products of this type where the dispenser is put on the bowl edge instead of inside the tank.) These are low-concentration products in use that serve more as maintenance products. There has also been a recent development that combines the cleaner with nonwoven pad to give the in-bowl cleaner on an implement, ready to use. Surfactant in these products serves one or more of the following purposes—cleaning through soil wetting/solubilization, foaming to let the product reach higher than the water level on the bowl wall, and signal to the consumer that the product is still present and active (for *automatic* cleaners).

5.2.2.1.1 "Automatic" Cleaners

One kind of toilet cleaning product is called *automatic* because the consumer adds it to the toilet once and then the dosing of the product is done, either by dissolution or a dosing dispenser, for the life of the product. These can be added to the toilet in two different places: in the tank or fixed to the rim of the bowl. These cleaners run the range in terms of strength of cleaner. In general, most tend to be weak cleaners, composed largely of surfactant, filler, and dye. These can be acidic, neutral, or alkaline. The simplest forms are neutral, but products with more cleaning or disinfecting claims tend to be acidic or alkaline, based on the other ingredients needed to make the stronger claims. They are dispensed as liquids or slow-dissolving tablets, which then give a small concentration of surfactant and relatively high concentration of dye to the bowl water. For these products the main function is to *freshen* the toilet after each flush, including giving a burst of fragrance, which may be claimed as an advantage of the cleaner [14]. The high dye concentration in the product (compared to other household cleaners) gives a visible color that appears in the toilet bowl water, signaling that the product is still active. Some also find this effect aesthetic. Products of this type also make statements about keeping the bowl cleaner between physical cleanings [15] or long-lasting antimicrobial action just by virtue of having the disinfectant agent always present in the bowl [16]. If the disinfecting agent is bleach, then the product is usually colorless due to the susceptibility of dyes to bleach attach, but there are those who claim that colored bowl water can still be produced even in the presence of bleach [17].

Automatic cleaners have two main forms: solid (also called *pucks* or tablets) and liquid. If the product is in the form of a liquid, then the dispensers can become quite elaborate to hold the product and release a small amount into the water with the flush. (For example see Refs 18–21.) Usually they work on some sort of siphon device. Devices are also placed along the rim of the toilet bowl, to dispense either continuously or on every flush, depending on how the device is made (For examples see Refs 22–24.) There has even been an effort to apply the talents of a designer to the shape of the dispenser, in this case a rim dispenser (Figure 5.1—picture of Alessi surfer). Examples of ingredients and their typical amounts are given in Table 5.3. The amounts of active ingredients in the

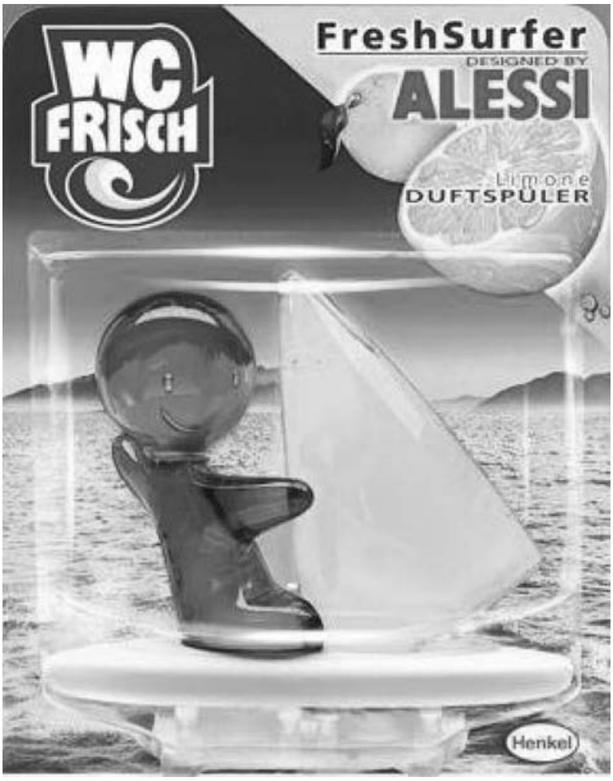

FIGURE 5.1 Unusual rim attached toilet bowl cleaner dispenser.

formulas are high, but this is because only a very small dose is given at a time and is diluted in use by the volume of water in the bowl.

The other form, the puck, consists of solid tablets in a variety of forms. In this case, the majority of the formulation effort is devoted to making a stable pellet that dissolves at a near constant rate. This is accomplished with a variety of tablet ingredients, including plasticizers, binding agents, and fillers. Various issued patents are directed to the rate of dissolution or release of product from the tablet [25–28]. It seems from the literature to be difficult to make stable tablets when they contain bleach [29]. Tablets are also convenient for delivering formulations with mutually incompatible ingredients, which patent applicants say can be done by making dual tablets [30,31]. There are also limits on the ingredients, depending on the method used to make the block. The two main methods are molding and extrusion, each with its own drawbacks [32]. This type of formulation is shown in Table 5.4.

TABLE 5.3
Automatic Liquid Toilet Bowl Cleaners Formulation

Ingredients (with Some Typical Examples)	Purpose	Concentration (w/w%)
Surfactant: linear alkyl sulfonates, ethoxylated alcohols	Cleaning, wetting; if germicide present, needs to be compatible	0.5–20
Polymer: polyester, polyacrylate	Thickening, surface modification	0.05–10
Solvent: alcohol	Rheology, solubilization of ingredients	10–20
pH control: NaOH		0–2
Germicide: modified phenols, quaternary ammonium surfactants	Disinfection, bacteriostatic action	0.5–6
Perfume	Aesthetic	0.5–1
Dye	Coloring of bowl water	0–5
Water		q.s.

TABLE 5.4
Solid Tablet Toilet Bowl Cleaners Formulation

Ingredients (with Some Typical Examples)	Purpose	Concentration (w/w%)
Surfactant: linear alkyl benzenesulfonate, lauryl sulfate, ethoxylated alcohols, ethoxylated alkyl sulfate, paraffin sulfonates, betaine	Cleaning, wetting; need to be bleach stable if bleach is present	2–60
Disinfection: chloroisocyanurates, chloro hydantoins, calcium hypochlorite, quaternary ammonium surfactant	Germ killing; also, stain removal from bleaches	0–80
Polymer: polyacrylate, cellulose, hydrophobically modified cellulose	Binder	1–35
Plasticizer: stearates, ethanolamines, polypropylene, limonene, EO-PO copolymers, silicone oil	Make tablet less friable	0.25–25
pH adjustment/chelation: alumina, silicate, tripolyphosphate	Stability and cleaning	10–20
sodium citrate, sodium bicarbonate, sodium carbonate		
Perfume	Aesthetic, deodorization	1–15
Dye	Coloring of bowl water	8–25
Filler: sodium sulfate, sodium chloride		0–50

In most cases, these products are neutral, depending on the action of chelants/builders and surfactants to maintain the cleanliness of the bowl. Unlike with the manual products, there are few citations of products that are acidic. Products that are not neutral usually are alkaline, because of the inclusion of chlorine bleach or quaternary ammonium surfactants as disinfection agents. Bowls with organic staining may need bleaching, so the hypochlorite bleach can also supply this need. Bleach does not seem to be usually found in the liquid products, but it is often present in the tablets in the form of chloroisocyanurates, which break down on contact with water to hypochlorite. Toilet-cleaning products are some of the few household cleaners that have formulas in the literature with peroxygen bleaches as well as chlorine based [33]. The other type of staining that may be found in the toilet bowl are iron or rust stains, which seem to require chelators to attack [34].

5.2.2.1.2 In-Bowl Cleaners

In-bowl cleaners are used with mechanical cleaning by the consumer. These products are usually liquids, usually thickened in the range of 200–700 cP. The idea is that the product is dispensed up under the rim of the toilet and then runs down the bowl wall until it encounters the water. The package for the product often has a specially shaped bottle that enables placement of the product under the rim (Figure 5.2). The product should be thick enough to cling to the vertical wall and yet not be so thick that the product does not spread well. It should also have a foam profile that collapses quickly so that the product rinses away well. As in the case of many bathroom cleaners, these also come in two types, the acid and the hypochlorite.

The surfactant concentration is higher in use with the manual in-bowl cleaners than in the automatic cleaners, but lower in the product formulation as packaged. This is because the manual cleaners are used *as is* from the package, whereas most of the in-tank and on-rim products go through a dilution step before they get to the bowl. Especially different between the two types is the very high concentrations of dye and perfume in the automatic cleaners as compared to the in-bowl cleaners.

Disinfection is a high concern in toilet bowl cleaners, and many are claimed to have germ-killing action. Hypochlorite bleach is a very effective disinfectant ingredient, and this is used in toilet bowl cleaners, so the surfactant choice for this product needs to be compatible with bleach. For the acid cleaners, often the disinfectancy is derived from the acid itself; although this can be achieved with organic acids like citric or lactic, the active ingredient quoted on many toilet bowl cleaner labels is hydrochloric acid, which is antimicrobial at concentrations over 9.5% [35]. (It would be anticipated, however, that this level of mineral acid would be irritating to a consumer's hands. Use of hydrochloric acid therefore suggests that consumers' hands are minimally involved in the job of toilet bowl cleaning, as opposed to other jobs such as bathtub scrubbing.) As bleaches have the desirable side effect of bleaching susceptible (organic) stains in the toilet bowl, similarly an acid such as oxalic may also have the side effect of being able to remove rust stain; formulas

FIGURE 5.2 Tops of manual toilet bowl cleaning products.

have been claimed to have this action [36]. Occasionally, quats are added as the disinfectant; in this case the surfactant needs to be chosen to be compatible with both acid and quats. This essentially eliminates most anionic surfactants because of the tendency to precipitate with the cationic quat. This is also in favor of nonionics (which are compatible with quats), because they tend to be lower foaming than anionics.

Also (conveniently) in many cases, the surfactant system itself is self-thickening. This is especially the case with amine oxide/soap combinations that are used with hypochlorite bleach systems, as is well known, as well as variations on this theme [37], and amine oxide/soap systems that are shown to be supplemented by polymer [38]. There is also a citation for a system using alkyl ether sulfate, solvent, and electrolyte to thicken the system [39]. For systems with lower surfactant levels, sometimes the addition of polymers such as hydroxyethyl cellulose [40,41] or colloidal thickeners [42] are mentioned. The targets for these cleaners tend to be in the 200–1000 cP range, especially in the 300–700 cP range.

Toilet bowl cleaners are one of the few household cleaning products that also use oxygen bleaches as well as hypochlorite. Persulfate salts were used in powder toilet cleaners, but there are few of the powder forms left in developed markets. However, persulfates are now also appearing in liquid forms as well, which combines bleaching action with an acid pH [43]. Peroxides are stabilized by acidity, and then activated as the pH shifts up during use. Therefore, the acid can take care of the hard water deposits and rust, and then the peroxide can do its destaining and disinfection. Hypochlorite containing cleaners work in the reverse, being stabilized by alkalinity and then becoming activated as the pH is lowered by interaction with soils or dilution on use. Typical ingredients and amounts for in-bowl manual cleaners are seen in Table 5.5.

Given the apparent unpleasantness of the job of cleaning the toilet, there are two developments meant to go beyond making cleaning more effective. The first of these that are mentioned are the

TABLE 5.5
Manual Toilet Bowl Cleaners Formulation

Ingredients (with Some Typical Examples)	Purpose	Concentration (w/w%)
Surfactant: alkylbenzene sulfonate, paraffin sulfonate, ethoxylated alcohol sulfate, ethoxylated alcohol	Cleaning, wetting	0–20
Cationic surfactant	Quaternary ammonium	0–2
pH adjustment; acid: phosphoric, hydrochloric, oxalic, citric, sulfuric; base: sodium hydroxide		0.5–10
Disinfection (nonbleach): quaternary ammonium surfactant	Disinfection	0–1
Electrolyte: nitrate, chloride, sulfate	Assist with thickening	0–10
Bleach; acid: persulfate salts, hydrogen peroxide; alkaline: sodium hypochlorite	Stain removal Disinfection	0–10
Thickening agents: polyoxyethylene, cellulose gums, polyacrylate	Cling on surface need to be stable to bleach if bleach is present	0–1
Antisoiling agent: fluorosurfactant, fluoropolymer, ethylene oxide/propylene oxide copolymer	Longer-lasting clean, nonadhesion of soils (not usually used with bleach)	0–1
Perfume, color, etc.	Aesthetic	<2
Water		q.s.

addition of antisoiling polymers [44,45] or surfactants [46] to the formulations. These are meant to lengthen the time between cleanings, therefore making the job more acceptable by making it less frequent. The second of these is the production of integrated systems of implements with the cleaner. Similar to the mopping systems that have changed floor mopping, these systems are often listed as having a long handle with a detachable head made of a pad of nonwoven material [47–49]. This nonwoven is impregnated with the cleaning solution, similar to a diluted in-bowl cleaner. This has the advantage that when the job is done the implement, its cleaner exhausted, can be disposed of. This can be a problem if a rag or sponge is used to clean the bowl—what does one do with the implement after the job is done? Many consumers find storing a toilet brush unappealing, so the disposability of the soiled part of these utensils is very attractive.

5.2.2.1.3 Toilet Wipes

Related to the cleaner/implement systems are the toilet-cleaning wipes. These are not so much for cleaning the inside as the outside of the toilet. Although this can be done with typical all-purpose or bathroom cleaners, once again there is a higher than normal concern with disinfecting the surfaces of the toilet. It is also important to clean the surfaces thoroughly and leave them shiny. Toilet wipes are formulated very similarly to general household disinfecting wipes. However, some of them are different in that the wipe substrate itself is formulated to be flushable. (In general, cleaner wipes are not flushable and are supposed to be disposed of in the ordinary garbage.) However, not all toilet wipes are claimed to be flushable, and indeed what constitutes *flushable* is under dispute [50]. It is generally understood that wipes that contain a high proportion of cellulosic material are more likely to be claimed to be *flushable*.

The advantage of wipes for disinfection cleaning is that the consumer cannot use them incorrectly. A disinfecting cleaner usually has a recommended concentration and time of contact that results in disinfection (as determined by standardized testing). With ordinary liquid cleaners, one could overdilute the product in use, either when it is added to an implement or when it is applied to the surface. When a wipe is used, the cleaner at its proper dilution is already on the implement, which needs only to be applied to the surface. Most disinfecting toilet wipes contain only a cleaning solvent (like alcohol or glycol ether) and the disinfecting quat.

5.2.2.2 Mildew Cleaners

Another major category of specialty cleaner is mildew cleaners. Mildew is largely a problem in the bathroom, but it can occur in trash cans, refrigerators, and other kitchen surfaces. The main focus of mildew cleaners tends to be their use in the bathroom, especially in the shower enclosure. Mildew cleaners are a subset of the general category of bleach cleaners, which were discussed in a previous chapter.

The main purpose of the mildew cleaners is to get rid of the black mildew on bathroom surfaces. It can be argued whether or not these are cleaners if the consumer does not wipe the surface. This is because a distinction can be drawn between decolorization and cleaning. If the mildew cleaner is simply sprayed on the surface and left, the characteristic color of the mold will be bleached. However, the actual *body* of the mold is still left on the surface until the surface is wiped or scrubbed. The surface is therefore not cleaned until the surface is physically wiped so that the surface infestation is removed.

Mildew cleaners are overwhelmingly bleach cleaners, and predominately trigger spray products. The bleach choice shown in commercial products is almost entirely hypochlorite bleach. This has the virtues of being powerful, fast, and inexpensive as an ingredient. The surfactant choices to go with this active ingredient are those that are stable to high pH and bleach attack, typically amine oxide either by itself or combined with other surfactants; the choices are the same that are used in bleach-containing toilet cleaners and also usually contain ingredients needed to produce and maintain a high pH, which is required to stabilize the hypochlorite; indeed, the object of some

TABLE 5.6
Mildew Remover Formulation

Ingredients (with Typical Examples)	Purpose	Concentration (w/w%)
Surfactant: alkyl sulfate, soap, linear benzene sulfonate, alkanol amide fatty acid, amine oxide, sarcosinate	Cleaning, wetting, thickening; often used in combination	1–15
Builder: carbonates	Stabilize pH	0–2
Alkalinity: sodium hydroxide, silicate	Stabilize bleach	0.25–5
Solvent: lower-carbon number alcohols	Soil softening	0–10
Bleach: hypochlorite bleach	Stain removal and disinfection	0–5
Polymers: polyacrylate.	Thickening for cling (if not done with surfactants)	0–0.1
Perfume, color, etc.	Aesthetic	<1
Water		q.s.

formulations is directed to increasing the stability of bleach formula [51], as they tend to degrade due to the activity of the bleach. Typical composition of these types of cleaning products is shown in Table 5.6.

Surprisingly, oxygen bleaches find very little application in this type of product, although examples do exist in the literature [52]. Generally, peroxide bleach systems show slower action on the stains to be decolorized, although such cleaners would show greater soap scum cleaning due to their low pH. Soap scum is usually a coexisting soil with mildew, and many mildew cleaners also are claimed to remove soap scum. However, acid cleaners generally are better at cleaning soap scum than alkaline cleaners, so the hypochlorite-containing mildew products tend to be inferior on soap scum, although they are superior at mildew bleaching. However, there are alkaline/bleach-containing formulas for which assertions are made for soap scum cleaning; they tend to include, for example, formulas solvents (such as alcohol) [53] or strong chelating agents [54]. It is interesting that, when cleaning results are shown for these cleaners, they are usually only compared to other alkaline- or bleach-containing cleaners.

Many of the surfaces in a shower enclosure are vertical. The formulator therefore takes whatever steps he/she can to encourage cling of the product to the surface. The product cannot bleach a mildew stain on a shower wall if, after it is sprayed, it simply runs down the wall and pools on the floor. There are usually two approaches to this problem. The usual one is to optimize the droplet size, so that the resulting spray is fine enough to be spread and cling on the surface. Care must be taken, however, to make the droplets large enough that they do not tend to linger in the air to irritate the nose of the consumer. The second approach is to actually thicken the product so that both droplet size is increased and individual droplets have less tendency to flow, which is also said to decrease misting [55–57]. The droplet size of the spray is affected because, for a given spray head's actuation force, a thicker product will tend to produce larger droplets.

5.2.2.3 Soap Scum Cleaners

Soap scum cleaners are by far the largest group of bathroom cleaners. Soap scum is a prevalent problem in almost any bathroom. Hard water deposits are more of a problem in very hard waters area such as Europe, but the precipitation of soap caused by hard water salts can become a problem even in areas with moderate hard water. This tends to be less of a problem in households that use shower gels or synthetic detergent (*syndet*) bars, because the detergents used in these products are more resistant to hard water precipitation. Bars made of real soap (sodium salts of fatty acids) are still very popular products for showering and whole body bathing, however, and using these products will produce soap scum. It is interesting to speculate on whether soap scum becomes less of a problem as use of shower gels continues to increase.

Soap scum tends to be built up as fine layers of calcium or magnesium fatty acids on the bathroom surfaces, gradually dulling the surface and serving as a matrix for trapping other soils, such as sloughed skin cells, dirt, lint, and mildew. Many bathroom surfaces are fabricated to be shiny, and the soap scum, which is white or cream colored, tends to become apparent when the shine is dulled. As the more popular bathroom colors are pale or white, it is hard to see the soap scum itself on the surface, owing to the lack of color contrast. Soap scum is much more apparent on dark surfaces (like black ceramic tiles) or on transparent surfaces (like transparent shower doors). It is therefore somewhat hard for the consumer to determine that the soap scum has been completely removed from the surface except by the reappearance of the native shine of the surfaces.

Acid cleaners are speculated to be effective because they help to reverse the reaction that formed the soap scum, the calcium or magnesium precipitation of the fatty acid. However, the soil being waxy and hydrophobic, the acid, an aqueous agent, could not make effective contact with it if not for the surfactant, which encourages the effective contact of the aqueous cleaning solution with the soil. The criteria for surfactant selection become ruled by compatibility with the acid, which fortunately is quite wide. Unlike in the toilet bowl cleaners, there is no great concern about foaming, as long as the product rinses easily. Indeed, foaming can be a mechanism for helping the product to cling to vertical surfaces to increase contact time with the soil. (However, if the product is made disinfectant by the addition of quat surfactants, then the cleaning surfactant must be compatible with the quat, which usually means a nonionic. Quat surfactants are active as germ killers at both acid and alkaline pHs [58].) Thickening is also said be a way to try to increase cling to surfaces [59,60].

There are bathroom cleaners formulated at alkaline pH, but these tend to be older formulations, whereas more acid formulas have launched in recent years. The alkaline cleaners are almost all disinfectant formulas with quats. It is known that quat surfactants can be boosted in their efficacy with chelating agents like ethylene diamine tetraacetic acid (EDTA) [61], which are active at alkaline pHs. Between the use of nonionic surfactants (to be compatible with quats) and the alkaline pH, these are generally less effective soap scum cleaners than those based on anionic surfactants and acid. Some acids are recognized as disinfectant agents [62], which is convenient to the formulator because one gets *two for one* – an agent claimed to contribute both to the disinfection and to the cleaning [63,64]. However, there is some literature that purports that nonionic surfactants are the best for cleaning soap scum [65]. However, one thing to be said for alkaline cleaners is that they would be easier on the bath surfaces such as grout and some ceramic tiles that are worn by acid attack. However, there are systems that are formulated to avoid this type of damage [66]. Still, acid formulations are very popular, both in the literature and as commercial products. Unlike the toilet bowl cleaners, where hydrochloric acid seems to dominate in commercial products, the bathroom cleaners are more likely to use organic acids commercially, and this is shown in the literature [67–72]. Several patents make reference to the increased mildness to a consumer's hands in using the organic acids, which supply acidity at *moderate* acid pHs, as opposed to the very low pHs of mineral acids. Typical composition of acid soap scum cleaners is shown in Table 5.7.

Modern bathroom cleaners in developed countries tend to come as liquids in spray trigger bottles. This form is now venerable in bathroom cleaners, dating back almost to the invention of spray triggers in the 1980s. Before that, bathrooms were cleaned with dilutable all-purpose cleaners, cleansers, or cream cleansers. Some consumers still use these products today in bathroom cleaning, although the specialty products are preferred by a large margin, to judge by their presence on store shelves. Rarely, spray bathroom cleaners are also available as aerosol sprays, but the *unenvironmental* image of aerosols (left over from the chlorofluorocarbon bans) seems to have made them less popular.

TABLE 5.7
Spray Bathroom Cleaner Formulas

Ingredients (with Some Typical Examples)	Purpose	Acid Cleaner Amount (w/w%)	Alkaline Cleaner Amount (w/w%)
Surfactant: alkylbenzene sulfonate, paraffin sulfonate, alkyl sulfate, ethoxylated alcohol sulfate, ethoxylated alcohol, alkanol amide fatty acid, carbamates, amine oxide, ethoxylated alcohols, betaines	Cleaning, wetting, foaming must be compatible with specific ingredients—acid, base, bleach, quats, polymers, etc.	0–10	0–10
Builder: carbonates, citrates	pH stabilization	0	0–2
Chelator: EDTA	Adjunct to cleaning, disinfection	0	0–15
Alkalinity: sodium hydroxide, alkanolamines, sodium carbonate		0	0.25–5
Acid: phosphoric, dicarboxylic (like glutaric), citric, sulfamic, acetic		0.5–10	0
Solvent: alcohols, glycol ether	Soil softening, penetration	0–10	0–10
Disinfectant: quaternary ammonium surfactants	Germ killing, bacteriostatic action	0.1–3	0.1–3
Bleach; acid: peroxide; alkaline: hypochlorite bleach	Stain removal (may also disinfect)	0–3	0–3
Polymers: xanthan gum, polyacrylate, fluorosurfactants, siloxanes	Thickening, surface modification	0–0.1	0–0.1
Perfume, color, etc.	Aesthetics	0.05–1	0.05–1
Water		q.s.	q.s.

As in toilet bowl cleaning, there are also now wipes intended for general bathroom cleaning that are said to clean soap scum. Again, these are not simple wipes like those used for exterior toilet cleaning or general household cleaning. The bathroom cleaner wipes tend to be more like the toilet bowl cleaning wipes, where a replaceable nonwoven wipe or pad is attached to a wand or handle, presumably to add leverage to the use of the wipe on the surface. They tend to be shown as formulated similarly to the mainline trigger spray products but more dilute [73].

Another claim being made for bathroom cleaners is that they can also keep the surfaces clean longer, usually by the inclusion of a polymer or other ingredient. An example is a bathroom cleaner with *Teflon*. Teflon® has become associated in the consumer mind with soiling resistance and easy soil removal. In general, as an ingredient, it refers to fluorocarbon polymers. However, in this case the polymer used as the antisoiling ingredient was not a fluoropolymer [74]. Given the size of the surfaces to be cleaned and the tenacity of the soil in bathroom cleaning, decreasing the frequency with which the job must be done or the difficulty of the job is a highly desirable trait. There are other examples in the literature that have given fluorosurfactants or fluoropolymers as antisoiling ingredients [75–77]. These compounds might tenaciously adhere to the surface and change its wettability properties, either to more hydrophobic or to more hydrophilic. Usually the ingredients cited are polymers such as siloxanes [78] and other types [79,80], but sometimes surfactants, such as zwitterionic surfactants [81], are also shown. One literature example even uses chitosan [82]. This tendency to formulate ingredients that contribute to these effects is a trend that has been noted several times recently [83,84]. Again, the surfactant systems have to be chosen so as not to interfere with the deposition of these agents on the surface.

Some formulas are being described as containing suspended material [85,86]. Unlike other cleaners with suspended abrasive (like some toilet bowl cleaners or cream cleansers), the literature is not forthcoming with the purpose of the *beads* in the formula.

5.2.2.4 Shower Sprays

A recent development in bathroom cleaning was the emergence of the *shower sprays* in the 1990s [87]. These were products formulated to remove the immediate deposits of a showering or bathing occasion before it can dry out on the surface. They can either be used to clean the surface (slowly) over time with repeated use or to be applied to cleaned surfaces to keep them clean. They are usually based on the chelation of hard water salts [88–90], probably in an attempt to prevent the interaction of the salts with soap on the bathroom surfaces. These are formulated to be neutral or slightly acid, and the usual surfactants used are also neutral, being nonionics, which are said to be able to interact equally with anionic or cationic residues [91,92]. Some of the patent literature expresses concern with using nonionics on plastics [93], and so the use of amphoterics is also shown in formulas [94].

The most recent development in this area is the use of a mechanized system to distribute the cleaner. Previously, these products were dispensed from spray trigger bottles. Of course, if it is desired to protect all the surfaces of the shower enclosure, then there could be some hand fatigue on the part of the consumer trying to cover all these surfaces in discrete sprays. This device is directed to a replaceable reservoir of the cleaning solution mounted on a motorized base, which hangs in the enclosure. When a button is pushed, the motor is activated and the cleaning solution is dispensed through a nozzle that moves back and forth, distributing the product [95]. This product is formulated similarly to the other shower sprays, the main innovation being the packaging and dispensing of the product.

5.2.3 TESTING METHODS FOR BATHROOM CLEANERS

There are multiple tests for the performance of bathroom cleaners. There are tests for cleaning performance that must be conducted separately for different soils. There are disinfection tests, given the importance of germ killing to this particular cleaning segment. For some products, there are also foaming tests, usually for the ease of collapse of the foam, which seems to relate to the ease of rinsing. Importantly, there are also tests of surface safety—whether or not the different bathroom surfaces might be damaged by the chemistry of the cleaner. Given the aggressive chemistry of some bathroom cleaners and often directions to let the cleaner sit on the surface for periods of time, for cleaning or disinfection, this is an important consideration.

5.2.3.1 General

5.2.3.1.1 Cleaning Tests

A very important tool in household cleaning tests is the Gardner Abrasion Tester (Figure 5.3). This instrument is quoted in many standardized testing methods, particularly for testing the effect of abrasion on a coated surface (as its name implies). However, it is also used in many methods for cleaning because it can objectively scrub a surface without the biases of a human operator. For instance, the American Society for Testing and Materials (ASTM) has published a soap scum cleaning method, which was revised in 1997 and again in 2006 [96]. The main item that has undergone revision over the years is to account for the development of different types of products such as trigger sprays, which changes how products are applied to the surface and how the cleaning implement is handled. Published tests often mix other materials, like dirt or sebum, into the precipitated soap scum so that it is not a pure soap scum soil. This is evidently considered more realistic and predictive than pure soap scum.

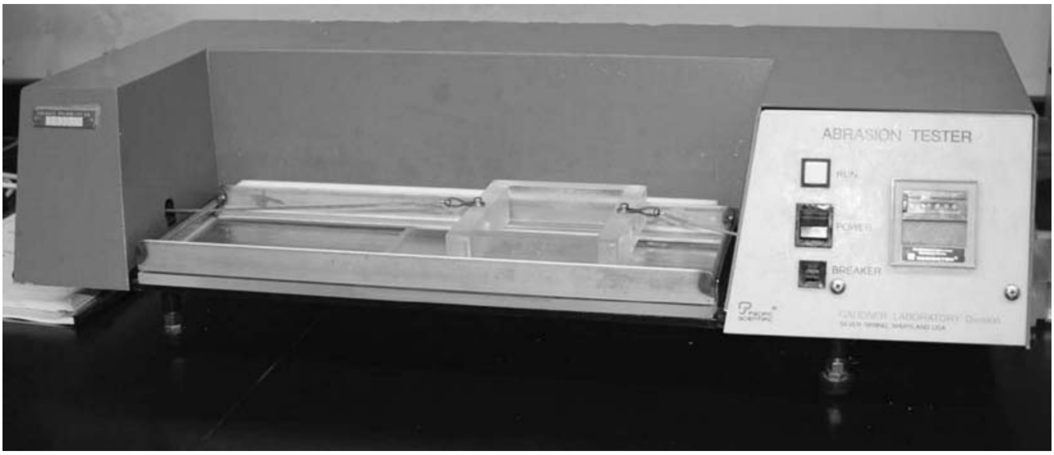

FIGURE 5.3 Gardner abrader.

Cleaning tests for toilet bowl cleaners can be a little more difficult. The first problem in any cleaning test is acquiring a soiled surface. Hard water deposits can be done fairly simply by allowing hard water to evaporate from a ceramic surface, as is done for other bathroom cleaners. However, the more organic soils that occur in the toilet bowl can be more difficult to mimic. There are formulas for synthetic feces [97] (as incredible as that seems) that make it possible in theory to soil a ceramic surface and test the soil removal of a cleaner. Rust stains are another soil that is common in toilet bowl cleaning tests. This is sometimes made by treating a ceramic surface with a ferric chloride solution subsequently fixed by the addition of sodium hydroxide after heating [98]. However, there are some examples where the testing is actually done in a working toilet, particularly when the product is one of the automatic cleaners. Soils can be produced *in situ*; hard water buildup can be done by filling the toilet with hard water and waiting for evaporation in the bowl. Similarly, for rust stains a a piece of mild steel can be placed in the tank and left to generate rust that deposits [99]. The test product is then added to the toilet and the removal of the deposits measured either by number of flushes or time resident in the bowl until removal. Prevention would be tested by putting the test product in the toilet at the same time as the hard water or the steel and monitoring the bowl to see if deposits develop. Monitoring can take place on the toilet surface itself or on ceramic tile suspended in the bowl.

Mildew cleaning can be a little more problematic to test. Real mildew is a living system that can be hard (in a laboratory) to reproduce at need on the desired surfaces. In point of fact one is not testing *cleaning* (in the sense of removing soil from a surface) but decolorization. The difficulty is in establishing the stained surface so that a realistic estimate of the bleaching ability of the cleaner under real conditions can be assessed.

5.2.3.1.2 Foaming, Rinsing, and Residue Tests

Household cleaners in general are often screened for their foaming ability with simple inverted cylinder tests. In general, these involve adding a set amount of an appropriate dilution of the product to a large graduated cylinder and then turning over the cylinder either by hand or by machine. The foam amount produced is then easily determined by the volume markings on the cylinder. However, this does not necessarily predict the foaming behavior of a cleaner that is dispensed from a spray trigger. For measurements of the actual foam behavior the cleaner must be dispensed from the actual spray trigger that will be used.

Rinsing tests vary by the type of product. After applying the product to a surface, the area can be rinsed with water of set flow speed and temperature. A way then needs to be devised to collect the rinse water so that the volume of water used to completely rinse the surface can be measured and compared. Rinsing tests are more straightforward for toilet bowl cleaning; the number of flushes for there to be no foam can be measured. Ideally this would be one flush.

Residue tests are very important for bathroom cleaners given that many of the bathroom surfaces are designed to be smooth and shiny. Usually, the product is applied to a clean surface and then left to dry or wiped, whichever is appropriate to the use of the product. Applying the product without soil serves two purposes: any residue left on the surface is assured to have come from the cleaner (and not from any unremoved soil), and it gives the product maximum interaction with the surface itself unmediated by soil interactions. The surface can then be inspected for spotting, streaks, or filming, and these defects rated by a panel. It is also common for the surface to be measured with a glossmeter before and after treatment. If gloss has decreased, then the surface is judged to have lost some of its shine.

5.2.3.1.3 Dispensing Tests

A related topic is dispensing tests. These are especially important for the in-tank toilet bowl cleaners. Usually the brute force method is used whereby the product is placed in an actual toilet tank, and the number of flushes to exhaust the product is measured. Alternatively, the product can be placed in a container of water; the time required for the solid tablet or puck to dissolve completely is measured. (This is not relevant for liquid automatic cleaners.) The difference between the two methods is that the first uses repeated aliquots of fresh water to dissolve the item (as in real use), whereas the second uses the same volume of water for the whole experiment.

Dispensing is also important for spray trigger containers. There is now even a published method to give guidance to evaluating spray trigger dispensing [100]. The spray produced by the trigger can be evaluated for area of coverage, particle size distribution, and ability of the spray to cling to a vertical surface. Particle size distribution can contribute to how pleasant the product is to use, because it is one factor in whether or not the spray will linger in the air for the consumer to breathe the particles. If the spray particles are very low or high pH, contain bleach, or have certain other formula characteristics, it can make the spray irritating or even unsafe for a consumer to breathe.

Cling to a vertical surface can be important for any bathroom cleaner, but especially important for in-bowl toilet bowl cleaners. It is important that the cleaners cling to the surface without decreasing the cleaner's ability to spread on the surface and cover as much as possible in one application. Spray triggers can also dispense product as foam, which can make it more likely to cling to a surface. Simple tests for *cling* involve applying the product to a vertical surface under specified conditions and then timing how long it takes for the product to flow down the surface to the bottom.

5.2.3.1.4 Surface Safety

As noted before, the chemistry of some of the bathroom cleaners can be somewhat aggressive. Not every home surface is resistant to every type of cleaner chemistry. Aluminum, which can be used in shower door tracks or some fixtures, is sensitive to high pH, which tarnishes it. Glass surfaces are gradually eroded by very high pH. Marble and some glass tiles are sensitive to acidity, which can roughen and dull the highly polished surface. In the case of marble, one is actually dissolving the surface. Grout between bathroom tiles, being basically concrete, is also sensitive to acidity. Plastic surfaces—toilet seats, shower enclosures, countertop materials—can be sensitive to surfactant or solvent ingredients, resulting in *crazing* or other surface defects.

For all these reasons, it is advisable to check the interaction between the cleaner and a number of surface types likely to be encountered. This usually consists of simply placing an aliquot of the cleaner on a clean, unsoiled surface, covering to prevent evaporation, and leaving for a predetermined amount of time. After the time has elapsed, the cover is removed, the cleaner is rinsed off, and the surface is checked either visually or instrumentally for damage. Loss of glossiness of the surface, measured by a glossmeter, can be an early warning of damage before other visual signals become apparent.

5.2.3.1.5 Stability

It is also important to know that the product will be stable on the shelf before sale and for a time in the consumer's home. Therefore the product is usually put under conditions of set temperature and humidity, and stored under these conditions for a predetermined time. At the end of that time, the product is inspected or measured for changes in appearance, odor, chemical composition, and performance as appropriate. There are organizations that seek to standardize the conditions of aging, such as the International Conference on Harmonization, which has guidelines for stability testing [101].

5.2.3.2 Disinfection

Tests for the disinfection or sanitization of bathroom surfaces are usually mandated by local law, which dictates both the need for testing and the methods of testing. Consumers cannot see the bacteria being killed and therefore have to rely on some authority to certify that the product actually does the job claimed for it. Two main protocols on disinfectant cleaners are those set down by the Environmental Protection Agency (EPA) in the United States [102,103] and the European Committee for Standardization (abbreviated CEN for Comité Européan de Normalization) CEN-TC216 Technical Committee for Disinfectants and Antiseptics of the European Union [104,105]. Many other countries follow these methods or use them as a model for their own rules. Both of these sets of regulations depend on testing data as part of the submission for application for disinfectant labeling. Canada is a country that uses a monograph system [106], in which data is accumulated on products and ingredients over a period of time, ultimately being incorporated into a monograph. Products that conform to the description in the monograph are allowed to be labeled as disinfectant.

Testing protocols generally take into account how the product will be used. This includes the amount of time anticipated for contact with the surface, what product concentration will be used, and how the product will be dispensed. For instance, one of the oldest disinfectant product tests in the United States was developed for dilutable liquid cleaners. The exact dilution used for disinfection is indicated in the testing details. The test protocol includes an organic component to simulate a soil load as would be encountered in cleaning. There is a chance that the disinfection ingredient can be trapped or inactivated during the cleaning of the surface. (Many disinfection products actually give the instruction to disinfect only after the surface has been cleaned to ensure good contact of the cleaner with the surface to be disinfected. This would actually be directing the consumer to go over the surface twice with the cleaner during one cleaning occasion.) For toilet bowl cleaners that make disinfection claims, the dilution method would be appropriate because the product would be diluted in use.

Trigger spray products use a different protocol in the United States, where the product is sprayed directly onto the test surface according to anticipated label instructions. Therefore, the tester must stipulate how much product is sprayed and how far the product is held from the surface when sprayed, as this can influence how much of the cleaner reaches the surface. As new product forms develop, like disinfectant wipes, this requires new EPA methods; modifications of the germicidal spray test for wipes-type products are now being seen in some of the literature [107,108].

The type of testing determines the claims that are possible. For instance, the U.S. EPA test gives the option of testing against one to three different organisms. Which organisms are successfully reduced determines the label claim language that can be used. The regulations can also determine what needs to be on the label and how the claims are worded there. For example, in the United States, the active disinfectant ingredient must be listed on the front label with its active amount and the directions for use (derived from the testing protocol) on the back. This varies from country to country, as to what claims are allowed and how they must be worded, and a formulator must consult the local regulatory agency to determine the legal requirements.

There are other tests for specific kinds of germicidal activity, for example those published by the Association of Official Analytical Chemists (AOAC) or the ASTM. There are tests for specific microorganisms as well as tests of sporicidal and fungicidal action in the AOAC compendium, some of which have been accepted by the EPA as substantiating methods [109]. There is also a test published by the ASTM International for action against viruses on hard surfaces [110]. These last two are different from the use dilution test of the EPA, which is only for different classes of bacteria. Distinction needs to be made between action against bacteria, against fungi and mold, and against spores. Although a consumer may view a *disinfectant* or antimicrobial cleaner to be good against all these, regulatory agencies may require separate testing for separate classes of microorganisms. In the United States, for example, testing against the bacteria specified in the use dilution test can gain a *disinfectant* labeling for the product as a whole, but no claims can be made on the label for fungicidal, viricidal, or sporicidal action unless separate tests are done for specific organisms, and then only those specific organisms can be listed on the label.

Similarly, there are also tests for microbial inhibition. In these tests, the surface is pretreated with the cleaner and then inoculated with a mixture of nutrient and microorganism of interest. The surface is then incubated, and the amount of growth observed after incubation indicates the inhibitory effect of the cleaner. In particular, the literature gives an example of this type of test to exhibit antifungal property [111].

5.3 GENERIC FORMULATION

5.3.1 NONSURFACTANT INGREDIENTS

5.3.1.1 Acids, Bases, and Bleaches

As commented previously, these cleaners depend largely on the nonsurfactant ingredients. The chemistry of the cleaner is tailored more closely to the chemistry of the soil than the chemistry of all-purpose cleaners, which seek to remove the broadest variety of soils from the widest variety of surfaces. However, in practical fact, *all-purpose cleaners* are generally tailored to the removal of grease. This means that they can still remove soap scum or dirt or mildew from a surface, by virtue of their surfactancy, but not to the depth or with the efficiency or ease that the specialty cleaners do. This is the *raison d'être* of specialty cleaners—if all-purpose cleaners were really that efficient on all surfaces, then the specialty cleaners would not exist.

Among the pH-altering ingredients used, there is generally more variety of acid ingredients than basic. Sodium hydroxide is the overwhelming favorite for supplying alkalinity to a product. Occasionally organic amines such as alkanol amines or morpholine are used, but this tends to be more prevalent for all-purpose cleaners. Ammonia can sometimes be mentioned, but this tends to be more prevalent for window cleaners. However, there is a wide variety of acids. For instance, both mineral and organic acids are seen in bathroom cleaning formulas. Some toilet bowl cleaners simply use hydrochloric acid, and some soap scum cleaners use phosphoric acid. There are advantages to using the organic, particularly the buffering. This allows the cleaner to maintain its acidity during the stress of the cleaning operation, but also gives a moderate acidity that is more tolerable to the bare skin of the consumer using the product. Organic acids such as lactic or citric acids can also have chelating abilities that assist in the hard water or soap scum cleaning. Acids such as these can also be touted as naturally derived cleaning agents. Oxalic acid is widely known for its ability to interact with iron salts, and therefore is often added to toilet bowl cleaners to eliminate rust stains.

These pH conditions can also serve to stabilize bleaching ingredients. As previously discussed, hypochlorite bleach is stabilized by high pH, and peroxide bleaches by low pH. As the pH shifts during cleaning, due either to exhaustion of the acid or base against the soil or to dilution during use, the pH could rise or fall, destabilizing the bleach and making it more active. Bleaches are excellent ingredients for, of course, stain removal, but also as disinfection ingredients. Hypochlorite bleach is one of the most effective disinfecting agents, active against virtually all types of bacteria, viruses, and molds [112,113]. So, when hypochlorite is used it not only decolorizes the mildew stain, but can also be used to kill the mold organism causing the stain.

5.3.1.2 Solvents

Solvents, predominately the glycol ethers, are used somewhat in these specialty cleaners. In cases like soap scum, where it is an organic soil capable of softening, the glycol ethers are useful. They serve less use in removing inorganic soils like hard water deposit, where attack by acidity is far more effective. Alcohols are also sometimes used, especially in products like the shower sprays, where the soil load is light. Alcohols could also be used to adjust the viscosity of some cleaners. Solvents are also used in wipes formulas to help speed both the action of the cleaner on the surface (since it has to work essentially within the time of a *swipe*) and in the evaporation of the cleaner on the surface, since these are no-rinse products.

5.3.1.3 Adjunct Ingredients

Chelating agents are widely used in bathroom and other specialty cleaners. Hard water salts are a primary target of this ingredient, but chelating agents can also be used to increase the effectiveness of quat surfactants as disinfectants [114]. For this reason, traditional chelators like EDTA are common in the alkaline bathroom cleaners. Because the cleaners are alkaline, their effect on the soap scum due to pH is limited, but it is speculated that the chelating ingredients help the cleaner to remove the hard water ions from the soap scum and therefore loosen the soil. The primary acid-active chelating agents are organic acids like oxalic or citric. These have the added benefit in attacking soap scum that the low pH also helps as well as chelation.

As was also noted previously, cling to vertical surfaces can be important in some product groups. In many cases, such as the toilet bowl cleaners, the formula may be self-thickening due to its surfactants. However, some products also use polymers such as cellulose gums, polyoxyethylenes, or polyacrylates, depending on the formula chemistry. Cellulose gums, depending on their structure, can be acid unstable, as can be polyoxyethylenes in bleach systems.

Outside of functional ingredients or those like the thickeners that adjust the product form, the use of dyes and perfumes is widespread. These are practically nonexistent in drain or oven cleaners (due to the highly chemically aggressive nature of these products), but essentially all other products use them. Many consumers feel that the bathroom, of all the rooms in the house, can be an area of unpleasant odors. Therefore, a pleasantly scented cleaner whose fragrance lingers somewhat serves to eliminate the odors due to the bathroom soils (during cleaning), to make the cleaning process more pleasant for the consumer, and to signal that the bathroom has been cleaned after the job is done. Dye serves largely to make the product aesthetic for the consumer, but in toilet in-tank cleaners, it serves to signal the continuing presence of the product. When the color in the toilet bowl fades, it signals the consumer that the tank should be opened and new product added.

5.3.2 SURFACTANT USE IN HARD-SURFACE CLEANERS

As in the all-purpose cleaners, specialty cleaners generally have a combination of surfactants for most effective cleaning. These are usually combinations of anionic and nonionic surfactants. However, as was noted in the discussions above, there are times when solely nonionic surfactants are needed. Over the past 20 years, the household cleaners have gradually made more and more use of amine oxide, betaines, and more specialized nonionics. Amine oxides were always well used in hypochlorite-containing products, but are now used in other cleaners as well. However, the use of linear alkyl benzene sulfonates, alkyl sulfates, and ethoxylated alkyl sulfates are still very prevalent. As stated before, the main choice of surfactant is dictated by the other chemistry in the cleaner—acid, alkaline, bleach, and quats.

5.4 CONCLUSION AND FUTURE TRENDS

Specialty cleaners are an interesting subset of household cleaners. Their use tends to cluster in the bathroom, where cleaning tasks are laborious and time-consuming, therefore creating a demand for products that are formulated for higher efficacy targeted against specific soils or cleaning tasks. The products tend to be extremes of pH, where the all-purpose cleaners tend to be mildly alkaline. A wider variety of surfactants are seen in these products due to the broader chemistry requirements. Use of specialty cleaners are not well spread through the rest of house, the second most frequent use of specialty cleaners being in the kitchen for the oven and drain. There are few examples as yet, but it can be anticipated that there will develop antiallergenic cleaners for more whole-home use similar to disinfectant cleaners whose target is bacteria and viruses. These antiallergenic cleaners would probably become a new class of specialty cleaner. It will be interesting to see how the aggressive chemistry of these specialty cleaners develops in the face of the growing *natural* movement, with its attendant side issues of water conservation and ingredient sustainability. There is growing appetite (apparently) among consumers for products with ingredients that are derived from renewable or plant sources. There is also increasing awareness of the prodigal use of fresh water by consumers in developed nations. Bathroom cleaning operations tend to use large volumes of water—will products develop to minimize this? Similar to all-purpose cleaners, the actual surfactant ingredients in these cleaners have not changed significantly in 20 years, but this may change in the near future as petroleum-derived surfactants increase in price.

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6 Application of Personal Care Detergent Formulations

Louis Ho Tan Tai and Veronique Nardello-Rataj

CONTENTS

6.1 INTRODUCTION

Personal care products are applied directly to parts of the human body such as the skin (soaps, shower gels, bath foams), the hair (shampoos, hair conditioners), and also intimate parts such as the mouth mucous membranes (toothpastes). Many different products are available as personal care products. This chapter deals only with the most representative products on the market:

- Skin care products—soap, toilet bars, shower gels, bath foams
- Hair care products—shampoos and conditioners
- Oral care products—toothpastes

Some specific cosmetic products have been excluded from this consideration. A wide range of components may be used to obtain a similar functionality but only the most commonly or widely used are discussed in this chapter.

6.2 SKIN CARE PRODUCTS

6.2.1 Toilet Soaps

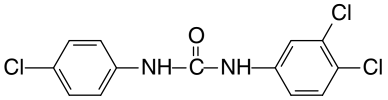
Toilet soaps are commonly used for cleansing the human body. They are typically prepared from sodium salts of stearic, palmitic, and oleic (C_{16}–C_{18}) acids obtained by saponification of tallow (animal fat from beef or sheep), fish oil, and vegetable oils like palm oil that comes from the skin of the palm fruit, and palm kernel oil that comes from the kernel of the palm fruit. To increase solubility and to provide satisfactory lathering of soap, these oils are usually mixed and combined, for example, tallow/coconut, tallow/palm kernel, palm/coconut, or palm/palm kernel. Actually, it is established that soaps derived from shorter-chain length fatty acids such as coconut fatty acids are known to produce a much richer lather than soaps produced from longer-chain length fatty acids such as tallow fatty acids. It has thus been common practice in toilet soaps to add coconut fatty acid to the tallow fatty acid feed stock used to make the soap. Thus, toilet soaps can contain 10–40% coconut or palm kernel oils (usually ~20%) and 60–90% tallow or palm oils. In Europe, a mixture of tallow and coconut oils is generally used. Palm oil and palm kernel oil are more frequently used in the producing areas, such as Africa and Southeast Asia. Toilets soaps are excellent cleansers, but sometimes they can irritate the skin. There are several types of soaps:

- *Domestic "household" soap.* The old household soap was simply a 63% fatty acid raw soap, which was cooled and cut into bars.
- *Superfatted soaps.* Some formulations may also contain varying amounts of *free* fatty acids in combination with emollient agents. Actually, addition of superfatting agents, such as free coconut fatty acid, improves the volume and richness of the lather produced by toilet soap. Moreover, these added *free* fatty acids neutralize any residual soda, leading to a decrease of the aggressive behavior on the skin. The percentage of *free* fatty acids is usually ≈5%, added into the liquid soap under high pressure and before flash-drying.

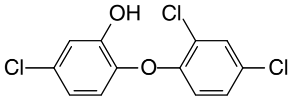
Soaps must also contain an appropriate preservative system, which is usually a combination of a chelating agent such as ethylene diamine tetraacetic acid (EDTA) to complex any free metal ions and an antioxidant to prevent possible oxidation of the fatty constituents. For example, the presence of copper or iron can cause discoloration and unpleasant smells resulting from a catalytic oxidation of unsaturated oils (Table 6.1).

There are also specific toilet soaps that exhibit secondary functions, for example, germicidal soaps. These are obtained using antimicrobial agents such as 2,4,4′-tricholoro-2′-hydroxyldiphenyl ether (Triclosan or Irgasan DP300 from Ciba-Geigy) and 3,4,4′-trichlorocarbanilide (trichlocarbon [TCC]). They are very effective at destroying gram-positive and some gram-negative microorganisms.

TCC tends to be used less frequently, as it can form trichloroanilines that cause skin problems. Triclosan has other disadvantages, in that it tends to color under light. This phenomenon can be reduced by the presence of free alkali (Table 6.2).



3,4,4′-trichlorocarbanilide (TCC)



2,4,4′-tricholoro-2′-hydroxyldiphenyl
ether (Triclosan)

TABLE 6.1
Typical Formulations of Toilet Soaps

Ingredients	**Nonsuperfatted (wt%)**	**Superfatted (wt%)**
Nominal composition of fats	80–20 (Palm/palm kernel)	65–35 (Tallow/coconut)
Sodium soap	83–88	80–85
Free fatty acids	—	4–6
Sodium EDTA	0.015–0.030	0.015–0.030
Sodium EHDP	0.010–0.025	0.010–0.025
Orthophosphoric acid	0.1–0.2	0.1–0.2
Color	+	+
Opacifiers (titanium oxide)	0.1–0.7	0.1–0.7
Brighteners	+	+
Perfume	+	+
Deionized water, salts	Balance	Balance

Note: EHDP = ethylene hydroxydiphosphonate (e.g., Dequest 2016).

TABLE 6.2
Typical Formulations of Germicidal Soaps

Ingredients	**Formulation A (wt%)**	**Formulation B (wt%)**	**Formulation C (wt%)**
Nominal composition of fats	80/20 or 75/25 Tallow/coconut Palm/palm kernel	80/20 or 75/25 Palm/coconut	80/20 or 75/25 Tallow/coconut Palm/palm kernel
Sodium soap	75–85	80–85	85–88
EDTA acid	0.01–0.05	0.01–0.05	0.02–0.05
EHDP acid	0.01–0.05	0.01–0.05	0.02–0.05
Orthophosphoric acid	0.005–0.015	0.005–0.015	0.1–0.2
TCC	0.1–0.5	0.03–0.1	—
Triclosan	0.1–0.5	—	0.1–0.5
Color	+	+	+
Perfume	+	+	+
Brighteners	+	+	+
Titanium oxide	+	+	+
Deionized water, salts	Balance	Balance	Balance

6.2.2 NONSOAP DETERGENT BARS

Nonsoap detergent bars do not contain soaps. They are synthetic detergents made from petroleum derivatives (Table 6.3) [1–3].

The main advantage of this kind of bar is that, unlike toilet soap, they are not sensitive to calcium in the water. Therefore, they lather equally well in hard and soft water, whereas soap detergent does not produce a lather until all the water hardness has been neutralized. In addition, they also leave a certain soft feeling on the skin, like shower gels and foam baths (Table 6.4).

Germicides can also be included in detergent bars. As for toilet soaps, TCC or Triclosan can be used.

6.2.3 BATHROOM PRODUCTS: SHOWER GELS AND BATH FOAMS

These products are very similar to shampoos, which will be discussed later. There are two categories of shower/bath products, differentiated by consumer habits, that is, whether they prefer the feeling of a fatty product that leaves the skin slippery after the bath or shower. The first category of

TABLE 6.3
Main Ingredients with Their Functions in Nonsoap Detergent Bars

Ingredients	Functions
Sodium cocoyl isethionate[a]	Foaming and cleaning agent
Sodium linear alkylbenzene sulfonate	Foam booster (speed and volume)
Anhydrous soap	Gives a creamy feel to the foam/plasticizer
Sodium isethionate[b]	Hardener
Sodium stearate	Hardener
Stearic acid	Plasticizer, softness
Titanium oxide	Opacifier, whiteness
Mineral oil	For marketing, for example, *bath oil*

[a] Sodium cocoyl isethionate = $CH_3(CH_2)_nCH_2COO(CH_2)_2SO_3Na$.

[b] Sodium isethionate = $HO(CH_2)_2SO_3Na$.

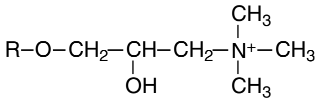
Source: Taken from Helliwell, J. F., Unilever, WO 9403151; Madison, S. A., Massaro, M., Rattinger, G. B., Wenzel, C., Unilever, WO 9514661; Cherrey, M., Filiciano, D., Wivell, S., Chesebrough. Ponds, U.S. 5441671.

TABLE 6.4
Typical Formulation of Nonsoap Detergent Bar Detergents

Ingredients	wt%
Sodium cocoyl isethionate	44–60
Sodium alkylbenzene sulfonate	0–2
Anhydrous soap	7–8
Sodium isethionate	2
Stearic acid	15–19
Sodium sulfate	5
Preservative + complexing agent	+
Titanium oxide	0.2
Deionized water, perfume	Balance

products, which do not contain soap, is favored in Europe and in the United States; the products of the second category contain soap and are favored in Asia (Table 6.5) [1].

Jaguar C13S, or guar hydroxypropyltrimethyl ammonium chloride, is a cationic conditioning polymer with the formula



$$R{-}O{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{N^+}}}}{-}CH_3$$

where R is a polysaccharide residue.

The second category of products contains the same ingredients as above but with fatty acids such as lauric, myristic, or oleic acids (Table 6.6) [1].

TABLE 6.5
Typical Formulations of Shower Gels and Bath Foams

Ingredients	Formulation A (wt%)	Formulation B (wt%)
Sodium isethionate	9	5
Sodium lauryl ether sulfate	—	2
Cocobetaine[a]	6	—
Cocoamidopropyl betaine	—	8
Silicone oil	5	5
Jaguar C13S	0.1	0.1
Preservative	+	+
Perfume, deionized water	Balance	Balance

[a] Cocobetaine = $H_3C–(CH2)_{11}–N^+(CH_3)2–CH2COO^-$.

Source: Taken from Helliwell, J. F., Unilever, WO 9403151.

TABLE 6.6
Typical Formulations of Shower Gels and Bath Foams with Soap

	Formulation A	Formulation B
Ingredients	Transparent Base (wt%)	Opaque Base (wt%)
Myristic acid	5–8	5–8
Lauric acid	5–8	5–8
Oleic acid	2–4.5	2–4.5
Glycerin	10–15	10–15
NaOH 45%	7–10	7–10
Formaldehyde	0.05–0.25	0.05–0.25
Cocoamidopropyl betaine	12–20	12–20
Silicone emulsion 60%		2–6
Sodium EDTA	0.05–0.15	0.05–0.15
BHT	0.02–0.07	0.02–0.07
NaCl	+	+
Color	+	+
Perfume	+	+
Deionized water	Balance	Balance

Notes: BHT, or butylated hydroxytoluene, is an antioxidant.

Source: Taken from Helliwell, J. F., Unilever, WO 9403151.

6.3 HAIR CARE PRODUCTS

If we examine a long hair in its entirety, we observe four different states:

1. Near the root, the hair is new, so in good condition.
2. Five centimeters from the root, the hair is already older and has been subjected to the aggression of combs, brushes, and drying.
3. Toward the end of the hair, most of the cuticle has disappeared for the mechanical reasons and also due to exposure to the environment (chemicals, light, etc.).
4. The end of the hair is in several parts: if all the cuticle has gone; the cortex is completely exposed and is easily broken.

Soil on hair is varied and comes from many sources. Sebum and its derivatives are the main ones. Other sources of hair soil are: keratin debris from flaking of the scalp; proteins; organic and inorganic compounds from sweat; dust from the atmosphere; and remains from hair care products including hair sprays, gels, and hair creams. Hair lipids are a complex mixture whose composition changes according to sex, age, diet, and seasons. They are subject to chemical changes, such as hydrolysis and oxidation, which change physical properties such as their consistency or their polarity. These are important factors in their capacity to resist removal.

Dandruff. It is normal for superficial cells from the horny tissue layer (stratum corneum) of skin to deteriorate and cause numerous tiny fragments of keratin or invisible flakes (squama). However, this flaking becomes abnormal if visible flakes (dandruff) form. These flakes are gray or brownish in color and appear in the hair, falling onto the collar of clothes. These flakes can be quickly washed away, but they very quickly reappear. This is referred to as dry scalp or dandruff.

6.3.1 SHAMPOOS

Shampoos may be liquids, creams, pastes, aerosol, or dry. The main role of a shampoo is to wash hair and to remove soils such as dust, grease, and the other dead cells discussed above. However, hair shampoo formulations need to provide many other benefits to the consumer to be competitive in the marketplace. They must

1. Dissolve easily whatever the water hardness, and not form precipitates.
2. Clean well in any water hardness.
3. Leave hair supple, soft, easy to comb, and with less static.
4. Foam quickly and abundantly (consumer need). Foam should rinse away easily and not cause irritation (except very momentarily) if in contact with the eyes.
5. Perform well at neutral or slightly alkaline pH.
6. Have a pleasant smell.
7. Be nonirritating to the hands.
8. Be nonirritating to the scalp.
9. Have a pleasant appearance (color, pearlescence, and a good viscosity).
10. Be reasonably priced.

Certain shampoos, such as antidandruff shampoos, can be considered as therapeutic.

The main ingredients of a liquid shampoo are detergents (i.e., surfactants), thickeners, foam stabilizers, foam boosters, perfumes, preservatives, conditioning agents, pearlescing agents, opacifiers, colors, and water. Some of them are multifunctional [4–12].

6.3.1.1 Detergents

The following table summarizes the most frequently used surfactants in shampoos, along with their advantages and disadvantages. Clearly, no raw material is ideal, and none will meet 100% of the requirements. Nevertheless, good quality shampoos can be made from a variety of surfactants combined with additives.

The surfactants used in a shampoo will be selected on the basis of several criteria such as detergency, foam volume and texture, irritation, cost, compatibility with other ingredients, color, odor, purity, and biodegradability. Usually, primary surfactants used in shampoos are anionic and inexpensive. They may be combined with secondary surfactants, such as nonionic or amphoteric surfactants (Table 6.7).

In Europe, sodium lauryl ether sulfate is the most commonly used primary surfactant. In the USA, α-olefin sulfonates will be preferred, with sulfosuccinates, which are very mild but more expensive.

Nonionic surfactants, such as fatty ethoxylated alcohols, are rarely used as primary surfactants in shampoos because of their poor foaming properties (Table 6.8).

The most commonly used alkanolamide for enhanced foam stability and viscosity is cocamide monoethanolamide (MEA). Most products in today's market no longer use the cocamide diethanolamide (DEA). Stearyl ethanolamide is used as a pearlescent thickener, whereas oleyl ethanolamide is also used for its conditioning effect (Table 6.9).

Cocamidopropyl betaine (CAPB) is a common secondary surfactant in shampoo formulations. It improves mildness and viscosity, and enhances the foam properties. It is milder on the skin than linear alkylbenzene sulfonate (LAS), so adding it to the mix reduces the amount of the harsher detergents needed. It is thicker than the other ingredients, so it can be added to make the mix have the right viscosity. It also has antistatic and moisturizing properties. In many shampoos, CAPB is used in combination with sodium lauryl ether sulfate (LES) (Table 6.10).

A hair shampoo formulation is usually a combination of sodium lauryl sulfate (SLS), LES, CAPB, and cocamide MEA. A desirable pH of 5–6 is achievable with the addition of citric acid. An optimum viscosity is usually obtainable by incorporating an electrolyte such as sodium chloride. A formulator will typically add preservatives, perfumes, and dyes to complete the formula. To realize all end-use properties and marketing claims, some modifications with other additives are necessary [13].

6.3.1.2 Conditioning Agents

Shampoos with pure anionic surfactants may have a strong degreasing effect on hair and also on hands. Actually, the detergent tends to adsorb on the hair, making the hair brittle and difficult to style and to comb. Hence, conditioning agents are added to keep the hair cuticle smooth and slippery. These compounds deposit on the surface of the hair and improve its feel, softness, and combability, while reducing static charge. Shampoos that specifically feature conditioning as a benefit are called 2-in-1 shampoos, because they clean and condition hair in the same step. Special ingredients such as lanoline or lecithin may be incorporated to counteract these effects. Lanoline and its derivatives give good results at low incorporation (if the level is >2%, the foaming properties of the shampoo are affected). Lecithin can also be used at low levels. Egg and egg yokes, which contain lecithin, cholesterol, and proteins, are also used. They act as softeners. Long-chain fatty alcohols like cetyl, stearyl, and oleyl alcohols also lubricate the hair.

Cationic surfactants also improve the wet and dry combing and reduce fly-away. However, they are incompatible with anionic surfactants and cannot be used in shampoo formulations. Cationic surfactants, which are mainly quaternary ammonium, are used in hair conditioners. They are called *quats* and can also be used to thicken the formulation (Table 6.11).

The use of cationic polymers as conditioning agents precludes the problem of incompatibility with anionic surfactants. These compounds are cationic homopolymers and copolymers obtained by polymerization of a vinyl monomer bearing a quaternary ammonium group or a quaternized amine with another water-soluble monomer such as acrylamide or methacrylamide. The most frequently used polymers are those derived from guar gum, such as guar hydroxypropyltrimethyl ammonium chloride (Jaguar C13S, C17, etc.).

TABLE 6.7
Anionic Surfactants Used in Shampoo Formulations

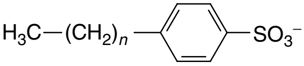
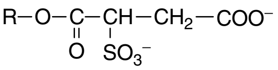
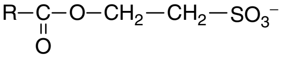
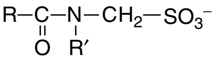
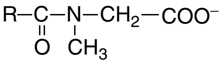
Names and Formulas	Advantages	Disadvantages
Soaps $R{-}COO^-(Na^+ \text{ or } K^+)$	Inexpensive Very little risk to eyes Leave hair soft Good detergency and foaming properties in soft water	Alkaline solutions Cleaning and foaming properties reduced in hard water
Alkyl sulfates $R{-}OSO_3^-\ (Na^+ \text{ or } NH_4^+)$	Long chains = good detergency, good emulsification and solubility	
Alkyl ether sulfates $R{-}(OCH_2CH_2)_n{-}OSO_3^-\ (Na^+ \text{ or } NH_4^+)$, R: $C_{12}{-}C_{14}$, $n \approx 2$ or 3 Example: lauryl ether sulfate (LES-Na)	Good lather Good tolerance on skin	When *n* is weak, solubility diminishes in cold water
Diglycolamide sulfates $R{-}CONH{-}CH_2CH_2O{-}CH_2CH_2{-}OSO_3^-$	Stable in aqueous solution	
Linear alkylbenzene sulfonates 	Good degreasing (3–4% for special *greasy hair* shampoos) No alkaline hydrolysis Inexpensive Good stability at low pH Good tolerance to hard water	
α-Olefin sulfonates $H_3C{-}(CH_2)_m{-}CH{=}CH{-}(CH_2)_n{-}SO_3^-$ $n + m = 9{-}15$	Good lather in the presence of sebum Low cloud point Good solubilization properties Little color and odor Good tolerance on skin	
Sulfosuccinates  $R{-}O{-}\underset{\underset{O}{\Vert}}{C}{-}\underset{\underset{SO_3^-}{\vert}}{CH}{-}CH_2{-}COO^-$	Good detergency Good lather Very mild on skin Nonirritating (eyes)	Hydrolyzation of their ester group Best used at a pH of 6.5
Acyl isethionates  $R{-}\underset{\underset{O}{\Vert}}{C}{-}O{-}CH_2{-}CH_2{-}SO_3^-$	Properties comparable to sulfosuccinates	Same problems of stability Poor solubility in cold water Best used in opaque shampoos
Sulfoalkylamides of fatty acids Example: *N*-acyltaurides  $R{-}\underset{\underset{O}{\Vert}}{C}{-}\underset{\underset{R'}{\vert}}{N}{-}CH_2{-}SO_3^-$ R′ = CH3 → *N*-methyl tauride	Good lather Good dispersion of calcium salts	
N-acyl amino acids Example: acyl sarcosinates  $R{-}\underset{\underset{O}{\Vert}}{C}{-}\underset{\underset{CH_3}{\vert}}{N}{-}CH_2{-}COO^-$	Good lather Good detergency More soluble in hard water than soaps Not irritating to hair and skin Give hair and skin a soft feel Satisfactory detergency Good dispersion of calcium salts Easy to rinse	
Polyoxyethylene carboxylates $R{-}(OCH_2CH_2)_n{-}O{-}CH_2{-}COO^-$	Same properties as *N*-acyl amino acid salts Soluble in weak pH Compatible with cationic surfactants if *n* is high	Foam less than lauryl ether sulfates

TABLE 6.8
Nonionic Surfactants Used in Shampoo Formulations

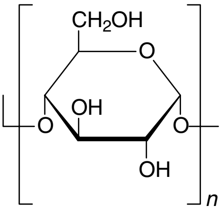
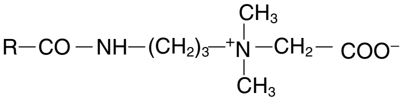
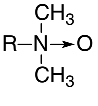
Names and Formulas	Properties
Fatty alcohols ethoxylate $R–O–(CH_2CH_2O)_n–H$	Good detergency When n is high, irritation is reduced Poor foaming properties
Fatty acid polyglycol esters $R–COO–(CH_2CH_2O)_n–H$	Exceptional foaming properties Extremely compatible with skin Very mild Basic ingredients for baby shampoos
Alkyl polyglycosides  $R = C_{10}–C_{14}$ and $n \approx 1–3$	Good synergy with anionic surfactants Excellent environmental compatibility Improve rheological properties and sebum solubilization Good foaming properties Very mild on skin
Alkanolamides Example: monoethanolamide $R–CO–NH(CH_2CH_2OH)$ Example: diethanolamide $R–CO–N(CH_2CH_2OH)_2$	Increase foaming properties

TABLE 6.9
Amphoteric and Zwitterionic Surfactants in Shampoo Formulations

Names / Formulas	Properties
Alkylamidobetaines  $R–CO–NH–(CH_2)_3–{}^{+}\overset{CH_3}{\underset{CH_3}{N}}–CH_2–COO^-$ Example: cocamidopropyl betaine	Strong substantivity (used in shampoos for gray or dyed hair) Less toxic and irritating than cationic surfactants Usually combined with anionic or nonionic surfactants to make mild shampoos (for babies)
Amine oxides  $R–\overset{CH_3}{\underset{CH_3}{N}}\rightarrow O$	Multifunctional Stabilize foam Adjust the viscosity Conditioning effect Potential anti-irritant

Silicones can also be very effective as conditioning agents. These include the high-molecular weight (above 200,000) polydimethyl siloxanes or dimethicones, which are hydrophobic compounds used to make the hair shiny and slippery.

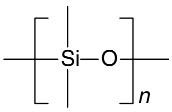
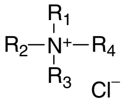
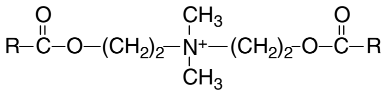


TABLE 6.10
Properties of the Most Common Combination of Surfactants Used in Shampoo Formulations

Surfactants	Features
Primary surfactant	Nontoxic
	Good detergency
	Good lather
	Low irritation
Lauryl ether sulfate	Little/no color
	Little/no odor
	Easily available
	Moderate cost
Secondary surfactant	Increases foam in the presence of soil
Cocamidopropyl betaine	Increases viscosity
	Decreases dryness of skin
	Moisturizing properties

TABLE 6.11
Cationic Surfactants Used in Hair Conditioners

Names/Formulas	Properties
Quaternary ammonium (quats)	Condition hair after washing
 $R_2-\overset{R_1}{\underset{R_3}{N^+}}-R_4 \quad Cl^-$	Behave like flocculants Poor detergency Physiologically active and irritating Poor biodegradability
with two or three methyl and one or two alkyl chains derived from tallow or coconut oil.	
Esters quats	
 $R-\overset{O}{\overset{\|}{C}}-O-(CH_2)_2-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-R$ R = alkyl, typically C_{16}–C_{18}	Better biodegradability

Finally, certain mild surfactants can also be used as additives, such as sorbitan polyoxyethylene monostearate (Tween 60). These conditioning agents would be effective because they are more rapidly adsorbed on hair than anionic surfactants. Other theories state that the conditioning agents fix themselves during rinsing (strong dilution) or that they surround the surfactant micelles.

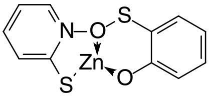
6.3.1.3 Antidandruff Agents

There are different ways of dealing with dandruff:

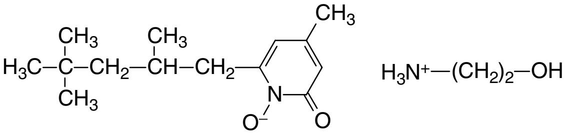
1. Reduce the speed of renewal of the cells. It might be possible to strengthen the stratum corneum of skin to limit flaking. In this case, the use of keratolic products such as sulfur or selenium sulfur could give good results. However, these products can also cause thinning of the cornea, which can cause a greasy condition favorable to microorganisms. It should

also be noted that selenium disulfur, which is relatively toxic, is usually used in shampoos sold in drugstores.

2. Inhibit the growth of yeast, which seems to be responsible for the production of flakes (*Plasmodium ovale*). Germicides are used to reduce the growth of microorganisms, including the yeast *P. ovale*. The most common are

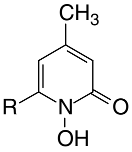


Zinc pyridinethione (ZnPTO)

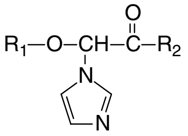


Piroctone olamine (Octopirox)

ZnPTO can cause stability problems at low temperatures, and also toxicity. So, piroctone olamine is generally preferred. It is more soluble in the presence of surfactants, not very toxic, easy to use, and stable, but it costs more than ZnPTO. Other derivatives are mentioned in the literature:



Hydroxypyridone derivatives



Imidazolylketone derivatives

6.3.1.4 Other Ingredients

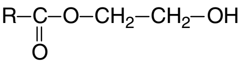
Other ingredients can either improve the aesthetic and the physical aspects of the product, such as viscosity, pH, stability, or preservation, or make the products more attractive to the consumer (color, appearance, perfume, etc.).

6.3.1.4.1 Opacifiers and Pearlescent Agents

These are generally long-chain alcohol sulfates such as sodium cetyl sulfate. Opacification can be simply obtained by addition of a small amount of fine white polymer dispersion. There are also

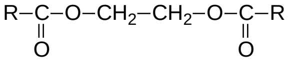
- Poorly soluble alkanolamine salts of fatty saturated acids in C_{18} or more fatty alcohols (tallow, cetyl, and steryl alcohols), which are good for conditioning but reduce foaming properties.

- Vinyl or styrene polymer emulsions.
- Esters of ethylene glycol, propylene glycol, or glycerol. The most frequently used are glycerol monostearate and ethylene glycol distearate. Different stearates give different effects.



$$R-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-OH$$

GMS



$$R-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-O-\underset{\underset{O}{\|}}{C}-R$$

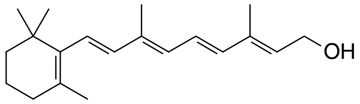
EGDS

6.3.1.4.2 Thickeners/Adjusters of Viscosity

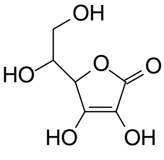
Shampoos can be thickened by inorganic electrolytes such as NaCl, alkanolamides, especially coconut mono- and diethanolamides, and polymers such as soluble cellulose derivatives, that is, carboxymethyl cellulose, methyl cellulose, hydroxymethyl, or hydroxyethyl cellulose. These derivatives are thickeners for opaque formulations and can also have other functions, such as foam stabilizers and antiredeposition agents. By leaving a thin film after rinsing, they help to untangle hair. Carboxyvinyl polymers (Carbopol from B.F. Goodrich Chemical Co.) can be very good thickening agents, particularly in the presence of ethoxylated fatty alcohols. They give creamy foam and prevent decantation of silicones or silicone emulsions, particularly when the product is stocked in a hot place. Viscosity can be adjusted using ethylene glycol and glycerol polyethylene glycols (PEGs) of various molecular weights.

6.3.1.4.3 Vitamins

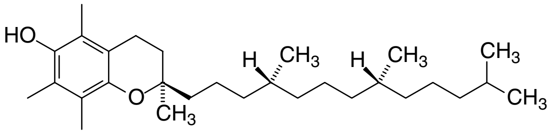
Vitamins A, B, C, and E are the most frequently used. All these vitamins, and in particular vitamin E, help to control oxidoreduction and can favor blood circulation in the scalp.



Vitamin A or retinol



Vitamin C or ascorbic acid



Vitamin E or tocopherol

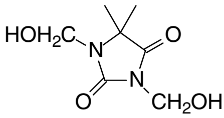
6.3.1.4.4 Preservatives

They stop mould and fermentation. Making the right choice of preservatives is important because

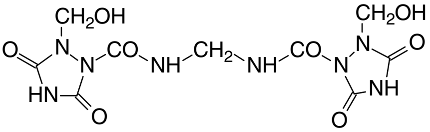
1. Their efficacy must not be inhibited by surfactants
2. They must be stable and not lose their activity too quickly

3. Some of them can be irritant
4. Others, such as phenolic derivatives, give a *brownish* color

Two widely used preservatives, DMDM hydantoin and imidazolidinyl urea, are found in many shampoos, to prevent fungal and bacterial spoilage. They release formaldehyde to kill germs. Other broad-spectrum biocide are isothiazolinone and the related methylisothiazolinone and methylchloroisothiazolinone. Sodium benzoate is another preservative used in shampoos. It kills bacteria, fungi, and yeasts, and works well in acidic mixtures.

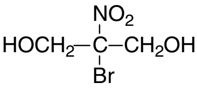


DMDM hydantoin



Imidazolidinyl urea

Many other preservatives can be used, such as *p*-hydroxy benzoic acid, sorbic acid, and hydroxy quinoline sulfate. Another bactericide used is 2-bromo-2-nitropropane-1,3-diol (Bronopol).

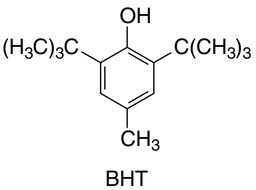


$$HOCH_2-\underset{Br}{\overset{NO_2}{C}}-CH_2OH$$

Bronopol

6.3.1.4.5 Antioxidizing Agents

Butylated hydroxytoluene or 2,6-di-*tert*-butyl-4-methylphenol is frequently added as an antioxidizing agent to prevent catalytic oxidation induced by transition metal traces present in certain raw materials. Its chemical formula is



BHT

6.3.1.4.6 Colorants and Perfumes

These are chosen according to qualitative criteria, but must also be compatible and stable with the other ingredients. In shampoos for sensitive skins, particularly baby shampoos, the perfume must be free of irritant molecules (Tables 6.12 and 6.13).

It is noteworthy that there are many patents covering the formulations. The greatest care should be taken to check patents before using a product, to avoid all risk of infringement (Tables 6.14 through 6.16).

TABLE 6.12
Main Ingredients of Shampoos and Their Functions

Functions	Ingredients (Examples)
Detergency—lather	Anionic surfactants (primary and mild surfactants): Na or Mg or NH_4 lauryl ether sulfate (LES), Na or Mg cetyl ether sulfate, sodium sulfosuccinate
	Extra mild surfactants (nonionic): polyethoxylated sorbitan ester
	Combination with amphoteric or zwitterionic surfactants: cocamidopropyl betaine
Conditioning	Surfactants/glycol soap agents
Aids deposition of conditioners	Cationic surfactants
	Cationic polymers
	Silicones and derivatives
Therapeutic effect	
Dry hair	Oil, fatty alcohols, proteins
Greasy hair	Proteins, vitamins
Antidandruff	Antimicrobials, keratolytic agents
Pearlescent effect	Ethylene glycol distearate
Thickening	Inorganic electrolytes (NaCl), carboxymethylcellulose and derivatives, carboxyvinyl polymers, PEG
Preservative	DMDM hydantoin, imidazolidinyl urea, sodium benzoate, and derivatives
Antioxidant	Butylated hydroxytoluene, EDTA
pH	NaOH, citric acid

TABLE 6.13
Typical Formulations for Normal Hair

	Formulation A (Transparent) (wt%)	Formulation B (Opaque) (wt%)
LES	10–15	10–15
CAPB	2–4	2–4
Stabilizing opacifiers	0	0.5–2
Antioxidants	+	+
Preservatives	+	+
Viscosity regulators	−/+	−/+
pH adjusters	−/+	−/+
Perfume, color, water	Balance	Balance

6.3.2 CONDITIONING PRODUCTS

In the 1960s, these products were used only in salons, but they have grown now into large markets in most developed countries, and particularly the USA. They are best used when the hair is long and dried with an electric hair dryer. They provide the following benefits:

1. Supple hair, when damp
2. Easy untangling, when damp
3. Easy brushing, when dry
4. Shine, silkiness, volume
5. Protection, particularly for the ends of the hair

TABLE 6.14
Typical Formulations with Conditioners (Known as 2 in 1 Shampoos)

Ingredients	wt%
LES	10–15
CAPB	1–4
Silicone emulsion	0–1.5
Carboxyvinyl polymer (Carbopol)	0–0.3
Ethylene glycol stearates	0.5–1.5
Guar hydroxypropyltrimethyl ammonium chloride	0.1–0.5
Perfume	+
Butylated hydroxytoluene	0.025–0.06
NaCl	0.5–1.5
Color	+
Citric acid/NaOH	+/– To adjust pH
Water	Balance

TABLE 6.15
Typical Formulations for Baby Shampoos

Ingredients	wt%
Na or Mg lauryl ether sulfate with 2, 6, or 8 ethylene oxides or Na, Mg oleyl ether sulfate or Na sulfosuccinate	5–7
Polyethoxylated sorbitan ester	0.5–1
CAPB	3–4
Preservatives/antioxidants	+
Perfume, water	Balance

TABLE 6.16
Typical Formulations of Antidandruff Shampoos

Ingredients	wt%
LES	10–15
CAPB	1–2
Piroctone olamine or zinc pyridinethione	0.05–0.15
Selenium sulfide or salycilic acid	2
Opacifiers, preservatives	Balance

Conditioning products can be divided into two groups:

1. Classical conditioners (without thickening polymers)
2. Conditioners with thickening polymers

6.3.2.1 Basic Ingredients

In both cases, conditioners contain a cationic surfactant and a fatty alcohol as basic ingredients. The cationic surfactant adsorbs easily on the hair (negatively charged) and produces a light conditioning effect, which particularly helps dry or wet combing. Its main negative effect is that it can irritate the eyes. The addition of fatty alcohol improves both the safety and the functional aspects of cationic solutions, because mixed bilayers are formed, which are dispersed in the aqueous phase. This lamellar phase has the following functions:

1. It helps deposit active product on hair in a more organized way.
2. It reduces irritation due to cationic surfactant by reducing the concentration of free monomer.
3. The network formed is an efficient system to maintain suspension, and the product is stable.

6.3.2.2 Other Ingredients

They may include

- Polyethylene glycol that is used as a wetting agent
- Hydroxyethylcellulose that acts as a thickening agent and makes the product easier to handle during processing
- Electrolytes that strongly influence the viscosity of formulations when hydroxyethylcellulose is not used (Tables 6.17 and 6.18)

TABLE 6.17
Typical Formulations of Conditioners

Conditioning Agents		Thickening and Pearlescent Agents	
Ingredients	**wt%**	**Ingredients**	**wt%**
CTAC	0.5–1.2	Monostearate glycerol	0.5–1
Cetyl-stearyl alcohol	1.5–3	Stearyl stearate	03–0.7
Polydimethylsiloxane (>5000 Cps)	0.5–2.5	Cetyl palmitate	0.3–0.7
		Paraffin	0.5–1.5
		Hydroxyethylcellulose	0.7–1.5

Note: CTAC = cetyltrimethylammonium chloride.

TABLE 6.18
Typical Formulations for "Intensive" Care

Ingredients	Formulation A (wt%)	Formulation B (wt%)
CTAC	0.8–1.2	1–1.5
Cetyl/stearyl alcohol	2–3	2–4
Cetyl alcohol	0.5–1.5	—
Paraffin	—	0.5–1.5
Stearyl stearate	1.5–3	—
Hydroxyethyl cellulose	1–2	—
Hydroxypropylmethyl cellulose	—	1–2
Polydimethylsiloxane (5000 Cps)	0.5–1.5	—
Preservatives	+	+
Perfume	+	+
Color	+	+
Water	Balance	Balance

6.4 ORAL CARE PRODUCTS

Most tooth problems are directly related to dental plaque. This is a whitish substance that collects on teeth and gums, which is removed by brushing. About 70% of plaque is made up of millions of bacteria, which lodge in a mass of insoluble carbohydrate. Plaque starts with a deposit of salivary mucus on the teeth containing aerobic bacteria that need oxygen to develop. With time, anaerobic bacteria appear; they are the principal cause of problems related to plaque.

A lack of dental hygiene allows the plaque formation, causing gingivitis or inflammation caused by toxins produced by the bacteria. With time, the gum recedes, the fragile root dentine is exposed, and finally, the tooth will fall out.

Tartar is calcium phosphate from saliva that deposits on plaque. Saliva is supersaturated in calcium phosphate, whose crystals therefore precipitate easily. Tartar is strongly attached to the tooth surface and cannot be removed by simple brushing.

Gums, receding with age, expose first the root dentine (under the protective layer of enamel) and then the pulp. The nerve cells of the pulp are then exposed to outside stimulation (such as heat and cold), causing discomfort. Dentine can also be exposed by excessively hard brushing, which causes the gum to retreat.

Stains. Dyes that fix themselves to enamel cannot be removed by simple brushing with water. Dentifrice must contain a soft abrasive which does not attack the enamal of the dentin.

Bad breath. Compounds containing sulfur, called thiols, are produced by the bacterial metabolism responsible for halitosis or bad breath. Advanced caries can also cause bad breath.

Caries are holes in the enamel. They represent irreversible damage and can cause pain and discomfort. Left untreated, the tooth will be completely destroyed.

Dental caries result from a process that locally destroys the structure of the tooth. Organic acids demineralize the enamel, which liberates enamel ions such as calcium, phosphate, carbonate, magnesium, fluoride, sodium, and other trace elements.

The presence of acid-forming bacteria capable of transforming sugars into acids is the essential condition for the process to start. These bacteria known as *"Streptococcus mutans"* are highly acidogenic and significantly increase the risk of caries. Acids that attack the enamel are produced by fermentation of carbohydrates in food by the bacteria flora that has accumulated in dental plaque. These carbohydrates come from different sources such as sucrose or fermentable carbohydrates. The acid can also come from beverages. Factors that influence the activity of acids on enamel are the time during which the food remains on the tooth surface, the quantity of acids, and their capacity to favor the formation of dental plaque. Normally saliva plays a protective role, since it buffers the flow of acid on the tooth surface [14], has certain antibacterial properties, and provides elements that participate in the remineralization of dental tissue (such as calcium and phosphorous). But saliva alone is not enough. Good oral hygiene is essential if caries are to be avoided.

A dentifrice must fulfil two primary functions:

1. It must clean teeth and refresh the mouth (*cosmetic function*).
2. It is the vehicle for certain therapeutic agents such as fluoride against caries (*therapeutic function*).

Toothpastes are complex mixtures of abrasives and surfactants, anticaries agents, tartar control ingredients, pH buffers, humectants, and thickeners [15]. All the ingredients must pass Food and Drug Administration regulations.

6.4.1 WATER AND HUMECTANTS

Water dissolves and dissipates the therapeutic agents, detergents, thickeners, and sweeteners. Humectants permit a reduction in the amount of water in the formula, which helps preserve the product to some extent, and reduces drying out by retaining moisture (if the cap is left off for instance). The humectants therefore play a small role in the aspect of the toothpaste and give a slight shine. The main compounds used in toothpastes as humectants are polyols such as sorbitol ($HOCH_2–(CHOH)_4–CH_2OH$), which gives a mild and refreshing feeling, and glycerol or glycerine ($HOCH_2–CHOH–CH_2OH$), which gives a feeling of warmth. Others include propylene glycol ($HOCH_2–CHOH–CH_3$), xylitol ($HOCH_2–(CHOH)_3–CH_2OH$), and PEG ($–CH_2CH_2O)_n–$). PEG may also be used to structure and solubilize both the flavors and the surfactant. A toothpaste may contain up to ≈70% humectants.

6.4.2 Detergents

Detergents (i.e., surfactants) in toothpaste formulations have three main functions:

1. To help clean teeth by removing dental plaque
2. To provide the desired foam
3. To dissolve and disperse flavors that are insoluble in water due to the formation of micelles

Two anionic surfactants are predominant in toothpaste formulations. These are SLS and sodium dodecylbenzene sulfonate (SDOBS) that exhibits excellent foaming properties. A good quality and quantity of foam may be obtained by mixing SLS and SDOBS. Sodium lauroyl sarcosinate ($H_3C(CH_2)_{10}CON(CH_3)CH_2COONa$) was used extensively in dentifrices, but was found to be a cause of oral mucosal irritation. Nowadays, its use is limited. Surfactants also play the role of inhibitor of enzymes responsible for tooth decay.

6.4.3 Abrasives

The abrasive cleans the teeth and also contributes to ensuring the right viscosity for the toothpaste. Cleaning is done by abrasion of the stained/colored film on the surface of the teeth. Dentin, which is softer than enamel, has to be taken into account in the choice of an abrasive. The abrasive also contributes to the viscosity of the toothpaste, particularly at high concentrations (>30%). The choice of abrasive also depends on the choice of therapeutic agents, as there may be some incompatibilities, and whether the desired product is opaque or transparent. The three abrasives most frequently used are

- Hydrated silica precipitates (SiO_2)
- Calcium carbonate ($CaCO_3$)
- Aluminum hydroxide ($Al(OH)_3$)

Precipitated calcium carbonate is inexpensive and efficient. However, it reacts easily with fluoride and hence, its use is limited to sodium monofluorophosphate dentifrices. $CaCO_3$, in addition to its abrasive properties, has other interesting qualities. It buffers the pH of saliva, which contributes to the formation of caries. After brushing with a toothpaste containing calcium carbonate, it dissolves into the saliva, where it works as a pH buffer. The suspended particles then adhere into certain cavities in the tooth structure and in the plaque. From there, they dissolve slowly into saliva, thereby prolonging the buffering effect [16].

Other abrasives include dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$), which is not stable in toothpaste formulations and converts into $CaHPO_4$, which is much harder. Nevertheless, $CaHPO_4 \cdot 2H_2O$ can be stabilized by addition of tetrasodium pyrophosphate. Insoluble sodium metaphosphate ($(NaPO_3)_x$), calcium pyrophosphate ($Ca_2P_2O_7$), and sodium bicarbonate may also be encountered in toothpaste formulations.

These ingredients should not harm either the enamel or the dentin, but must be efficient in removing colored stains. Their efficiency depends on

1. Hardness
2. Particle size and shape
3. Concentration in the finished product

6.4.4 THICKENERS

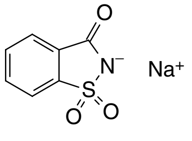
These help to avoid sedimentation of the abrasive and bring the desired rheological properties to the product, such as easing the flow from the tube while ensuring it remains firm on the brush. Thickeners structure the liquid phase of the product, holding the abrasive in suspension. This structure disappears when pressure is applied to the tube, only to reform when the pressure stops (thixotropic behavior).

Either organic or inorganic thickeners can be used. Among organic ones, there are polymers such as sodium carboxymethylcellulose (SCMC) and xanthan gum. SCMC is available in many forms, with different thickening abilities and electrolyte tolerance. Xanthan gum is a high-molecular weight natural polymer (polysaccharide), obtained by the fermentation of *Xanthomonas campestris* in a glucose environment. It has some advantages over SCMC, including better mouth feel, better electrolyte tolerance, resistance to microbial deterioration, and good stability over time. Other organic thickeners include cellulose ethers, carrageenans, sodium alginate, and polyacrylates.

The main inorganic thickeners used are silicas (pyrogenic, precipitated, aerogels), sodium aluminium silicates, and also certain clays (laponite or hectonite).

6.4.5 SWEETENERS

These make the product more acceptable in terms of taste, by masking the bitter taste of some ingredients in the formula. Ingredients used today are not sugars and are nonfermentable, which help to avoid caries. The most commonly used is saccharin, which is sodium salt of *o*-sulfobenzimide.



Saccharin

6.4.6 OPACIFIERS

Titanium oxide (TiO_2) is added to white opaque toothpastes to improve whiteness and to vary the shade of a colored product.

6.4.7 DYES

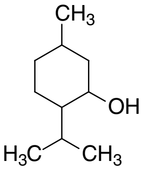
Dyes used must meet safety, stability, and cost norms. They are therefore food-quality and can be soluble or insoluble (pigments). It is sometimes possible to add small quantities of color stabilizers such as magnesium sulfate.

6.4.8 STABILIZERS AND pH ADJUSTERS

Previously, alumina-based toothpastes were packed in nonlacquered aluminum tubes. Stabilizers were added to avoid chemical reactions between product and pack, using sodium monophosphate (NaH_2PO_4), which is still used today, but rather to stabilize the pH. (Tubes today are of better quality, lacquered or plastic.) Zinc citrate is also used as a buffer, reducing pH to neutral. It should not be used together with phosphates, as this forms insoluble zinc phosphate salts. To increase the pH of formulations containing high sorbitol, trisodic phosphate (Na_3PO_4) can be used. For reasons mentioned above, this cannot be used with zinc citrate, in which case sodium hydroxide should be used to adjust pH.

6.4.9 FLAVORS

The taste of a toothpaste is critical for the consumer. Apart from very specific exceptions, such as flavors for children, the range of flavors is very limited. Eighty percent of tastes are based on mint, peppermint, or a mixture of the two. Most of the remainder is methyl salicylate from the gaultheria plant. In some countries, there are variations from these norms; for example: fruity notes in Japan, aniseed in the Mediterranean, and spicy notes in South America. Flavors must be pleasant and associated with a *clean* feeling. This is the reason mint/peppermint oils together with menthol account for 60–80% of flavor bases for toothpastes. The flavor sources are either natural or synthetic.



Menthol

6.4.10 PRESERVATIVES

The humectants help to preserve the product, but in formulations with little water, other products such as sodium benzoate, potassium sorbate, and methyl parabenzoate can be added to inhibit mold and growth of bacteria. Sodium benzoate and potassium sorbate are used at pH <5.5, as they are more efficient in their nonionized form. *p*-methylbenzoate, however, is more efficient at neutral pH.

6.4.11 THERAPEUTIC AGENTS

6.4.11.1 Antitartar

Pyrophosphate salts ($P_2O_7^{4-}$) have been the standard ingredient, usually in a mixture of tetrasodium pyrophosphate, which has a poor solubility at low temperatures, and potassium tetraphosphate, which has a better solubility, but salty taste.

6.4.11.2 Desensitizing Agents

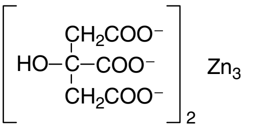
The first agent to be authorized was strontium, but this also has a salty taste and is not compatible with fluorides. The next generation was strontium acetate, with a less salty taste, and better compatibility with fluoride. Potassium salts (chlorides, nitrates, citrates) are the most widely used today, as they are compatible with fluoride and they provide a neutral taste.

6.4.11.3 Antiplaque Agents

There are two main groups:

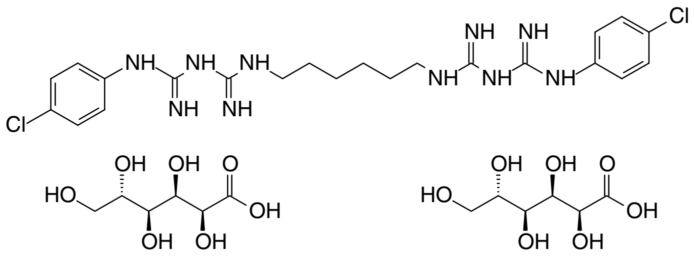
1. Antimicrobials with a metallic ion. This class includes water-soluble salts of zinc, copper, or tin. Zinc salts, in particular zinc citrate, are the most widely used in toothpastes. Other sources of zinc ion are zinc chloride, zinc sulfate, and zinc thiocyanate.

2. Organic antibacterial agents. Among organic antimicrobials, the best known is chlorhexidine digluconate, but it has a bitter taste and stains teeth; it has not been very successful in toothpastes.



$$\left[\begin{array}{l}\ \ \ \ \ \ \ CH_2COO^- \\ HO{-}C{-}COO^- \\ \ \ \ \ \ \ \ CH_2COO^- \end{array}\right]_2 Zn_3$$

Zinc citrate



Chlorhexidine digluconate

On the other hand, Triclosan is widely used. However, it would seem that the use of only one bactericide in toothpaste may be less effective than the combination of two, such as zinc citrate and Triclosan. Plaque reduction is then improved and gingivitis is retarded.

6.4.11.4 Anticaries

There are a certain number of options to control and reduce dental caries, the biggest problem in tooth care. The use of fluoride salts is one of the most effective methods to prevent or slow down demineralization that causes tooth decay [16,17]. The action of fluoride can be explained by its antimicrobial action, its interaction with enamel to form a fluorinated hydroxyapatite compound (hydroxyfluorapatite or fluorapatite $Ca_5(PO_4)_3F$) by substitution of an hydroxyl ion in hydroxyapatite $Ca_5(PO_4)_3(OH)$, which is more resistant to acid than enamel on its own, and its *repairing* effect by formation of calcium and phosphate, which remineralize the tiny lesions in which caries begin.

It is well known that fluoride inhibits bacterial growth, but the concentration required to be effective is far higher than the amount delivered in a toothpaste [18]. The generally accepted explanations for the efficacy of fluoride are the last points above, that is, the formation of the fluoridated hydroxyapatite compound, which is stronger against acids [19], and the inhibition of demineralization of the enamel [20,21]. The therapeutic efficiency of fluoride would therefore appear to be due to a reduction in the solubility of enamel and to the remineralization of areas under attack. Remineralization of enamel is the consequence of adsorption of fluoride on the enamel surface [20]. The remineralized lesion stops, neither increasing nor decreasing with time.

The correct use of a fluoride toothpaste ensures a fluoride concentration sufficient to prevent caries from forming, or to cure them. Concentration of 0.01–0.02 ppm fluoride is enough to form fluorinated hydroxyapatites that reduce enamel solubility and help to fix calcium onto the caries (remineralization) [22,23].

People usually brush their teeth 1–3 times per day. If a fluoride toothpaste is used, the level of fluoride in saliva is twice as high as for nonfluoride toothpaste users. This is due to the fact that the fluoride is absorbed by different parts of the mouth after brushing, and is then gradually released into the saliva [18]. Elimination of fluoride occurs in two phases:

1. After brushing, concentration falls quickly to ~0.08 ppm of fluoride after 30 min.
2. In the second phase, the concentration falls more slowly to an almost stable level of 0.02 ppm of fluoride between two brushings.

A well-formulated product will ensure a level of fluoride in the saliva above 0.02 ppm for several hours [18]. Fluoride ions are present in toothpaste formulations largely in the form of stannous fluoride (SnF_2), sodium monofluorophosphate (Na_2PO_3F), and sodium fluoride (NaF). But we can also find in the literature potassium fluoride, lithium fluoride, aluminum fluoride, zinc fluoride, acidic phosphate fluoride, ammonium fluoride, titanium tetrafluoride, and amine fluoride.

Every year, the World Health Organization issues a world map of caries in 12-year-olds, which clearly reflects eating habits. Developed countries are experiencing relatively little problem as a result of preventive programs. In France for instance, a decree requires all 15-year-old adolescents to visit the dentist, with any necessary dental work to be paid for by the Government.

The use of fluoride toothpaste is therefore the main way to fight caries. Other factors seem to be relatively unimportant. For instance, limitations on sugar consumption and other foods that could give rise to carbohydrates have very little effect on numbers of caries (Table 6.19) [24].

For illustration, some examples of toothpaste formulations are given in Tables 6.20 and 6.21 [25,26].

The above example contains both antimicrobials and anticaries agents. Products sold in the trade will generally contain only the anticaries agents for reasons of cost.

For a toothpaste to be efficient against caries, it is not enough simply to add fluoride salts. It is vital that all ingredients be stable during the life of the product. It is not unusual to find products in the trade (particularly those manufactured in Third World countries), which no longer contain active fluoride ions. Large brand manufacturers have the advantage of knowing how to keep anticaries agents stable, for example, by selecting the right raw materials and manufacturing processes and using stabilizing systems. Moreover, through research, they are always improving the anticaries

TABLE 6.19
Main Ingredients of Dentifrices and Their Functions

Functions	Ingredients (Examples)
Detergent—foaming agent	Sodium lauryl sulfate, sodium dodecylbenzene sulfate
Humectant	Sorbitol, glycerol
Abrasive	Hydrated silica, carbonate, alumina, calcium phosphate
Thickener	Cellulose derivatives, xanthan gum, precipitated silica
Sweetening agent	Saccharin
Opacifier	Titanium oxide
Flavor	Mint and peppermint oils
Preservative	Sodium benzoate
Therapeutic agents against caries, tartar, bacteria (plaque, gingivitis, bad breath, periodontal disease), sensitive teeth	Fluoride derivatives Pyrophosphate Bactericides (zinc salt or Triclosan) Strontium acetate, potassium salts

TABLE 6.20
Typical Formulation of a Toothpaste Containing Sodium Fluoride as the Source of Fluoride Ion (Anticaries) and Zinc Chloride as the Antimicrobial

Ingredients	wt%
Zinc chloride	2
Sorbitol (70%)	35
Glycerol	10
Hydrated silica	23
Sodium methyl cocoyl taurate[a]	3.75
Xanthan gum	1
Hydroxyethyl cellulose	1
Sodium gluconate[b]	0.80
Titanium oxide	0.80
Sodium saccharinate	0.7
Saccharin	0.10
Sodium Benzoate	0.20
Flavor	1.3
Demineralized water	Balance

[a] Sodium methyl cocoyl taurate: R–CO–N(CH_3)–CH_2CH_2–SO_3Na (R ≈ 12C).

[b] Sodium gluconate: $HOCH_2$–$(CHOH)_4$–COONa.

Source: Asano, A. and Gaffer, M. C., Johnson & Johnson, EP 0162574B1.

TABLE 6.21
Typical Formulation of a Toothpaste Containing Sodium Monofluorophosphate as the Source of Fluoride and Two Combined Antimicrobials

Ingredients	wt%
Trihydrated alumina	50
Sorbitol (70%)	27
Sodium lauryl sulfate	1.88
Sodium dodecylbenzene sulfonate	0.63
Sodium carboxymethylcellulose	0.8
Trihydrated zinc citrate	1
Triclosan	0.5
Sodium monofluorophosphate	0.85
Flavor	1.2
Sodium saccharinate	0.18
Formaldehyde	0.04
Demineralized water	Balance

Source: Taken from Roger, M. L. et al., Unilever, U.S. 4759562.

efficacy of their products, for example in the search of yet more effective fluoride compounds such as alkylamine fluorophosphates [27] or combinations of fluoride compounds with other agents such as silicones (to help the adsorption of fluoride on teeth) or a mixture of fluoride salts with xylitol, which improves anticaries properties (Table 6.22) [28, 29].

TABLE 6.22
Typical Formulation of a Multiphase Toothpaste Comprising Clear and Opaque Phases

Ingredients	wt%
First phase = clear gel phase (25% v/v)	
Sorbitol (70%)	63
Sodium lauryl sulfate	1.8
Abrasive silica	8.0
PEG 32	4.0
Thickening silica	9.25
Sodium carboxymethylcellulose	0.9
Sodium fluoride	0.32
Water	12.73
Second phase = opaque phase (75% v/v)	
Sorbitol (70%)	63
PEG 32	4.0
Sodium fluoride	0.32
Titanium dioxide	0.5
Sodium lauryl sulfate	1.8
Abrasive silica	8.0
Thickening silica	9.2
Sodium carboxymethylcellulose	0.9
Water	12.48

Source: Taken from Argawal, R. K., Faravelli, I., Gregory, D. P., and Groves, B., Unilever, WO 2006081934.

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7 Body-Cleansing Technology

Syed H. Abbas

CONTENTS

7.1 INTRODUCTION

Soap is one of the earliest cleansing agents known to mankind. There are different biblical references for the use of soap as a cleansing agent [1]. It is believed that the Phoenicians developed the art of making soap in 600 BC. Early records show that the Egyptians and Babylonians were using a saliva-like preparation produced by boiling oils and plant ashes as cleansers [2].

Although the history of soap is very old, its importance as cleansing agent was recognized only after the first century. Greek physician Galen (about AD 130–200) and the well-known chemist Gabir ibne Hayyan (eighth century) are among the first few who have mentioned the use of soap as a body-cleaning agent in their writings [3,4]. In the ninth century, Marseilles was famous for soap making, and by the fourteenth century, soap manufacture became very common in Britain [5]. Though the interest in soap as a cleansing agent is known from the first century, its manufacture and use was not very common. Its process was kept strictly secret, and for the first time it could be published in the year 1775 [3]. Soap industries flourished further as a result of the discovery by LeBlanc in the year 1787 of how to produce soda ash from common salt.

Some of the present soap makers like Unilever, Procter & Gamble, Colgate-Palmolive, Dial Corporation, and Jergens started manufacturing soap in the nineteenth century. The oldest and the most well-known transparent soap *Pears* was developed by Andrew Pears and first sold in England in the year 1789 [6]. Even now it is one of the most famous transparent soap brands in the world. The soap-making process was considered an art up to the end of nineteenth century. With the understanding of unique molecular structure and physical properties of surfactants, soap technologists started thinking toward scientific explanations of the properties and process of soap making. Different theories and phase diagrams of soap systems started emerging in literature, and slowly soap making became not an art, but a separate branch of science.

The objective of this chapter is to review the developments in the area of body-cleansing products. For the sake of convenience, this chapter is divided into four sections. The first section covers the changing consumer needs and increasing demand for cleansing products. Structural aspects of cleansing products are covered in the second section, whereas the third and fourth sections deal with formulations and an overview of processing aspects of bar cleansers.

7.2 CHANGING CONSUMER NEEDS

Consumer needs for body-cleansing products are based on socioeconomic conditions and geographical location. Consumers have certain requirements in the developing countries, although the expectations of the consumers in the developed countries are completely different. In most of the developed countries, the consumers dictate the quality of the product, and successful industries follow the philosophy of "the consumers come first" [7]. To be successful in the global market, industries need to design products to meet the specific needs of consumers in various parts of the world.

With the increase in the level of literacy and awareness, created by media, people are becoming very health conscious. In the past, cleansing products were expected to deliver only the basic needs of cleaning benefits, but now consumer's expectations have gone beyond cleaning into the area of health and cosmetics [8]. These expectations have led the industries to develop products that can satisfy the needs of consumers. It became the key reason for the development of products with different functional properties. In body-cleansing products, for better performance in hard water and improved mildness, syndet, combar, and mild liquid products were developed. Transparency is perceived as a cue for mildness and purity, which has led to the development of different types of transparent bar products. Demand for antibacterial products increased with health consciousness and awareness of hygiene and cleanliness.

By effective communications through media, using the Internet, television, and newspapers, industries have helped the consumers in increasing their awareness and expectations. Environmental awareness associated with biodegradability issues, global warming, and ozone depletion will have a major effect on the approach toward the development of environmentally friendly products in the future. There are consumer guidance societies, government bodies like the Food and Drug Administration (FDA) and consumer awareness programs, which help the consumers to understand both the positive and negative aspects of products. Jawaorski [9] has described in detail the changing consumer needs and market trends in personal care industries.

7.3 STRUCTURAL ASPECTS OF SURFACTANTS

Surfactants are organic compounds that possess surface-active properties. This unique property of the surfactant is due to the presence of hydrophilic and hydrophobic qualities in the same molecule. The hydrophilic part of the molecule has affinity toward the aqueous phase and the hydrophobic part of the molecule interacts with the oil phase. This unique property of the surfactant molecules helps in its movement toward the interface and reduces the surface tension between the two immiscible phases. This dual behavior of surfactant molecules is responsible for their wide range of application in products such as cleansers, creams, lotions, shampoos, agricultural products, and medicines.

In fully formulated products, based on the solvent medium, other components, their concentrations, and the temperature, the surfactant molecules form different types of aggregates. These aggregates have a major effect on the product attributes and the processing properties. To have a better understanding of the formulation and process, it is necessary that a cleansing product technologist should have a basic knowledge of these interactions and the physical properties of these aggregates. One can always have a good understanding of these phases in model systems, but it becomes difficult and complicated to predict the formation of these phases in products, where the surfactant molecules interact with other additives.

The Krafft point (KP) of a surfactant plays a very important role in the formation of different phases. It is the temperature at which there is a sudden increase in the solubility of surfactants in water [10,11]. Below the KP, a surfactant forms solid phases, whereas the liquid phases are formed above the KP of the surfactant. In general, we can classify these phases into the following three groups:

- Micellar solution
- Liquid crystalline phases
- Solid phases

There is plenty of information available in literature on liquid crystalline and isotropic phases of different surfactants, but the study of the solid phases is limited to only soaps [12–19]. The basic reason for the lack of solid phase studies of synthetic surfactants is their limited use in solid form. The low KP of these surfactants limits their use to liquid products. Owing to a relatively high KP, sodium cocoyl isethionate (SCI), alkyl glycerol ether sulfonate (AGES), and sodium cocoyl monoglyceride sulfate (CMGS) form solid phases at room temperature, but there is hardly any information available on these solid phases.

A detailed discussion about these phases is beyond the scope of this chapter. It is worthwhile to mention briefly some of the relevant properties of these phases and their significance in product formulation, process, and user properties.

7.3.1 Micellar Solution

At a low level of surfactants in water, a molecular solution is formed, and with the increase in concentration, after a particular level, the surfactant molecules aggregate to form micelles. This concentration is called critical micelle concentration (CMC). Owing to the formation of micelles at CMC, there is a sudden change in the physical properties of surfactant solution. At the KP the CMC of the surfactant is equal to its solubility. Micellar solution is very important for liquid products such as liquid soaps and shampoos. The level of synthetic actives such as sodium lauryl ether sulfate, triethanolamine lauryl sulfate, ammonium lauryl sulfate, and alpha olefin sulfonate (AOS) can vary from 10 to 20% in these formulations. At this concentration, in water, these surfactants form spherical micellar solution. The viscosity of the spherical micellar solution is very low. For better aesthetics and proper handling of products, depending on the requirement, the liquid formulations need particular rheological properties. Normally common salts are used to convert the spherical micelles to rod micelles, which give high viscosity in these formulations. It is possible to increase the viscosity of the product by using polymers or formulating it in such a way that it forms stable viscous liquid crystalline phases with required rheological properties. Spherical and rod micelles are isotropic in nature. A significant amount of work has been done on the study of the micellar solutions and their physical properties. A packing constrain model based on the molecular dimensions, proposed by Israelachvili et al. [20], gives a theoretical prediction of the micelle shape.

Sodium and potassium salts of coconut fatty acids in liquid soaps, at a 15–25% level, give spherical micellar solution. Owing to the low electrolyte tolerance of soaps resulting from the use of common salt, soap gets salted out without the formation of rod micelles. Polymers such as hydroxyethyl cellulose, xanthan gum, hydroxylpropyl cellulose, or any other viscosity modifier do not change the aggregation behavior of these types of micellar solutions, but due to the interaction with water, they give desired rheological properties and are successfully used as viscosity builders in soap-based liquid products.

7.3.2 LIQUID CRYSTALLINE PHASES

Liquid crystalline phases are very important for the products having a high level of surfactants. The type of liquid crystalline phases formed depends on the nature of the surfactant, its level, the solvent medium, the additives, and the temperature of the medium [21–25]. The various liquid crystalline phases have different physical properties, such as optical behavior, rheological properties, refractive index, density, and translucency.

The most common phases encountered in surfactants used for skin-cleansing products are hexagonal, lamellar, and cubic liquid crystalline phases. There are different inverted and complex intermediate liquid crystalline phases that have hardly any use in the formulation and process of cleansing products. Cubic phase is isotropic, whereas lamellar and hexagonal liquid crystalline phases are anisotropic in nature. Optical microscopy, x-ray diffraction (XRD), and nuclear magnetic resonance (NMR) are the main techniques used for the identification of these phases [22,23]. Based on different structural and thermodynamic parameters, theoretical models have been developed to construct phase diagrams and predict the phase behavior of different surfactant systems [24]. A good understanding of these phases helps in the prediction of the product attributes and their processing properties.

Different materials such as salts, free fatty acids, polyols, fatty alcohols, fatty esters, and perfumery components can influence the formation of liquid crystalline phases. Free fatty acids and fatty alcohols promote the formation of lamellar liquid crystalline phase [26]. One can expect solid, isotropic solution, and hexagonal liquid crystalline phases coexisting in normal soaps, but in superfatted soaps, part of the hexagonal liquid crystalline phase is converted to lamellar, which is responsible for product softness during processing.

A substantial amount of work has been carried out on thermotropic transitions of anhydrous soaps and other surfactants using high-temperature XRD and NMR. The mobility of the hydrocarbon chains increases with temperature, which leads to the formation of mobile solid phases (waxy phases) and liquid crystalline phases [27–29]. These transitions have very limited application in cleansing products. Some of these transitions take place during processing of soap at elevated temperatures.

7.3.3 SOLID PHASES OF SOAP AND THEIR PROPERTIES

The amphiphilic nature of surfactants is responsible for the arrangements of surfactant molecules in a bilayer form, giving crystalline structure in the solid phase. Low-angle XRD studies indicate the formation of an ordered bilayer structure in solid surfactant systems [20].

There is not enough information on the solid phases of the synthetic surfactants. A substantial amount of work has been done on solid phases of soap and their correlation with product attributes. Most of this work started in the third and fourth decades of the past century. These phases have been characterized mainly on the basis of XRD pattern in the range of 15–35° of 2θ value, and are formed during soap processing. Mostly the phase transformation depends on the processing temperature, soap composition, moisture, and additives such as salt, free fatty acid, and perfume [3,30]. A number of different solid phases of soap have been reported in the literature, but the most relevant solid phases affecting the product attributes and the processing properties are beta, delta, and omega phases (β, δ, and ω). Their main characteristic XRD peaks are summarized in Table 7.1.

All these three phases are observed in commercial soaps and can coexist, but based on processing conditions, the relative ratios of these phases can be changed [31]. The formation of omega phase is favored at high temperature and low moisture level, with low-molecular weight saturated fatty acid soaps, whereas delta phase is favored by low temperature, high moisture content, and high-molecular weight soaps, preferably in the presence of superfatting agents [32,33]. Beta and delta phases are formed during mechanical working of omega phase under controlled conditions of temperature, moisture, and fatty acid composition [34–36]. This conversion is easier in mixed fatty

TABLE 7.1
Main Characteristic XRD Fingerprints of Different Soap Phases

Phases	d-Value (Å)
Beta	2.75
Omega	2.95
Delta	2.85, 3.55

TABLE 7.2
Effect of Soap Phases on Product Attributes

Attributes	Omega	Beta	Delta
Mush	Intermediate	High	Low
Use-up rate	Low	High	Medium
Lather	Inferior	Good	Intermediate
Appearance	Opaque	Translucent	Opaque

acid systems of common soap formulas. During soap manufacturing, the mass coming out of the dryer is predominantly in the form of omega phase. On working during the mixing, milling, and plodding stages, based on the moisture level and the processing temperature, omega phase is converted to delta or beta phase. Depending on the composition and electrolyte level, a certain minimum level of moisture is required to form delta phase in the formulation [34,37,38]. The general properties of these phases are illustrated in Table 7.2.

Sometimes it is very difficult to predict soap properties based on the phases formed, because these properties can also be highly influenced by the crystal size, and their orientation and interaction with each other [31]. It is very difficult to control the processing conditions to form a desired phase.

7.4 SKIN-CLEANSING PRODUCTS

Based on the product forms and rheological properties, the existing body-cleansing products can be categorized into four forms, namely, solid bar cleansers, liquid cleansers, cleansing creams, and implements. Different types of products associated with these four forms are shown in Table 7.3.

7.4.1 Cleansing Bar Products

Soap is the most widely used cleansing product in the world. Chemically it is the salt of fatty acids, derived from oils and fats. The reaction of alkali with triglyceride, referred to as the *saponification process* gives one mole of glycerin and three moles of soap. In another process, oils and fats can be converted to glycerin and fatty acids by splitting triglycerides. After removing glycerin, the fatty acids can be converted to soap by direct neutralization, using alkali (Figure 7.1).

In bar soap formulations, the product attributes are highly affected by the types and ratios of different oils and fats. A detailed description of the quality of oils and fats used for soaps has been given by Shirhatti et al. [39].

7.4.1.1 General Bar Ingredients

George and Serkadowski [40] have described the physical properties of bar soaps and the use of different functional additives in various traditional and synthetic soap bases.

TABLE 7.3
The Three Forms of Body-Cleansing Products

Cleansing products

Cleansing bar	Cleansing liquids	Cleansing creams	Implements
Normal soaps	Body wash	Facial creams	Wipes
Filled low-TFM soaps	Shower gel	Facial lotions	Pillows
Transparent soaps	Hand wash		Scrubs/mechanical devices
Superfatted soaps	Antibacterial liquid soaps		
Syndet bars			

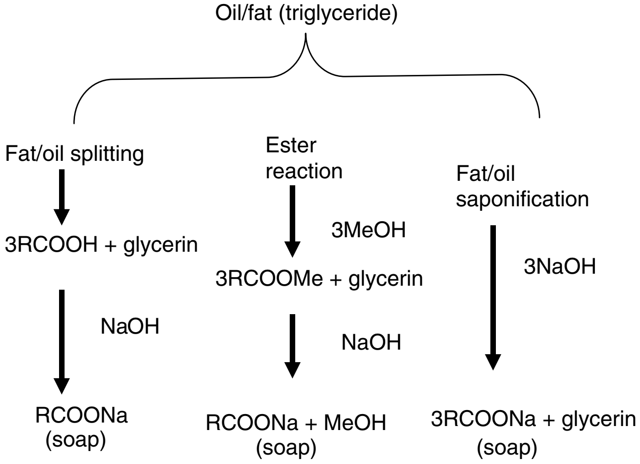

FIGURE 7.1 Chemical reaction during soap-making process. (From Abbas, S.H., Goldberg, J.W., and Michael, M., *Dermatol. Ther.*, 17(Suppl. 1), 35–42, 2004. With permission.)

A summary of the general ingredients of solid cleansing products, based on their functional properties, is as follows:

1. *Lathering agents.* Lather plays a very important role in skin-cleansing products. In normal soaps, the lathering component is sodium and potassium salts of fatty acids. The higher-chain saturated fatty acid components, such as stearate and palmitate derived from tallow or hydrogenated oils, act as structurants for bar soap formulations, whereas lower-chain fatty acid components derived from coconut and palm kernel oils contribute to the lathering properties of the product. Salts of unsaturated fatty acids, such as oleate and linoleate derived from vegetable oils and tallow, help in the dissolution process of lower-chain fatty acid salts by reducing the KP of the mixture.

SCI, sulfosuccinates, AGES, and CMGS are the main synthetic detergents used in combars and syndet bars. The KP of surfactants plays a very important role in the selection of a particular surfactant for the product. Vel Beauty Bar, launched by Colgate in 1948, was the first syndet bar, followed by Zest and Dove in 1952 and 1955, respectively, by P&G and Lever Brothers.

2. *Opacifiers*. In the absence of opacifiers, products look translucent and it is difficult to control the color of the bar. Titanium dioxide is the main opacifier used in bar soaps. Owing to an exceptionally high refractive index, fine particles of titanium dioxide strongly scatter light, and effectively opacify the product [41].
3. *Brighteners*. Tinopal CBS, supplied by Ciba-Geigy, is one of the most commonly used brighteners for soap, and at a level of 0.02–0.05%, it gives very good brightness to the product. Optical brightening agents absorb the invisible ultraviolet portion of the light and convert this energy into the longer-wavelength visible portion of light [42]. This helps in the perception of the brightness of the product.
4. *Perfume*. Perfume is one of the most important and the most expensive ingredients in body-cleansing products. Besides providing a pleasant smell, it is widely used to convey product concept and helps in positioning of the product in the marketplace. Depending on the need, perfume level can vary from 0 to 2.0% in the product. Normally, the fragrance components are hydrophobic and can have physical interaction with surfactants and other components. As a result of this interaction, they have the capability of influencing physical properties of the products such as hardness, lather, and rate of wear. The perfumers have to take great care in developing a fragrance to avoid any negative interaction with the product.
5. *Color*. The popular colors used in soap bars are green, white, and pink [7]. Based on positioning of the product in the market, soaps with some other colors such as blue, yellow, and orange are also available. Most of the time, these types of colors are used for products that have hygienic properties and are positioned as antibacterial or medicinal products. Consumer likings and the positioning of the product are major factors in the selection of color. One has to be very careful of the stability of color in the product. If the color is not stable to light, pH, or temperature, it can create major issues in the marketplace.
6. *Preservatives*. To preserve the unsaturated component from oxidation, antioxidants such as butylated hydroxytoluene (BHT) and *tert*-butylhydroquinone (TBHQ) are added at a 50–100 ppm level in the formulations [43]. Chelating agents such as ethylenediaminetetraacetic acid (EDTA) and hydroxyethylidene diphosphonic acid (EHDP) are added in the formulation to complex the metal ions, which when free, accelerate the oxidation process of unsaturated components [44].
7. *Specialty ingredients*. Minor ingredients such as vitamin E acetate, fatty alcohol, fatty esters, fatty acids, antibacterial agents, glycerin, mineral oils, and lanolin are used in the products for added benefits [45–47]. Based on the need and the product concept, these benefits can be emotional or functional. With increasing awareness about the benefits, consumers are now slowly moving to the products with real as opposed to emotive benefits.

7.4.1.2 Bar Soap Formulation

A product created by boiling oil with plant ashes was the stepping-stone for the use and manufacturing process of cleansing products [2]. The major developments in soap formulations have taken place just during the past two centuries. Parallel advancement of formulation and process technologies combined with the accelerated interest in the fundamental studies of soaps and synthetic surfactants during the last half of the twentieth century are the main drivers of the emergence of new product concepts and applications. A general cleansing bar formulation is given in Table 7.4.

TABLE 7.4
Bar Soap Formulation

Functional Ingredients	Examples	Level (%)
Surfactants	Natural soaps and surfactants	20–90
Structurants	C_{16}–C_{18} fatty matters (acids, esters, alcohol, triglycerides, soaps, etc.)	10–50
Water		4–35
Opacifier	Titanium dioxide	0–2
Brighteners	Tinopal	0–0.1
Chelating agents	EDTA, EHDP	0.02–0.1
Rheology modifiers	Common salt	0.3–2.0
Cosurfactants	Betaine, AOS, SLS, etc.	0–5
Antibacterial agents	Tricloson, TCC, etc.	0.1–1.0
Moisturizers, skin-benefit components	Fatty acids, esters, emollients, hydrocarbons, lanolin, herbal extracts, etc.	0–40
Perfume		0–2
Antioxidants	BHT, TBHQ, etc.	0.005–0.01
Colorants	Colors for aesthetics	0.001–0.1

The most important raw material for cleansing formulations is surfactant. Owing to cost constraints and demand for cost-effective surfactants, the surfactant industries have not devoted sufficient resources to the development of new molecules. This has negatively affected the developmental process for new technologies in the soaps and cosmetic industries. The soaps and cosmetic industries have done an excellent job of utilizing the limited available surfactants to bring new and mild products with different functional benefits. It appears that for further growth of the soap and cosmetic industries, there is a strong need for the development of new cost-effective and mild surfactants.

In general, the selection of surfactants for different cleansing products depends on their key physical properties that are directly or indirectly related to the KP of the surfactants. All the surfactants above their KP are soluble in water and form liquid phases (isotropic solution and liquid crystalline phases), but below their KP they have poor solubility and are crystallized in the form of solid phases. Surfactants with a high KP can be used for solid cleansing products, whereas low KP surfactants are suitable for liquid products. For proper process and product attributes, it is necessary that the average KP of the primary surfactant used for solid bar products is above room temperature. The KP of a mixture of tallow and coco soap is in the range of 40–45°C, and is ideal for processing bar soaps. Common surfactants used in different types of liquid and solid products are given in Table 7.5.

Cationic and nonionic surfactants are not very common for bar products. However, they can be used at very low levels for certain functional properties. Anionic and amphoteric surfactants are more cost-effective, and have balanced mildness with excellent lathering properties. Some of the nonionic surfactants such as sugar esters and amphoacetates have very good mildness and lathering properties, but are not cost-effective. These surfactants are suitable mainly for liquid products. In combination with fatty acid soaps, SCI, sulfosuccinate, AGES, AOS, and CMGS have been used as surfactants in syndet and combars.

Solid bar products can be categorized as normal soaps, superfatted soaps, transparent soaps, combars, and syndet cleansing bars. These products have different formulations and manufacturing processes. Formulations, physical properties, and the process of making these types of products have been described in different publications [48–59]. A general schematic diagram for the split of various ingredients in different types of bar products is given in Figure 7.2. Unique

TABLE 7.5
Common Surfactants Used for Cleansing Products

Product

Cleansing bar

Soap (C_8–C_{18} fatty acid salts)	40–80%
Sodium cocoyl isethionate	40–60%
Sulfosuccinate	10–20%
Sodium lauryl ether sulfate	2–5%
Cocoamidopropyl betaine	2–5%
Alfa olefin sulfonate	2–20%

Cleansing liquid

Sodium lauryl ether sulfate	5–15%
Ammonium lauryl ether sulfate	5–10%
Cocoamidopropyl betaine	2–10%
Alfa olefin sulfonate	5–15%
Cocomono ethanol amide	2–5%
Amphoacetates	2–10%
Glucose esters	2–10%
Soaps (C_8–C_{12} fatty acid salts) Soaps (C_{18} unsaturated fatty acid salts)	10–20%

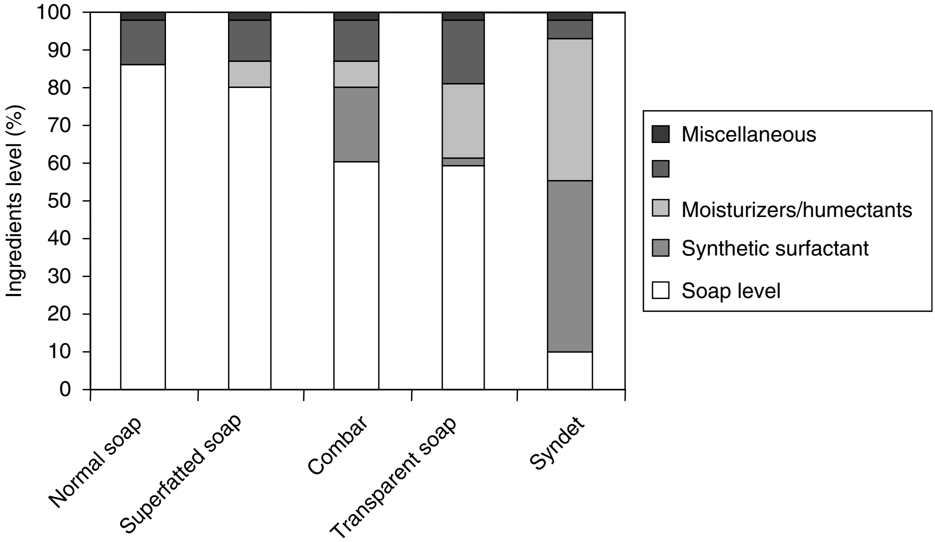

FIGURE 7.2 Relative levels of functional ingredients in different types of cleansing bars. (From Abbas, S.H., Goldberg, J.W., and Michael, M., *Dermatol. Ther.*, 17 (Suppl. 1), 35–42, 2004. With permission.)

physical properties and better mildness to skin tissues make SCI a unique surfactant suitable for syndet bars.

A substantial amount of clinical studies have been conducted to establish the irritancy potential of different types of bar products. Soap-based formulations have a high level of irritancy potential, and by damaging the skin barrier structure, they can produce a dry feel and skin irritation, particularly for delicate skin in cold weather. Different methods have been used to establish and quantify the difference in irritancy potential of these products [60–65]. The Forearm Controlled Application Test (FCAT) is the most commonly used method to quantify relative mildness of

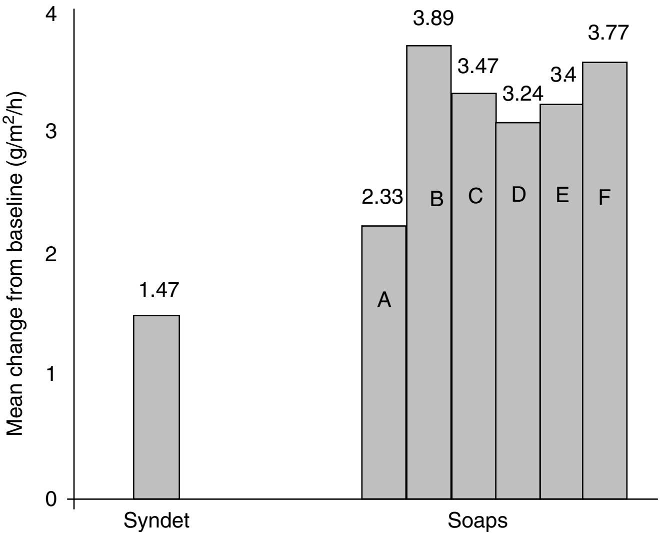

FIGURE 7.3 Relative transepidermal water loss by FCAT with syndet and soap formulation (5-day repeat wash clinical test). (From Abbas, S.H., Goldberg, J.W., and Michael, M., *Dermatol. Ther.*, 17(Suppl. 1), 35–42, 2004. With permission.)

body-cleansing products [66]. Transepidermal water loss (TEWL) measured by the FCAT method for different bar products clearly demonstrates the superiority of the syndet bar over other toilet soaps (Figure 7.3).

TEWL is the measure of barrier integrity of skin. Frosch and Kligman [60] developed soap chamber test and used it to evaluate several commercial bar products available on the market to check their relative mildness.

7.4.2 Body-Cleansing Liquids

Essential components in liquid products are surfactants, skin conditioning and moisturizing components (emollients), specialty ingredients for required benefits, fragrance, color, and preservatives. An extensive list of these ingredients and their suppliers are published in the book *Cosmetic Additives* by E.W. Flick [67]. The physicochemical properties, chemical structures, applications, and safety of these ingredients are well summarized by A.L.L. Hunting in *Encyclopedia of Shampoo Ingredients* [68].

In the beginning of past century, liquid soaps were prepared by dissolving potassium salt of coco fatty acids in glycerin [69]. With time, glycerin has been replaced by water, and fatty acid salts have been replaced by milder, more soluble, synthetic surfactants in liquid products.

Starting with a user-friendly, quick-lathering liquid cleansing product during the third quarter of the twentieth century, now the liquid cleansers have become very sophisticated, with excellent skin health and cosmetic benefits. The consumer acceptance of liquid products is due to changing consumer needs, product performance, good hygiene, and ease of use. At the same time, it gives a high level of flexibility for formulators to develop liquid products. Most of the skin-benefiting components being liquid, they can easily be incorporated in liquid formulations using suitable rheology modifiers. Most of the mild surfactants have a low KP, and are suitable only for liquid products.

Formulators have adopted the criteria of fulfilling consumer needs by modifying the sensory profile of the product using required benefit components.

Soap-based liquid formulations provide voluminous, creamy lather and a squeaky-clean feel. However, they lead to drying and irritation of the skin in cold weather. Soap-based liquids are formulated by using potassium salts of lower-chain fatty acids that are derived from coconut oil.

Owing to the high alkalinity of soaps, the pH of these formulations is high and hence they are harsh to skin. Furthermore, high pH limits the choice of skin care agents and fragrances that can be incorporated in these products.

Formulations of liquid cleansers sold in most parts of the world, especially in Europe and North America, are based on synthetic surfactants. These surfactants are much milder to skin than the soap-based surfactants and can be used in products to give skin-neutral pH. Products formulated with these surfactants are much more compatible with a wide variety of skin care agents and fragrances.

Liquid cleansing products can have a single anionic surfactant, or it can be formulated with a mixture of different anionic and amphoteric surfactants. The most common surfactant used in liquid products is alkyl ether sulfate, with different levels of ethoxylation having different solubilizing cations, such as sodium, potassium, and ammonium. Surfactants such as acyl isethionates, sarcosinates, sulfosuccinates, alkyl phosphates, sugar esters, sulphoacetates, lauramide diethanolamine (DEA), cocamide DEA, amine oxides, and amphoacetates are used as cosurfactants to improve mildness and lathering properties of the product. Cocoamidopropyl betaine is one of the most widely used amphoteric surfactants in liquid products. Amphoteric surfactants not only help in improving lathering properties, but also provide mildness to the product. In combination with other surfactants, AOS is another cost-effective surfactant being used in developing markets for liquid cleansers [70].

Liquid products can be formulated as transparent isotropic solution, or they can be opacified by using suitable opacifiers, which are typically high-molecular weight fatty matters such as esters, fatty alcohols, or waxes. The main opacifying ingredients used in liquid products are ethylene glycol distearate and ethylene glycol monostearate. These opacifiers can provide a very attractive shimmering and pearly effect by proper control of their crystallization. Some of the specialty liquid products are being formulated by using mica-coated titanium dioxide.

Owing to oxidative and rheological instabilities, it was difficult to formulate liquid cleansers using a high level of liquid benefit components. During the past two decades, with improved understanding of formulation technology, it is now possible to use as high as 25–30% liquid emollients in formulations [71].

To have proper product aesthetics and controlled application dosage, it is essential for the liquid products to have suitable rheological properties. There is a very common practice in industries to adjust the viscosity of liquid cleansers by using cogel, which is formed by polymers or rod micelles developed by interaction of surfactants with common salts. With proper selection of surfactants and other ingredients, it is now possible to structure liquids by using suspended particulates or by forming liquid crystalline phases [72,73]. Because of a high level of water activity and low pH, it is necessary to use proper antimicrobial preservatives in the formulation.

7.4.3 CLEANSING CREAMS

These are mainly facial-cleansing products. Use of facial-cleansing products is not a new phenomenon, having been used by women for centuries. It was very common in Indian culture to apply an aqueous paste of turmeric and mustard seed powder to the face and body of brides before marriage to make the skin soft and clean. There are different herbal and natural paste formulations from Ayurvedic and Unani medicines, which are used to improve the facial or body skin texture. Before the development of synthetic surfactants, soap was the main product used as facial cleanser. Owing to superior mildness, products based on synthetic surfactants are preferred over soap.

During the past few decades, facial cleansers are getting special attention from consumers. These cleansing products are available in different forms and can be formulated as a solid dispersion in liquid medium or as an emulsion in the form of high-viscosity creams or low-viscosity lotions with a high level of emollients and moisturizing components. The requirements of facial cleansers are different from those of other body-cleansing products. A high level of attention is given to the skin benefits in comparison to the foaming properties of these products. In general, these products have a low level of surfactants and a high level of ingredients such as glycerin, propylene glycol, fatty acids, hydrocarbons, and triglycerides. Besides these common ingredients, there can be ingredients for specific needs of the facial skin, such as antiwrinkle, antiacne, antiaging, and sun screen agents.

Mildness and moisturization of facial cleansers are assessed in the same way as bar and liquid cleansers, by controlled-application wash testing. The maximization allergy testing (patch) method is another very common test used for relative mildness studies of cleansing creams and lotions.

7.4.4 IMPLEMENTS

Implements in the form of pumice stones or hard porous objects have been known for a long time as effective tools for the removal of dirt and dead skin. There are plenty of body, face, hand, and foot scrubs in the market that are based on pumice, loofa, and other scrubbing materials. Loofa, a natural vegetable cleansing sponge, has been extensively used as exfoliating material for dead skin cells. Products based on these hard substrates are harsh to skin. Industries during the past few decades have come up with inventive ideas for implements with a mild effect on skin using products such as wipes, pillows, and mechanical devices.

Traditionally, liquid, gel, or bar soaps have been used in personal care as the main cleansing products. However, with increase in hygiene and skin care awareness, along with the busy and fast pace of life, different types of implements and tools are being accepted by consumers. Many of these implements are based on the use of textile or fabric articles. Wipes without surfactants, along with suitable solvents, benefit components, and perfumes, have been used as facial refreshing cleansers. Additionally, these products are very convenient to carry and use. Dry wipes and pillows with mild surfactants, moisturizing components, and other performance ingredients provide effective facial and body-cleansing benefits [74–76]. These are disposable, single-use articles, and are convenient because they are more hygienic in comparison to sponges, washcloths, or other cleansing implements intended for multiple use. Single-use facial or hand wash products have been developed using water-soluble starch with the required level of surfactants and other ingredients. These products are sold as dry sheets that dissolve during use without leaving any residue.

7.5 PROCESSING OF BODY-CLEANSING PRODUCTS

There is a large difference in the manufacturing process of solid and liquid products. Luis Spitz [1,5] has described in detail the manufacturing process and equipment for making solid bar cleansers.

Equipment for manufacturing transparent soap can have very different specifications where translucency is achieved by applying the right amount of mechanical work on the soap mass within a narrow range of temperature. The actual technology used to achieve translucency varies from manufacturer to manufacturer, but the principle of shearing/mechanical work that leads to phase transformation and translucency remains similar. Besides having extruded transparent soaps with

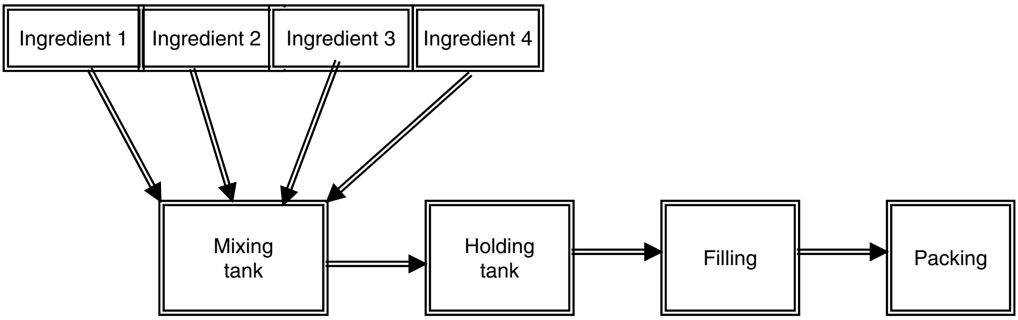

FIGURE 7.4 Process for body-cleansing liquids and creams.

high fatty matter, the majority of the transparent soaps available in the market are made by melt cast using a high level of solubilizers. Formulations for the products made by the two types of processes are significantly different.

The process for manufacturing liquid products is relatively simple and cost-effective. This is one of the reasons why, to avoid large capital investments, soap manufacturers are moving toward copackers for manufacturing bar products. The differences in the manufacturing processes between bar and liquid cleansers can be shown in schematic flow diagrams (Figures 7.4 and 7.5). These clearly show the complexity of the soap-manufacturing process. The soap-making process requires

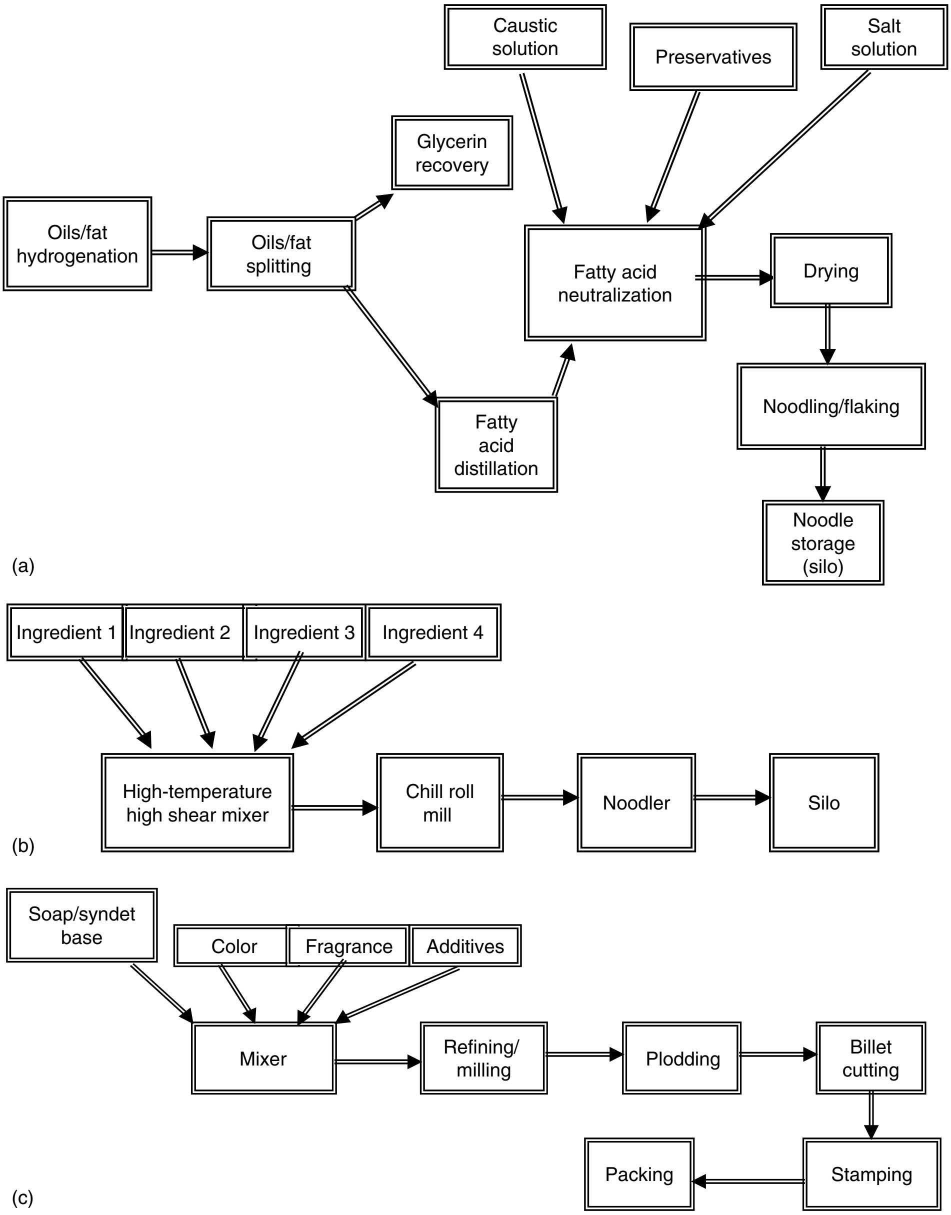

FIGURE 7.5 (a) Process for making soap base, (b) process for making syndet base, and (c) process for finishing line of soap/syndet bars.

huge base-making and finishing lines, with very high capital investment, whereas the process for liquid cleansers is relatively very simple and cost-effective.

The process conditions, and sometimes the equipment needed for making various types of bar products, are very different, leading to a huge investment to achieve formulation flexibility. Normal fatty acid soap making requires fat splitting, distillation, neutralization, drying, base mixing, milling/plodding, cutting, stamping, and packing equipment. The base-making process of soap is replaced by high-temperature, high-shear mixers attached to a chill roll mill for syndet bar products. Processing conditions for the finishing line can be significantly different for normal soaps, transparent soaps, syndet, and combars. In short, it is easier to have a high level of process flexibility with minimum capital investment for manufacturing of liquid cleansers, whereas soap-making equipment has limited flexibility for processing different types of formulations.

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8 Applications of Surfactants in Shampoos

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CONTENTS

8.1 INTRODUCTION

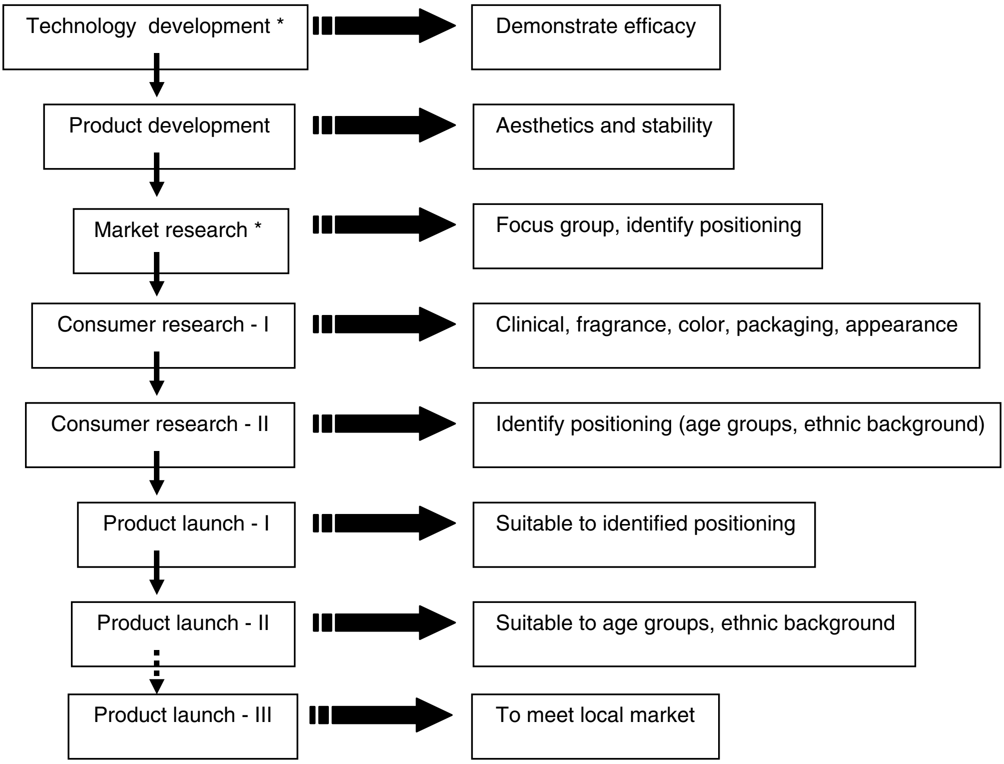
Effectiveness of hair care products is dependent on several factors such as combination of surfactants, conditioners, polymers, fragrances, and active ingredients present in the formulations and their compatibility with each other. Hair care products also include coloring agents, preservatives, and actives (antidandruff agents) for both instantaneous and sustained benefits. The range of hair care products available in stores today is quite large and ever increasing. Numerous brands and various shampoo formulations, encompassing wide-ranging claimed benefits, are found not only in department stores but also in favorite salons, and drug and discount stores. Researchers have proposed a model and measurement methodology to aid managers in designing new frequently purchased consumer products.[1] The model is structured as a trial and repeat process that produces an estimate of long-run share for a new brand. Physical and psychological product attributes are linked to the trial and repeat probabilities through multidimensional scaling procedures. Generally, cost, fragrance, cleaning efficiency, and foam are the factors most people consider when purchasing a product. It seems that every year the competition is becoming more challenging, and major manufacturers constantly produce a new range of products featuring new and improved benefit claims with more complex formulations, and some manufacturers provide appeal by including costly and exotic ingredients.[2,3] Though some of these changes and benefits are consumer perceivable, many of them are not.

In addition to types of ingredients present in the hair care products, the compatibility among them and therefore the overall stability are the key to the success of a product. Physical appearances such as phase separation, precipitation, haziness, and discoloration are definitely known to deter consumer's interest from buying the product.[4,5] Factors such as unstable emulsions, cosmetic changes due to climatic changes (specifically temperature) from the point of manufacturing, transportation, and storage to the point of selling, and photooxidation of the ingredients are some parameters that could be responsible for the lack of aesthetic appeal to consumers. In some cases, specifically products with emulsions, although the technology is novel[6] and products could deliver consumer perceivable benefits, extremely slow interactions lead to precipitation of active and other ingredients, which might not impress consumers. That means the parameters overlooked in the research laboratories become visible while the product is sitting on the shelf for longer durations or while sitting on the counter or sink in the bathroom. Care should be taken to understand the parameters that affect overall stability, so that such unstable products are not exposed to consumers. Sometimes, specific instructions such as *shake before use*,[7,8] and *store in a dark place*[9] provided on the label might negatively impact the consumer decision to buy such products. To overcome all the stability issues, manufacturers are spending enormous amounts of money and resources. There are mushrooms of organizations and contract laboratories that have the ability to test tens and even hundreds of products at a time in establishing acceptable stability over longer durations for these products. From the manufacturer's viewpoint, it is worth spending to ensure stability rather than facing the situation of product recall where cost, product trustworthiness, and company credibility will be at stake.

Other appealing factors, not limited to hair care products, such as product color, packaging, labeling, and display in the store are also identified as contributing factors for the consumers to buy specific product(s) among the several choices available in the store.[10] Although product performance and efficacy are important, brand-loyal consumers look for the products of their choice, and the majority of consumers can be swayed simply by the appealing aesthetics of other products. Major manufactures spend millions of dollars in consumer research and market research to obtain answers to questions and concerns related to concepts and products to identify key points that influence consumer decision.[11] Manufacturers also establish a connection over a period of time by consistently providing a specific color and product attribute for targeted benefits[12] coupled with packaging for positioning and differentiating against competition.[13] Such spending also includes over-and-above charges or incentives paid to the store for product display in a highly visible area, at times in multiple locations in a single store. Consumers of different age groups and ethnic background are influenced differently in making decisions to buy products.[14] The nonbrand-loyal consumers could be easily swayed, and visually and sensually appealing products could also influence and sway brand-loyal consumers to try novel and innovative products. Marketing research has revealed that celebrities of dissimilar age groups and diverse ethnic background influence different groups of consumers.[15,16] To identify the key points that impress consumers of dissimilar age groups and diverse ethnic background in every possible way and influence *buying* decision, major manufacturers spend heavily both on consumer research and market research as well as on advertisement. In addition to product aesthetics, fragrances perceived at the point-of-purchase also play a pivotal role[17] in making the decision to *buy* in the store. Additionally, fragrance perceived during product use and after use is a key factor in the decision of repurchase. It is also to be noted that unlike previous generations, families of today end up having more than one kind of hair care product in each household. Consequently, there are opportunities wherein fragrance perceived in the bathroom after use by other household member(s) could also influence and impress consumers. Identifying the right fragrance(s) that appeal to the majority of consumers is a tough job, and care must also be taken to resolve challenges associated with changing fragrance on compatibility issues in the finished product without affecting performance benefits (foaming, cleaning, overall efficacy, etc.) and aesthetic attributes that are consumer perceivable. It is therefore not surprising that major manufacturers spend huge amounts of money on research[11] to identify the right sensory cues using fragrances.

The efficacy of products such as ease of combing, feel and shine, luster, manageability, and flyaway are undoubtedly important aspects from the technological end of the formulations.[18] Most often, it is the delivery of efficacy as claimed on the package and advertisement that makes consumers loyal to specific brands.[19] Manufacturers therefore try to establish a strong brand name and create a position in the consumer's mind in the marketplace.[13] Generally, by providing line extensions in terms of different fragrances, colors, and aesthetics (clear and opaque) that are suitable to families[20] with different age groups, and diverse ethnic communities,[21] manufacturers try not only to retain brand-loyal consumers, but also to lure nonloyal consumers. There are also observations in today's consumer market that some manufacturers use the same fragrance and color in different line extensions. Generally, both color and fragrance go together, showing point-of-difference between the main product and a line extension product. Various events between product development and developing potential line extensions suitable to meet consumers from all walks of life are shown in the chart below (Figure 8.1).

It therefore becomes imperative that technology development demonstrating efficacy is the primary step in introducing a strong brand, followed by developing line extensions with different colors and fragrances. Multinational companies that are advantageously positioned plan strategically to



** Several instances these are interchangeable*

FIGURE 8.1 Chart showing sequence of events from technology development to product launch.

take the technology developed and by modifying slightly, develop products suitable to market globally with the theme, color, and fragrance suitable to each region or country.

Since hair care products (shampoos, conditioners and 2-in-1 shampoo-conditioners) are of the wash-off types, in addition to fragrance perceived during product use, clean feel and foaming experience are considered to be the most important parameters that influence the perception of a product by consumers.[18] Additionally, parameters such as feel, consistency, and spreadability of the product influence the perception of benefit and performance of the product.

In this review, the applications of surfactants in shampoos are discussed using representative samples and examples from published work and data from new studies in the patent literature. Applications of surfactant combinations for improvement in cosmetic stability or efficacy based on compatibility issues are also discussed. Functional benefits of surfactants from the viewpoint of wetting, cleaning, and foaming are discussed with some examples. Also included in this review is the role of surfactants in providing stable and aesthetically appealing products that contain emulsions and agents that are nondetergent soluble actives. The role of detergents in the solubilization of actives such as antibacterial and antidandruff agents and fragrances is also discussed.

8.2 GENERAL FEATURES OF SURFACTANTS

There are several Surfactant Science Series volumes published by Marcel Dekker that specifically illustrate properties and applications of different types and classes of surfactants and their mixtures.[22–29] There are also innumerable references available in the literature that provide general features of surfactants, their properties, and applications in cosmetics,[30,31] including shampoo formulas. Since this review is focused on the applications of surfactants in shampoo formulas, only a brief description on their general features and broad classification are given here. Although surfactants are mainly responsible for cleaning, they are also responsible for providing a battery of benefits that will be discussed separately in this review. Surfactants can be soap, a synthetic detergent, or a combination. Detergents (cleaning or washing products) commonly found in households, contain synthetic, organic surface-active agents called surfactants that are derived from petroleum and vegetable oil product precursors. Surfactant molecules have the ability to be both hydrophobic and hydrophilic, and this is achieved by having both functional groups attached to each other. Surfactants are effective cleansing agents because they have the common property of lowering the surface tension of water for easier wetting. This helps the lipophilic part to stick to oil and dirt, whereas the hydrophilic part allows the oil and dirt to be washed away. Surfactants also help in the solubilization of hydrophobic ingredients, emulsification, and building viscosity, and are responsible for lather generated during applications. The choice of a cleaning agent is based on its compatibility within the product and lathering characteristics, feel on the skin, and how easily it rinses off during use conditions. Depending on the nature of the hydrophilic (ionic) functional group, surfactants can be classified into the following four groups:

- *Anionic* surfactants—carry a negative charge when ionized
- *Nonionic* surfactants—have no charge on the molecule
- *Amphoteric* surfactants—carry both positive and negative charges when ionized
- *Cationic* surfactants—carry a positive charge when ionized

8.2.1 ANIONIC SURFACTANTS

Shampoo compositions generally comprise one or more anionic cleansing surfactants, which are cosmetically acceptable and suitable for topical application to hair. Anionic surfactants (negatively charged molecules) provide a lot of lather and detergency in the shampoo. The most commonly used anionic surfactants are sodium lauryl ether sulfate (SLES), ammonium lauryl sulfate (ALS), and ammonium lauryl ether sulfate (ALES), and sodium lauryl sulfate is also occasionally used.

Extensive use of C_{12} anionic surfactants is attributed to the physical properties (solubility, wetting, cleaning, etc.) of the alkyl sulfate, in the form of sodium or ammonium salts, which provides desirable attributes of a shampoo.[32] In fact, by controlling the degree of ethoxylation of the alcohol prior to sulfation and utilizing appropriate neutralizing bases, a wide variety of shampoos representing many consumer needs can be formulated.[33]

Anionic surfactants used in shampoo formulations include individual or combinations of alkyl sulfates, alkyl ether sulfates, alkaryl sulfonates, alkanoyl isethionates, alkyl succinates, alkyl sulfosuccinates, *N*-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulfonates, especially their sodium, magnesium, ammonium, and mono-, di-, and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulfates, alkyl ether phosphates, and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide (EO) or propylene oxide (PO) units per molecule. The total amount of anionic cleansing surfactant in shampoo compositions is generally in the range of 8–20% by weight based on total weight of the composition.[33]

Shampoo formulations generally contain sodium and combinations of ammonium lauryl/laureth sulfates to overcome and improve any issues of solubility and precipitation. By using the combinations, increased steric hindrance and lower ionization level of the ammonium group help prevent precipitation in the presence of conditioning agents in a 2-in-1-type formulation and precipitation of surfactants due to the common ion effect if many sodium ions are otherwise present in the formulation.[34]

In general, the skin absorption of anionic surfactants is reported to be very low.[35] Although there are many choices of anionic surfactants available, their use is restricted because of potential limitations, solubility, cost, and compatibility issues in some cases. For example, sodium lauryl sulfate is not highly soluble at room temperature, but solubility increases with increasing temperature.[33] ALS and triethanolamine salts not are only soluble at higher levels, but also eliminate any precipitation issues occurring in hard water.[36] Additionally, by using sequestering agents such as citric acid or salts of ethylenediaminetetraacetic acid (EDTA), solubility in hard water could be mitigated.[18]

Sulfosuccinates that contain both a carboxylate and a sulfonate group are used in combination with alkyl and alkyl ether sulfates to produce shampoos that exhibit reduced eye and skin irritations, conditioning benefit, and improved lathering.[37–40] However, traditionally sulfosuccinates are known to exhibit good foaming properties,[41] but not as good as alkyl and alkyl ether sulfates. Additionally, there are concerns about compromised foaming properties, especially in the presence of lipids.[41] *N*-acyl-methyl taurates known for their low irritancy and claimed to protect hair against cuticle damage,[42] find limited applications in shampoo because of poor solubility and foaming properties, especially in hard water.[43] *N*-acyl sarcosinates exhibit good detergency and foaming performance in soft and moderately hard water and are compatible with a wide range of cationic surfactants.[44] However, detergency and foaming performance decrease in the presence of hard water and at low pH.[45] Acyl isethionates are very mild to scalp and hair, and produce a creamy lather both in soft and hard water[46]; however, limited solubility at room temperature and ease of hydrolysis at low and high pHs limit their use in shampoo formulations. Anionic linear alkyl benzene sulfonates are widely used in laundry detergents, but have very limited use in shampoos.[33] Linear alkylbenzene sulfonates are relatively more irritating to the skin than the corresponding branched alkylbenzene sulfonates. The detergent forms light and airy foam, but leaves a dry feel on the hair.[47] Because of these mixed benefits, linear alkylbenzene sulfonates have only been used marginally as a secondary surfactant and that too in very few expensive formulas.[48]

In recent years, protein-based surfactants are finding some applications in personal care products due to their abilities to interact with skin and hair.[49] *N*-acyl polypeptide condensates (protein derivatives) belong to the mild surfactant category with foaming performance inferior to alkyl sulfates, but they produce creamy lather[50,51] and leave hair feeling soft and manageable. However, it appears that extra attention and care should be taken to ensure preservation of these protein derivatives due to compatibility with other anionic surfactants when present in shampoo formulations.

Polyalkoxylated ether glycolates (organic salts) yield a creamy lather and also provide some conditioning properties to the hair. Monoglyceryl sulfates exhibit properties similar to lauryl sulfates and do not offer any other additional advantages. Fatty glyceryl ether sulfonates exhibit mildness and superior flash foam and have the additional benefit of hydrolytic stability.[52]

8.2.2 NONIONIC SURFACTANTS

Nonionic surfactants (uncharged molecules) are often not included in shampoos as primary surfactants due to low foaming capacity, less stable foam,[53] and harshness of their detergency.[36] The poor quality of the foam has been attributed to the large surface area per molecule and the lack of any charge on the surface films.[54] The detergency power, however, is as good as, and in many cases may be even better than, those of anionic surfactants that are used in shampoo formulations.[55,56] They can strip the hair and lead to scalp irritation due to excessive defatting. However, they are mostly included as secondary surfactants, since many of them are very mild and act as foam stabilizers and thickeners, and may be more necessary in formulations for greasy hair types. Some examples include laureth-3 or 4, cocamide diethanol amides (DEA) or coco glucosides. The use level is in the range of ~1 to 8% total weight of the shampoo composition. Examples of other nonionic surfactants that can be used in shampoo compositions include condensation products of aliphatic (C_8–C_{18}) primary or secondary, linear or branched chain alcohols or phenols with alkylene oxides, usually EO, generally having from 6 to 30 EO groups.

Amine oxides, in their nonionic forms (depending on the pH), are best known for their functionality as secondary surfactants, since they enhance foam characteristics and provide thick, creamy, and more stable lather at moderate acidic pHs.[57] They are also mild to skin and hair,[58] and since the N–O bond is highly polarized and exists in a protonated form at low pHs,[18] they may provide some conditioning and antistatic benefits.

Polyethoxylated surfactants represent the largest group of nonionics and include the ethoxylated derivatives of alkylphenols, fatty alcohols, fatty esters, and diglycerides. They exhibit excellent detersive power and cleansing properties, but because of poor foaming, their use has been restricted to solubilizing of shampoo fragrances and other oleophilic additives.[59,60] Both polysorbate-20 and PEG-80 sorbitan laurate (ethoxylated sorbitan monoester of lauric acid), when used as cosurfactants, reduce eye irritation of anionic surfactants without affecting foaming attributes.[36] For these reasons these nonionic surfactants find wide applications in baby shampoos.

Another class of nonionic surfactants included in shampoo compositions is alkyl polyglycosides (APGs). Typically, an APG is one that comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. APGs are defined by the formula $RO–(G)_n$. APGs are commercially available and have different trade names, as several manufacturers are making them. Some examples include Oramix NS10 marketed by Seppic, and Plantaren 1200 and Plantaren 2000 marketed by Henkel. Other sugar-derived nonionic surfactants that can be included in shampoo compositions are C_{10}–C_{18} *N*-alkyl (C_1–C_6) polyhydroxy fatty acid amides, such as the C_{12}–C_{19} *N*-methyl glucamides.[61,62]

8.2.3 AMPHOTERIC SURFACTANTS

Amphoteric surfactants are finding increased use in shampoo formulations because of several benefits that are consumer perceivable. Amphoteric surfactants in general are known to be poor foamers when used alone,[31] and milder than traditional primary surfactants. Their use therefore is in many baby shampoos that often consist entirely of them, and also they are often incorporated in formulations to mitigate the effects of harsher primary surfactants.[63,64] Amphoteric surfactants also maintain their compatibility with all anionic, cationic, and nonionic surfactants over a wide pH range.[52] Combination of these surfactants with other anionic surfactants provides decreased irritancy of a formulation while increasing the active content level of the product and therefore the quality of the lather produced.

Amphoteric surfactants are divided into two groups based on their response to pH. One class of compounds that contain carboxylated imidazoles and *N*-alkyl betaines are zwitterionic at pHs at, and above, their isoelectric points and cationic at lower pHs.[18] Sulfobetaines and phosphobetaines, on the other hand, exhibit zwitterionic characteristics as the anionic portion is dissociated at all pHs. Although the former are the major ingredients in many baby shampoos or those products that provide mildness, they also function as foam and viscosity enhancers when utilized as secondary surfactants, having good water solubility over a wide pH range.[30,52]

The major applications of this class of surfactants are shampoos and body washes, and they are often found in conditioning shampoos due to their compatibility with quaternary compounds.[65,66] The shampoo compositions mostly include from 1 to ~8% by weight of amphoterics to help impart aesthetic, physical, or cleansing properties to the composition. Amphoterics also find broad applications in hard surface cleaner formulations and homecare applications, due to their excellent detergency and pH stability.

By far the most widely developed and used amphoteric surfactant is cocoamidopropyl betaine, and occasionally cocoamido betaine.[52] It is to be recognized that betaines can exist only in nonionic and cationic states, depending on pH. True amphoteric surfactants contain dual functional groups in the same molecule that, depending on pH, allows them to exist in anionic, nonionic, and cationic states. Other examples of amphoteric surfactants summarized in the literature[18] include cocoamidopropyl hydroxy sultaine, sodium cocoamphoacetate, and sodium lauroamphoacetate. The amphoteric and zwitterionic surfactants that are less frequently used include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulfobetaines (sultaines), alkyl glycinates, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates, alkyl amidopropyl hydroxysultaines, acyl taurates, and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms.

Amphoteric glycinates and propionates exhibit characteristic mildness to the skin and eyes. However, at low pHs they become positively charged, and this could result in increased irritation.[18] Commonly used ones include cocoamphocarboxyglycinate, cocoamphocarboxypropionate, cocoamphoglycinate, and cocoamphopropionate. Alkyl-substituted amino acids (amino and imino propionates) can impart a light conditioning effect to the hair.[33] Some examples include sodium lauraminopropionate and sodium lauriminopropionate. Since the foam characteristics of this class of amphoterics are best in alkaline pHs, the conditioning benefits may be compromised if the pH of the system is not optimized.[33]

8.2.4 CATIONIC SURFACTANTS

Cationic surfactants (positively charged molecules) have the ability to adsorb strongly to negatively charged surfaces and are not efficiently removed during washing and rinsing. In the case of hair surface, the cationic surfactants strongly bind to the hair's negatively charged surface and are very difficult to remove by washing. This results in leaving the hair surface more hydrophobic, due to surfactant tails extending out.[64] The attraction between the hydrophobic tails and oily dirt makes it harder to remove such soil from hair and increases the tendency for resoiling.[33] This electrostatic interaction accounts for low surface friction and reduction of electrostatic charge, making both hair combing and manageability easier. This charge neutralization also manifests itself as increased hair body and luster, possibly due to alignment of surfactant molecules on the hair surface. Dialkyl ammonium salts are used in rinse formulations for shampoo containing alkyl sulfates and alkyl ether sulfates as the main ingredients.[67]

There are some novel cationic surfactants that are presently being produced. Quaternary ammonium salts made from long-chain Guerbet alcohol form lamellae liquid crystals even in cold water that are readily adsorbed onto hair.[68] Amido guanidine cationic surfactants with methylene groups as spacers between amide and guanidine groups[69] are used for providing conditioning benefits and also have excellent moisturizing properties even under low-humidity conditions.

Quaternary ammonium compounds have been used in combination with amine oxides and alkyl betaines, and with hydrocarbons and vegetable oil to impart luster and combability.[70,71] Shampoo formulations with polyglycol amine derivatives in combination with betaines have been reported to provide excellent conditioning properties.[72] Polyglycerolated cationics were reported to provide ideal characteristics of a surfactant for shampoo, that is, good foaming, cleaning, and conditioning properties with low irritation.[73–75]

In contrast to the benefits discussed above, cationic surfactants are generally incompatible with anionic surfactants, the primary surfactants used in shampoo formulations, which further limits their applications. The cleaning and foaming properties of cationic surfactants are considerably inferior to those of the anionics, and another major downside is the weighing-down effect on hair.[52] Because of these limitations and compatibility issues, cationic surfactants are not used very often in shampoo formulations, and applications are limited mainly to conditioning, lubricating, and anti-static benefits in conditioners.

Cationic surfactants are used more widely and effectively as antibacterial agents[76,77] than other kinds of surfactants, and are generally employed as disinfectants and antiseptic agents. They are also used in germicide and sanitized products, but seldom as cleansers *per se*. The cationic agents are therefore better exploited in the form of conditioning and antistatic agents.[78] For example, as identified previously, cationic surfactants bind to hair surfaces thereby reducing the static charge, resulting in greater ease of combing and improved manageability. Cationic agents generally employed in hair care products include quaternary surfactants, and cationic polymers are the most widely used species for this purpose. As expected, the complexation of the anionic surfactant that provides the primary shampoo function of removing soil from hair with the cationic surfactant poses difficult challenges to formulation chemists. Although cationic surfactants are compatible with both nonionic and amphoteric surfactants, they are generally not employed as secondary surfactants because of their irritancy. Some anionic surfactants, such as carboxylated nonionics, show some tolerance toward cationic surfactants, and these combinations may have potential application in future years.

8.3 MOST FREQUENTLY USED SURFACTANTS IN SHAMPOO FORMULATIONS

There are several types of surfactants that are being used in shampoos, soaps, and skin cleansers. Selection of surfactant is generally based on cleansing efficiency, foaming ability, compatibility, cost, mildness, and safety. Generally, anionic surfactants are the primary surfactants, whereas nonionics and amphoterics serve as secondary surfactants to help improve product attributes including those that are consumer perceivable. Table 8.1 lists most of the surfactants that are commercially used in today's shampoo, conditioning, and 2-in-1 formulations. Some of the more frequently used surfactants are discussed in the following sections, along with the rationale for their selection and some benefits they deliver to the product(s).

8.3.1 SODIUM LAURYL ETHER SULFATE

Sodium laureth sulfate or SLES (CAS no. 3088-31-1) is one of the most commonly used anionic surfactants in shampoo formulations. An aqueous concentrated SLES is derived from fatty alcohols, ethoxylated to an average of 2 moles (2EO), and sulfated via a continuous SO_3 process. There are a large number of synonyms for SLES available in the literature. Those most frequently cited are provided in Table 8.2 along with structural formula of the surfactant.

SLES and its ammonium counterparts, ALS and ALES, are the primary surfactants currently used in most formulations and have dominated the shampoo market.[80] Solubility in water and at increased temperature, and compatibility with hard water make SLES an automatic choice for formulators around the world. This anionic surfactant is attractive for its foaming ability and as a cleansing agent that is suited for both high-viscosity and low-pH products. Additionally, it thickens

TABLE 8.1
List of Surfactants Used in Commercial Hair Care Products

Sodium Lauryl Ether Sulfate	Alcohol Sulfates	Alcohol Ether Sulfates
ALES	Alkanolamides	Ethoxylated alcohols
	Alkyl sulfonates	Ethoxylated fatty acids
ALS	Amine oxides	Lauryl sulfates
Sodium lauryl sulfate	Amphoteric surfactants	Mono and diglycerides
Tea laurel sulfate	Anionic surfactants	Nonionic surfactants
Olefin sulfate	Cocoamidopropyl betaine	Phosphate esters
Decyl glucoside	Betaine derivatives	Quaternary surfactants
Dodecylbenzene sulfonic acid	Amido guanidines	Sorbitan derivatives
Glycerol esters hydrotropes	Disulfonates	
Ethoxylated alkyl phenols		

Source: Barker, G., *Surfactants in Cosmetics*, Surfactant Science Series Vol 16, Marcel Dekker, New York, 1985, pp. 251–292; Rieger, M.M. (Ed.), *Surfactants in Cosmetics*, Surfactant Science Series, Vol 16, Marcel Dekker, New York, 1985; Rieger, M.M. (Ed.), *Surfactants in Cosmetics*, Surfactant Science Series, Vol 68, Marcel Dekker, New York, 1997; Reich, C. and Chupa, J., *Hair Shampoos, Harry's Cosmeticology*, Chemical Publishing Company, New York, 2000; Wilkinson, J.B. and Moore, R.J. (Eds), Shampoos. *Harry's Cosmeticology*, Chemical Publishing Company, New York, 1982, pp. 427–469.

TABLE 8.2
Frequently Cited Synonyms for Sodium Lauryl Ether Sulfate

Commonly used synonyms	Sodium POE(2) lauryl ether sulfate; Sodium diethylene glycol lauryl ether sulfate; 2-(2-dodecyloxyethoxy)ethyl sodium sulfate; Diethylene glycol monododecyl ether sodium sulfate; Diethylene glycol monododecyl ether sulfate sodium salt; Diethylene glycol monolauryl ether sulfate sodium salt; Lauristyl diglycol ether sulfate sodium salt; Lauryl diethylene glycol ether sulfonate sodium; Sodium diethylene glycol dodecyl ether sulfate; Sodium dioxyethylenedodecyl ether sulfate; Sodium lauryl alcohol diglycol ether sulfate; Sodium lauryloxyethoxyethyl sulfate; Sodium laurylglycolether sulfate
Structural formula	$CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_2OSO_3Na$

Source: http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=18335#Synonyms.

when sodium chloride is added to the formula and produces high levels of lather. SLES-2EO is also shown to remove sebum more effectively than ALS,[81] and is generally very stable compared to other lauryl sulfates. In addition to all these benefits, SLES is very inexpensive, which is an important factor for its commercial use.

Alkyl ether sulfates (AESs) are better tolerated on the skin, and it is generally reported that the irritancy is lower than that of alkyl sulfates (e.g., sodium lauryl sulfate). Alkyl chain lengths of 12 carbon atoms are found to be more irritating to the skin compared to other chain lengths.[82,83] Addition of increasing levels of ethoxylation is shown to decrease the skin-irritating properties of alkyl ether sulfates.[84,85] Concentrated AES solution is generally considered a strong irritating ingredient; dilute solutions of 10% are shown to provide moderate to strong effects. However, only mild or slight irritation is reported when a nonspecified AES was applied at 1% to the skin.[86]

Effects of ethoxylation of alkyl ether sulfates on solubility, surface properties, and detergency have been discussed in the literature.[87] Ethoxylation of alkyl surfactants not only increases solubility, but also helps reduce the tendency for precipitation and decrease in foam volume in the presence of calcium and magnesium ions from hard water.

From shampoo formulas, consumers have a great preference for thick, creamy, and luxurious lather cleaning. Ether sulfates, especially SLES, fail to produce light and airy foam that collapses rapidly.[33] For this reason, shampoo with SLES as the primary surfactant is formulated with a secondary surfactant to improve the foaming and viscosity attributes.[88,89] Foam boosters interact with primary surfactants, thereby affecting the micellar properties in formulas and decreasing the electrostatic repulsion between the molecules in the foam films. In certain cases, the mixed surfactant systems could also have a beneficial impact by solubilizing fragrance and other detergent-soluble hydrophobic molecules present in the formula. Further, the structure and nature of surfactants could also influence the viscosity of the formula at a given concentration.[18] The ordered structures of linear molecules over branched ones, coupled with the reduction of opposing intermicellar force due to the addition of salts and alkanolamides, helps the buildup of viscosity.[90] Here again, it is evident that manufacturers and formulators constantly strive to identify ingredients and conditions that help generate thick and viscous lather from shampoo formulas to have a better cosmetic appeal among consumers.

8.3.2 AMMONIUM LAURYL ETHER SULFATE

ALES (CA 32612-48-9) is one of the other commonly used anionic surfactants in shampoo formulations. It is derived from fatty alcohols, ethoxylated to an average of 3 moles. A few commonly used synonyms used for ALES available in the literature are listed in Table 8.3 along with the structural formula.

Although solution properties appear to be very similar between sodium and ALESs, from the viewpoint of applications in hair care formulas, there are differences purely attributed to the change in the ionic (head) groups. For example, as discussed earlier, the increased steric hindrance and lower ionization level of the ammonium group helps prevent precipitation in the presence of conditioning agents. Addition of ALES to SLES can also prevent precipitation of surfactants due to the common ion effect if a lot of sodium ions (added to increase viscosity) are otherwise present in the formulation. It is easier to thicken hair care formulations containing ALS/ALES solutions alone by adding salt than those containing SLES,[18] producing high levels of foam. For these reasons, ALES is suited for high-viscosity products and low-pH liquid cleaning products, and is therefore used as a foaming and cleansing agent for shampoos and cleansers. Also as discussed previously, the foaming ability is relatively unaffected in hard water, is useful in many cleansing applications. As observed for SLES, in the case of ALES also, the degree of ethoxylation reduces the irritation potential, and since higher degree brings the lowest irritation, ALES with 3-mole EO is more commonly used.

TABLE 8.3
Frequently Cited Synonyms for Ammonium Lauryl Ether Sulfate

Commonly used synonyms	Ammonium diethylene glycol lauryl ether sulfate Ammonium laureth sulfate Alpha-sulfo-omega-(dodecyloxy)-poly(oxy-1,2-ethanediyl) ammonium salt
Structural formula	$CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_3OSO_3NH_4$

Source: Household Products Database, http://householdproducts.nlm.nih.gov/cgi-bin/household/brands?tbl=chem&id=131.

TABLE 8.4
Frequently Cited Synonyms for Ammonium Lauryl Sulfate

Commonly used synonyms	Ammonium lauryl sulfate Ammonium dodecyl sulfate Dodecyl ammonium sulfate Sulfuric acid, monododecyl ester, ammonium salt Dodecyl ester of sulfuric acid, ammonium salt Dodecyl sulfate ammonium salt
Structural formula	$CH_3–(CH_2)_{10}–CH_2OSO_3NH_4$

Source: Household Products Database, http://householdproducts.nlm.nih.gov/cgi-bin/household/brands?tbl=chem&id=5.

Also, ALES surfactant with 3-mole EO generates slightly wetter foam than either 1-mole EO or 2-mole EO sulfate. Shampoos and bubble baths formulated with ALES-3EO and Calamide alkanolamides generate profuse foam, and the product has been characterized to be mild and gentle, and perform well under use conditions.

8.3.3 AMMONIUM LAURYL SULFATE

ALS (CAS no. 2235-54-3), a member of the alkyl sulfate group, is also a widely used anionic surfactant in shampoo formulas. The most frequently cited synonyms for ALS in the literature are provided in Table 8.4, along with the structural formula.

ALS is generally used as a surface-active agent for its wetting, foaming, dispersing, and emulsifying properties. ALS is a preferred surfactant in the United States, whereas sodium and ALSs with an average of 2–3 moles of EOs are preferred in many other countries.[93] Because of lathering quality and good stability, in addition to being more stable than the sodium salt with regard to hydrolysis at acidic pH (upto 4.5),[52] ALS is an ideal surfactant for use in acidic shampoos and other personal care formulations such as hand soaps and bath products. It can also be used in many detergent applications. The surfactant also displays excellent foaming and cleansing properties, and is compatible with hard water. Although a very effective cleanser, this surfactant, especially at high concentrations, has a tendency to irritate the scalp and remove lipid constituents of the hair cuticle. By adding cosurfactants, shampoos with ALS are less irritating to the scalp and reduce damage to the hair. ALS also has excellent viscosity response when formulated correctly with alkanolamides and amphoterics, and generates large quantities of foam. Since ALS is a high-foaming surfactant, it is very often used together with ALES.

From the viewpoint of safety and toxicity, both sodium and ALSs are considered as cosmetic detergents that exert emulsifying action, thereby removing oil and soil from the hair and the skin. The review panel that evaluated the safety and toxicity wishes to point out that although these two ingredients produce eye or skin irritation for some users of cosmetic formulations, the effects are similar to those produced by other detergents.[94] The review panel concluded that both sodium and ALESs are safe ingredients for use in cosmetic products.

8.3.4 COCOAMIDOPROPYL BETAINE

Cocoamidopropyl betaine (CAS No: 61789-40-0) is an amphoteric surfactant that contains both cationic amine and anionic carboxylate groups in one molecule. Some of the synonyms used for cocoamidopropyl betaine in the literature and trade industry are given in Table 8.5, along with the structural formula.

These quaternary carboxylates are derived from trimethylglycine, where one methyl group is replaced with a $C_{12–18}$ fatty alkyl radical. Cocoamidopropyl betaine could exist only in its zwitterionic and cationic forms at high pHs.[18] Consequently, the solution properties and performance of this

TABLE 8.5
Some of the Frequently Cited Synonyms for Cocoamidopropyl Betaine

Commonly used synonyms	Cocoyl amide propyldimethyl glycine *N*-(3-Cocoamidopropyl)-*N,N*-dimethyl-*N*-carboxymethylammonium hydroxide, inner salt *N*-(3-cocoamidopropyl)-*N,N*-dimethyl-*N*-carboxymethyl betaine 1-Propanaminium, 3-amino-*N*-(carboxymethyl)-*N,N*-dimethyl-, *N*-coco acyl derivative, hydroxides, inner salts *N*-Cocamidopropyl-*N,N*-dimethylglycine, hydroxide, inner salt
Structural formula	$RCONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$

Source: Household Products Database, http://www.householdproducts.nlm.nih.gov/cgi-bin/household/brands?tbl=chem&id=118.

molecule in a shampoo formula is pH dependent and affects foaming attributes, solubility, and intermicellar properties.

Cocoamidopropyl betaine functions as a foam and viscosity enhancer, and therefore is mostly utilized as a cosurfactant in shampoo formula.[96] Its application as a viscosity enhancer is due to the formation of complexes with surfactant molecules that maximize intermolecular attractive forces in the surface film, thereby increasing viscosity, a phenomenon very similar to that reported for alkanol amides.[90] This surfactant is reported to be extensively used to formulate baby shampoos that are mild, and as a mollifying agent in more irritating anionic compositions. Since free amine content is generally regarded as the major contributor to irritation, combinations with betaines are formulated to provide mildness and optimize performance. When the carboxylic group of cocoamidopropyl betaine is replaced with a sulfonic group, the modified molecule is milder to skin and eyes. Betaines can only form hydrophobic bonds with proteins in the skin, which is considered one of the possible explanations for the low protein denaturation potential compared to the ion-binding properties of other surfactants that contribute to such denaturation.

The high solubility of surfactants in water is very important in the preparation of cosmetic products, and their compatibility as cosurfactants makes them even more useful. In this regard, cocoamidopropyl betaine is generally compatible with most anionic, nonionic, and cationic surfactants that are used in the shampoo industry. In combination with anionic surfactants, a positive synergistic effect with regard to skin compatibility is often found. For example, although alkyl and alkyl ether sulfates produce abundant lather, these are often loose, and the foam quality decreases significantly in the presence of sebum.[97] When cocoamidopropyl betaine is used as a secondary surfactant, a significant boost in foam characteristics is observed.[98] Additionally, decreased erythema was observed for a combination of 20% C_{12} alkyl sulfates and 10% cocoamidopropyl betaine compared to a 20% solution of C_{12} alkyl sulfate (sodium lauryl sulfate) alone, 1 h after the removal of patches.[99] The combination of cocoamidopropyl betaine and C_{12} alkyl sulfate is also shown to reduce swelling of the skin, and this is attributed to interactions between the amphoteric and alkyl sulfates that produce less swelling and result in milder skin reactions.[100]

8.3.5 ALKYL POLYGLUCOSIDES

Alkyl polyglucosides (CAS No. 110615-47-9) are a relatively new class of nonionic surfactants, fully based on renewable vegetable resources and easily biodegradable, and hence they are finding increasing applications in many industrial fields, including the personal care industry. There is a book published by VCH publishers discussing their history, production, physicochemical properties, toxicity, and applications in various industries.[101] There is also a Surfactant Science Series

TABLE 8.6
Some of the Frequently Cited Synonyms for Alkyl Polyglucosides

Commonly used synonyms	Fatty alcohol C_{12}–C_{14} alkylglycoside
	Glucopon 600
	APG + so 600 glycoside
Structural formula	$H–(C_6H_{10})_n–O\text{-}C_XH_{2X+1}$ ($X = 10-12$)

Source: http://www.kemcare.net/unitrader/shop/product/779; Dow Surfactants, http://www.dow.com/surfactants/products/alkyl_po.htm.

volume published by Marcel Dekker that discusses synthesis, structure and nomenclature, properties (both chemical and surfactant), toxicology, and dermatology, as well as applications of alkyl polyglucosides.[102] The synonyms used for alkyl polyglucoside in the literature and trade industry are given in Table 8.6, along with the structural formula.

Alkyl polyglucosides are divided into several groups based on carbon chain length. For example, Dewolf Chemical[105] has several fractions with variable carbon chain length including C_{10}–C_{16}, C_8–C_{10}, C_8–C_{16}, and C_9–C_{11}. Alkyl polyglucosides are considered to have the advantage of combining properties from both conventional nonionic surfactants and anionic surfactants.[106] Current utilization of this promising class of surfactants, in the personal care industry and other industries, does not appear to be up to its full potential. $C_{8/14}$ polyglucosides appear to be the largest in commercial products used for cleansing formulations that are characterized by their skin and hair care products. It is reported that $C_{12/14}$ alkyl polyglucosides act as an emulsifier in specific formulations and particularly in microemulsions.

Alkyl polyglucosides offer many attractive properties, such as being toxicologically safe, readily biodegradable,[107] compatible with other surfactants, and able to provide beneficial cost/performance, and therefore have drawn the attention of scientists across industries and in cross-category applications. In addition to compatibility, these surfactants exhibit synergistic benefits in combination with traditional surfactants.[106] They are considered as specialty surfactants suitable for mild, nonionic products with good detergency and wetting properties. While combinations of betaines and quaternary active substances provide conditioning effects in the presence of anionic surfactants, in combination with cationic surfactants alkyl polyglucosides significantly reduce wet compatibility with or without the addition of betaines.[108] Addition of sodium caproyl lactylate to betaines or alkyl polyglucosides is shown to significantly boost foam and increase foam stability.[109] Alkyl polyglucosides are used in household, industrial, and institution detergent formulations, where high-stable foam is required, or high caustic concentrations are necessary. Alkyl polyglucoside with the trade name TRITON CG-110 is used in personal care applications, shampoos, bar soaps, skin creams, and lotions.

8.3.6 POLYOXYETHYLENE BLOCK COPOLYMERS

Polyoxyethylene block copolymers are nonionic surfactants composed of a hydrophobic alkyl chain (fatty alcohol), which is combined with a number of ethoxylate or EO units through an ether linkage. Alcohol alkoxylates (AA) normally contain both EO and PO (PO) in their hydrophilic moiety, whereas butylene oxide (BO) is less frequently used. The abbreviation AA designates nonionic surfactants with a hydrophilic part containing PO (or BO), frequently in combination with EO. Alcohol ethoxylates are used in many types of consumer and industrial products, for example, laundry detergents, all-purpose cleaning agents, dishwashing agents, emulsifiers, and wetting agents. Alcohol alkoxylates are used as weakly foaming and foam-mitigating surfactants in household cleaning agents, dishwashing agents, and cleaning agents designed for the food industry.[110]

Other applications of alcohol alkoxylates also include textile lubricants, agricultural chemicals, rinse aid formulations, and personal care products. Polyoxyethylene block copolymers exhibit properties similar to surfactants, such as the presence of micelles in aqueous solutions, micelle structure, and association number, and are therefore termed polymeric surfactants. These diverse subsets of nonionic surfactants are unique and offer several advantages in manufacturing, and they could be designed for specific uses and applications. A complete Surfactant Science Series volume dedicated to the chemistry, physicochemical properties, applications, and toxicity was published in 1996.[111] Because of these beneficial attributes, alcohol ethoxylates and alcohol alkoxylates are the most important nonionic surfactants in terms of volume usage in consumer products.

The foaming characteristics of Pluronic surfactants, polyoxyethylene block copolymers, are poor compared to other types of surfactants. Their usage is related to the ability to reduce ocular irritation without affecting the foaming characteristics of the shampoo formula.[112] There are very limited studies that were devoted to test the applications of polyoxyethylene block copolymers in shampoos. Pluronic F-68 (a difunctional EO/PO block copolymer terminating in primary hydroxyl groups) was tested in an antidandruff shampoo, where the active agent was a metal salt of pyridinethione,[113] and was claimed to be more efficacious than the traditional shampoos containing anionic surfactants. The patent also states that when a pyridinethione metal salt in platelet form, with a specified particle size, is combined with any of a group of specific synergizers (polyethylene glycols, polypropylene glycols, polyoxamer block polymers, polyethylene oxide fatty glycerides, polyethylenimines, polyethoxylated polyethylenimines, polyethylene oxide carbohydrates, ethoxylated nonylphenols, ethoxylated alcohols, and mixtures thereof) in a shampoo matrix, an improvement in antidandruff efficacy is realized. Such compositions are stable, safe, and effective in cleaning the hair while treating the scalp for dandruff.

Benzoic acid esters of a polyalkoxylated block are claimed to show enhanced capabilities as foam boosters, emollients, conditioners, clarifiers, solubilizers, and carriers (diluents).[114] The studies with several Pluronics were also shown to provide better conditioning effect as well as controlling flyaway. These esters could also solubilize both oxybenzone (protection as a sunscreen agent) and benzocaine (an anesthetic agent), like other surfactants. Such enhanced characteristics of the esters make them ideally suited for use in hair care compositions. Another patent discusses an invention relating to shampoos useful for cleaning and conditioning hair as well as the coats of animals.[115] Also discussed in the invention are medicated shampoos that include the use of medicaments such as topical therapeutic agents, antimicrobial agents, and the like. The composition involves the use of a fatty acid monoester of a polyhydroxy alcohol, such as monolaurin, as an antimicrobial agent. In addition to the killing of bacteria and fungi, the shampoo composition was also shown to have activity against *Pityrosporum ovale*, the fungus that is associated with dandruff.

Generally, swelling mechanism of the skin in the presence of a surfactant involves a combination of ionic binding of the hydrophilic group as well as hydrophobic interactions of the alkyl chain with the substrate. Nonionic surfactants do not carry any net charge, and hence can bind to proteins only through hydrophobic bonds. For this reason, generally proteins are not denatured by nonionic surfactants, and proteins with poor solubility are not solubilized by nonionic surfactants. For example, studies with C_{12} alkyl ethoxylate containing 23 EO groups showed that the nonionic surfactant caused little or no swelling of the stratum corneum of guinea pig skin.[116]

8.3.7 SILICONE SURFACTANTS

Silicone polymers that exhibit good surface modification effects are classified as surfactants. Silicone polymers are derived from a polysiloxane backbone, wherein the reactive sites could be attached to this backbone. The reactive sites are typically reacted to organic moieties forming organomodified siloxane polymers.[117] Such derivatives form a different class of surfactants providing unique properties and applications that differ significantly from traditional surfactants. A Surfactant Science Series volume was published in 1999 that covers a wide spectrum of topics related to the chemistry, physicochemical properties, and applications of silicone surfactants.[118] Two review papers covering the emulsification properties and application in personal care products provide an excellent source for enhanced understanding of silicone surfactants.[119,120] Several patents discuss the use of silicone surfactants for developing transparent shampoo and for providing conditioning benefits.[121,122]

Applications of silicone surfactants and polymers in personal care in general, and shampoos in particular, are wide ranging. Silicone surfactants and polymers mostly provide conditioning benefits, and other benefits include shine, static control, and high lubricity, manifested, for example, by easy combing.[123] While dimethicones and common silicones depress lather, some silicone surfactants act as foam builders, exhibiting better compatibility with anionic surfactants, and therefore are considered as suitable additives for enhancing foam. Also, some of these silicone polymeric surfactants are exceptionally mild to skin and eyes. Although silicone polymers are quite substantive to hair substrates, many of them have better rinse-off and do not show any disadvantage of building up on the hair.[124–126] Although cost seems to be an inhibitory issue for the use of silicone surfactants, their synergy with dimethicone copolyols allow their use in small amounts. Such low level of copolyols is adequate for providing significant improvement in conditioning benefits and tactile properties; thus, they remain attractive for hair care applications.[119]

The functional benefits of silicone polymers depend on the nature of organic modification, which could be ionic or nonionic. The phenyl modifications, generally labeled as phenyl trimethicones, are known to provide good glossy appearance. Hydroxyterminated polysiloxanes, generally labeled as dimethiconols, are extensively used in conditioning products.[119] They contribute to emollience, gloss and shine, and also provide good combing characteristics. Dimethicone copolyols that consist of EO or PO groups or their mixtures (EO/PO) provide unique surfactant properties to the formulations. Whereas the hydrophobic dimethylsiloxane moiety provides characteristic alignment at the surface of the aqueous medium, the EO moiety, which is hydrophilic, attaches itself to the aqueous medium. Because of the presence of polyether groups, the dimethicone polyols exhibit cloud points, which could drop when the PO content is increased. The influence in the variation of EO/PO ratio is so profound that any influence due to small variations in the dimethylsiloxane content is not meaningful.[127]

The majority of silicone polymers/surfactants that are used in today's personal care industry are of the nonionic types. Since the derivatives of polysiloxanes could be ionic completely or partially, the properties exhibited by such compounds are different and therefore provide an entirely new range of properties and benefits. For example, cationic and amphoteric functional groups, because of increased substantivity on the hair surfaces and durable surface covering, provide antistatic effects. Polymethoxylsiloxanes modified with cationic and amphoteric groups provide both antistatic benefit as well as high gliding ability, which are very useful in personal care applications.[119]

Although silicone betaines and silicone quaternaries are excellent hair additives, the latter are more substantive than the former and compatible with anionic surfactants.[128] Both silicone betaines and silicone quaternaries give better rinse and avoid buildup issues on hair substrate, thereby providing good antistatic benefits. Furthermore, silicone betaines and silicone quaternaries give hair a silky silicone gloss and feel, which pure organic polymeric quaternary compounds fail to provide. Unlike their organic counterparts, silicone quaternary compounds are also good conditioning agents and are mild to skin and eyes. In spite of being very costly, the synergism between diquaternary silicone compounds with copolyols allows very low usage for providing efficacy. Additionally, these formulations end up being mild and can be formulated over a wide pH range.[119]

Another type of ionic silicone surfactant is the silicone phosphobetaines, which exhibit positive or negative charge depending on the pH of the formulation.[129] This further expands the diverse applications of silicone surfactants. This not only provides wider options in making formulations, but also delivers multiple benefits. Like other alkyl betaines, phosphobetaines are also high-foaming agents, nonirritating and mild, and deposit on hair substantially, bringing out enhanced benefits due to surface modifications.[119]

Among ionic silicones, anionic siloxanes (corresponding sulfates and thiosulfates) have not yet been commercially exploited. In limited investigations, the thiosulfate-modified siloxane was found to be an effective conditioner, and efficacy was perceived even when hair samples with damaged structures (due to bleaching) were employed.[119] The anionic thiosulfate groups, also known as Bunte salts, could bind electrostatically with the amino acid groups on the hair,[130] and therefore the hair surface becomes very smooth after treatment. Even differences in tactile properties of the hair surface were claimed to be evident in such cases, due to the incorporation of thiosulfate-modified siloxanes. Such differences could therefore simply manifest as shine and easily combable surface. Because of the polymeric nature of the anionic siloxanes, substantivity is significant when compared to traditional sulfates/thiosulfates. Such unusual properties make the ionic silicone surfactants suitable for treatment of damaged hair. Additionally, because of the strong electrokinetic interactions with hair, these surfactants also bring shine to the hair appearance. Shampoos and conditioners that deliver such benefits are well received in the ethnic markets.

8.4 FUNCTIONAL BENEFITS OF SURFACTANTS

Surfactants provide various benefits in shampoo formulations ranging from wetting of hair surfaces to cleaning, and might help the deposition of hydrophobic ingredients for sustained benefits. A shampoo or shampoo-conditioning formula becomes ideal if it can deliver the following benefits and meet safety and environmental requirements:

- Proper detergency of the hair without degreasing
- Ability to form thick and rich lather
- Easy rinse-off
- Provide good feel after wash
- No chemical damage to the hair
- No irritation to skin/eye/scalp

No one surfactant is able to successfully deliver all the above benefits from a shampoo formula. For these reasons, shampoo formulations and 2-in-1 shampoo conditioning formulations generally contain one primary surfactant and other surfactants, referred to as secondary surfactants. Table 8.7 lists some of the commercial hair care products available in the market and their corresponding surfactant systems. As evident from the table, these products contain dominantly anionic surfactants, and some examples contain secondary surfactants.

As discussed earlier, whereas the primary surfactant provides principal detergency and foaming benefits, the secondary surfactant provides improved detergency/cleaning, foaming, and mildness, and in some cases delivers actives more effectively. The following sections provide some specific examples demonstrating improved benefits achieved by the use of combinations of surfactants.

8.4.1 FOAMING

Among products in the personal category, shampoo formulas face the greatest challenge in the marketplace. In addition to cleaning, foaming characteristics are very important from the viewpoint of successful marketing. Foaming occurs when surfactant molecules gather around air instead of oil during mechanical action. Foam perception is quite different among consumers, manufacturers, and the scientific community. Although consumers show a preference for products that provide thick, luxurious, silky, and smooth foam, formulators feel that clouds of luxurious foamy lather only mean that too much shampoo was used. As discussed earlier, it is generally accepted that C_{12} sulfates provide voluminous foam and C_{14} sulfate richer and creamier foam.[33] It was also discussed earlier that foaming attributes for various surfactants and their combinations are different in the presence and absence of sebum and hard water. It is generally accepted that hydrophobic ingredients such

TABLE 8.7
Some Hair Care Formulas Showing the Surfactant Systems

Brand	Product	Surfactant Combination
Neutrogena	T-Gel Shampoo	Sodium lauryl ether sulfate Cocodiethanolamide Cocamidopropyl betaine
Suave Originals	Salon Formula Shampoo Daily	Ammonium lauryl sulfate
	Clarifying Shampoo	Ammonium laureth sulfate Cocamidopropyl betaine
	Balsam & Protein Shampoo	Ammonium lauryl sulfate
	Volumizing Shampoo	Ammonium laureth sulfate
Pantene Pro V	Shampoo + Conditioner 2-in-1	Ammonium laureth sulfate
	Shampoo Hydrating Curls	Ammonium lauryl sulfate
Pert Plus	Shampoo Plus Light Conditioner	Ammonium laureth sulfate
	Refreshing Shampoo plus Conditioner	Ammonium lauryl sulfate
Fructis	Kraftigendes Pelegeshampoo	Sodium lauryl ether sulfate Cocobetaine
Schwarzkopf	Schwarzkopf Professional Bonacure Men Phytobiogin Shampoo	Sodium lauryl ether sulfate Disodium cocoamphodiacetate
Sedal	Hidraloe	Sodium lauryl ether sulfate Cocoamidopropyl betaine
	Ceramids	Sodium lauryl ether sulfate SodiumC_{12}–C_{13} pareth sulfate
L'Oreal	Smooth Intense Shampoo	Sodium lauryl ether sulfate Cocobetaine
Sunsilk	Straighten-Up Shampoo	Sodium lauryl ether sulfate Cocoamidopropyl betaine
Dove	Moisturizing Cream Shampoo	Ammonium lauryl sulfate Ammonium laureth sulfate
Hairplus	Shampoo	Ammonium lauryl sulfate Sodium lauroamphoacetate
Herbal Essence	Natural Volume	Sodium lauryl ether sulfate
	Texturizing Shampoo	Sodium lauryl sulfate Cocoamidopropyl betaine
Caprice	Shampoo	Ammonium lauryl sulfate
	Botanicals	Ammonium laureth sulfate
	Shampoo/Conditioner	Sodium lauryl ether sulfate
Palmolive	Optims	Ammonium lauryl sulfate

as oils quickly destroy foam. A manifestation of this is that with the same product, depending on the frequency of use and the amount of soil, sebum, and other deposits present on the hair, foam perception could vary. Also, the amount of lather and foam generated by a shampoo does not affect its ability to clean hair. It is only necessary to lather hair once under normal washing conditions. Shampoo manufacturers know that consumers equate lots of foam and suds with the cleaning power of a shampoo. To ensure good foaming in the products, they either increase surfactant loading or often add foam-enhancing agents (cosurfactants) to their shampoos. A surfactant may have high foaming power, but that does not always mean it has high cleaning properties.

SLES is often used in high-foaming shampoos, dishwashing detergents, and many industrial cleaners. The physical properties of this surfactant enable its applications in liquid detergents, foaming agents, heavy-duty alkaline cleaners, emulsifiers, textile mill boiling bleach assistants, and neutral and alkaline scouring. In addition, foam stability in the presence of soap is much improved

TABLE 8.8
List of Agents with Their Contribution to Foaming Attributes

Agents	Attributes	References
Cetyl alcohol	Foam stabilizer	133
Stearyl alcohol	Foam stabilizer	132
Lauryl alcohol	Foam booster	54
Fatty acid diethanolamide	Foam booster	54
Amine oxides	Foam booster	54
Ethoxylated carboxylic acids	Foam booster	135
Ethoxylated alcohols	Foam booster	132
Ethoxylated polyhydric alcohols	Foam booster	132
Alkyl polyglucoside	Foam booster	102
Alkanol amides	Foam booster	99

over other anionic surfactants, therefore this surfactant is recommended for cleaning products containing soap as an ingredient.

The foaming potentials of alkyl sulfates and alkylether sulfates have been extensively studied using various foaming tests in the absence and presence of lipids.[131] By themselves, both alkyl and alkyl ether sulfates produce voluminous flash foam,[88,89] but the foam collapses (~60% reduction in volume over 3 min) due to rapid drainage, and thus fails to meet consumer expectation. Such collapse is even more severe in the presence of lipid soil. The presence of lauryl alcohol seems to reduce the rate of foam collapse, leading to innovative ways to improve foam attributes. One investigation with the deliberate addition of fatty alcohols to SLES confirmed these results.[132] Studies with sodium lauryl sulfate and SLES showed that fatty alcohols such as lauryl alcohol, myristyl alcohol, and cetyl alcohol reduce foam drainage of sodium lauryl sulfate, whereas cetyl and stearyl alcohols stabilized foam drainage.[133] These findings led toward exploring several ingredients that were not just compatible with sebum, but also improved foaming attributes. A list of agents with their contribution to foaming attributes (stabilizer and booster) is given in Table 8.8. While foam stabilization seems to depend on the additive's ability to increase viscosity, foam boosters affect both the bulk viscosity of shampoos and the foam liquid network.[134] Also, the foaming of straight chain alkyl ether sulfates seems optimal at about C_{12}–C_{14}, with an ethoxylation level of about 3. In general, parameters such as surface tension, Gibb's excess concentration, minimum area per surfactant molecule, theoretically considered important in foaming, do not seem to correlate with foam production.

Different methods are used to assess the nature of foam. Generally speaking, flash foam volume, maximum volume, size of the foam bubble, drainage efficiency and density are the most widely monitored parameters. Different methods employed in understanding foaming attributes have been published elsewhere.[136] How consumers perceive foam will continue to be a key objective in developing successful shampoo formulations and products that can be marketed locally and globally.

8.4.2 WETTING

Wetting in its most general sense is the displacement from a surface of one fluid by another. A wetting agent is a substance that increases the ability of water or an aqueous solution to displace air from a solid surface. In the case of shampoo and cleaning formulas, wetting is applied to the displacement of air from a solid surface by water or an aqueous solution. The degree of wetting attained is determined by free energy changes in the case of small surfaces, and in the case of large surfaces, wetting is determined by the kinetics rather than the thermodynamics of the wetting process.[54] Different types of wetting and their fundamentals are discussed elaborately in the prior reference.

The primary requirement for any agent or product to clean a surface is to wet it first. By lowering the surface tension of aqueous solutions, surfactants can act as wetting agents and enhance the spread of water over surfaces. Further, the surface properties of a solid surface determine the adsorption capacity of a surfactant. In the case of shampoo and other hair care wash-off type cleaning formulas, wetting of the hair is a necessary phenomenon (and not the adsorption of surfactant to hair), so that detergents from the shampoo have the opportunity to interact with deposits on hair that include hydrophobic soils, residues from hair care products, and any deposits from the environment, and lift them from the surface. These deposits also include secretions from the body, referred to as sebum, from the sebaceous glands. There are innumerable papers[81,135,137,138] discussing the specific composition of sebum, how it varies among individuals, its physical properties, and interactions with detergents present in shampoo, conditioners, and 2-in-1 formulas. Additionally, wetting of surfaces also helps in washing and removal of solid deposits and agents that are hydrophilic and water soluble.

Although wetting efficiency is dependent on the surface activity of a given surfactant and its concentration, and is lower at low surfactant concentrations, this is not an issue at the level of surfactants used in shampoo, usually in the range of 10–20%.[139] In principle, any surfactant that reduces the surface tension of water would be able to provide better wetting of the hair surface. However, the presence of hydrophobic substances on the hair surface could hinder the wetting process. Therefore, surface-active agents that have better cleaning efficacy are perceived to be better surfactants for use in hair care products.

8.4.3 CLEANING

The primary function of a shampoo formulation, in short-term use conditions, is cleaning ability, and consumer expectations on this attribute are very high. Deposits of sebum, soil, sweat, salt, dust (a combination of airborne contaminants, microorganisms, pollution, etc.), and the ingredients that are left from previous cleaning processes, styling, and other treatments need to be removed from a mass of flexible hair fibers under short-term use conditions. Although some deposits that are physically adsorbed on the hair could be washed away by water alone, a vast majority of deposits adhere and stick to the hair surfaces and continue to remain there even after washing. There are also instances wherein the agents used for cleaning could resoil the hair surfaces. Also, the sebaceous glands attached to the hair follicles provide a continuous supply of sebum to the surface of hair.[140] This sebum further gets spread within the hair mass and redistributes during brushing and combing.[137] Ingredients used for hair grooming that include waxes, hair spray, and residues from mousses are all hydrophobic in nature and cannot be removed by just water rinsing and washing.[141] Further, consumers oil their hair in a prewash treatment, as it is believed that oils nourish the hair and protect it during the washing process, and postwash oiling is also done for manageability and styling. The oiling habit is believed to be practiced widely by around 800 million people across Central Asia and the Middle East region. These processes leave hair soiled and sticky due to its contact with dust and other particulate matter from the environment and to a greater extent from sebum secreted by the scalp. The buildup of the sebum causes the hair to have a dirty feel and unattractive appearance, a situation requiring frequent hair shampooing. However, in the case of consumers who oil their hair, the problem arises from oil on the hair that may interfere with the action of the shampoo.

The mechanisms associated with cleaning and removal of soil from hair include emulsification and mesophase (liquid crystal) formation.[142] Emulsification involves breaking down an oily soil into smaller particles that can form a stable suspension. This requires a low interfacial tension between the oily soil and the bath medium, which may be accomplished by adsorption of surfactant from the shampoo onto the soil surface. Mechanical work can help in breaking up the soil. Amphiphilic compounds in soils, such as fatty alcohols or fatty acids, can greatly aid the emulsification process by interacting with surfactant from the shampoo to spontaneously emulsify the soil. Since shampooing is a short process, emulsified soils need to be resuspended for a shorter duration to accomplish cleaning. Phase diagrams for surfactants in aqueous systems exhibit large regions wherein mesophase (liquid crystals) is formed. Such regions can incorporate amphiphiles or oily soils containing amphiphiles, constituting another way of removing soil and cleaning hair.

Solubilization of hydrophobic and detergent-soluble ingredients from hair surfaces is an efficient way of cleaning, and for this reason detergency becomes an integral and mandatory part of shampooing. All the cleaning has to be achieved without either damaging hair or irritating scalp, and yet consumers expect the experience to be invigorating and rejuvenating. Mixed surfactant combinations (anionic and nonionic) could impact the intermicellar properties and their ability to solubilize hydrophobic agents; the use of other types of cosurfactants, in addition to improving product and foaming attributes of a formula, could also improve cleaning efficiency. This is achieved mainly due to the following two reasons:

1. *Adsorption of nonionic surfactant.* Adsorption of nonionic surfactants to various surfaces is very poor due to the absence of any electrostatic forces. However, lipids present on the hair and the skin surfaces provide sites for the adsorption of nonionic surfactants. Although nonionic surfactants combine only poorly with water-soluble proteins, they interact strongly with lipophilic proteins, e.g., membrane proteins.[143] Also, nonionic surfactants and some proteins do not show any interactions at all and if any, the interactions are weak in nature.[144] However, when introduced along with an anionic or a cationic surfactant, there appears to be significant adsorption of nonionic surfactants. Schwuger and Smolka[145] have shown that the adsorption of anionic surfactants onto hydrophobic surfaces decreased drastically by the addition of nonionic surfactants, whereas the adsorption of nonionic surfactant molecules are favored. Such adsorption of nonionic surfactants therefore results in improved wetting of the surface, facilitating cleaning by easier lift-off of hydrophobic soils from the surfaces.
2. *Critical micelle concentration for mixed surfactant system and micelle size.* For similar chain-length system, nonionic surfactants generally exhibit lower critical micelle concentration (CMC) than either cationic or anionic surfactants.[146] In a mixed system above the micellar concentrations, mixing can be anticipated to be nonideal, because nonionic surfactant molecules markedly decrease the ionic repulsion of the ionic components in the micelle, leading to hydrophobic interactions in the interior of the mixed micelles. In fact, there are some examples wherein the CMC of the mixed micelles is lower than that of the single surfactant, demonstrating nonideal mixing.[147–150] It is also known that some surfactant systems containing a ratio of 10:90 (nonionic and anionic) exhibit very low CMC (lower than the nonionic alone).[145] In the mixed micelle system containing substantial amount of nonionic surfactant, the repulsion among the anionic head groups is reduced by incorporating nonionic surfactant molecules, and the micelle size (aggregation number) is expected to be as high and close to that of the nonionic alone. Consequently, the amount of detergent-soluble hydrophobic soil that is solubilized in the mixed micelle would be higher than that of the anionic single micelle system. This results in a mixed surfactant system that could solubilize soils of a hydrophobic nature from hair and scalp more effectively and provide effective cleaning/removal of soils. Additionally, the improved cleaning process provides a cleansed surface for the delivery of some active agents that are required for conditioning, shine, softness, increased volume, easier manageability, and possible antidandruff benefits.

Surfactants, in general, are excellent cleaners and rinse easily from the hair with no issues of buildup. It is also expected that surfactants do not precipitate onto the hair or in hard water, nor should they leave a residual sticky or tacky feel on the hair surface. Whereas ALS is the principal primary surfactant used in the United States, other countries use SLES (with 2- or 3-mole EO). There is a trend to use sodium pareth sulfate, a synthetic version that performs similar to SLES. Because of their excellent cleansing properties, combinations of these surfactants are used in many shampoo formulations to ensure effective cleaning.

There are many instances wherein a third surfactant is added to boost the cleaning performance of the shampoo formula. Manufacturers allocate huge resources to identify such agents and would like to have intellectual ownership by patenting the technology. For example, a patent application published in Japan[151] describes a shampoo containing a lauryl trimethyl quaternary ammonium salt in conjunction with anionic and amphoteric surfactants. The shampoo is said to show good foaming attributes and softening properties without damaging the hair. The compositions of the invention also claimed to exhibit improved deposition of cationic polymer onto the hair (conditioning benefit) as well as enhancing oil removal from the hair. Other examples reported[152,153] include shampoo compositions that contain a combination of anionic surfactant, cationic polymer, and a monoalkyl quaternary ammonium compound with an alkyl chain length of C_8–C_{14} acting as a stabilizer, giving superior conditioning on one hand and oil removal on the other.

8.4.4 STABLE EMULSIONS

Developing successful hair care formulations that are cosmetically stable, aesthetically appealing, and that deliver desired benefits poses tremendous challenges, since these formulations often contain a variety of ingredients that are both incompatible and water insoluble. For example, the silicones used for delivering conditioning benefits are hydrophobic and both water and detergent insoluble. Surfactants help in such cases by the formation of emulsion with the hydrophobic molecule. An emulsion is defined as a stabilized mixture of two or more insoluble materials. In the case of personal care products, emulsion formulation often consists of water mixed with a variety of water-insoluble ingredients, such as emollient oils, moisturizers, and sunscreen oils. The water-insoluble ingredients are dispersed in water in the form of tiny droplets that are stabilized by a layer of emulsifiers that prevent the oil droplets from coalescing. If not prevented, coalescence leads to change in the texture and appearance of the formulation, eventually causing separation of oil droplets, which grow in size. A high shear mixing process causes the oils to break into droplets of desired particle size; however, the stability of the resulting droplets is mainly dependent on the choice of the detergent used to stabilize the oil droplets.

It is customary to refer to the droplet size as the particle size, although the oils are liquid droplets. The particle size of the emulsion formulation must be small enough to produce a smooth texture, which requires droplets with an average size of ~30 to 40 μm. If the particle size is bigger, the emulsion droplets move within the product, which eventually leads to creaming if not controlled. Creaming is driven by the fact that the oils typically have densities lower than that of water, and therefore as the oil droplets move, they come to the surface. Stokes law predicts the rate of movement of droplets in a formulation as a function of the difference in density between the droplets and the water phase.[154] It is therefore imperative to slow down the oil droplet movement as much as possible to give reasonable shelf life to the product. Two methods commonly utilized to control such movement are reducing the particle size to even smaller than that needed to give a smooth texture and increasing the viscosity. Since emulsions are thermodynamically unstable systems, and scientists formulate them against the laws of nature, they use both size and viscosity to maximize the stability of formulations.

Emulsions usually contain silicone oil, water, surfactant, and biocide. Although there are emulsions supplied by manufacturers that can be added to formulas, there are others that are formed during the formulating process in the manufacturing plant. The type of surfactant used to make the emulsion determines if the emulsion is cationic, anionic, or nonionic. In addition to the ability to disperse an emulsified fluid in water, emulsions are much lower in viscosity than many silicone oils, which increase their flowability in dispensing equipment. As described earlier, creaming is a natural occurrence in an emulsion that is dependent on age and storage conditions. Creaming is used to describe a condition when a dense creamy phase (usually white or tan) appears at the top or bottom of a silicone emulsion. This creamy phase appears when an oil-rich phase of an emulsion separates on standing from an oil-lean phase. Emulsions showing signs of creaming should be stirred before

TABLE 8.9
List of Most Commonly Used Emulsifiers

Nonionic	Cationic	Anionic
Stearyl alcohol	Tallowtrimonium	POE(4)lauryl ether
Cetyl alcohol	Chloride	POE(23)lauryl ether
Cetyl stearyl alcohol	Trideceth-12 Cetrimonium	Dodecylbenzene sulfonate
Ethylene glycol distearate		C_{12}–C_{14} Sec-pareth-7 and -5
		C_{12}–C_{14} sec-pareth-5
Octoxynol-40		C_{12}–C_{13} Sec-pareth-3
Isolaureth-6		C_{12}–C_{13} Sec-pareth-23
Polypropylene glycol		
Polyethylene glycol		
Behenyl alcohol		

TABLE 8.10
Examples of Multiple Surfactants for Stabilization of Emulsions

Silicone Fluid	Surfactant System
Amidomethicone	Tallowtrimonium chloride and nonoxynol-10
Amidomethicone	Octoxynol-40 isolaureth-6
Amidomethicone	C_{12}–C_{14} Sec-pareth-7 and -5
Dimethicone	Cetyl stearyl alcohol
Dimethicone	C_{12}–C_{13} Sec-pareth-3 and -23
Dimethicone	Laureth-4 and laureth-23

use to assure consistency. A list of emulsifiers is given below in Table 8.9. In many cases, although one individual surfactant could provide emulsification, more than one is used to better control particle size as well as stability. Some examples of emulsions wherein more than one surfactant is used are given in Table 8.10.

8.4.5 Solubilization of Hydrophobic Actives and Fragrances

Many hair care products are designed to provide treatment against dandruff. For example, zinc pyrithione bactericide-fungicide has been used as an effective antidandruff agent. Its unbeatable combination of high antimicrobial efficacy and safety has made it the biocide of choice for antidandruff shampoo manufacturers worldwide. It is a highly active, broad-spectrum antimicrobial agent that is registered around the world for use in both personal care as well as industrial product applications. Zinc pyrithione is listed in the Food and Drug Administration (FDA) Final Monograph on Dandruff and Seborrheic Dermatitis as a Category I substance (i.e., generally recognized as safe and effective). Hair care products are approved for use by the Environmental Protection Agency and allowed by the FDA. The agent climbazole, a conazole fungicide, although not approved for use in the United States, is approved for use in Europe, Asia, Africa, and Latin America. It is also used in shampoo and cleansers as an antidandruff agent and antibacterial agent. It exhibits pronounced growth-inhibiting activity against a broad spectrum of both gram-positive and gram-negative bacteria in cosmetic preparations. It also inhibits the growth of fungi, yeast, and mold in cosmetic preparations.

Many formulations contain one of the antidandruff agents; there are also formulations wherein a combination of two is used to exploit synergistic behavior or improved efficacy over a single agent. For example, a combination of agents such as piroctone olamine and salicylic acid showed slightly improved efficacy over zinc pyrithione in reducing the severity and area affected by scaling.[155] A caveat in this study is that the efficacy of the agents when used alone and the impact of increased concentrations in the formula need to be understood prior to making such conclusions. Also, a note of caution is that if these antidandruff agents and fragrance molecules are not effectively solubilized or suspended, the products exhibit phase separation of fragrance oil droplets or precipitation of hydrophobic particles that appear suspended or settled at the bottom. The latter becomes more visually damaging if the product targeted is a clear formula. Surfactants added to the formula for other benefits (wetting, foaming, cleaning, etc.) also promote solubilization of water-insoluble actives and fragrances, resulting in a stable formula.

A list of generally used antidandruff agents is shown in Table 8.11. Most of the antidandruff agents listed in Table 8.11 and fragrance molecules are generally insoluble in water, and any limited solubility is not enough to provide the desired benefits. The high level of surfactants (10–20%) used in most hair care formulations is adequate to solubilize or at least suspend particles of the listed antidandruff agents. In the case of a formula with antidandruff agent, manufacturers claim that any of the following methods would be able to provide a clear antidandruff shampoo with piroctone olamine:[156]

1. A dispersion of piroctone olamine is made in water (*snow-like*), and surfactants are added as solubilizers afterward.
2. Piroctone olamine is dissolved in an alcohol as solvent (e.g., propylene glycol), and this solution is added to the surfactant mixture.
3. A gel in water at 80°C is formed under stirring, cooled, and then added to the surfactant phase.

Although it is not clear why this is true only with piractone olamine, from the formulation viewpoint the above three methods employed in solubilizing piroctone olamine using surfactants should also work for other water-insoluble agents. In all shampoo and hair care (rinse-off) type formulations, although solubilization/suspension of hydrophobic agents and fragrances are important from the viewpoint of aesthetics of the product, it is also important to deliver and deposit these agents onto the hair surface, providing both immediate benefits (cleaning experience and fragrance perception) and prolonged ones (relief from dandruff).

TABLE 8.11
List of Commonly Used Antidandruff Agents

Antidandruff Agents	Synonyms	CAS Number
Zinc pyrithione	1-Hydroxypyridine-2-thione, zinc salt; mercaptopyridine *N*-oxide, zinc salt	13463-41-7
Piroctone olamine	1-Hydroxy-4-methyl-6-(2,4,4-trimethypentyl)-2-pyridon and its monoethanolamine salt	27503-81-7
Resorcinol	4-(2′-Pyridylazo)resorcinol, sodium salt *meta*-Benzenediol Resorcin	16593-81-0
Undecylenic acid	9-Undecylenic acid	112-42-5
Salicylic acid	2-Hydroxybenzoic acid	69-72-7
Sodium shale oil sulfonate	Shale oils	68308-34-9
Selenium sulfide	Selenium (II) sulfide	7446-34-6

8.5 ISSUES AND FUTURE

For successful marketing and to have winning sales, over-the-counter shampoo formulas need to demonstrate cleaning efficacy and good lather that is consumer perceivable. Compatibility of varieties of ingredients that constitute the final product, its thermal stability on the shelf and at home, and the cost of entry of a new product dictate the success of hair care products. There are some safety issues attributed to shampoos, specifically due to surfactants, which can irritate and cause scalp problems. These are rare with modern products when made by reputable manufacturers, and even less frequent if they have been designed for sensitive skin and used appropriately. From the viewpoint of specific requirements of the consumers, overwashing may exhibit some of the following effects:

- The pH of the skin surface may change. By using the claim "pH balanced" for the shampoo formulas, manufacturers make the products appealing to consumers.
- The number and type of bacteria and yeasts on the skin surface may change, resulting in dandruff or seborrhoeic dermatitis.
- The surface oil film (sebum) is removed or the surface horny cells may be loosened, disturbing barrier function. This allows greater water loss through the epidermis to the skin surface, from where it evaporates. The skin becomes more permeable to chemicals from other hair care (both rinse-off type and leave-on) products.
- Defatted skin may become excessively dry. This could become more prone to infection with *Staphylococcus aureus*, resulting in impetigo.
- Irritant contact dermatitis (red, dry, chafed skin) may develop. This may be provoked by dry skin itself, or by a particular surfactant in the shampoo. For example, sodium lauryl sulfate is more irritating than sodium laureth sulfate.
- Stinging, especially if dermatitis is already present.
- Protein-contact dermatitis, a rare mixture of contact urticaria and allergic dermatitis, due to a protein component such as peanut or oatmeal.

Identifying the gap between what is already available in the market and future needs of consumers helps manufacturers streamline and focus their efforts on the development of new products with novel technologies. Effective solutions to consumer need and a consistent message linking performance with product can lead to a successful product in the marketplace. Although the role of marketing and sales is important in identifying the gap, it is the scientists and formulators who, finally, make the impossible possible by developing stable, aesthetically appealing, mild, and cost-effective formulas that deliver fragrance and agents for better aesthetic experience and cleaning efficiency, and yet leave long-lasting benefits including antidandruff action, shine, and easier combing. The key ingredient(s) in hair care formulations that most often help to address all these requirements and meet consumer expectations is undoubtedly the surfactants, either a single surfactant (that is a rare phenomenon in the modern age), or a combination of surfactants.

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9 Fabric Softening

Amjad Farooq and Charles J. Schramm, Jr.

CONTENTS

9.1 INTRODUCTION

Fabric-softening agents or fabric softeners are compounds used to improve fabric feel or handling. Softeners lubricate fabrics and prevent direct contact between fibers. This reduces bending and shear resistance, improving the feel and drapability of the fabrics. Softeners impart fluffiness and a fresh and pleasant smell to the laundry after washing. The bulking effect is induced by softeners probably due to two reasons: prevention of direct contact between the fibers by the adsorbed lubricating softener and by electrostatic repulsion among the adsorbed cationic head groups of the softener. Fabric softening agents possess useful antistatic properties. Untreated garments, in particular synthetic and cotton synthetic fiber blends, develop static charge during machine drying or when worn in dry conditions. The charges impair the comfort of handling and wearing clothes. Softeners, by reducing frictional force and by their possession of positive charge, tend to eliminate charges on the surface of the fibers.

Both the microstructure and the *hand* of the fabric are changed as a result of shrinkage due to repeated washing, damage to the fibers from mechanical friction in the washing machine, chemical action of detergents, deposition of inorganic salts present in detergents, and insoluble calcium salts present in hard water. Softeners help to reduce shrinkage, and help protect fabrics from undergoing damage due to mechanical friction in the washing machine and chemical action of detergents. Berenbold reports that the use of a softener, distearyl dimethyl ammonium chloride, protects the fabrics from enhanced inorganic deposits (reduced on the order of 35% in case of air drying) caused by repeated washing [1]. He also reports an improvement in the water permeability of the fabric with the use of the softener. Increased water permeability may have a beneficial effect on fabric comfort in wear. Water permeability of cotton increases with the use of the softener up to a level of 1.0 g of distearyl dimethyl ammonium chloride per kilogram fabric. Past the usage amount of 1 g/kg fabric, the water permeability decreases. In contrast to cotton, the water vapor permeability of polyester continues to increase up to ~20%, compared to the value for the untreated fabric.

Berenbold also reports a 20% reduction in fabric abrasion (cotton) during wearing and washing on using a fabric softener. In addition to the above attributes, softening agents offer the following benefits:

- Reduce energy costs by reducing the drying time in the tumble dryer
- Facilitate ironing
- Contribute to wrinkle reduction
- Have a germicidal effect
- Carry fragrance to the fabric surface

There are several drawbacks to use of softeners. Repeated use of softeners may cause reduced water absorbency of garments (particularly with distearyl dimethyl ammonium chloride). Softeners may also reduce the effectiveness of anionic fluorescent brighteners [2]. They may impart a greasy feel, and may stain fabrics when overdosed or too thick. Softeners can also reduce the effectiveness of flame retardancy agents on fabrics.

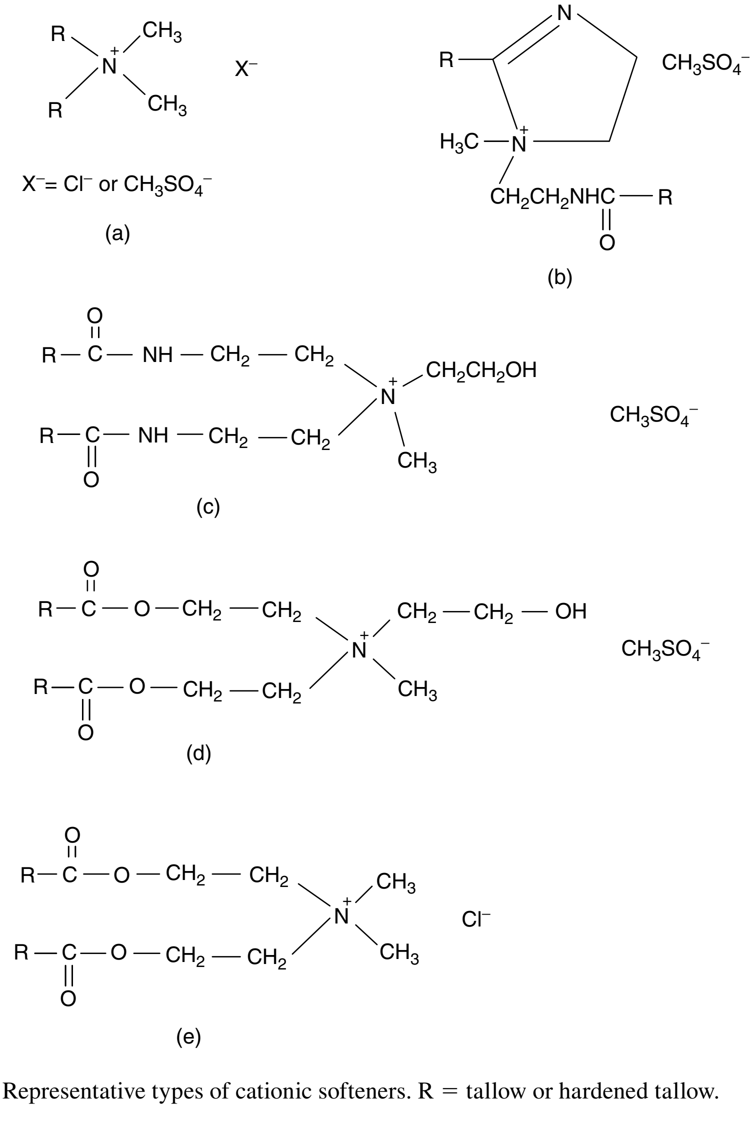


FIGURE 9.1 Representative types of cationic softeners. R = tallow or hardened tallow.

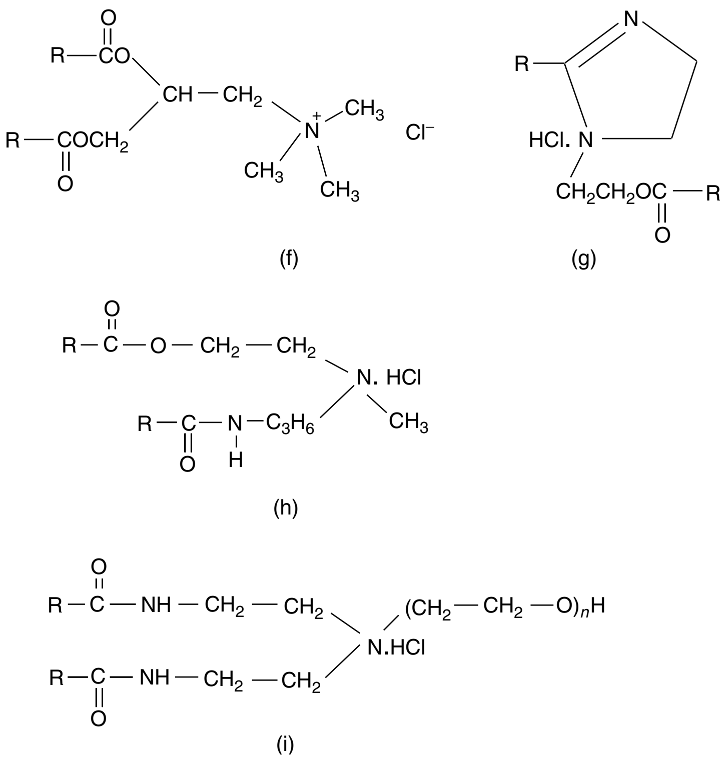


FIGURE 9.1 (*Continued*)

Fabric softening agents most commonly used by the detergent industry are nitrogen-containing cationic compounds with two long-chain hydrophobic alkyl groups. The alkyl groups are usually from tallow fatty acids or triglycerides with a high C_{16}–C_{18} alkyl content. Cationics of the quaternary ammonium and imidazolinium type are the preferred materials (Figure 9.1).

Fabric softeners used in the early 1960s were mainly based on simple aqueous dispersions of dihydrogenated tallowdimethyl ammonium chloride, DTDMAC (Figure 9.1a). Some were based on imidazoline (Figure 9.1b) or amidoamine derivatives (Figure 9.1c). For more than three decades, DTDMAC was the most extensively used raw material in the production of liquid rinse cycle softeners. In 1990, the European environmental authorities, in particular the German and Dutch, classified DTDMAC as harmful to the environment, although no perceptible environmental damage had occurred over a period of 30 years, as demonstrated by simulated field trials [3]. The German and Dutch government officials based their concern largely on the poor biodegradability and aquatic toxicity data obtained in laboratory tests. Thus, in 1991 and later, major manufacturers volunteered to replace DTDMAC with new environmentally safe actives such as diester quaternaries, imidazoline ester, and ester amidoamine or amidoamine acid salts (tertiary amine acid salts) (Figures 9.1d through 9.1i). These materials pass the European environmental safety guidelines that were published by the EEC commission in the 12th Commission Amendment 91/325/EEC [4]. The environmental compatibility of ester quat and its comparison with DTDMAC (Figure 9.1f) is discussed by J. Waters et al. [5]. The materials (Figures 9.1c through 9.1i) are also suited for high-active dispersions.

There are many new and less well-known types of softening compounds such as pentaerythritol ditallowate [6], glycerine-based polyol esterquats [7], 1,1-ethylene-*bis*(2-tallow-alkyl-3-methylimidazolinium) methyl sulfate [8], β-hydroxyethyl ethylenediamine derivatives [8], polyammonium compounds such as propylenediammonium chloride with fatty acid ethoxy-ester substitutes [8], diquaternary compounds [8], alkylpyrimidinium [8], pyridinium compounds [8], clays [4], and silicones [4] such as polydimethylsiloxane polymers or organo-modified polydimethylsiloxanes, which have been discussed in the scientific and patent literature. There is a considerable effort by chemical companies to synthesize new softening molecules with some unique attributes such as thiodiglycol alkoxylate derivatives, nitrogen-free softeners with good softening that is unaffected by water hardness and allows formulations in the range of pH 4–11 [9], polyalkyl ester or amido ammonium compounds [10], amido ester amine and its corresponding quaternary ammonium compounds [11], alkoxy-2-ethyl hexyl-alkyl methyl quaternary ammonium compounds and their precursor amines having high water dispersibility [12], ribose diester quaternary [13], and glycerol- and betaine-derived softeners [14].

9.2 FORMS OF SOFTENING PRODUCTS

There are four major forms of softening products:

1. Rinse cycle softeners
2. Dryer-added softeners
3. Wash cycle softeners
4. Softergents

Of the four forms, rinse cycle softeners provide the most effective softening [4]. These are added to the laundry during the last rinse cycle, after the soil and the detergent residues are removed. Rinse cycle softeners are most effective because their addition after the main wash prevents

1. Formation of ineffective neutral salts with detergent anionic surfactants
2. Redeposition of the suspended soil
3. Nonuniform coverage

Domestic rinse cycle softeners are supplied as liquids [15–20]. They are available in solid forms for institutional washing. Household fabric softeners were first introduced in the U.S. market in the mid-to late 1950s and were launched in Europe and Japan starting in the 1960s by detergent manufacturers. Rinse cycle softeners are far more important in Europe than in the United States, because there are considerably fewer tumble dryers in West European households, and therefore the wet washed clothes are dried outside in the open atmosphere. In 1991, only 20% of West European households owned a dryer as compared to 75% of U.S. households [21].

Rinse cycle softener dispersions are easily prepared at regular strength (3–8 wt%), by slowly mixing melted softener into water at ~50 to 70°C. For example, a 5% by weight dispersion of DTDMAC can be prepared in the laboratory by the following procedure.

Slowly add the melted 70°C oil phase (33.3 g, 75% active DTDMAC) to hot water (466.7 g) at 70°C with stirring. Then add the NaCl solution (0.4 g of 10% NaCl solution; active concentration of NaCl in the emulsion, 0.008% or 1.368×10^{-3} M) and cool the stirring emulsion to room temperature with an ice water bath. ***Characteristics*:** Brookfield viscosity (spindle 4, 20 rpm, RT) = 40 cP; average particle size = 23 μm (LS Coulter 130); pH = 5.5.

For three decades, rinse cycle fabric softeners were essentially 3–8 wt% active dispersions [22], which were considered regular strength. In the past 10–15 years, a market for less bulky, more concentrated products has emerged as a result of the desire to cut packaging and transportation costs, reduce the shelf-space, and utilize smaller, easier-to-handle containers. Section 9.6 discusses the concentrated rinse cycle fabric softeners.

The launch of Downy Rinse Free (Libre Enjuagne) rinse cycle fabric softener in Mexico in 2004 had a significant impact on the fabric conditioner market in Mexico [23]. The product, which addressed a consumer habit and need, rapidly gained market share. Along with executing on the primary fabric conditioner benefits of fabric softening and fragrance delivery, the product addressed the behavior of the Mexican consumer (hand wash and machine wash) to do a prerinse before the rinse containing fabric conditioner. The first rinse with water only provided for removal of anionic surfactant carried by wash solution left in the damp cloths. In Mexico, use of high-surfactant powdered detergents at a high concentration results in visible foam in the first rinse. The prerinse removal of detergent residue involves additional labor, time, and use of a scarce resource: water. Utilizing a standard rinse conditioner in the first rinse often generates some level of fabric residue resulting from interaction of the cationic softener active with the anionic surfactant.

No rinse fabric conditioners are formulated with defoamers that eliminate the visible foam from the anionic surfactant carried over into the rinse by the washed fabrics [24]. These formulations are also formulated to minimize the interaction of the cationic softener and anionic surfactant or to prevent the formation of large aggregates of cationic softener/anionic surfactant complexes [25]. Mexican consumers have shown their appreciation for the time savings of only one rinse step and the ability to save on water use. Significant consumer interest has resulted in additional entries into the category such as Suavitel Sin Enjuague rinse cycle fabric softener.

Dryer softeners are placed in the tumble dryers along with the moist laundry. The most commonly used dryer softeners are made from sheets of polyurethane foam or nonwoven material impregnated with active matter, to act as a carrier [8]. U.S. Patent 5300238, European Patent Application 0544493 A1, and U.K. Patent Application GB 2240791 A give examples of fabric conditioning compositions produced by coating a flexible substrate for use in a mechanical dryer [26–28].

Wash cycle softeners are added to the main wash bath along with detergents. They provide convenience to the U.S. consumers with washing machines having no automatic dispenser for the rinse-cycle fabric softener. Effectiveness of the wash cycle softener is reduced by the anionic surfactants used in laundry detergents [29,30]. They have gained only limited commercial importance [4]. There are numerous examples of through-the-wash fabric conditioning systems in the patent literature [31–35].

Recently unit dose wash cycle fabric softeners have been introduced into the European market. Unit dose represents additional ease of use, as the product is supplied in the form of preweighed separate amounts that are added directly to the wash. This eliminates the need to measure and prevents possible messes from spillage. Compared to a softergent (detergent softener combination), this product form presents an added challenge, as the formulator has no control over the detergent system or proportion of softener to detergent used.

Soupline Hearts and Comfort Pearls were launched in France in late 2003 and in the United Kingdom in 2004, respectively. Soupline Hearts has the form of a heart-shaped tablet and contains an organic-modified clay and fragrance [36,37]. The organo clay–based softener system had been previously used in powdered softergents [38]. Significant effort was involved in preparing a tablet that would effectively release the softening system while minimizing fabric residue [39]. Comfort Pearls is a nonaqueous liquid using *Cocos nucifera* (coconut oil) and additional fatty acids and salts of fatty acids as the softening system, in an oval water-soluble sachet [40]. Triglycerides can be hydrolyzed at the high pH of a wash solution typical of detergent systems in the U.K. Salt of fatty acids precipitated by hardness ions will deliver a softening benefit. Both products have achieved small market penetration and may turn out to appeal more to nonrinse fabric conditioner users.

Softergents combine a detergent system for cleaning fabrics with softener system for delivering softening benefits. These products are a compromise between easier handling and performance [8]. The product form offers consumers the convenience of not having to catch the rinse to add a rinse softener (automatic washers without dispensers). Minimizing the impact of the detergent system on softening and the softener system on cleaning requires a compromise on performance as compared to products delivering only a single benefit. They do not match the performance of a rinse cycle

TABLE 9.1
Composition of a Powder Soft Detergent

Component	Weight%
Sodium linear C_{10-13} alkylbenzene sulfonate	6.0
Zeolite 4A (hydrated)	19.0
Sodium silicate ($Na_2O:SiO_2 = 1:2$)	3.5
Sodium maleate methacrylate copolymer	1.1
Ethylene diamine tetra(methylene phosphonate) sodium salt	0.5
Sodium carboxymethyl cellulose	0.4
Stilbene fluorescent brightener	0.2
Sodium sulfate anhydrous	13.54
Sodium carbonate anhydrous	10.0
Sodium perborate monohydrate	9.0
Tetraacetyl ethylene diamine	1.8
Hydroxylamine sulfate	0.5
Enzyme blend	0.36
Sodium aluminosilicate (Tixolex 28)	0.4
Perfume	0.55
Calcium bentonite or calcium montmorillonite	18.0
Pentaerythritol distearate	4.25
Nonionic surfactant (C_{12-15}) fatty alcohol (7 EO)	6.0
Water	4.9

Source: Doms, J.R.P., Gillis, M.J.E.G., Lambert, P.M., Heckles, P.A., Puentes-Bravo, E.E., A. Hermosilla, M., Grandmaire, J.-P.M.H.F., and Tack, V. E. A. U.S. Patent 5332513, Colgate-Palmolive Company, 1994.

softener. These types of products are available both in powder [8,41–43] and liquid forms [8,44,45]. Tables 9.1 and 9.2 show examples of a powder soft detergent, containing pentaerythritol distearate as softener [46], and of a heavy-duty liquid laundry detergent composition containing the fabric-softening agent lauryl trimethyl ammonium chloride [47].

Softergents were a product form that although significant in the late 1980s and early 1990s became very minor by the late 1990s. A new interest in the form began in 2004 with the launch of Tide with a Touch of Downy, both powder and liquid. This example of cobranding the market-leading Tide brand with the market-leading Downy brand resulted in a renewed interest in softergents. Tide with a Touch of Downy is described as working by using detergent surfactant to remove soil. This exposes negative sites on the fabric surface, which attract positively charged softener ingredients [48,49]. The Touch of Downy liquid patent indicates softening can be achieved with a range of cationic softener actives used at preferably levels between 1 and 8% [50]. The softener actives claimed are mainly di-long alkyl chain–containing compounds. Quaternary cationic surfactants in the Touch of Downy powder patent are mainly mono-alkyl chain and preferably C_6—C_{10}. Another preferred cationic surfactant type included mono and *bis*-alkoxylated quaternary ammonium surfactants. The cationic surfactants in Touch of Downy powder appear more directed to antistatic and cleaning benefits than to fabric softening. Based on the published patent art, Tide with a Touch of Downy powder also is formulated with a clay type fabric softener. Sodium or calcium montmorillonites are

TABLE 9.2
Composition of a Liquid Soft Detergent

Component	Weight%
Sodium C_{12-15} alkyl polyethoxylate (2.5) sulfate	18.0
Lauryl trimethyl ammonium chloride	5.0
C_{12-13} alkyl polyethoxylate (9)	2.0
C_{12} alkyl glucose amide	5.0
Citric acid	3.0
C_{12-14} alkyl fatty acid	2.0
Ethanol	3.7
Propanediol	8.0
Monoethanolamine	1.1
Boric acid	3.5
Tetraethylenepentamine ethoxylate (15–18)	1.2
Sodium cumene sulfonate	3.0
Protease enzyme	0.9
Lipase enzyme	0.1
Cellulase enzyme	0.08
Sodium hydroxide	To pH 8.0
Water, perfume, and minor ingredients	Balance to 100

Source: De Buzzaccarini, F., Farwick, T.J., and Zhen, Y., WO 95/29217 A1, The Procter & Gamble Company, 1995.

particularly preferred. Clay flocculating agents are also mentioned as a potential active. The most preferred type is polyethylene oxide of molecular weight ranging between 200,000 and 1,000,000.

Whether or not the softergent product form will continue to have consumer impact remains to be seen.

9.3 RELATIVE SOFTENING AND ANTISTATIC PROPERTIES

To date, the best method of determining softness has been by our sense of touch of the fabric. Relative softening values, on a prearranged scale, are assigned to different fabrics by trained panelists. Statistical analysis of these reveal the relative performance differences among various softeners [51,52]. Softeners are usually tested at 0.1–0.2% of fabric weight. They are usually added to the rinse water as aqueous dispersions providing ~100 to 250 ppm of softener in the rinse water. Terry cloth swatches are excellent for evaluating the relative softening of various softeners. They yield best results after being desized by a mixture of a household laundry detergent and sodium tripolyphosphate (about two washing cycles followed by plain water wash) and harshened by a mixture of sodium sulfate, metasilicate, and sodium tripolyphosphate (about six cycles). It is highly useful to include fabrics treated with standard material DTDMAC as reference samples and also a harshened fabric swatch to which no softener has been applied. The softening of a new material can be reported in comparison to the standard material. Farooq and Mastrull report the softening of a new softener on the EQ scale [19]; EQ stands for equivalent amounts of DTDMAC. The EQ is the DTDMAC concentration of a hypothetical composition needed to deliver the same softness as the tested composition under the standard test conditions (given earlier). The EQ value of a softener product can be determined experimentally by comparing the softness performance of the product to those of known concentrations of DTDMAC dispersion through laboratory paired comparison tests with a trained panel. The softening of 5% dispersion of DTDMAC is reported as 5 EQ. Eight times diluted softener dispersion (28% by weight based on fatty amidoamine and diester quaternary ammonium compounds) that provided equal softening efficacy to the 5% DTDMAC dispersion was reported as 40 EQ. Washing conditions (detergent composition, dosage, drying conditions, etc.) could strongly influence the delivered softness and EQ values.

Since softening is inherently subjective because human sensory perception is involved, no instrumental method has been identified to date as the perfect one to quantitatively relate human perception of softening to instrumental data. The Kawabata method measures the mechanical properties of fabrics [2]. These properties are used to quantify the effects of fabric softeners. Softening is associated with lubrication, flexural rigidity, and compressibility of whole fabrics. Fabric lubricity is related to fabric friction, which can be measured by Instron tests.

A number of methods have been used to measure the static electricity of fabrics [53]. The most frequently used method has been a subjective evaluation by an experienced operator. Using this method, the operator removes the fabric from the dryer one swatch at a time and gives each piece a subjective rating on, for example, a 1–5 scale, where 1 = no static or cling, and 5 = large amounts of static, crackle, and cling. The most common instrumental method has been with an electrostatic meter [53]. This is a device that measures the electric field around a charged object and requires multiple measurements on the fabric. Tiede has devised an improved instrumental method based on a Faraday cage, for evaluating static control in laundry [53]. Test swatches are removed from the dryer and placed in an insulated stainless steel tank. As each swatch is removed from the tank, a charge equal and opposite to the charge on the fabric is induced on the tank, which is measured by a high-impedance voltmeter. Figure 9.2 shows the range of results (static current) seen over several cycles with multiple products in each category (softener added in rinse, dryer sheet, etc.) [53]. For the softergent, the values ranged from 3700 to 9300 V, and by subjective evaluation these

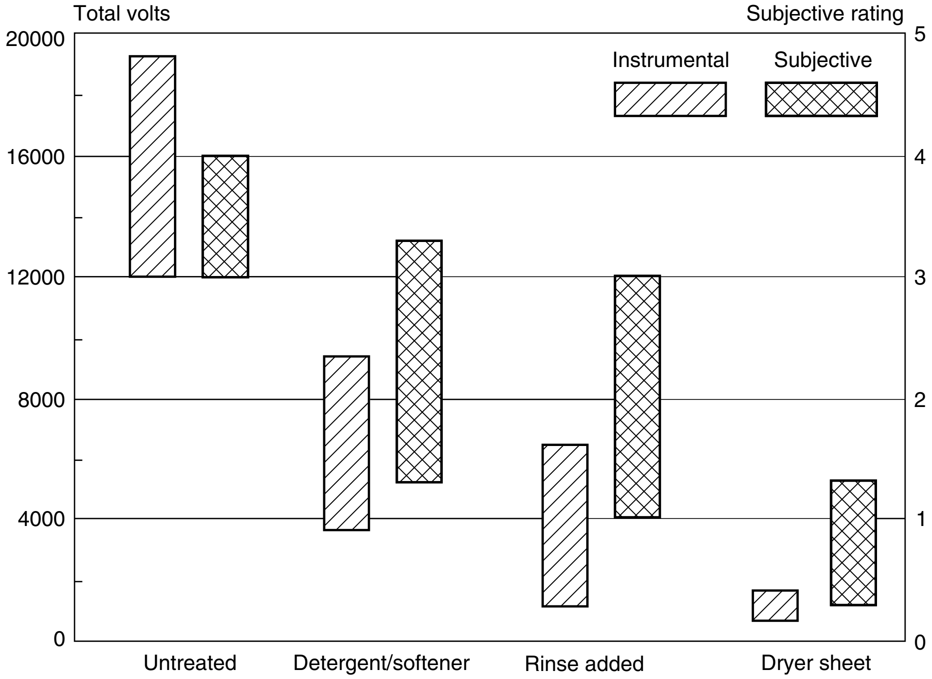
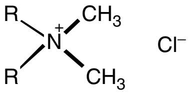
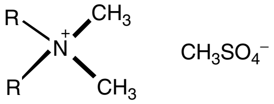
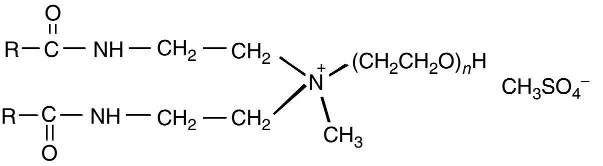
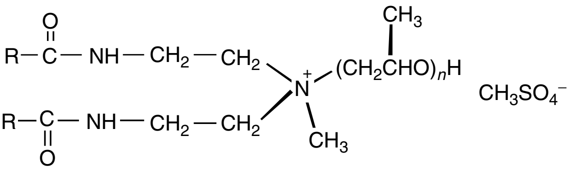
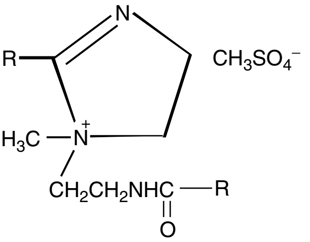


FIGURE 9.2 Subjective versus instrumental comparison of methods. (From Tiede, M.G., *J. Am. Oil Chem. Soc.*, 65, 811–815, 1988. With permission.)

formulations gave results ranging from 1.3 to 3.3 on a 0–5 rating scale. It is apparent that similar patterns of performance are achieved with subjective and instrumental methods.

McConnell reports the relative performance rating of five quaternary type of surfactants at the indicated wt% (based on dry weight of fabric) solids levels (Table 9.3) [54].

TABLE 9.3
Performance Rating

Softener	Softening (0.1 wt%)	Antistatic (0.075 wt%)	Hand (0.1 wt%)	Stable Dispersion Range, (wt%) Solids
 R= Hydrogenated tallow alkyl	1	3	Very slick	4–8
 R = Hydrogenated tallow alkyl	2	2	Slightly slick	4–8
 R = Tallow alkyl	3	1	Slightly slick	4–12
 R = Tallow alkyl	4	4	Dry	3–15
 R = Tallow alkyl	5	5	Dry	3–15

Note: 1 = best, 5 = poorest.

Source: McConnell, R.B., Softeners and ethoxylates, American Dyestuff Reporter, July 31–34, 1978.

9.4 FACTORS AFFECTING SOFTENING EFFICACY

The prerequisite for a softener to function is that it must deposit onto the textile fabric. A greater deposition, however, does not necessarily mean better softening. Factors that affect deposition and softening efficacy as perceived by human sensory evaluation include:

9.4.1 CHAIN LENGTH AND TYPE OF ALKYL SUBSTITUENT

The nature and number of long alkyl chains affects softening efficacy. Generally, the more hydrophobic the softener, the greater the amount deposited onto the fabric, and therefore (although not necessarily), the better the softening performance. Crutzen reports that DTDMAC at the same molar concentration performs better than dicocodimethyl ammonium chloride and monotallowtrimethyl ammonium chloride [55]. A. D. James et al. report performance testing of the softening efficiency of tetraalkyl quats to be in the order, $\text{mono}C_{18} < \text{di}C_{12} < \text{mono}C_{22}$ [56]. The degree of saturation of the alkyl chain also substantially influences softening efficacy. Hein shows an inverse linear correlation of the iodine number of the softener or its alkyl radical with its softening performance [57]. As the iodine number of an imidazoline type softener (fixed alkyl chain length of C_{16-18}) increases, the softness of the treated fabrics decreases linearly.

9.4.2 MOLECULAR STRUCTURE OF THE SOFTENER

The incorporation of polar groups such as hydroxyl and ethoxy within the softening molecules tend to reduce softening efficacy, although these polar groups do enhance dispersibility of the product [58]. The area that a softener molecule occupies on the fabric would probably affect the softening efficacy. The higher the area per molecule, the lower will be the softening.

9.4.3 TYPE OF FABRIC (COTTON, POLYESTER, WOOL, ETC.)

DTDMAC is adsorbed best on cotton and wool. Significantly lower amounts of softener are adsorbed on synthetic fibers, which are nonpolar and hydrophobic, such as polyester and polyacrylonitrile. Table 9.4 shows the relative amounts of softener sorption in percentage WOF (weight of fabric) from distearyldimethyl ammonium bromide (DSDMAB) solutions (wt/v%) [59]. Although a lower amount is adsorbed on polyester, in subjective sensory evaluations the softness rating of polyester fabric was similar to that of cotton [59].

9.4.4 PARTICLE SIZE OF SOFTENER DISPERSION

The particle size of the softener dispersion affects softening efficacy. Relatively smaller particle size dispersions would more uniformly deposit onto the fabric surface than larger sized dispersions. Okumura et al. report that a micronized dispersion (90% under 1 μm) of distearyldimethyl

TABLE 9.4
Sorption of Cationic Surfactant Distearyldimethyl Ammonium Bromide on Test Fabrics (No Finish) from Three Solutions

	Sorption in % WOF	From DSDMAB	Solutions (wt/v%)
Fiber content	0.0034	0.01	0.02
100% Cotton	0.097	0.297	0.319
50/50 Cotton/polyester	0.094	0.157	0.247
100% Polyester	0.024	0.069	0.144

Source: Beal, C.M., Olson, L.A., and Wentz, M., *J. Am. Oil Chem. Soc.*, 67, 689–697, 1990.

ammonium chloride has faster adsorption on cotton as well as superior softening and antistatic performance compared to a macronized dispersion (80% between 1 and 10 μm) [60].

Several other factors, such as pH of the rinse liquor [2,8], temperature [8,58], water hardness [2,4,8], and softener concentration affect deposition and softening efficacy. Deposition generally increases with pH in the range of 2–9; however, it is more advantageous to treat the fabrics in the neutral to slightly acidic pH range to promote uniform coverage of the fabric surface [8], and to avoid hydrolysis of the softeners containing ester moieties.

9.5 MECHANISM OF SOFTENER DEPOSITION

Laughlin [2] has discussed the physical processes by which softener deposition on fabrics occur. He suggests that deposition represents a combination of molecular ion exchange and physical adsorption processes. A cotton surface possesses a negative zeta potential due to carboxylic acid groups of oxidized cellulose. Considering earlier work, Laughlin suggests that an initial binding of the cationic softener to the cotton surface occurs by an exchange of positive counterions associated with the carboxylate groups of cotton with the softener cation. Following this initial ion exchange process, further adsorption of the softener takes place by physical adsorption, which does not require surface charges. Recently, Crutzen proposed a single mechanism to account for the deposition of ditallowdimethyl ammonium chloride onto cotton and charge-free synthetic fabrics [55]. According to this author, ditallowdimethyl ammonium chloride deposition onto the fibers does not result from an electrostatic attraction, but from a hydrophobic ejection of the softener molecule from the aqueous medium. In aqueous dispersion (neat product), ditallowdimethyl ammonium chloride exists as positively charged vesicles, where the fatty chains are completely out of the aqueous environment. At the rinse concentration during the fabric treatment, the vesicle structure is modified so that the fatty chains come into contact with water and the ditallowdimethyl ammonium chloride is hydrophobically ejected out of the aqueous phase and adsorbed onto the fabric surface (Figure 9.3).

Crutzen pointed out the unknown nature of the ejected species, which are represented in Figure 9.3 as individual molecules. Through scanning electron microscopy, Okumura et al. have reported that DTDMAC dispersion adsorbed onto the fabric surface not as mono- or bilayers, but as multilayered particles [60].

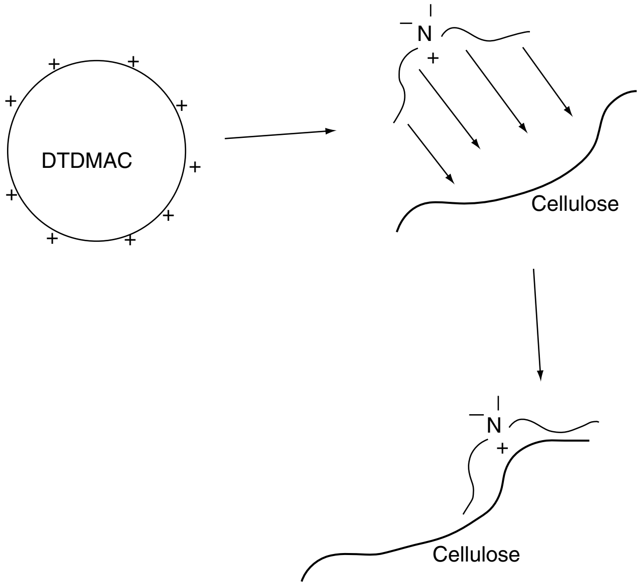


FIGURE 9.3 Hydrophobic model of DTDMAC (ditallowdimethyl ammonium chloride) deposition on cotton. (From Crutzen, A.M., *J. Am. Oil Chem. Soc.*, 72, 137–143, 1995. With permission.)

9.6 CONCENTRATED RINSE CYCLE FABRIC SOFTENERS

It is difficult to prepare concentrated aqueous dispersions containing more than ~20% of cationic softeners without encountering severe product viscosity and storage stability problems [57,61]. With the increase in concentration of the active ingredients of fabric softeners, viscosity increases, which inevitably results in nonpourable products. Furthermore, the physical stability of the formulation decreases because of the increased amount of the dispersed material and dissolved electrolyte. Product efficacy and dispersibility are also affected by increased concentration. This is true for DTDMAC, amido-imidazolinium compounds, and difatty diamido ammonium methyl sulfate [57,61,62]. The approximate upper active level (wt%) limits for these softeners are 12, 20, and 26 (iodine value = 40), respectively, for a typical soft-tallow–based dialkyl softener [62]. Low-viscosity concentrates (~10 to 20%) of fabric softeners, such as imidazoline derivatives and dialkyl ammonium compounds, are prepared by using high-pressure homogenization [63] or adding fatty alcohols, aliphatic fatty acids, fatty acid methyl esters [64], paraffin oils and paraffin waxes [65], ionogenic and nonionogenic emulsifiers (such as ethoxylated nonylphenol and oleyl alcohol) [57], or water-miscible organic solvents such as hexylene glycol [66]. A few other examples of softener concentrates include the use of water-soluble polymers [67,68], alkoxylated alcohols [69,70], organic solvents [71,72], and fatty groups in diester quaternary ammonium compounds, having a controlled level of unsaturation [73].

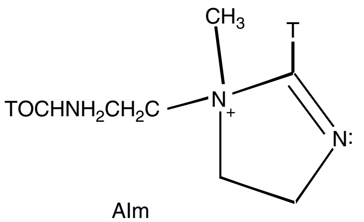
Farooq et al. [18,74–76] have prepared concentrated softener dispersions of *bis* (alkyl amidoethyl)-2-polyethoxy amine AA(H) by making use of the two complementary basic approaches:

1. Reduction in the crystallinity of AA(H) by low-melting softening molecules such as amidoamine AA(S), unsaturated imidazolinium quat, or triethanolamine diester quat (DEQ)
2. Use of electrolytes as viscosity-controlling agents (Figure 9.4)

The approximate upper active level (wt%) limit for the AA(H) system is 11. With the use of AA(S) and calcium chloride, the critical concentration of AA(H) dispersions (the concentration above which the viscosity increases to unacceptable values, that is, >700 cP at room temperature) is shifted from 11 to ~25% (Figure 9.5) [18,75]. AA(S) is an analogue of AA(H), with soft tallow moieties. In soft tallow groups, there is ~45% of unsaturated alkyl chains [mainly the oleyl moiety $CH_3(CH_2)_7CH{=}CH(CH_2)_7COR$] and 55% of saturated alkyl chains (C_{14}–C_{18}). Conversely, in hydrogenated tallow (also sometimes referred to as *hard tallow* or *H-tallow*), all of the unsaturated chains are converted to saturated chains. Therefore, the AA(H) molecule contains almost 100% of saturated alkyl chains.

Softening efficacy of the dispersions does not increase proportionally with the concentration of AA(H)/AA(S). While the 4% dispersion shows a product activity of 5 EQ, the 24% dispersion [AA(H)/AA(S); 22/2] exhibits a softening of only 14 EQ. This was ascribed to the higher average particle size and remains of undispersed amine at higher concentrations.

Another choice to reduce the crystallinity of AA(H) is to add difatty amido imidazolinium compound (AIm). This compound was chosen because it is a liquid (90% active in isopropanol) at room temperature, and higher dispersibility of AA(H) was expected by virtue of the reduction in the crystallinity of AA(H).



AIm
T = Soft tallow

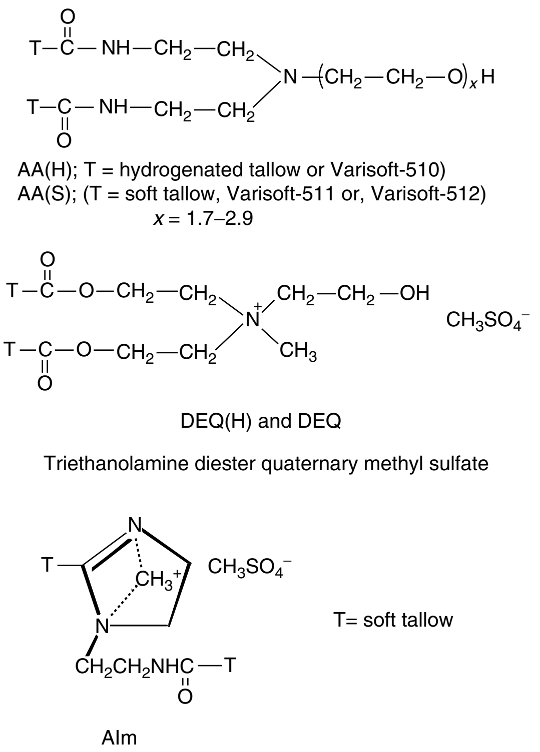


FIGURE 9.4 Structures of *bis* (alkyl amidoethyl)-2-polyethoxy amine AA, triethanolamine diester quaternary methyl sulfate [*bis* (alkyl carboxyethyl) 2-hydroxyethyl methyl ammonium methyl sulfate] DEQ and difatty amido imidazolinium methyl sulfate (AIm).

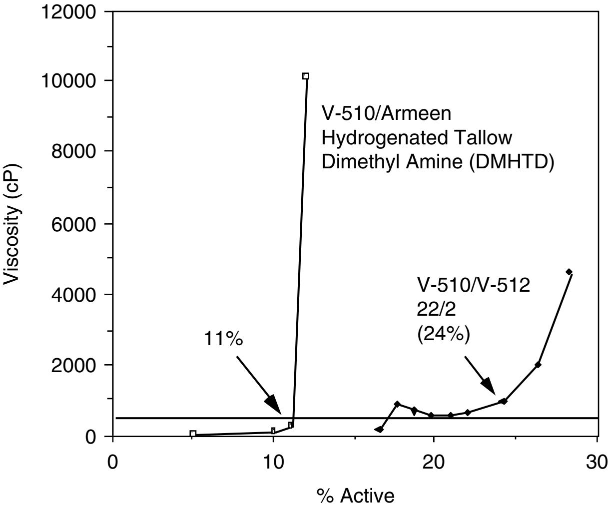


FIGURE 9.5 Shift of the critical concentration of AA(H), Varisoft-510 emulsions from 11 to 24% by AA(S), Varisoft-512 and $CaCl_2$. DMHTD: Hydrogenated Tallow Dimethyl Amine. (From Farooq, A., Cesar, R. and Deville, F., U.S. Patent 5501806, Colgate-Palmolive Company, 1996; Farooq, A., Mehreteab, A., Mastrull, J., Cesar, R. and Broze, G., *Concentrated and Efficient Fabric Softeners*, *Specialty Surfactants*, Marcel Dekker, New York, 2001.)

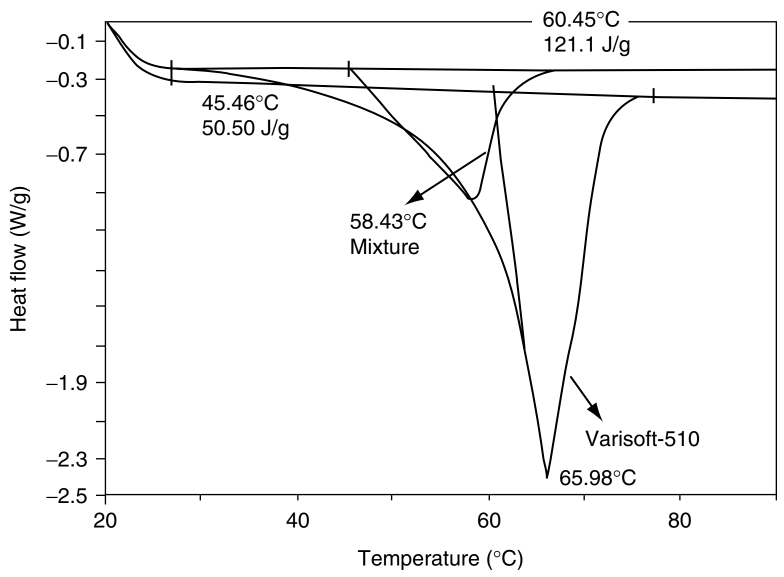


FIGURE 9.6 DSC thermogram of Varisoft-510 AA(H), and 1:1 mixture of AA (H)/AIm. (From Farooq, A., Cesar, R. and Deville, F., U.S. Patent 5501806, Colgate-Palmolive Company, 1996; Farooq, A., Mehreteab, A., Mastrull, J., Cesar, R. and Broze, G., *Concentrated and Efficient Fabric Softeners*, *Specialty Surfactants*, Marcel Dekker, New York, 2001.)

Evidence for the reduction in the crystallinity of AA(H) (or Varisoft-510), by AIm comes from the differential scanning calorimetric analysis (DSC) of AA(H) and a mixture of AA(H) and AIm (1:1) (Figure 9.6) [18,75]. A thermogram of AA(H) shows a melting temperature of 65.9°C (ΔH = 121.1 J/g). In contrast, a 1:1 mixture of AA(H) and AIm exhibits a melting temperature of only 58.4°C (ΔH = 50.5 J/g). Therefore, AIm serves as a dissolving matrix for the highly crystalline AA(H).

The characteristics of 1:1 mixtures (20–25% by weight) of AA(H) and AIm are listed in Table 9.5. The unique combination of fatty amidoamine AA(H) with the imidazolinium quat results in a synergistic softening of 35 EQ at the 25% level, an average particle size of 1 μm and a 1 week viscosity of only 360 cP at room temperature [74,75].

The combination system of fatty amidoamine AA(H) and imidazolinium quat (AIm) meets the needs of high-efficacy and low-viscosity fabric conditioner concentrate. The attributes of high efficacy and low viscosity of AA(H) in the presence of unsaturated softening molecules are ascribed to the high dispersibility of AA(H), decrease in the melting point, and looser packing of the softening molecules in solution.

A system based on environmentally safe AA and triethanolamine diester quaternary methyl sulfate (DEQ and DEQ-H) allows concentrates with as high as 37.5% actives [18,19,75,76]. The emulsions of fatty amidoamine and DEQ are of low viscosity (<600 cP) and exhibit acceptable viscosity stability with time [18].

Figure 9.7 shows the effect of concentration of AA(S) on the viscosity of the AA/DEQ(H) emulsions [18,75]. As can be seen, as the soft tallow amidoamine AA(S) increases, the viscosity decreases. These data correspond to samples stored at 4°C for 3 weeks (viscosity measurement at room temperature). The data clearly point out that to avoid gelation, the amount of soft tallow amidoamine in the amidoamine fraction must be above 45%.

The decrease in viscosity is ascribed to reduction in the crystallinity (loosely packed structure as opposed to well packed structure) of AA/DEQ(H) emulsions.

TABLE 9.5
Compositions and Physical Properties of Emulsions of AA(H)/AA(S) and AA(H)/AIm

Composition	#1 (wt%)	#2 (wt%)	#3 (wt%)	#4 (wt%)
Varisoft-510, AA(H)	10	10	12.5	
Varisoft-512, AA(S)	—	10		
AIm	10	—	12.5	20
HCl	0.72	1.08	0.9	
2-Propanol	4	4	5	
$CaCl_2$	0.37	0.38	0.45	0.27
H_2O	Balance to 100	Balance to 100	Balance to 100	Balance to 100
Physical properties				
Average Particle Size (μm)	1.1		1.1	11.7
Softening efficacy (EQ)	>24	≪20	35	<8
Viscosity (cP) 20 rpm, spindle 4-initial	60	30	140	120
Viscosity (cP) week 1	120	40	360	420

Source: Farooq, A., Cesar, R. and Deville, F. U.S. Patent 5501806 to Colgate-Palmolive Company, 1996; Farooq, A., Mehreteab, A., Mastrull, J., Cesar, R. and Broze, G., *Concentrated and Efficient Fabric Softeners, Specialty Surfactants*, Marcel Dekker, New York, 2001. With permission.

Ingredients	wt%
AA(H)	0–17.5
AA(S)	0–17.5
DEQ(H)	10.5
HCl	1.16
$CaCl_2$	0.40
Dye	0.03
Preservative	0.01
Perfume	2.4

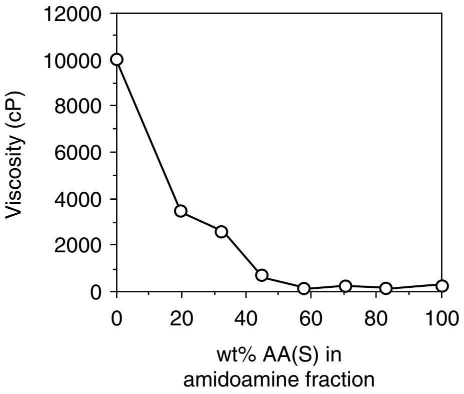


FIGURE 9.7 The effect of concentration of AA(S) on the viscosity of the AA/DEQ(H) emulsions. (From Farooq, A., R. Cesar, and F. Deville, U.S. Patent 5501806 to Colgate-Palmolive Company, 1996; Farooq, A., Mehreteab, A., Mastrull, J., Cesar, R. and Broze, G., *Concentrated and Efficient Fabric Softeners, Specialty Surfactants*, Marcel Dekker, New York, 2001.)

To see the effect of unsaturation on the flow properties of the emulsions, a number of rheological techniques were carried out. Figure 9.8 shows the flow curves of emulsions with various levels of AA(S) [18,75]. As the amount of AA(S) increases, the yield stress of the system decreases, and the emulsion moves toward Newtonian (waterlike) behavior.

Yield stress refers to the minimum stress (force) that is required to initiate flow. Below this stress, the system behaves like an elastic solid. The relatively higher value of yield stress for the emulsion with 0% soft tallow amidoamine is indicative of stronger interactions between the particles. The incorporation of AA(S) weakens the intermolecular interactions, thus leading to weakly or poorly structured systems.

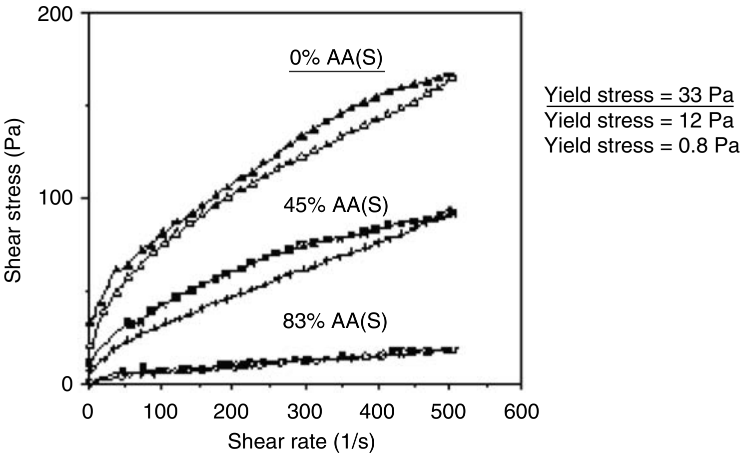


FIGURE 9.8 The flow curves of 28% emulsions with various levels of soft tallow amidoamine AA(S) in the amidoamine fraction. (From Farooq, A., Cesar, R. and Deville, F., U.S. Patent 5501806, Colgate-Palmolive Company, 1996; Farooq, A., Mehreteab, A., Mastrull, J., Cesar, R. and Broze, G., *Concentrated and Efficient Fabric Softeners*, *Specialty Surfactants*, Marcel Dekker, New York, 2001.)

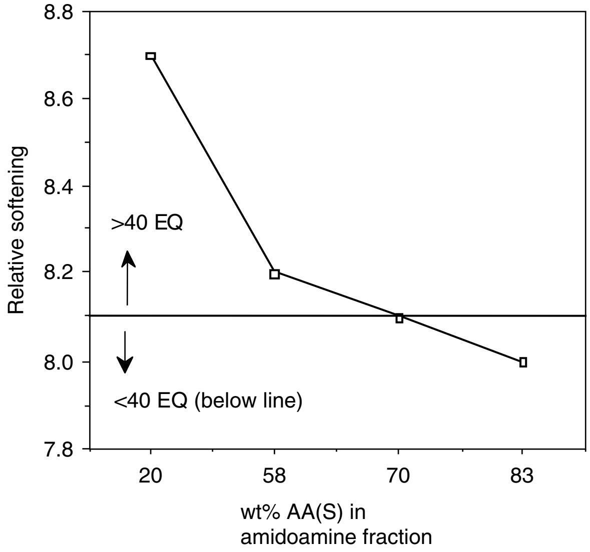


FIGURE 9.9 The effect of unsaturation on the softening of compositions (Figure 9.7) (8 times diluted samples, softening by DTDMAC (5% dispersion) gives a value of 8.1. (From Farooq, A., Cesar, R. and Deville, F., U.S. Patent 5501806, Colgate-Palmolive Company, 1996; Farooq, A., Mehreteab, A., Mastrull, J., Cesar, R. and Broze, G., *Concentrated and Efficient Fabric Softeners*, *Specialty Surfactants*, Marcel Dekker, New York, 2001.)

For oil-in-water emulsions, more structuring is induced probably due to more lamellar phase volume, where a higher amount of water is trapped inside the vesicles. Higher phase volume would result in higher viscosity. Unsaturation seems to lower the lamellar phase volume, thus breaking the structure. A microscopic study of the concentrated dispersions indeed revealed a decrease in the dispersed phase volume with an increase in the content of AA(S) [75].

Softening depends on the concentration of AA(S) (Figure 9.9) [18,75].

As expected, the softening decreases with the increase in the concentration of the unsaturated amine. To maintain low viscosity and have product activity of at least 40 EQ, it is preferred to limit the amount of soft tallow amidoamine (in the amidoamine content) to no more than ~70% and no less than ~50%.

The preparation of DEQ is well known in the patent art. The reaction of about two equivalents of fatty acid (or fatty acid methyl ester) with one mole of triethanolamine (followed by quaternization by dimethyl sulfate) results in a mixture of mono-, di-, and triesteramines quaternary ammonium salts. U.S. Patent 5750492 and U.S. Patent application 2002/0025915A exemplify that by adjusting the reaction conditions (molar ratio of fatty acid fraction to tertiary amine, temperature, ratio of cis to trans isomer in the unsaturated fatty group) to limit the amount of triesterquat content, liquid softener concentrates with as high as 22–28% actives can be produced. Some other useful examples of liquid concentrates can be found in patents U.S. 545340 and U.S. 5574179.

9.7 ADDED BENEFIT DELIVERY

Fabric Conditioners have been found to be an effective delivery system for benefits in addition to their primary function of improved fabric feel and reduction in buildup of static charge. Achieving additional fabric care benefits through use of a fabric softener requires the formulator to include sufficient chemistry to at least document the added benefit by an accepted test methodology. Acceptable product stability must also be maintained with an added cost that is not prohibitive.

Color care benefits are one example of added benefit. Fading of dark colors, particularly black or blue, has been achieved by use of a chlorine scavenger such as amine and its salts. Chlorine use by many municipal water systems to disinfect water causes a slow fading that is highly noticeable on dark color fabrics. Reduction in transfer of dyes from one fabric to another was claimed to be reduced by use of polyvinylpyrrolidone and poly (4 vinylpyridine *N*-oxide) in fabric conditioners [77]. Polycationic condensates have been claimed to prevent dye transfer and reduce dye release [78]. Chelants such as ethylene diamine tetraacetic acid have been claimed to prevent hue shifts in fabric dyes caused by heavy metal ion impurities (Fe^{3+} and Cu^{2+}) in water [76].

Although cationic fabric conditioning agents confer some wrinkle reduction and ease of ironing benefit themselves, additional actives may be added to enhance performance. Polyorganosiloxanes formulated into a fabric conditioner have been claimed to deliver reduction of micro creases on cotton polyester fabrics [79]. Ease of ironing and antiwrinkling were claimed based on incorporating into a fabric conditioner polymeric or glass water-insoluble particles with size in the range of 1–50 μm [80]. Also described as deliverable from a cationic softener–containing formulation are a combination of a polycarboxylic acid or derivative and a thermoplastic elastomer such as poly(styrene-butadiene-styrene) [81]. The system is claimed to deliver fabric elasticity and shape retention benefits.

Fabric rinse compositions containing a UV absorber based on hydroxyaryl-1,3,5-triazine have been claimed to increase the ultraviolet protection factor (UPF) rating of treated garments to provide added protection to skin covered by the garment from UV components of sunlight [82].

The commercial product Downy Plus Whitening has been launched, containing a hueing dye and an optical brightener to address the yellowing of white fabrics that occurs over many wear and wash cycles [83].

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10 Industrial and Institutional Cleaners

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CONTENTS

10.1 INTRODUCTION

Industrial and Institutional (I&I) cleaners constitute the second largest cleaning products category after household detergents. A brief description of I&I cleaners will delineate the topic in general and help understand in particular the diverse I&I cleaning world. I&I cleaning can be associated with any cleaning task that is done outside the residential home environment. Simply put, I&I cleaning can be described as any cleaning process that occurs in places such as hotels, restaurants, schools, office complexes, hospitals, slaughtering houses, meat/poultry processing plants, dairy parlors, dairy and food processing plants, workshops, machine plants, and car washes. The I&I cleaning tasks as shown in Table 10.1 may include laundering, ware washing, pot and pan cleaning, food-processing plant cleaning, floor cleaning, hand washing, metal cleaning, truck washing, or cleaning of food preparation equipment.

I&I cleaners are quite different and distinct from household cleaning products in formulation, product strength, product dispensing, and end usage, because I&I soils and substrates are different. Most I&I cleaning products are made with specific soils and substrates in mind, and a wide array of such soils and substrates are encountered in I&I settings. It involves much more than just converting a consumer product by making it stronger for an I&I application. I&I formulations are developed and optimized differently than the consumer products, and they are basically dictated by customers' specific needs. In general, I&I cleaners are more aggressive and more alkaline than the household and consumer products, because of short and aggressive wash cycles and high throughput. Workers in I&I settings routinely receive operational training on how to safely use I&I cleaning products. Typically, I&I cleaners are contained in closed containers for easy, automated dispensing that saves labor cost and prevents accidental spillage for safety. I&I cleaners are usually

TABLE 10.1
Some Typical Cleaning Tasks Performed in Industrial and Institutional Environments

Cleaning Categories	I&I Settings	I&I Establishments
Ware-washing detergents	Institutional	Cafeterias, restaurants, bars, hotels, hospitals, schools, nursing homes, etc.
Laundry detergents	Institutional	Hospitals, nursing and retirement homes, hotels and motels, cafeterias, commercial laundries, restaurants, bars, daycare centers, uniform rental places, etc.
Manual dishwashing detergents	Institutional	Quick service restaurants, regular restaurants, cafeterias, daycare centers, etc.
Janitorial cleaners	Industrial and institutional	Floor cleaning, general-purpose cleaning, window cleaning, odor control, bathroom cleaning, regular cleaning and maintenance in all I&I establishments
Transportation cleaners	Industrial	Trucks, buses, fleet cars, tank cars, airplanes, railroad cars, boats, etc.
Food process cleaners disinfectants/sanitizers	Industrial and institutional	Meat/poultry slaughtering houses, meat and food processing plants, beverage plants, grocery stores, food service establishments, etc.
Metal treatments and cleaners	Industrial	Metal surface preparation, coating, residue removal, paint removal, etc.
Hand cleaners	Industrial and institutional	Hospitals, food service and food processing/preparation industries, healthcare institutions, restaurants, daycare centers, etc.
General cleaners and sanitizers	Industrial and institutional	CIP cleaners for food-processing plants, beverage plants, breweries, dairy parlors, and teat dip applications for dairy animals

concentrated and require on-site dilution, whereas consumer products are made ready to use or require little or no dilution. I&I cleaners are distinct, contrasting in substrates, soils, and situations when compared to household cleaning products. For example, in a household setting, dust, mud, and soot are typical soils that are removed from carpet floor, as compared to ink, paint, grease, and hydrocarbon soils, which are scrubbed or extracted from what is usually a heavy-duty carpet in a commercial building. Home dish wares may be washed by hand or automatic dishwasher to remove light to moderate soils.

Likewise, restaurant wares are both hand and machine-washed, but soils may be harder-to-remove polymerized fats, greases, starchy dough, and the like. Much hotter water and much shorter wash time are normal in manual and ware wash. For a household floor, for example, a light mopping using mild cleaner is needed, but a shop floor must be scrubbed with stronger detergent and vacuumed up with a scrubbing machine. However, some similarities still exist in household and I&I cleanings, such as bathroom cleaning, window cleaning, and hand washing. Many I&I cleaners are similar to household types, with notable exceptions in that phosphate builders are still widely used in many I&I applications, and a wider range of surfactants are employed. For example, a high performance, liquid I&I cleaner may contain ~5 to 10% nonylphenol ethoxylate (NPE; there is now a trend to remove this particular surfactant for environmental concerns), sodium metasilicate (Metso), sodium tripolyphosphate (STPP) or sodium ethylenediaminetetraacetate (EDTA-Na_4), and sodium xylenesulfonate (SXS). The active ingredients may represent as high as 30–50% of the formula. An industrial-strength liquid hard surface cleaner may contain ~6 to 12% nonylphenol ethoxylate, 5–10% glycol ether solvent, some builder materials, and sodium silicate. Window cleaners may be formulated with ~1 to 5% of the alcohol ethoxylate (AE); glycol ether and isopropyl alcohol solvents may go as high as 30–50%. Typical household cleaning products are formulated with considerable less chemical strength because soil load is usually light and substrates are often pretreated, scrubbed and prewashed.

Some chemical ingredients that are widely used in consumer products are also found in I&I cleaners; however, some raw materials that are widely used in I&I cleaners are seldom found in the consumers products. In spite of their use in both cleaning worlds, the functions and performances of these ingredients are quite different. For example, the high concentration of alkalinity delivered from alkaline silicates or alkaline caustic sources are vital to many I&I cleaners, but consumer products may contain only moderate amounts of caustic elements, or silicates may be used more for corrosion protection. Sodium tripolyphosphate, a workhorse detergent ingredient, is much regulated in consumer products, but it is still widely used in I&I cleaners, and the level may be up to 30–40%. Zeolite A, frequently used in household products as a non-phosphate replacement, has yet to find a niche in I&I cleaners. Nonphosphate-based cleaners have not yet penetrated the I&I market as extensively as the consumer market. Sodium carbonate (soda ash) is widely used in both categories as a builder, a buffering agent, and a source of moderate alkalinity. Surfactants present in I&I cleaners such as laundry products or ware-washing detergents serve more as auxiliary agents, because the high alkalinity, high temperature, or high concentration of bleaching agents does most of the cleaning. Consumer laundry products, for example, are formulated with high surfactant concentration compared to I&I laundry detergents. Surfactants present in I&I products often provide functionality other than primary detergency. I&I cleaners consume ~10% of total surfactant tonnage produced in the United States and Europe. The workhorse surfactants that are widely used in I&I cleaners are linear alkylbenzene sulfonates (LASs), AEs, and alkylphenol ethoxylates (e.g., NPEs); the latter is not widely used in consumer products, however. These three major surfactants combined account for more than half of the surfactant tonnage used in I&I products.

I&I cleaners have some differences of their own. The major differences are in the three cleaning aspects: soils, substrates, and situations or environments. Industrial soils are generally more difficult to remove, because they are more hydrophobic in nature and more tightly bound. Industrial cleaning occurs in places such as manufacturing plant sites, fabricating operations, machine shops, metal treating or finishing operations, and printing shops, to name a few.

Institutional cleaning, on the other hand, occurs within offices, schools, restaurants, hospitals, and other commercial buildings. The soils found in the institutional settings are considerably lighter and less tenacious than in the industrial establishments. Industrial and institutional cleaners are also distinctly different in formulations and distinct in their use patterns, but both are always grouped together. They share similar definitions in that they are in the same market channel, that is different from the household or retail consumer market. The cleaning products that are supplied for both I&I markets have similarities in packaging and labeling, but they are distinctly different from household consumer products.

10.1.1 Industrial and Institutional Cleaners Market Trend

The I&I cleaners market is growing at a faster pace than the household category. Often I&I cleaners provide the leading edge technology for tomorrow's cleaning products and stay active ahead of the consumer cleaning products. Historically, the first mechanical washing machine was made for commercial use, and fluorescent whitening agents were used in I&I detergents long before they became part of consumer laundry products. The future growth of the I&I cleaners market is strong, and the growth is partly dictated by the customers' needs and demands for highly effective, multifunctional cleaners. A robust economy and an aging population are providing a boost to the I&I cleaners market. Consumers are spending more on leisure activities such as dining out and traveling more, because of their increased disposable income. As a result, the hospitality industry, including I&I food service and laundering business, is enjoying stronger growth. Older and retiring generations are choosing community retirement living, and vacationers including business travelers due to their international and domestic business expansions are traveling more; these new activities and incremental business are boosting the hospitality industry by increasing hotel and restaurant occupancy.

According to Kline & Co., Fairfield, NJ, which was published in HAPPI recently, U.S. sales of I&I cleaning products are approaching $9.5 billion and account for a healthy portion of global I&I sales of $22 billion [1]. Taking a closer look at the U.S. market segments: janitorial, $3.1 billion; industrial, $2.6 billon; food service, $1.8 billion; food processing, $1.15 billion; and laundry, $850 million. Growth has been steady and moderate. Food service has recorded robust growth because so much of the food dollar is being spent away from home. In February 2007, Kline published the fourth edition of Food Processing Cleaning Products USA [1]. The study examines 10 key end-use segments of the U.S. market, including dairy, meat and poultry, and beverage processing, as well as baking and retail food sanitation. Kline also rolled out the third edition of its Janitorial and Housekeeping Cleaning Products study. It provides a complete qualitative and quantitative analysis of janitorial and housekeeping product categories and end-use markets, industry dynamics and key trends. It includes data on all distribution channels, including industrial facilities and office buildings, hospitals, lodging establishments, nursing homes, schools, recreational facilities, fast-food restaurants, full-service restaurants, colleges and universities, and government facilities. The National Restaurant Association (NRA) estimates that sales from the country's 925,000 restaurants will top $511 billion this year, a gain of 5.1%. At the same time, the Travel Industry Association of America (TIA) expects U.S. travel expenditures to reach $683 billion this year, an increase of ~5%. TIA also notes that travel and tourism generate $1.3 trillion in economic activity every year. All these statistics underscore the health of the food and hospitality industries. Other sectors, such as healthcare, appear to be gaining at a 3% rate, according to sources.

10.1.2 Industrial and Institutional Cleaners: Past Market

Historically, the I&I market has had a steady growth curve. In 1996, people made 1.2 billion trips of 100 miles or more; this had been up from 1.17 billion such trips in 1995 [2], and it surpassed the TIA projection of industry growth from \$492 billion in 1997 to \$600 billion in 2000. Growth in production of durable and nondurable goods as manufactured items has also pushed toward greater demands for detergents in food service and other cleaning areas. The restaurants industry has been growing 4–5% annually with more than \$320 billion 1996 sales, which equaled ~43% of American dollars spent on food [3]. The top 10 quick-service restaurant chains in the United States accounted for about \$53.4 billion in 1996 sales [3]. The combined sales of I&I cleaners in the United States, Europe, and Japan reached \$12 billion in 1995 with United States commanding ~40% of the worldwide I&I market. It surpassed the \$14 billion projection in the year 2000 by SRI Consulting of Menlo Park, CA [3,4]. Freedonia Group Analyst of Cleveland, OH, through a past study, projected nearly a 5% growth in U.S. sales of I&I cleaners, reaching over \$7–8 billion by the year 2000 [5]. The U.S. I&I market reached over \$6 billion in 1998, according to the past study in Janitorial and Housekeeping Cleaning Products per Kline & Co. of Fairfield, NJ [4]. I&I cleaning products accounted for about one-third of the \$18 billion market of all U.S. cleaning chemicals.

Freedonia Group International estimated private companies' business in cleaning products growth of 3.5% annually through 2001, reaching \$21.8 billion, with gains in the I&I market outpacing the household category [4]. The growth was boosted by demands within several key end-use markets, including food and food service industries, hospitals, retirement communities, and healthcare service [4].

The janitorial market for I&I cleaners experienced the most rapid growth through 2000, according to a Freedonia study [5]. In the United States, janitorial products commanded the largest share of the \$6 billion I&I cleaning products market, accounting for over 45% [4]. Kline & Co. estimated the 1998 janitorial and housekeeping sector as nearly 38% of the total, at \$2.3 billion for the United States, as shown in Table 10.2 [4]. By product category, general I&I Cleaners projected growth of 4% a year to \$2.08 billion by 2000, floor care products growth of 4.7% annually to \$1.46 billion, and ware-washing detergents growth of 4.6% a year to \$815 million. Commercial laundry detergents were about half the size of the I&I ware-washing products market. The remaining I&I cleaners market was increased by 5.4% annually to nearly \$2.9 billion. I&I cleaners market expansion in the Asia-Pacific region and Latin America, with <20% of the I&I market, and also in other new territories helped further boost the growth. A comparative I&I cleaners market breakdown for 1993 and 2000 sales are given in Table 10.3 [6]. Kline and Company estimated U.S. sales of food processing cleaners for 1994 to be \$634 million, as shown in Table 10.4 [7]. Freedonia Analysts forecasted in a 1997 April study of detergent additives that I&I detergents tonnage would rise 1.9% annually to reach 2.6 billion pounds in 2001, as shown in Table 10.5 [4]. Freedonia expected I&I cleaning product demands in the United States to rise to \$7.6 billion by 2001. Although general all-purpose

TABLE 10.2
1998 U.S. Sales Estimate of Janitorial/Housekeeping Products

Products Categories	1998 Estimated Sales (Million \$)
Floor cleaners	800
Hard surface cleaners	775
Hand soaps	400
Carpet cleaners	175
Odor control	125
All others	75

Source: Adapted from Krawczyk, T., *INFORM*, 9(4), 274–291, 1998.

TABLE 10.3
U.S. 1992 & 2000 I&I Cleaner Market Share Comparisons

Products Categories	1992 Sales (Million $)	2000 Sales (Million $)	Annual Growth (%)
Alkaline cleaners	520	740	8.4
General-purpose cleaners	305	455	4.8
Ware-washing detergents and rinse-aids	425	695	6.8
Laundry detergents and bleaches	255	405	5.3

Source: Adapted from Carson, H. C., *Household and Personal Products Industry (HAAPI)*, 29(12), 28–48, 1992.

TABLE 10.4
1994 Sales of U.S. Food-Processing Cleaners

Food-Processing Cleaners	1994 Sales (Million $)
Alkaline cleaners and detergents	282
Disinfectants and sanitizers	96
Acid cleaners and detergents	68
Conveyor lubricants	37
Caustic soda cleaners	31
Teat dips	47
All others	74

Source: Adapted from Branna, T., *Household and Personal Products Industry (HAPPI)*, 31(11), 62, 1994.

TABLE 10.5
United States 1996 & 2001 I&I Detergents Volume

Products Categories	1996 Sales (Million Pounds)	2001 Estimated (Million Pounds)
I&I cleaners	2320	2550
Laundry detergents	1300	1440
Powder products	810	910
Liquid products	490	530
Dishwashing detergents	1020	1110

Source: Adapted from Krawczyk, T., *INFORM*, 9(4), 274–291, 1998.

cleaners and floor care products are the current leaders in sales, sanitizers and hand cleaners are projected to have the greatest growth rates through the next decade based on rising concerns over infectious diseases [4]. Demands for disinfectants and antimicrobial agents in the industrial markets rose 3.95% annually to 122 million pounds, with a price tag of $399 million for the year 2001 per a Freedonia prediction [4].

Many segments of the I&I Cleaners market will see rapid growth because of a healthy, buoyant economy, due to rapid new construction growth (8% annually), increased traveling, more food consumption and dining out, and use of long-term healthcare service by the aging population. There will be continuing demands for multifunctional, cost-effective, and efficient cleaners that will all the future I&I cleaners market to thrive. In general, the future is healthy for the I&I cleaners market. Expansion of the healthcare industry and long-term care facilities due to an increasingly aging population will provide a bigger boost for I&I cleaners. As the hospitality industry grows, the support industry will see similar growth, and this trend will help the I&I cleaners market with an annual growth of nearly 5% [2]. Although the I&I cleaners business is prospering, consumers are displaying more concerns about potential bacterial contamination of food, in particular food-borne pathogens in the food-processing and services industry. Thus, the I&I market is creating demands for more efficient disinfecting products.

This chapter on I&I Cleaners will briefly describe the formulations and compositions of the major product categories, such as manual dishwashing detergents; ware-washing detergents; liquid hand cleaners; laundry detergents; janitorial cleaners, including floor cleaners; all-purpose hard surface cleaners; glass and bathroom cleaners; degreasers, including heavy-duty degreasers; disinfectants; and sanitizers. Some specialty products, such as transportation cleaners, hard surface cleaners, oven cleaners, toilet bowl cleaners, drain cleaners, clean-in-place (CIP) products for cleaning food-processing plants and equipment, and products for treating dairy animals such as teat dips will also be included. Various aspects of detergent formulation, chemical ingredients used in the formulations, products criteria, and test methods will also be addressed, including some examples of typical formulations in each category.

10.2 MANUAL DISHWASHING DETERGENTS/ALL-PURPOSE DETERGENTS

Manual dishwashing detergents, also known as light-duty detergents (LDD) in household consumer products, are primarily used for hand washing of dishes, pots and pans, cooking utensils, serving wares, and any other cooking and kitchen items that are not generally washed in ware-washing machines. They are also used in all-purpose cleaning, in general degreasing such as cleaning tables, doors, windows, and the like. I&I cleaning products, unlike household hand dishwashing products, are generally made concentrated with high active surfactants, and are commonly dispensed through a metering device such as a sink-proportioner. The sink-proportioner dispenses detergent mixed with hot water at a desired preset use concentration. Dispensing tips with varied-openings are available and can be mounted onto the sink-proportioner to dispense detergent at preset use concentration. Since the dispensed amounts depend on the flow property of the liquid product, the product's viscosity plays an important role in controlling the dispensed amounts of detergent through the sink-proportioner. Although the liquid form of manual dishwashing detergent or light-duty liquid (LDL) is predominant and is generally preferred because of convenience, ease of dispensing, and use, the solid form is also available. Typically, the solid detergents, made either in solid block or paste, are highly concentrated and are virtually free of water. For dosing, hot water is injected onto the detergent block and the resulting detergent solution at a desired concentration is dispensed through a metering device. Ecolab Inc. has pioneered solid detergent block technology and perfected it over many years. Several reviews on light-duty liquid detergents and dishwashing detergents have appeared recently [8,9].

The major performance attributes of LDL that formulators strive to optimize within the cost and performance guideline include high foaming, excellent grease cutting, mildness to skin and environmentally benign products or raw materials. Two end points are generally considered and measured when evaluating the efficacy of manual dishwashing detergent. The first involves the end point at which the foam disappears in the wash liquor, and is considered a very important sensory signal to users. The second end point is that at which the nonemulsified grease or fatty soil starts to deposit on the washed items or floats on the wash liquor. Foam volume is also a very important characteristic of manual dishwashing detergents; higher foaming products generally equate with customer's perception of higher cleaning efficacy [10]. Both end points signal the users that it is time to recharge the detergent. Several important characteristics of manual dishwashing detergent should be considered during evaluation: foaming behavior and foam stability, foam stability in the presence of fatty soil, soil dispersing and emulsifying capacity, skin compatibility, and environmental impact. I&I manual dishwashing detergents available on the market today vary widely in choice of surfactants, surfactants concentration, viscosity, and aesthetic. Generally, I&I cleaners are highly concentrated in surfactants or ultra type formulations. Manual dishwashing cleaners composition consists of a primary surfactant that provides the cleaning performance and foaming properties, the two most important attributes of dishwashing detergent. Secondary surfactants are required in the composition to provide enhanced cleaning such as grease cutting and lowering irritation potential of primary surfactants, helping to improve mildness, and boosting and stabilizing foam properties. Typical dishwashing compositions may contain ~10 to 60% surfactants, foam or performance boosters, 0–10% hydrotropes, 0–10% viscosity regulators (e.g., electrolytes, salts), up to 3% other minor ingredients such as preservatives, dyes, and fragrances; water makes up the remainder. Although anionic, nonionic, and amphoteric or zwitterionic surfactants are widely used, the anionic surfactants are most commonly used and form the active base of the formulation. In typical dishwashing formulations, at least binary surfactants are required, and quite commonly a ternary system is used. In some cases, a quaternary system is needed.

Commercial dishwashing compositions typically comprise one or more of the following anionic surfactants, including some of the preferred primary surfactants: LAS, paraffin sulfonate (PS) or secondary alkane sulfonate (SAS), fatty alcohol sulfate (FAS), α-olefin sulfate (AOS), and alcohol ether sulfate (AES). LAS, AES, and SAS are predominantly used. The use of FAS has been decreased over time due to higher cost, lower solubility, higher skin irritation, lower performance, and instability at lower pH (<5.5). LAS with a C_{11}–C_{12} alkyl chain possesses the optimum dishwashing efficacy. LAS acid is more suitable, because of its flexibility of neutralization with desired counter-ions such as Na, K, Mg, NH_4, or other amines. The C_{13}–C_{18} alkyl chain length of alkane sulfonate is preferred. For ultra-type formula, alkane sulfonate is preferred over LAS because of favorable solubility with other surfactants. The best alkyl chain length of AOS is C_{14}. Fatty AES with C_{12}–C_{14} alkyl chain length and 2–3 moles of ethoxylation provides the maximum dishwashing performance. AES is preferentially used in formulation because it provides high foam and oil emulsifying power. AES with a 1:1 ratio of C_{12} and C_{14} alkyl chain and 3 moles of ethoxylation provides the optimum performance and skin compatibility. A 4:1 ratio of LAS:AES is an optimal binary surfactant mixture for dishwashing detergent. FASs are strongly absorbed on the skin and cause the most severe skin irritation. LAS and alkane sulfonate possess moderate skin irritation, whereas AES possesses high skin compatibility and low water hardness sensitivity.

In addition to the primary surfactants, some secondary surfactants are used in LDL as foam boosters to enhance foam properties. Typical surfactants include alkanolamides, amine oxides, or other amine- or nitrogen-based surfactant compounds. Their main function is to increase the amounts of initial foam and then to stabilize the foam in the presence of various soils typically encountered in I&I dishwashing. Nonionic surfactants (NIs) are also commonly used as secondary surfactants to enhance the performance of the primary surfactant. Some NIs widely used are alkyl polyglucoside (APG), alcohol ethoxylate, and fatty-acid glucoamide. APG with an alkyl chain length of C_{12}–C_{14} is preferred for manual dishwashing detergent [11]. Typical average degree of polymerization is ~1.4 of glucose units in APG. APGs provide a number of interesting properties: synergistic performance interactions with anionic surfactants, good foaming behavior, low skin irritation potential, excellent ecological and toxicological properties, derived from natural, renewable sources. APGs show pronounced synergisms with the three primary surfactants LAS, SAS, and FAS. These synergisms are far more pronounced than those observed with fatty AES [11]. α-Sulfomethyl ester (SME), an anionic surfactant, is also used as secondary surfactant. SMEs are sodium salts of α-Sulfo methyl esters of coconut fatty acids and have alkyl chain length distribution of C_{12}–C_{18} atoms with an average carbon length of 13.6. Outstanding foaming synergy exists between SME and sodium AES-3EO [12]. The foam height of SME has been increased by almost 30% by synergism with sodium laureth-3- sulfate [12]. Combination of SME with other anionic, nonionic, or amphoteric surfactants is formulated in LDL products [13,14]. Amphoteric surfactants provide a further boost in cleaning and foaming, including mildness. Amphoteric surfactants, such as cocoamidopropyl betaine and glycine-based coco or lauroamphoacetate, are particularly useful, but their use is limited in formulations because of higher cost. Foam stabilizers such as fatty alkanolamides (e.g., cocamide diethanolamine, lauric/myristic monoethanolamine), and amine oxides, such as dimethyl alkyl amine oxide, are commonly used. Recently, a study conducted on diethanolamine or its alkanolamide derivatives showed some carcinogenic properties on laboratory animals, and there are some growing concerns about using these materials in any cleaning products. Hydrotrope or coupling agent is used to help solubilize incompatible surfactants and stabilize phase. This is a particularly important in I&I applications, where a high active surfactant system is desired and is typically formulated as such. Although hydrotropes provide several key benefits to dishwashing formulations, they do not contribute in the performance of detergency. SXS, sodium cumene sulfonate, urea, ethanol, and SME are widely used as hydrotropes. Propylene glycol and other alcohols are also used. Concentration of hydrotropes used in the formula often dictates the product's clarity, physical stability, and viscosity. Minor ingredients used as preservatives are formaldehyde, glutaraldehyde, isothiazolones, benzoic acid, and hydroxy benzoic acid. Chelators such as EDTA-Na_4, hydroxy ethylenediaminetetraacetate (HEDTA-Na_4), and sodium citrate, are widely used. Viscosity modifiers such as NaCl, KCl, NH_4Cl, Na_2SO_4, $(NH_4)_2SO_4$, urea, and Mg salts are used to control viscosity of the product. Dyes and fragrances are used as desired to enhance aesthetic of the product. Special ingredients are used to meet the particular needs. For example, preservatives and antimicrobial agents are widely used. 2,4,4′-Trichloro-2′-hydroxy-diphenyl ether (Triclosan), 4-chloro-3,5-dimethylphenol (*p*-chloro-*m*-xylenol, PCMX), glutaraldehyde, Dowicil™, and the like are widely used. The incorporation of alkaline earth metals such as Mg and Ca tends to greatly reduce the surface tension at the critical micelle concentration (CMC) of anionic surfactant [15]. Along with lowering of CMC and increasing the micelle size, Mg ions introduced as either a counter-ion of surfactant or as an inorganic salt such as $MgCl_2 \cdot 6H_2O$ significantly reduce CMC and increase the micelle size compared to Na salt, and therefore can absorb or emulsify more oil [15]. A combination of anionic surfactant with Mg salt enhances the cleaning performance, especially in emulsifying greasy and fatty soils. The use of Mg salt of anionic surfactant (made by neutralization of sulfonic acid with MgO) is preferred over adding Mg^{2+} ions as counter-ions to an alkali salt of a surfactant. Water hardness ions such as Mg^{2+} and Ca^{2+} generally increase the cleaning performance in dishwashing process. Although divalent ions are recommended for inclusion in LDL formulations, their solubilization is sometimes difficult and can cause some anionic surfactant to be salted-out from the product. Combination of several major surfactants often performs better in hard water than in soft water. Institutional soils, especially in the food service industry, are primarily fatty, greasy, or oily, including protein, carbohydrate, and their polymerized or carbonized matrix, and this requires special formulation chemistry to address the problem soils. A general formulation guideline for conventional and concentrated manual dishwashing detergents is given in Table 10.6.

In the food service industry, the recommended procedure for manual dishwashing is typically a three-step process involving washing, rinsing, and sanitizing; all are done separately in a standard three-sink operation. Pots and pans, dish wares, or utensils are prescrapped promptly and thoroughly washed with a brush or plastic scrapper, preferably with a hot water prerinse sprayer; otherwise, a heavy accumulation of food soils can quickly contaminate and deplete the cleaning power of solution. The scrapped utensils or items are placed into the first sink containing detergent that is dispensed with hot water at 100–120°F at a desired preset concentration with a sink-proportioner. Utensil and dishware are presoaked and the entire surface of the items is scrubbed using a scrub or a plastic scouring pad (nylon or polyester). The scrubbed items are immersed in the wash solution momentarily to rinse off any gross soils. The utensils are removed from the wash solution, held inverted over the wash sink to allow the excess wash solution to drain off, and then placed in the second or intermediate sink for rinse. The intermediate rinse

TABLE 10.6
Formulations Guideline for Manual Dishwashing Detergents

Ingredient Categories	Name of Ingredients	Concentration (wt%)
Anionic surfactants	Linear alkylbenzene sulfonate, secondary alkanesulfonate, alkylsulfate, alkyl ether sulfate	10–40
Nonionic surfactants	Fatty acid glucoamide, fatty acid alkanolamide, alkyl polyglucoside alkyldimethylamine oxide, alkylpolyethylene glycol ether	<20
Amphoteric surfactants	Alkyl betaine, alkylamido betaine, alkylamphoacetate	<10
Minor ingredients	Emollients, proteins, polymers	<5
Hydrotropes	Aromatic sulfonates, some anionic surfactants or other additives	<15
Preservatives	Aldehyde, polyaldehyde, EDTA-Na_4, paraban/other well-known compounds	<1
Fragrances	Choice	<1
Salts thickener	Electrolytes (NaCl, Na_2SO_4, etc.)	<2
Colorants	Choice	<0.1
Solvents/diluents	Water, glycols and alkylene glycols	q.s.

sink contains hot water (100–120°F). The washed items are rinsed thoroughly and removed from the intermediate sink, drained momentarily inverted over the rinse sink, and then immersed in the final sanitizing sink for sanitation. Sanitation is usually done with either very hot water at 180°F or hypochlorite bleaches having 50–200 ppm of available chlorine at 90–100°F. Quaternary ammonium salts or another approved sanitizer solution may also be used. After 2 min of soaking in the sanitizing rinse, washed items are removed and allowed to dry in air on a dish rack without hand wiping.

Various test methods are used to evaluate the efficacy of dishwashing detergent. There is not a single test method available that is universally accepted for the performance evaluation of manual dishwashing detergents. Numerous test methods developed by the soap and surfactants manufacturers exist in the literature, and none is perfect. Surfactant and soap manufacturers modify the existing test methods and use one or many tests to satisfy their needs. Some test methods that are typically used for performance evaluation are listed in Ref. 16. Gravimetric evaluation methods (cup test, grease removal test, and static soaking test) measure the percent of soil (usually fats/oils) removed from a substrate in a specific test condition [17–19]. Turbidity measurement (emulsion stability test, cup test) involves measuring turbidity using a light source and measures the product's emulsification of grease [20, 21]. The dishwashing test method (plate count) measures the actual dishwashing process and is a very time-consuming test [22]. Foam performance tests that measure foam volume and foam stability are widely used. Some test methods that involve foam disappearing end point are: ASTM Test Method D1173-53 [23] (Ross-Miles Foam Test), Foam-Stability Test Methods such as Soil Titration Method [24], Terg-o-Tometer, Piston Plunger Test, and ASTM Test Method D4009-92 [25]. The dishwashing foam end point test, miniature dishwashing test (Mini-Plates test) [26], soil pellet test, and modified Schlachter–Dierkes cylinder foam test [27] are also used. Initial foam with a known detergent concentration is generated and soil is added gradually until foam is collapsed to determine the end point. The Baumgartner grease removal method is also used to measure the amount of grease removed.

Although dishwashing detergents are primarily intended for washing dishes, pots & pans, they are also used for other cleaning tasks. General cleaning of light soils from tables; countertops, doors, windows, and equipment are very common. The general formulations guideline for manual dishwashing detergents is shown in Table 10.6. Some formulation examples of liquid dishwashing detergent are shown in Tables 10.7 through 10.13 [28,29].

Fragrance and color are added to products, and the choice depends on a product's positioning and intended market. In addition to liquid manual dishwashing detergents, so-called solid blocks are also available in the American I&I market. Solid block and paste products are similarly formulated by making a very concentrated formulation with very little or no water. Sometimes a process-binding agents, such as high-molecular weight polyethylene glycol, urea, and other compatible agents, are necessary, and high-active solid ingredients are chosen to eliminate the excess water. Use of a very concentrated formula is very common in I&I cleaning category, because it can reduce the shipping cost and the packaging cost, and save storage space. Dosages of solid products are usually dispensed through a metering devise by predissolving the solid with a hot water jet at a desired preset detergent concentration, and are carried into the dishwashing liquor. For solid blocks, processing, hardness,

TABLE 10.7
Regular Dishwashing Detergent Using Sulfomethyl Easter (SME)

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)	IV Concentration (wt%)
Magnesium LAS	19.44	19.44	19.44	—
Sodium LAS	—	—	—	19.44
NH_4 laureth-4-sulfate	10.34	—	3.22	3.22
α-Sulfomethyl ester	—	10.34	7.12	7.12
Laura-myristamide monoethanolamine	4.05	4.05	4.05	4.05
Ethanol	5	5	5	5
Water	q.s.	q.s.	q.s.	q.s.
pH	6.8	6.8	6.8	6.8
# Mini plates washed	48	45	51	42

Source: Adapted from Sajic, B., Ryklin, I., Frank, B, and Rao, B. K., U.S. Patent 5616781, Stepan Company, 1997; Sajic, B., Ryklin, I., Frank, B, and Rao, B. K., U.S. Patent 5637558, Stepan Company, 1997.

TABLE 10.8
Antibacterial Dishwashing Detergent Using Alkyl Polyglucoside (APG)

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sodium lauryl sulfate	18	27	—
Alkyl polyglucoside	4	6	6
Cocoamide diethanolamine	—	—	6
Sodium laureth-2-sulfate	—	—	30
Cocoamidopropyl betaine	3	3	3
Antibacterial agent: Triclosan or PCMX	0–1.0	0–1.0	0–1.0
Ucarcide 250 preservative	0.1	0.1	0.1
Sodium chloride (viscosity regulator)	0–3	0–3	0–3
Water	q.s.	q.s.	q.s.
pH (Adjustment with citric acid)	6.5 ± 0.2	6.5 ± 0.2	6.5 ± 0.2

TABLE 10.9
Regular Dishwashing Detergent Using Sulfomethyl Ester (SME)

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)	IV Concentration (wt%)
α-Sulfomethyl ester	7.12	7.12	7.12	9.56
Magnesium LAS	19.44	—	19.44	—
LAS acid	—	—	—	28.56
MgO	—	—	—	2.20
Sodium LAS	—	19.44	—	—
NH_4 laureth-4-sulfate	3.22	3.22	3.22	4.38
Laura-myristamide monoethanolamine	4.05	4.05	—	3.3
Cocoamidopropyl betaine	—	—	4.05	—
$MgSO_4 \cdot 6H_2O$	—	3.0	—	—
Ethanol	5	5	5	5
Water	q.s.	q.s.	q.s.	q.s.
# Mini plates washed	51	45	48	>57

Source: Adapted from Sajic, B., Ryklin, I., and Frank, B., *Household and Personal Products Industry (HAAPI)*, 35(4), 94–100, 1998.

TABLE 10.10
Regular Dishwashing Detergent Using Alkyl Polyglucoside (APG)

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sodium LAS/DDBSA-Na	24.0	—	—
Alkyl polyglucoside-Glucopon 625	6.0	7.2	10.0
Alkanolamide-cocamide diethanolamine	3.0	3.0	6.0
Betaine-cocoamidopropyl betaine	3.2	—	—
Fatty alcohol ethoxylate	8.0	6.0	—
Fatty acid amidopropylamine oxide	—	3.0	—
Alcohol ethersulfate-Na laureth (EO 2/3) sulfate	—	28.0	30.0
Sodium xylenesulfonate	6.0	—	—
Ethanol	—	6.0	8.0
Preservative	0.1	0.1	0.1
Sodium chloride/sodium sulfate	—	5.0	—
Water	q.s.	q.s.	q.s.

Source: Adapted from Andree, H., Hessel, J. F., Kings, P., Meine, G., Middelhauve, B., and Schmid, K., in *Alkyl Polyglycosides Technology, Properties and Applications*, VCH Publishers, New York, 1997, 98–130.

and dissolving behavior are very important. The hardness of the blocks can be controlled by the ratio of fatty acid monoethanolamide to fatty acid diethanolamide.

Ultra or super concentrated liquid detergent for washing heavily soiled dishes such as restaurant utensils, pots and pans, and dish wares can also be developed [30,31]. The super concentrated liquid detergent composition is based on a primary surfactant, and is comprised of alkali metal,

TABLE 10.11
Solid Block Dishwashing Detergent Using Alkyl Polyglucoside (APG)

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sodium LAS/(DDBSA-Na)	13.2	13.2	13.2
Alkyl polyglucoside (Glucopon 625)	4.0	4.0	4.0
Fatty acid monoalkanolamide (cocamide monoethanolamine)	10.0	—	5.0
Fatty acid dialkanolamide (cocamide diethanolamine)	—	10.0	5.0
Betaine (cocoamidopropyl betaine)	6.0	6.0	6.0
Alcohol ethersulfate (Na laureth-2/3-sulfate)	12.0	12.0	12.0
Fatty acid	6.0	6.0	6.0
Nonylphenol ethoxylate	4.5	4.5	4.5
Ethanol	3.0	3.0	3.0
Urea	20.0	20.0	20.0
Sodium chloride/sodium sulfate	—	—	6
Sodium hydroxide	0.75	0.75	0.75
Water (from raw materials)	Balance	Balance	Balance

Source: Adapted from Andree, H., Hessel, J. F., Kings, P., Meine, G., Middelhauve, B., and Schmid, K., in *Alkyl Polyglycosides Technology, Properties and Applications*, VCH Publishers, New York, 1997, 98–130.

TABLE 10.12
High-Foaming Dishwashing Detergent Using Alkyl Ethoxylated Alcohol

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Ethoxylated alcohol: C_{9-11} alkyl 8 EO	12–16	—	15–20
Ethoxylated alcohol: C_9 alkyl 6 EO	—	15–24	—
Sodium/NH_4-lauryl sulfate	5–8	5–8	5–8
Cocoamidopropyl betaine	3–6	3–6	3–6
Alkanolamide-cocamide diethanolamine or lauramide/myristamide monoethanolamine	3–6	3–6	3–6
Ethyl alcohol	4–8	4–8	4–8
Sodium xylenesulfonate	5–8	5–8	5–8
Water	q.s.	q.s.	q.s.

TABLE 10.13
Liquid Dishwashing Detergent Using Fatty Acid Glucoamide

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Ethoxylated alcohol: C_{12-14} alkyl 8 EO	16	—
Alcohol ether sulfate	—	15
Fatty acid glucoamide	8	10
Alkylamine oxide	—	4
Betaine	2	3
Ethoxylated alcohol: C_{9-11} alkyl 8 EO	8	4
Magnesium ion source	0.25	0.25

Source: Adapted from Dyet, J. A. and Foley, P. R., International Patent WO 92/06171, Procter & Gamble Co., 1992; Rolfes, R. T., International Patent WO 92/06156, Procter & Gamble Co., 1992.

alkaline earth metal, amine or ammonium salts of LAS, α-olefin sulfonate, alkyl sulfate, and alkyl ether sulfate, whereas the secondary surfactant system is comprised of APG and SME, in a weight ratio of primary to secondary surfactant of at least 3:1 as shown in Tables 10.14 and 10.15. The grease-cutting efficacy of detergent has been boasted by a mixture of Na and Mg salts of LAS with a mole ratio of 1:3 to 3:1 [30,31].

TABLE 10.14
Super Concentrated Liquid Detergents

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Mg Dodecylbenzenesulfonate (Biosoft Mg 50, from Stepan)	44	39
Lauramide/myristamide monoethanolamine (Stepan Ninol NMP)	4	4
Alkyl polyglucoside (Glucopon 625 FE)	13.75	16.25
AES-2EO (Texapon NC 70)	8	8
Ethanol (SDA 3A)	5	5
Water	25.25	27.75
Foam height (mL)	440	425
Pellet suds end point	15/17	16/16

Source: Adapted from Ahmed, F. U., U.S. Patent Application 2003/0092594 A1, Kay Chemical Co. (Ecolab), 2003; Ahmed, F.U., U.S. Patent 6759382 B2, Kay Chemical Co. (Ecolab), 2004.

TABLE 10.15
Super Concentrated Liquid Detergents

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Dodecylbenzenesulfonic Acid (Biosoft S-100, from Stepan)	25	25	25.16
Magnesium oxide	1	0.8	1.61
Sodium hydroxide (50%)	2.32	3.15	—
Lauramide/myristamide monoethanolamine (Stepan Ninol NMP)	4	4	4
Alkyl polyglucoside (Glucopon 625 FE)	15	15	15
α-Sulfomethyl ester (α-Step Me 48)	—	—	17
AES-2EO (Texapon NC 70)	4	6	6
Ethanol (SDA 3A)	5	3	5
Sodium xylenesulfonate (40%)	—	5	—
Water	43.68	38.05	41.23
Foam height (mL)	475	600	535
Pellet suds end point	17/16	16/17	16/17

Source: Adapted from Ahmed, F. U., U.S. Patent Application 2003/0092594 A1, Kay Chemical Co. (Ecolab), 2003; Ahmed, F. U., U.S. Patent 6759382 B2, Kay Chemical Co. (Ecolab), 2004.

10.3 WARE-WASHING (MECHANICAL DISHWASHING) DETERGENTS

Ware-washing process would require several different cleaners: washing detergents for main wash, rinse-aids for removing film and spots from glassware and aid in drying, and presoak detergents for removing protein soils from silverware and flatware.

10.3.1 Ware-Washing Detergents

Ware-washing or mechanical dishwasher detergent is one of the largest segments of the I&I cleaners business, and its popularity is increasing also in the household category. I&I ware-washing detergents grew 1.7% annually to reach 1.1 billion pounds in 2001 according to Freedonia. For ware-washing expenses, labor accounts for roughly 40–45% of the total cost, energy costs are ~25 to 30%, water consumption contributes 20%, and the detergents and other cleaning chemicals make up the remaining 5–6% [4]. Machine dishwashing, whether done in private homes or in an institutional setting, simplifies the workload, and saves time and labor. The ware washing segment will see growing demand driven by the ever-increasing labor cost of manual dishwashing and the trend of continued dining out by people away from home. The ware washing process also includes some pots and pan manual dishwashing with detergents that resemble consumer products. The majority of dishes, tumblers, drinking glassware, and silverware used in restaurants and cafeterias is washed in ware-washing machines. Based on different applications, the dishwashing machines are classified as household dishwashers and institutional dishwashers, otherwise known as ware-washing machines. The construction and washing action mechanism of the two kinds of machines are substantially different.

Household dishwashers contain only one tank in which the whole dishwashing process goes through several short wash cycles of different functions, and for each wash cycle, fresh water is supplied. Food residues coming off from the substrate are dispersed by water in the prewash are removed, and do not affect the main wash cycle, where alkaline detergent is added. Typically, all washing programs consist of a prewash (rinse), a main wash with detergent, at least one rinse after the main wash, and a drying cycle. Detergent is generally dispersed in the main wash, and rinse-aid is normally added in the final rinse cycle that follows the main cycle. Finally, drying cycles, in which the cleaned articles are dried, complete the wash. An excellent review on household consumer liquid automatic dishwasher detergent has been published [32].

In I&I ware washing, typical wash cycles are very short; they may go up to 1–3 min, compared to up to 30 min for household automatic dishwashers. This allows the institutional establishments to operate more efficiently with a smaller inventory of dishware. Since wash cycles are very short (30–45 s), hotter wash temperature is needed in ware wash cleaning. Sanitation and detergent formulations are typically stronger and far more alkaline than the household products, to compensate for the short wash cycles. Builder and alkalinity levels are much higher than the household products. The higher wash temperature also helps cleaning. A rule of thumb is that for every 10°C increase in temperature, the chemical reaction in a particular cleaning application can double; the higher the wash temperature is, the better is the cleaning. By increasing the chemical and thermal energy in the ware wash and shortening wash time, labor and money are saved.

Institutional dishwashers are manufactured either as a single-tank or as multiple-tanks systems, and as low-temperature or high-temperature wash machines. Ware-washing machines like household dishwashers are spray-washing machines and are available with many variations and levels of sophistication, but all operate under the same basic principle: directing a high-pressure or high-volume spray onto the substrates that need to be cleaned. The detergent solution is sprayed through the nozzles onto the soiled articles. These nozzles are installed on rotating spray arms. A detergent cleaning solution is pumped from a wash tank through spray nozzles onto the wares to be cleaned, falls back to the tank and is recirculated through the spray system. A spray-rinse removes detergent residues and soils from the washed items. In some machines, there is a power rinse that is pumped from a rinse tank similar to the wash tank, followed by a final high-temperature (180°F) or chemical sanitizing rinse. In other machines, a single final rinse serves both wash and rinse functions.

A single-tank door-type machine may have a door on the front or on both sides of the machine. A rack of dishes is placed in the machine, where it may remain stationary or be moved back and forth during wash and rinse cycles. The wash cycle is initiated either manually or automatically. Detergent solution is pumped from the wash tank through spray nozzles that can also be either stationary or rotating, above and below the dish rack. The wash cycle is followed by a hot water spray rinse. A conveyor, which moves dish racks through the machine, distinguishes conveyor type machines. In a single-tank conveyor machine, hot detergent solution is pumped through fixed or rotating spray arms, spray boxes, or slotted pipes with nozzles located above or below the dish racks in the machine. Like the door-type machine, rinse is usually done at line pressure, and most of the rinse water goes into the wash tank.

A single-tank machine system differs from a home dishwasher in that it utilizes only one cleaning solution. The wash solution is not completely removed after the wash cycle, but is slowly diluted by the water flowing from the final rinse. Thus, no total water replacement takes place from wash cycle to wash cycle. This also means that the wash solution not only contains cleaning products, but also rinse-aid that was added during the previous final rinse cycle.

In an institutional multiple-tanks machine system, several tanks (prewash, main wash, and an intermittent rinse cycle) and a final rinse zone are connected with each other. A two-tank washing machine has both a wash tank and a rinse tank. A recirculated power rinse from the rinse tank precedes the final rinse. A three-tank machine is similar to the two-tank machine, with a prewash tank for removing gross soils. The flow of water is opposite to the path in which the wash articles pass through the machine. In other words, water flows from the final rinse zone toward the overflow in the prewash tank, where it drains from the dishwasher [9]. In institutional dishwashers, the articles are moved, and the spray elements are installed in a fixed position. Unlike the home dishwashers, the cleaning detergent and rinse-aid are intermixed during the washing cycle, and could affect each other's performance during the washing. Institutional dishwashers generally operate at much higher temperature, and the complete wash cycle is very short, typically less than 2 min.

A carousal-type or merry-go-round machine is a closed-circuit conveyor multitank machine. These machines may move racks on the conveyor; they may have built-in racks, or they may be flight-type machines. A flight-type machine is a multitank machine with a conveyor designed with pegs or bars to hold dishes for washing, making dish racking unnecessary. Glasses, cups, bowls, and silverware still must be racked for handling. Flight-type machines have a strike bar that turns off the conveyor if dishes or racks are not removed from the conveyor at the clean end of the machine.

Single-tank institutional machines are commercially available in both low- and high-temperature operations. In conventional high-temperature machines, the prewash temperature is moderately warm, 80–110°F. The purpose of this spray is to remove gross food soil. If the water is too cold, it will have a tendency to congeal grease, which will then be washed off in the wash tank, causing excess soil buildup. If water is too warm, it may have a tendency to bake some soils, such as dairy products. The wash temperature is generally between 140 and 160°F, depending on the make and model of the machine. Temperature in this range softens soils and melts grease so that they can be removed easily. The power rinse flushes the wash solution away. Temperature is generally maintained at 170–180°F to raise the temperature of the dishes to sanitizing temperature. The final rinse temperature is very high, 180–190°F, to provide a thermal sanitizing effect and fast air-drying at this elevated temperature. High-temperature machines usually operate at much higher temperature in wash and rinse cycles; therefore, they do not require chlorine bleach sanitation, as the high temperature provides the sanitation.

Low-temperature washing machines, on the other hand, operate at ~140°F in both wash and rinse cycles and require chlorine bleach sanitation. The National Sanitation Foundation (NSF) and most health codes define low-temperature ware washing as a wash cycle using 120–140°F water, followed by a chlorine sanitizing rinse also at 120–140°F. Although requirements vary, most localities require rinse water to contain 50–100 ppm of chlorine bleach for adequate sanitizing in low-temperature machines. Low-temperature ware washing saves considerable energy and usually eliminates the necessity for either an exhaust system or a booster heater, which further reduces equipment and operating cost. There are three basic types of low-temperature ware-washing machines [33]. The batch-type machine is a door type, timed cycle machine that can be either single- or double-rack units. All operate in a similar manner. After the wash cycle, the machine drains and then fills with rinse water, sanitizer, and rinse-aid, and then recirculates for rinsing. Rinse water that remains in the tank serves as wash solution for the next load. At the start of the wash cycle, detergent is dispensed, and the wash solution is sprayed over the dishes. Both wash and rinse solutions use the same pump and water distribution system. The complete wash and rinse cycle typically requires 90 s. The major difference between a batch-type machine and a door-type machine is that it uses a separate water pump and distributing system for wash and rinse, similar to conventional high-temperature machines. The wash water is diluted with fresh water from a rinse water holding tank and reused from cycle to cycle. In a low-temperature rack conveyor or flight machine, the wash tank is diluted by a final rinse bypass or by overflow of the final rinse tank. The rinse water can be circulated with a constant fresh water dilution or can be pumped from a fresh water holding tank, as in door-type recirculating machines.

Typically, wash cycle is <1 min (40–45 s) and is followed by a very short rinse cycle (<20 s). Ware-washing detergent, rinse-aid, and chlorine bleach sanitizer are dispensed directly onto the wash water in the machine through a metering pump during the wash and rinse cycles. The wash tank heater maintains the wash temperature at 150°F, whereas the booster heater will raise the temperature of the final rinse water to a minimum of 180°F. Delimers and descalers, which are typically acidic compounds such as citric acid or phosphoric acid, are used to remove hard water scale by dissolving the lime stone and calcium salts of cleaning solutions from the machine. Unlike the U.S. home dishwashers, the institutional dishwashers have stainless steel construction. Institutional dishwashers operation is fully automatic; when the dishwasher door opens or closes, the wash cycle begins, with automatic dispensing and controlling of detergent concentration. The subsequent automatic rinse cycle will sanitize the washed articles and dispense rinse-aid into fresh water final rinse.

Ware-washing detergents are available in liquid, solid block, powder, and gel or slurry form, and are generally dispensed automatically in the wash cycle. Conventional I&I spray-washing machines employ liquid or powder detergents that are generally added to the wash tank by means of an automatic dispensing system. All forms of such detergents, whether liquid or solid, must be very highly alkaline to be effective against I&I soils. High-performance products usually contain a very high concentration of hazardous sodium hydroxide, which poses safety problems in handling such a liquid product. However, a solid block or cast ware-washing product contained in a closed container is much safer. For example, Ecolab's ware-washing solid block detergent is made, packaged, and dispensed from a closed container for safe handling. After connected to the proprietary dispensing system, it is diluted with water for use as a liquid product. Regardless of the detergent form, the ware-washing machine measures the conductivity of the wash bath and dispenses detergent as needed. The ware-washing market is currently split, with ~50% of the detergent being liquid products; solid block and powdered products make up the rest. Powder or solid block detergent is predissolved with hot water, which is injected into the solid detergent, and the concentration of detergent dispensed into the machine is determined by a conductance probe. Into the wash cycle, a pump-dispenser can introduce liquids or slurry/gels that are already predissolved into the machine. Similarly, rinse-aids are available in both solid and liquid form, and can be dispensed by a similar mechanism. Overall cleaning in ware-washing machines is accomplished by a combination of three types of energy: mechanical, chemical, and thermal. There is also a fourth factor—wash cycle time—that determines the cleaning ability in a dishwashing machine. Soil removal is a function of water temperature, scrubbing action of the spray, time, and chemical action. The mechanical energy is provided by the kinetic energy of the pressurized water through the rotating spray arm nozzles. As the wash liquor is pumped through the spray arms, the water jets sprayed from the rotor arms help to dislodge soils from dishware or other articles. Increasing kinetic energy by either more water or higher pressure results in more soil removal from the substrates. Thermal energy, which contributes a great deal in cleaning performance, is provided by hot water. This is particularly important and critical in I&I dishwashers, considering that wash cycles are very short, which translates to a very short contact time between the detergent and soils/substrates. In institutional dishwashers, wash and rinse temperature is substantially higher than in home dishwashers, and is provided by a booster heater in the wash tank. High temperature helps the chemical hydrolysis and then subsequent removal of soils, specially the fatty soils from the substrates. The chemical energy in cleaning performance is provided by detergent chemistry. Like thermal energy, this is particularly important in institutional dishwashers, which have a very short wash cycle. Many types of soil are encountered in ware washing, and heat, age, and dryness add to the complexity of soils and make them attach more tenaciously to the substrates. Typical food soils consist of proteinaceous, starchy, and fatty soils, and oxidizable colored stains. Dishwasher detergent chemistry is formulated in such way that all potential soil types are denatured and degraded at least partially by the chemical and thermal energy to a point where they can be removed and washed away. A combination of all three types of energy play a synergistic action by complementing each other in removing soil from the wares and prevent them from redeposition. Further, rinse-aid and sanitizing agents help remove residual soil, eliminate spots and films, and increase the drying efficiency by repelling water from the washed wares by what is known as a sheeting action.

Ware-washing detergent chemistry in I&I applications is quite different from those of household dishwasher detergent because of the nature of the ware-washing process, machine configuration, and wash condition. Since the contact time between the soils and detergent solution in an individual tank is very short, a stronger and more aggressive chemical formulation is required than in the household dishwasher detergent, to compensate for the short wash time. Unlike the household dishwashing detergent, ware-washing detergents are very concentrated and highly alkaline formulated, with high concentration of caustic soda and phosphate builder. As mentioned before, I&I ware-washing detergents are available in liquid, solid, and slurry/gel form. However, solid and concentrated slurry forms are preferred. Basically, detergent functional materials are very similar to household products; however, certain exceptional and specialty ingredients are used in both product lines. Unlike the household dishwasher detergents, the major workhorse component is alkalinity, which is generally provided by alkali hydroxides or occasionally by metasilicates in ware-washing detergent. Typical ware-washing compositions and their functional materials are listed in a general formulation guide shown in Table 10.16**.** Thickener, bleach, and water are product-specific optional reagents. Silicate may also be an optional item.

Builder materials perform several essential functions in ware-washing detergent cleaning. Builders can provide high and rapid sequestration of water hardness ions Ca^{2+}/Mg^{2+} in the wash liquor, making the detergents work efficiently. They act as buffering and dispersing agents, suspending soils, preventing redeposition, and helping overall cleaning by contributing to alkalinity and emulsification of soils. The presence of Ca^{2+} and Mg^{2+} ions in the wash solution can lead to undesirable spotting, filming, and streaking on the washed items. The hard water metal ions form insoluble complexes with soils, surfactants, and other detergent materials and hamper the washing efficiency. Some common builders widely used in ware-washing detergent formulation are alkali metal (Na/K) salts of tripolyphosphates (TPPs), carbonates, citrates, polyacrylates, nitrilotriacetates (NTAs), copolymers of polyacrylate/maleate, silicates, and zeolites. Sodium TPP (STPP) is a multifunctional cleaning agent. Besides its efficient sequestration ability of hardness ions, sodium TPP works to disperse and suspend soils, enhances the surface activity of surfactants, solubilizes protein soils, and provides alkalinity and buffering action. TPP builders can provide the best detergency and are predominantly used in about all cleaning products. However, there are environmental concerns of using STPP, which causes eutrophication in lakes and leads to algae growth from wash water affluent. Silicates are also multifunctional builders like TPP and additionally provide corrosion protection. A combination of TPP and silicates is generally used and preferred in

TABLE 10.16
Ware-Washing Detergent Formulation Guide

Components	Functions	Concentrations (wt%)
Builder	Sequestration, soil suspension, alkalinity, emulsification, soil peptization (deflocculation)	10–20
Caustic alkali	Alkalinity, soil hydrolysis, soil removal	10–50
Surfactant	Wetting agent, soil removal, spot/film prevention, sheeting action, soil dispersion, drying aid	0–3
Silicate (optional)	Anticorrosion, alkalinity, soil hydrolysis, soil removal sequestration, machine and fine china glaze protection	0–20
Bleach (optional)	Soil removal, stain removal, sanitation, disinfection	0–3
Defoamer (optional)	Foam prevention, wash efficiency	0–1
Thickener (optional) for liquid/slurry product	Product stability, aesthetic enhancement, binder	0–2
Color, perfume	Aesthetic enhancement	<0.5
Water (optional)	Solvent, carrier, flow property	Balance

home dishwasher detergent, but its use is very limited in ware-washing detergent. Soluble silicates with varied SiO_2/Na_2O ratio are available, but 1:1 and 2:1 ratios are commonly used in detergent formulation. Zeolites are aluminosilicates, are insoluble in water, and work with water hardness by an ion-exchange mechanism. Particularly zeolite A is used in nonphosphate detergent formulation. Carbonates are not used as primary builder and are not very effective. It works with water hardness ions by a precipitation mechanism, and tends to deposit the insoluble $CaCO_3$ on washed items particularly in a hard water environment. Citrate is also used as a nonphosphate builder, but it is incompatible with NaOCl bleach. Low-molecular weight polycarboxylates, particularly polyacrylates, copolymers of acrylate/maleate, are also used as secondary builder. These polymers, in addition to sequestration of water hardness ions, prevent and reduce crystal growth of calcium precipitate. NTA is a superior builder, but its toxicity profile prevents its widespread use.

Surfactants are a minor ingredient in mechanical dishwashers and are used in low concentration compared to manual dishwasher detergent, where such a combination of high surfactant concentration provides the total cleaning performance: foaming, grease cutting, soil removal, and soil emulsification. In ware wash, grease and soil removal is accomplished by high alkalinity and bleaching agents. Surfactants also provide sheeting action on items, preventing soils from redeposition and then appearing as spots, films, and streaks. Ideally, a nonfoaming or very low-foaming NI is preferred in ware-washing detergent, but in chlorine bleach containing liquid or slurry products, it becomes incompatible with bleach. However, in powder or solid block, it is widely used. In liquid formulation, bleach-stable anionic surfactants such as alkyldiphenyletherdisulfonates (e.g., Dowfax™) or nonfoaming tertiary amine oxides are used. Foam generated from protein soils, as well as from surfactant, decreases the water pressure, reduces the spray arm rotor speed, and ultimately lowers the cleaning efficiency. Foaming contribution from surfactant can be avoided by selecting a very low or nonfoaming NI. Typical NIs include polyethylene glycol ethers, fatty acid alkanolamide, amine oxides, and preferably EO/PO block polymeric surfactants. To prevent foaming, bleach-stable defoaming agents like alkyl phosphate esters, polysiloxane, silicone oil, and ethoxylated esters are commonly used.

Bleach or oxidizing agents are commonly used in the formulation to remove oxidizable food stains from sources such as coffee, tea, cocoa, wine, and colored fruits and vegetables, and proteinaceous soils such as milk, eggs, meats, and gravy. In addition, bleach disinfects and sanitizes the washing machine and washed items. Sodium hypochlorite (NaOCl) bleach or its precursor materials, such as sodium dichloroisocyanurate, chloramine T, chloramine B, LiOCl, and $Ca(OCl)_2$, which generate the bleach species (OCl^-) in alkaline solution, are used. NaOCl bleach also reacts with some detergent ingredients, such as enzymes, citrates, and nonionic surfactants, and is avoided when formulating with these materials. Oxygen bleaching compounds that generate the hydroperoxide species OOH^- in alkaline solution, such as perborate, percarbonate, and persulfate, are also used, but they are very ineffective at low wash temperature (120–140°F). Peracids [R(C=O)OOH], often generated by activation of carboxylic acids by peroxide, are also used. Chlorine bleach is effective against tannins in coffee or tea stains and colored chromophores of fruits and vegetables. However, iron present in water or detergent in combination with coffee or tea makes the stain more tenacious and more difficult to remove.

Enzymes such as soil-specific protease (proteinaceous soils), α-amylase (carbohydrates), and lipase (fatty/greasy soils) are suitable, but because of their instability in the presence of chlorine bleach, their uses have been very limited in ware-washing detergents.

Thickeners are used to make liquid gel or slurry ware-washing formulations [34–36] as structure builders. Thixotropic or viscoelastic ware-washing detergents use specific thickeners. They are water-swelling, high-molecular weight cross-linked polyacrylates (e.g., Carbopol™), clays such as bentonite or laponite, colloidal alumina, or silica and fatty acid, or their salts are used in liquid formulations. Thickeners are especially used in liquid household dishwasher detergent for ease of dispensing and cup retention, so that detergent does not run out of the cup before the main wash. In ware washing, the detergent is directly dispensed into the wash liquor in the wash cycle, and as such it is not required to formulate under this constraint.

Fragrance and color can be added to products based on market positioning. Ware-washing detergents are commercially available in solid powder, solid block, liquid, and liquid gel or slurry. A solid ware-washing detergent can be made in a ready-to-use plastic container by heating 55 parts of liquid NaOH (50%) at 130–140°F, and then mixed with solid NaOH [37,38]. The mixture is stirred until all solid NaOH is dissolved and then 36 parts of anhydrous sodium TPP is added and mixed until all sodium TPP is homogeneously mixed but not dissolved. The mixing is continued without heating for 10–15 min or until the mixture begins to harden, but is still in a fluid state. The mixture is then poured into a receptacle-shaped mold containing a slightly tapered cylindrical plastic container and allowed to harden, which takes ~5 min.

Some formulation examples of ware-washing detergents are shown in Tables 10.17 through 10.22 [39,40].

TABLE 10.17
Low-Alkaline/Low-Viscosity Liquid Ware-Washing Detergent

Ingredients	Phosphate Concentration (wt%)	Nonphosphate Concentration (wt%)
Sodium tripolyphosphate	10–15	—
Sodium citrate	—	15–20
Sodium (potassium) hydroxide	8–12	4–6
Potassium carbonate	—	25–30
Sodium polyacrylate	2–5	8–15
Surfactant	1	1
Potassium silicate	1	3
Water	q.s.	q.s.
pH	13.5	13.5

TABLE 10.18
High-Alkaline Ware-Washing Block Detergent

Ingredients	Phosphate Concentration (wt%)	Nonphosphate Concentration (wt%)
Water	3–10	8–15
Sodium hydroxide (50%)	7–20	7–20
Sodium polyacrylate (50%)	8–20	2–6
Phosphino polycarboxylate	—	3
Dequest™ 2010	—	4
Nonionic surfactant	1.5–3	1.5–3
Sodium hydroxide bead	40–45	40–45
Sodium sulfate	5–10	5–10
Sodium chloride	3–6	3–6
Sodium tripolyphosphate	30–45	—
Phosphate ester defoamer	0.2	0.2
Solid chlorine bleach source	7.5	7.5

Source: Adapted from Lentsch, S. E. and Oakes, T. R., U.S. Patent 4846993, Ecolab Inc, 1989.

TABLE 10.19
Low-Alkaline Liquid Gel/Slurry Formulation

Ingredients	Clay Thickener Concentration (wt%)	Carbopol™ Thickener Concentration (wt%)
Water	q.s.	q.s.
Clay	2	—
Carbopol thickener	—	1
Sodium hydroxide	5–8	5–8
Sodium tripolyphosphate	20–25	20–25
Sodium silicate	6–10	6–10
Sodium polyacrylate (low mol. wt.)	2–5	2–5
Sodium carbonate	5	5
Dowfax 3B2	1	1
NaOCl (13%)	10	10

Source: Adapted from Ahmed, F. U., International/European Patent Application 96/908532, Kay Chemical Co., 1996; Ahmed, F. U., U.S. Patent Application 08/395875, Kay Chemical Co., 1995; Ahmed, F. U., U.S. Patent 5981457, Kay Chemical Co. (Ecolab), 1999.

Performance evaluation of ware-washing detergents is done by a variety of test methods. A multisoil cleaning test is routinely done using a variety of soiled items typically found in restaurants: plates, cutlery, glass tumblers, cups, bowls, silverware, and serving wares. Combinations of soils representing protein; starch; greasy/fatty soils; and stained soils including coffee, tea, colored fruits, and vegetables all are used. Soil removal is visually rated and given a percent soil removal score. Spotting and filming test is done following a standard ASTM D3556 method [41]. Glass tumblers are soiled with homogeneous milk and an extra soil load of margarine and powdered milk is added in the wash cycle. Performance evaluation is done at different water conditions, including up to 300 ppm of water hardness, which is made with 2:1 Ca^{2+}/Mg^{2+} salts. Consecutive wash cycles in hard water are used, and an average cumulative score of four wash cycles on spotting and filming is

TABLE 10.20
High-Alkaline Ware-Washing Gel Composition

Ingredients	Bleach-Free Concentration (wt%)	NaOCl Bleach Concentration (wt%)
Water	q.s.	q.s.
Carbopol™	0.5–1.0	0.5–1.0
Sodium hydroxide (50%)	20	20
Sodium tripolyphosphate	10–20	10–20
Sodium hydroxide (beads)	20–30	20–30
Stearic acid	0–0.5	0–0.5
Sodium polyacrylate (50%)	0–8	0–8
Sodium hyphochlorite (15%)	—	15–20

Source: Adapted from Ahmed, F. U., International/European Patent Application 96/908532, Kay Chemical Co., 1996; Ahmed, F. U., U.S. Patent Application 08/395875, Kay Chemical Co., 1995; Ahmed, F. U., U.S. Patent 5981457, Kay Chemical Co. (Ecolab), 1999.

TABLE 10.21
Solid Block Ware-Washing Detergent

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sodium hydoxide (50%)	55	54	53.5
Sodium hydroxide (solid)	9	9	8.8
Sodium TPP-anhydrous	36	36	35
Defoaming agent	—	1	1
Encapsulated chlorine bleach source $Ca(OCl)_2$ or Na dichloroisocyanurate 59.7%, Veegum WG 14.4%, dendritic NaCl 25.9%	—	—	2.7

Source: Adapted from Fernholz, P. J., Copeland, J. L., and Penttila, R. C., U.S. Patent 4569780, Economics Lab, 1986; Fernholz, P. J., Copeland, J. L., and Penttila, R. C., U.S. Patent 4569781, Economics Lab, 1986.

TABLE 10.22
Low-Temperature Cast Ware-Washing Detergent

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)	IV Concentration (wt%)
Sodium hydroxide (50%)	7	16	12	19
Water	8	—	2	3
Polyacrylic acid	2	10	7	5
Sodium hydroxide bead	45	35	40	38
Sodium chloride	3	3	3	3
Ethoxy alcohol benzyl ether	3	12	9	5
Sodium TPP	32	23	27	26

Source: Adapted from Morganson, S. A., Heile, B. J., and Ashton, K. A., U.S. Patent 5080819, Ecolab Inc, 1992.

given. Foam measurement is done by a CSMA Compendium Method DCC-001 [42], and fine china glaze protection test is done according to ASTM test method D3556-89 [43].

10.3.2 RINSE-AID PRODUCTS

Rinse-aids or additives are used in the final rinse cycle of the dishwashing process. To minimize the deposition of residual water-soluble minerals and surface-active soil components on washed items, particularly on glasses, rinse-aids are routinely used in both household dishwashers and ware-washing machines. Rinse-aid performance agents reduce the interfacial surface tension between the cleaned articles and water during the final rinse cycle, and therefore, achieve a uniform draining film of wash water on items; otherwise uneven wetting results in spotting, filming, and streaking on the items when dried. The term *sheeting action* is often used to describe the action of a rinse additive. Sheeting is the ability of the rinse additive to cause the water droplets to spread out and form an even wet sheet over the surface of the item. The sheet of water then drains off and evaporates uniformly so as to leave no water spot or streak. Rinse-aids properties for I&I wares are different than for household wash. I&I wares are air-dried, whereas at home dishes are usually heat-dried. Rinse-aids provide a sheeting action that decreases drying time. This is important in ware washing when washed wares are dried by air.

Rinse-aid formulations are typically aqueous solutions containing nonfoaming NIs (10–50%), a metal complexing agent (0–30%) to bind the water hardness ions, and hydrotropes or coupling agent as needed. Ware-washing rinse-aids composition also contains a defoaming agent. Propylene oxide/ethylene oxide block polymers, propoxylated and ethoxylated fatty alcohol and its glycol ether, and ethoxylated alcohol are widely used in the rinse-aid formulations. Complexing or sequestering agents like TPP and citric acid are also used. Citric acid is preferred, as it contributes to the brilliancy or shiny appearance on glass surface. Hydrotropes are used to increase solubility of NI in water. Fragrance and color are usually added to product. Fragrance generates pleasant odor on opening the dishwashing machine and is also usually used. Rinse-aids are available in liquid and solid block. Solid block is also packaged like a hanging basket. Some formulation examples of rinse-aids are shown in Table 10.23.

10.3.3 FLATWARE PRESOAK CLEANERS

Flatware presoak products are formulated to loosen and dissolve tough food soil deposits prior to the flatware being washed in the machine. Flatware and cutlery over long usage tend to deposit on their surface a fine mono layer of hazy film of protein and carbohydrate soils, which appear as a distinct bluish hue. This filmy deposit is believed to be starchy and proteinaceous materials. The presoak products also remove silverware tarnishing. Silverware tends to develop brown tarnishing due to air oxidation. When silverware contacts aluminum surfaces while soaking in detergent solution in an aluminum container or aluminum foil-lined plastic container, a reduction-oxidation reaction occurs. Oxide and sulfide tarnishing substances are removed from the silverware by reducing the

TABLE 10.23
Rinse-Aid Formulations

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Ethoxylated/propoxylated fatty alcohol	50	17.5
Ethoxylated/propoxylated fatty alcohol	40	17.5
Isopropyl alcohol	24	12
Citric acid	—	25
Water	q.s.	q.s.

TABLE 10.24
Flatware Presoak Cleaner

Ingredients	Concentration (wt%)
Sodium tripolyphosphate	15–25
Sodium carbonate	20–35
Sodium sulfate	15–25
Nonionic surfactant	3–6
Sodium silicate	5–15
Protease	1–4
α-Amylase	1–4

silverware surface, whereas aluminum surfaces become black by oxidation. In a dishwashing pan lined with aluminum foil, presoak detergent is dissolved in hot water and tarnished silverware or separately stainless steel flatware are added and soaked for 0.5 h. The oxidation-reduction reaction that takes place is very rapid. In ware-washing processes, flatware is typically presoaked in a cleaning solution to remove the filmy soil and also to remove the brown oxidation film from silverware prior to washing in ware-washing machines. Dual enzymes in the presence of alkalinity remove this stubborn film layer of protein and starch and make the surface shiny. Flatware presoak formulations usually contain some builder salt, alkalinity source, NI, and very soil-specific protease and α-amylase enzymes in a solid or powder form.

A typical example of a flatware presoak cleaner is given in Table 10.24.

10.4 LIQUID HAND CLEANERS

In all I&I establishments, all employees are required to wash their hands after using the toilet. Although using warm water removes most bacteria, use of soaps and especially antibacterial soaps ensure bacteria-free hands when they return to work. Liquid hand soaps currently used in I&I establishments are regular hand soap, antimicrobial hand soaps, and hand sanitizer.

10.4.1 Regular Liquid Hand Soaps

The liquid hand soap category in recent years, in the consumer market, has been growing rapidly as evidenced by introduction of a variety of liquid soaps and some with antibacterial efficacy claims. Early users of liquid hand soaps were institutional, hospital, and healthcare establishments. The I&I cleaning market also introduced a variety of liquid hand wash soaps, including the antibacterial varieties. The liquid hand soap provides many advantages, such as ease of use and dispensing with a pump dispenser, avoiding the liquid mushy mess of bar soap. Liquid soap also provides high-quality cleaning; good lather; good skin feel during and after wash; pleasant aesthetic and other sensory attributes such as fragrance, color, and rich and creamy consistency; and above all an inexpensive value-added product. I&I liquid hand soaps are not much different in composition from the household hand soaps, except in their antimicrobial versions. Major differences are usually in packaging and mode of dispensing. General-purpose hand soaps for institutional restrooms might be similar to consumer products, but for food service, food handling, or medical use, antimicrobial soaps having much higher strength or antimicrobial efficacy are needed. I&I liquid hand cleaners are usually packaged in bulk, such as gallon containers, and are mechanically dispensed through a pump dispenser or packaged in a pouch fitted with a dispensing nozzle for easy dispensing through a pump dispenser. Generally, liquid hand soap is fully formulated as ready to use without any dilution. Typically, ~1 to 1.5 mL of liquid soap is dispensed through a pump dispenser by a single stroke and is adequate for normal hand wash with moderately soiled hands. I&I hand soaps are generally used in the kitchen, restrooms, bathrooms, hospitals, hotels, restaurants, and cafeterias. It is mandatory by federal and state laws that all employees are required to wash their hands every time they use the toilet in work places such as hospitals, food preparation and services industries, and child-care centers. Because of inadequate hand washing by workers who prepare, process, or handle food in retail food stores, restaurants, or plants, food-borne illness caused by fecal-oral transfer of microorganisms from workers continues to be a problem. As a result, consumers demand that employees in the food service industry wear gloves when serving or preparing food items. The use of glove by workers in the food industry is perceived to prevent pathogenic microorganism transfer that may remain on the surface of fingernails when individuals do not wash their hands or fingertips at all or wash them inadequately, after using toilet or touching contaminated surfaces, or raw foods. A simple hand-washing program that adequately prevents the transfer of pathogenic microorganisms must be used and removal of transient pathogenic microorganisms from hands and fingertips is assured [44]. Mildness to skin and hands is a very critical requirement for hand soap where hand washing is being required and done frequently as often as 10–40 times for restaurant workers or hospital nurses. An excellent review of liquid hand soap was published [45].

There are several important aspects of hand soap formulation that need to be considered in developing liquid hand soap. Early liquid hand soap formulation used fatty acid soap, which had performance deficiencies, such as inadequate flash foam in hard water and alkaline pH, which tends to irritate skin when compared to synthetic detergent. A good overview of a wide variety of liquid soap compositions is available [46]. Ideal hand soap formulation requires optimization of high flash foam generation, quick and easy rinsing, creamy lather, skin/hand feel, and mildness. The end users gauge the liquid soap by the degree of flash foam and mildness, followed by creamy or silky feel characteristics.

Structurally, liquid hand soap formulation can be broken down into several parts.

- Primary surfactants or deep cleaning agents are used to provide basic cleaning.
- Secondary surfactants or skin mildness agents are added to supplement the primary surfactants and also to lower skin irritation of primary surfactants.
- Skin-conditioning agents or emollients are used to provide skin smoothness and good feel, and to provide moisturizing or refatting effect.
- Physical property regulators control important sensory attributes such as flow property, dispensability, viscosity, and pH.
- Aesthetic contributors in the formulations usually dress up the product with attributes such as colors, fragrances, pearlizing, and opacity.
- Preservatives are used to prevent bacterial growth in the product during production and extended usage, thereby increasing product shelf life.
- Specialty agents are needed for individual product categories such as antimicrobial agents for the antibacterial soap category.

Primary cleaning agents are used in liquid hand soap to provide deep skin cleansing and plenty of lather during washing. Examples of some anionic surfactants used are: alcohol sulfate (sodium lauryl sulfate); olefin sulfate (sodium C_{14}–C_{16} α-olefin sulfonate); LAS (sodium alkylbenzene sulfonate); alkali soap of coco, oleo, tallow or other fatty acids (sodium cocoate); AES with 2–3 degrees of ethoxylation (sodium laureth-3EO sulfate); isethionate (sodium isethionate); and fatty acid isethionate (sodium cocoylisethionate). The most widely used anionic surfactants in hand soap formulations are sodium lauryl sulfate and sodium laurethsulfate. Sodium C_{14}–C_{16} α-olefin sulfonate is also widely used.

Secondary surfactants are used to further boost the performance of primary surfactants. Furthermore, many secondary surfactants lower the skin irritation of the primary surfactants, improve mildness and smooth skin feel, and increase the creamy character of lather when used in conjunction. Examples of some secondary surfactants are betaine amphoterics (cocoamidopropyl betaine), glycine-based amphoterics (cocoamphoacetate or lauroamphoacetate), APG nonionic (Glucopon 625), alkanolamide nonionic (coca or lauramide diethanolamine), and sulfosuccinates (sodium sulfosuccinate). Secondary surfactants are usually used at lower concentration for viscosity-building, flash-foam–enhancing, and foam-stabilizing purposes. Occasionally, a combination several secondary surfactants are used. Skin-conditioning agents and emollients are often used to provide moisturizing effect (humectancy) and soft skin feel (superfatting or refatting agents). Furthermore, they provide lubricity and skin smoothness during washing and rinsing. Examples of some skin conditioning agents are: glycerin, sorbitol, propylene glycol, PEG-7-glyceryl cocoate, stearic acid, polyquaternium-7, hydrolyzed silk peptide and silk protein, aloe vera gel, vitamine E acetate, guar hydroxypropyltrimonium chloride, stearic acid, fatty monoglyceride, glycerylmonostearate, and glycol distearate.

Examples of aesthetic or pearlizing agents that are widely used are stearic acid, glycol stearate, distearate, and styrene/acrylate copolymer. Preservatives are generally used to prevent contamination during manufacturing and prolong extended usage of the product. Glutaraldehyde, methyl paraben, propyl paraben, formaldehyde or its precursors such as DMDH hydantoin, and DMDM hydantoin are commonly used. Other additives such as Na_4-EDTA and Na_3-EDTA that also act as sequestering agents are widely used. Product rheology and viscosity controls a product's physical properties, including flow and dispensing. A product must be sufficiently viscous not to appear runny and stringy. Soaps should be able to dispense easily and disperse quickly into foam with minimum rubbing. Generally, polymeric thickeners such as cellulose, polyacrylates, PEG-120 methyl glucose dioleate, and inorganic electrolyte salts (e.g., NaCl, Na_2SO_4) are widely used to control the viscosity of the product. Typical product viscosity ranges from 300 to 6000 cP, and a thicker hand soap product is preferred. The product pH ranges from neutral range 6.5–7.5 to alkaline range 8.0–9.5. Ideally, the pH of the soap should be in the neutral range (6.5–7.5), matching skin lipid pH and hence making the hand soap skin compatible. Citric acid is typically used to adjust the pH of the product. A wide variety of colors, opacifiers, and pearlizing agents are used in hand soap. A very common color family is gold, amber, or peach, particularly for the antibacterial soap category.

10.4.2 ANTIMICROBIAL LIQUID HAND SOAPS

The importance of proper hand washing by employees in a food service establishment cannot be underestimated. Pathogenic bacteria can be found on the hands after using the restroom, handling raw foods, or touching soiled surfaces. Proper hand washing with effective antimicrobial soap is vital to prevent the transfer of these pathogenic bacteria to cooked food items that will be served to the customers. A field study evaluating the effectiveness of different hand soaps and sanitizers was published [47]. The microflora of the skin is generally grouped into two categories: resident and transient microorganisms [47]. Resident bacteria have been defined as organisms representing particular species that are recovered in >75% of time; whereas the transient bacteria are those that appear <25% of the time in a sampling study over 7 months. The resident group of microflora contains only one commonly accepted food-borne pathogen, *Staphylococcus aureus,* which is believed to be on the skin of ~35% of normal adults. These organisms are usually buried deep within the pores of the skin, where they are protected by fatty secretions of the sebaceous glands and are not easily removed during hand washing. The transient bacterial group represents a major concern for the food service industry, because these organisms are loosely attached to the skin surface and can easily cross-contaminate food products if the employees do not wash their hands adequately. Although transient organisms can be any organisms that the restaurant workers come in contact with, the major bacteria comprising this group are the gram-negative organisms, including *Escherichia coli* and *Salmonella* species. Low levels of *E. coli* and *Salmonella* usually result from contact with raw food products of animal origin, and a high level of contamination usually comes from improper hand washing after using the restroom. Since transient organisms are picked up from the food service environment and are loosely attached to the outer epidermal layer, they can be readily removed during proper hand washing with antibacterial soap.

An effective hand washing program that kills a broad spectrum of bacteria, including both transient and resident microorganisms, should be established and maintained in all related I&I establishments. Washing hands with plain hand soap and water removes the transient bacteria, whereas the resident flora are controlled by the use of antiseptic or sanitizing agents after the application of hand soap. Several varieties of antibacterial hand soap and lotion are available in

TABLE 10.25
USDA Classification of Hand Soaps/Sanitizers for Use in Meat-Processing Plants

E1 Compounds: *Hand Washing Compounds for Use in All Departments*

The compounds must be dispensed from adequate dispensers located at a sufficient distance from processing lines to prevent accidental product contamination. After the use of the compounds, the hands must be thoroughly rinsed with potable water. Under conditions of use, there can be no odor or fragrance left on the hands.

E2 Compounds: *Hand Washing and Sanitizing Compounds*

The compounds must be dispensed from adequate dispensers located at a sufficient distance from processing lines to prevent accidental product contamination. The hands need not be washed prior to use of the compounds. After the use of the compounds, the hands must be thoroughly rinsed with potable water. The compounds must always be used at dilutions and according to applicable directions provided on the label. The compounds have been accepted on the basis of their antibacterial kill equivalency to 50 ppm of chlorine.

E3 Compounds: *Hand Sanitizing Compounds*

The compounds must be dispensed from adequate dispensers located at a sufficient distance from processing lines to prevent accidental product contamination. The hands must be washed and rinsed thoroughly prior to sanitizing with the compounds. The compounds may be injected directly into the wash and rinse water. The hands need not be rinsed with potable water following the use of compound. The compounds must always be used at dilutions and according to applicable directions provided on the label. The compounds have been accepted on the basis of their antibacterial kill equivalency to 50 ppm of chlorine.

E4 Compounds: *Hand Creams, Lotions, and Cleaners*

The use of such compounds is limited to toilets and dressing rooms. Employees who handle edible food products may use the compounds only when leaving the plant.

the I&I segment. The U.S. Department of Agriculture classified liquid hand soaps and sanitizers into various classes for use in employee hand care in the meat & poultry processing industries as shown in Table 10.25 [48]. E classifications of hand soaps and sanitizing compounds apply only to U.S. Department of Agriculture (USDA)-approved meat and poultry processing plants. Currently, there is no such classification for hand-washing products relating to food service establishments; however, they follow the USDA guidelines for hand wash protocol. The medical industry's standard for hand surgical scrubbing further emphasizes the necessity of incorporating sanitizing ingredients into the soap base and the importance of mechanical removal of skin flora. Removing resident and transient bacteria is vital for health care personnel, since nonpathogenic bacteria may become pathogens when introduced into open wounds or in contact with vulnerable sick patients. There are many surgical scrubs available that have different active ingredients, such as alcohols, iodophors, chlorhexidine gluconate or acetate, and others based on polymeric polyhexamethylenebiguanides.

Generally, antimicrobial agents are added to the liquid soap formulations to provide adequate antibacterial property against a wide variety of gram-positive and gram-negative bacteria. It is required by federal and state laws that health care personnel, hotels and restaurant workers, workers in food-manufacturing and service establishments, and day care providers wash their hands very frequently with antibacterial hand soaps.

There are available a wide variety of antimicrobial agents including nonionic chlorophenols and quaternary ammonium compounds (quats). Two of the most effective and widely used bactericides in hand soaps and other hard surface consumer products are Triclosan and PCMX. Triclosan is a nonionic, broad-spectrum antimicrobial agent. Triclosan exhibits a moderate degree of substantivity, and to many products it imparts a remnant antimicrobial effect and produces a sustained reduction in skin, and in the growth, of auxiliary bacteria. Triclosan is milder with greater sustained activity, but is less effective in the immediate reduction of microbial counts than other antimicrobial agents. Triclosan, although being odorless and effective against broad-spectrum bacteria, shows poor kill property against gram-negative bacteria such as Pseudomonas, and it costs almost three times as much PCMX.

PCMX is a highly effective and broad-spectrum antimicrobial agent, and also acts as preservative at a very low concentration. PCMX is not a residual bacteriostat like Triclosan; therefore, it does not give a measure of long-term protection. PCMX leaves a sustained medicinal odor that is not acceptable to many customers. Unlike Triclosan, PCMX is a skin irritant, but it is very effective against gram-negative bacteria, such as Pseudomonas. PCMX is more of a germicidal agent, whereas Triclosan is more of a static material. Both Triclosan and PCMX are not soluble in water and need cosolvent like ethanol or propylene glycol. PCMX is a lower-cost material, making it an ideal candidate for I&I products such as surgical scrubs and E2 hand soap/sanitizer, but it requires a higher concentration to meet the E2 antibacterial standard. 3,4,4′-Trichlorocarbanilide (TCC), like Triclosan, is a nonirritant, substantive, odorless, and very effective antimicrobial agent, but is poor on gram-negative bacteria. Its use as antimicrobial agent is limited only in solid products such as deodorant and bar soap, because of its poor solubility in liquid products. 3,4,4′-Trichloro-*N*-*N*′-diphenyl urea (Trichlocarban) and quaternary salts such as benzalkonium chloride are also used in antibacterial hand soap. Glutaraldehyde (Ucarcide™ 250 Preservative) is a broad-spectrum biocide, and its ability to cross-link primary amines, such as those found in lysine residues in the microbial cell wall, makes it a very effective preservative. This fixative action ultimately prevents a microorganism from carrying on its metabolic functions by limiting the cell permeability, resulting in cell death. Glutaraldehyde or other aldehydic compounds or their precursors are widely used as preservatives.

It requires a high concentration of antibacterial agents in the product to meet the E2 standard for antibacterial kill property, and it is almost cost-prohibitive to incorporate such a high amount of Triclosan. It is very undesirable, on the other hand, to use such a high concentration of PCMX as needed for E2 efficacy, because of its strong sustained odor and skin irritation potential.

There are other antibacterial agents that are well known and widely used in many applications, such as hard surface sanitizations, and topical use applications, such as skin care products including hand soap, hand lotion, and teat dip applications for dairy animals. Iodine-based germicides such as iodophor complex, chlorine dioxide, hydrogen peroxide, peroxy acids, hypochlorite, hypochlorous acid, alkyl fatty acids, dodecylbenzene sulfonic acid (LAS), lactic acid, salicylic acid, methyl salicylate, benzoic acid, benzyl alcohol, lower carbon alkanols, glycolic acid, phosphate, polyhexamethylenebiguanide (PHMB, Ventocil®), chlorhexidine gluconate or acetate, ethylenediaminetetraacetic acid (EDTA), 2-bromo-2-nitropropane-1,3-diol (generates aldehyde in solution, Bronopol), dimethyl hydantoin, dichlorodiethyl hydantoin, and dibromodimethyl hydantoin are well-known germicides and are widely used in many such antibacterial products formulations.

Several *in vivo* and *in vitro* test methods are used to evaluate antimicrobial hand (AMH) soaps for their efficacy as well as skin irritation. Minimum inhibitory concentration (MIC) values of test substances provide growth inhibition of the test organism (based on turbidity) after 48 h of contact. The greater the dilution, the more effective is the test substance. This test is good for individual antimicrobial agents and is not widely used to evaluate completely formulated product. Time kill values are widely used to assess the antibacterial efficacy. Performance is considered standard if the germicide time-kill value is greater than 1 $\log_{10}$ reductions in total bacterial count, expressed as organism/mL, after 1 min of contact. A standard test method for the assessment of the rapid germicidal (time-kill) activity for antibacterial wash products has been proposed to the U.S. Food and Drug Administration (FDA) [49]. Bactericidal activity is measured by the time-kill kinetic method, whereby the killing of bacteria when exposed to an antibacterial agent over time is recorded. A dilution of the test material is brought in contact with a known population of the test bacteria for a specified period of time at a specified temperature. The antibacterial active is neutralized at the end of the test period, and the sample is plated to enumerate the surviving bacteria. The percent reduction from the original population is calculated [50]. A United States FDA tentative final monograph recommends greater than 1 $\log_{10}$ reductions in total bacterial count, to justify a claim of *antimicrobial* efficacy [51]. Currently, antimicrobial hand soaps and sanitizers are generally tested for their available germicidal equivalent concentration with respect to *Staph. aureus* and *Salmonella typhi* following the AOAC standard method [52]. The E2 and E3 compounds are authorized by the USDA based on the 50 ppm of chlorine equivalency antibacterial kill test, a standard *in vitro* test that is widely used in the food industry to assess antibacterial property [52]. An *in vitro* antibacterial efficacy test—per European standard tests such as EN1040-Chemical Disinfectants and Antiseptics (quantitative suspension test for the evaluation of bactericidal activity of chemical disinfectants and antiseptics), EN 1656-Chemical Disinfectants and Antiseptics (quantitative suspension test for the evaluation of bactericidal activity of chemical disinfectants and antiseptics used in veterinary field), and EN 1276-Chemical Disinfectants and Antiseptics (quantitative suspension test for the evaluation of bactericidal activity of chemical disinfectants and antiseptics used in food, industrial, domestic, and institutional areas) [50]— the Glove Juice Technique, employing a panel to evaluate AMH product, is also used [53]. Skin and eye irritation tests are widely used and usually done at an outside laboratory. Draize test [54] and skin patch test are standard and are routinely used to measure the skin irritation potential of the hand soap.

Some formulation examples of liquid hand soap are shown in Tables 10.26 through 10.32. Fragrance and color can be added according to product's marketing positioning. Solid hand soaps

TABLE 10.26
Sanitizing Hand Soap E2 Rated

Ingredients	Concentration (wt%)
Water	83.90
Nutrasol 250 HHR (thickener)	0.5
Cocoamidopropyl betaine	5.5
Cocodimethylamine oxide	3.5
Alcohol etheramide-amidox C-5 (Stepan)	1.6
Benzyltrimethylammoniumchloride (50%)	5.0

TABLE 10.27
Health Care Personnel Hand Wash

Ingredients	Concentration (wt%)
Tripropylene glycol	8
PCMX	3
TEA lauryl sulfate	20
Alkyldimethylamine oxide	3
Water	65
Sodium chloride	q.s. for desired viscosity

TABLE 10.28
Antimicrobial Hand Soap

Ingredients	Concentration (wt%)
Coco/oleic fatty acid	6–12
Monoethanolamine	1–6
Cocamide diethanolamine	0.5–2
Anionic surfactants mixture: (Sodium lauryl sulfate, sodium lauryl ether sulfate and betaine)	1–12
PCMX	0.5–1
Salt, color, fragrance, aesthetic agent	<1

are not typically available expect in the form of a bar soap because of the inconvenience of automatic dispensing.

A very mild and highly efficacious E2-rated antimicrobial hand soap with excellent skin condition has been reported [55], as shown in Table 10.31.

Waterless gel hand sanitizers, which are typically E3 rated, are also available, as shown in Table 10.32. These products are formulated with a high concentration of ethanol, organic

TABLE 10.29
Surgical Scrub Formulation

Ingredients	Concentration (wt%)
Sodium lauryl sulfate	20
Cocodimethylamine oxide	1
Tripropylene glycol	8
Cocamide diethanolamine	1
PCMX	3
Water	65
Sodium chloride	2

TABLE 10.30
E2 Sanitizing Hand Wash

Ingredients	Concentration (wt%)
Triethylene glycol	3.5–8
PCMX	2.5–3
Sodium lauryl sulfate	15–22
Sodium α-olefin sulfonate	0–15
Cocoamidopropyl betaine	1–5
Thickener (Nutrasol 250 HR)	0–1
Water	q.s.

TABLE 10.31
E2 Antibacterial Hand Washing Soap

Ingredients	Concentration (wt%)	Concentration (wt%)
Nipacide PX-R (PCMX)	1	1.20
Irgasan DP-300 (Triclosan)	0.30	0.20
Sodium lauryl sulfate (29%, Standapol WAC)	3	1
Sodium lauryl ether sulfate (60%, Sulfotex NL-60S)	8	10
Cocoamidopropyl betaine (35%, Velvetex BA 35)	3	3
Alkyl polyglucoside (50%, Glucopon 425N)	8	6
EDTA-Na_4 (30%, Hampene 100)	1	1
Polyethylene glycol-7 glycerylcocoate (Cetiol HE)	0.25	—
Glutaraldehyde (50%, Ucarcide™ 250)	0.25	0.25
Polyquaternium 7 (Mackernium 007)	0.25	0.25
Sodium chloride	0.70	0.20
Propylene glycol	1	1.50
Glycerin	—	1
Citric acid (50%)	0.20	0.20
Water	q.s.	q.s.
Color, perfume	Choice	Choice
Viscosity (cP)	1200–1500	1200–1500
pH	6.5–7.0	6.5–7.0

TABLE 10.32
E3 Hand Sanitizer

Ingredients	Concentration (wt%)
Ethyl alcohol	40–70
Carbopol and derivatized cellulose thickener	1–3
Emollients	1–6

polycarboxylic thickener, and some emollient. Ethanol acts as antimicrobial agent, and its activity wears off soon after it evaporates from the hand.

10.5 LAUNDRY DETERGENTS

There are two types of laundry operations that are very common in the I&I segment. Some big establishments such as hotels and hospitals typically have laundry operations done on their premises, whereas smaller outfits can have their laundry operations done off-site and often contracted out.

10.5.1 Institutional Laundry Detergents

Institutional laundry is one of the largest segments in I&I cleaners, such as the ware-washing detergents market. The global I&I laundry market was about $1.6 billion, which was roughly one fourth of the $6.6 billion household laundry market recently [56]. According to Freedonia, I&I laundry detergents segment grew 2.1% annually to reach 1.4 billion pounds in 2001, with powder and solid block products dominating over liquid by a 2:1 ratio. Although commercial laundries predominantly use powdered detergents, a switch over to liquid detergents has been progressing steadily. Historically powder dominant European markets now use more liquid products, which account for more than 60% of the market.

Laundry detergents, often identified as heavy-duty detergents, are generally recommended for nearly all laundry washing processes. Washing machines, washing temperatures, types of soil and soiled fabrics, and other factors determine the widely differing detergent compositions. I&I laundry detergents like ware-washing detergents vary in physical forms and compositions. They very much depend on the type of wash and soil loads. Detergents for I&I and commercial laundries perform fundamentally like household detergents, but differ in many aspects. In I&I laundry, wash cycles are shorter: about 15 min compared to 30 min or more for a household machine. I&I laundry detergent products are more alkaline, and they contain phosphates (which may be as high as 40%), soda ash, silicates, and surfactants. The phosphates are not yet regulated in I&I detergent products. Surfactants are used at lower concentration compared to household laundry detergents. I&I laundering processes are different from the household tasks for various reasons, such as differences in the laundry compositions, the use of softened water, machine types, heating of the washing liquors with steam, automatic and special dosing systems, short washing processes, and bleaching methods. Efficient detergents are formulated tailored to the special needs. All laundry processes are widely different, each having characteristic wash items with characteristic soils.

In a typical industrial laundry, the wash load may consist of severely soiled cleaning rags, mops, floor mats, roll towels, and working uniforms. In contrast, hospital laundries and wash articles may range from lightly soiled bed sheets, pillowcases, towels, protective work clothing, lab coats, and professional uniforms to severely bloodstained operating room clothing. In a commercial laundry, for example, in hotel settings, very lightly soiled wash items such as linens, bed coverings, towels, wash clothes, table covers, and work clothing from restaurants are generally washed.

In regular restaurants or quick service restaurants, wash loads widely vary from work uniforms, table linens, wash clothes, towels, and napkins to heavily soiled items such as greased wipe towels.

These institutional washing machines handle large quantities of laundry every day. It is obvious that the huge laundry operations require conditions assuring economical washing processes. Soft water is usually used in commercial laundry, and it is generated by water ion-exchange column-type water softening systems. In comparison to household detergents, commercial products require, therefore, smaller amounts of water softening or hard water metals complexing agents.

10.5.2 On-Premise Laundering Detergents

Many hospitals, hotels, motels, and restaurants have their own laundering operation. The basic requirement for operating an on-premise laundry (OPL) must justify the economics of owning linens and garments, rather than renting them, buying and maintaining the equipment, and managing a none-core business. Alternatively, establishments that cannot justify an OPL seek industrial laundries that furnish garments, industrial wipes, and dust control items. Linen supply laundries will rent bed items, table linens, towels, pillowcases, and restaurant items as well as garments. Commercial laundries wash and finish linens for institutions, which prefer to own linens but do not want to be in the laundry business.

Hospitals frequently do their own laundries, although there is a trend toward a central laundering system serving several hospitals. The hospital laundry uses large commercial wash wheels and dryers, and will usually use flat work irons and presses for uniforms. The soils and stains found in a hospital typically are urine, feces, blood, some oils, and medicines. Generally, a well-designed washing machine can handle these laundries without any problem. Nursing homes uses similar versions of commercial washer. Sheets, bedpans, diapers, gowns, and personal clothing are major types of laundries, and soils level can vary from light to very heavy. Urine, feces, and medicines are major soils and stains.

Most large hotels have their own laundering operation using large commercial wash wheels and dryers. The bulk of the laundry is linens, including sheets, pillowcases, wash clothes, bath towels, and bath mats. The soil content is generally light and is predominantly makeup, cosmetics, shoe polish, and body oils. In hotels and regular restaurants, food soils and stains include coffee, tea, and wine; salad dressings or fatty/oily sauces are typically found on linens and garments. The non–food service garments worn by maids and other maintenance personnel contain a variety of soils and stains. Motels, depending on the size, will use any washer from a medium size commercial type to a top-loading household machine. Soils and stains in motel linens and garments are similar to those found in hotels. The laundries are normally washed and bleached for colored and oxidizable stains.

Commercial laundry machines widely vary. Generally, they are washer-extractors, continuous batch washing machines with a counter-flow system. Conventional washers consist of an outside stationary shell that holds water and a rotating inside cylinder holding the laundries. Both the outside shell and the inside cylinder have openings. The inside cylinder is perforated to allow free flow of water between the clothes and water bath. The inside cylinder, in rotating, raises the clothes on ribs and drops them. This dropping and pounding action gives the mechanical energy needed for washing. Institutional machine sizes vary from a household 25 pound load-type to a massive 1200 pound capacity-type that bears little resemblance to a consumer washer. Cylinder sizes vary in diameter from 24″ to 60″ and in length from 18″ to 126″. These washers do not have the capability to extract the laundry. The laundry has to be removed wet from the washer and extracted separately.

Most OPLs contain washer-extractors. These machines, similar in construction to a conventional washer, have the ability to wash and extract excess water by spinning. The washing processes are frequently programmed automatically. Smaller OPLs use top-loading washers similar to household machines. These can be of either porcelain or stainless steel construction. For a conventional washer, a separate extractor is used. Centrifuge, hydraulic, and pressure are the three basic types of operation that control washing processes. Most OPLs use the centrifuge type, because of smaller volume of work processed. Most commercial washers have automatic controls, in which the washing operations are programmed. For a fully automated machine, the programmer will automatically add detergents, bleaches, and other supplies at proper times. For a hopper type dispenser, powder supplies are dispensed usually through five hoppers: two for detergents, one of each for bleach, souring agent, and softener. The supply containers are filled with dry supplies prior to starting the washer. On command of the controller, the hopper dumps or water spray carries the supply into the washer. Liquid supplies are measured by an electronic measuring tank and dispensed into the washer by air pressure. In a simple liquid system, a timer-activated addition of liquid detergents is made either using small pumps or by a venturing mechanism, which is controlled by a command controller.

Tunnel washers can use multiple detergents, each having specific functions such as prewash (enzymes), builder boosters, bleach, neutralizers, sour, and disinfectants. The large washers are tunnel systems with computer-controlled automation and are capable of washing 3–8 million pounds of wash per year. Multiple compartments accommodate each stage of the wash with controlled addition of detergents for individual components. Liquid detergents are favored because of easy dispensing and dosing.

A spinning process uses centrifugal force to extract and drive out the water. The remaining water is removed by flat work ironing, where flat pieces are passed through a series of padded heated rolls. Thus it drives off the water and presses the laundry. Dryers are often used to dry the clothes. Tumble dryers or tunnel dryers are commonly used.

The load capacity of the washer-extractor can reach up to a 600 pound wash load, which is washed, rinsed, and extracted within 30–60 min. The high rotational speeds of modern washing machines dictate the application of especially low-foaming detergents. In a continuous batch washer, up to two tons of wash can be processed hourly. The machines operate by the counter-current process, that is, water flows toward the dirty laundry. The dirty fabric is brought in on conveyor belts or suspension conveyors and stays for a few minutes, sequentially, in individual zones in which wetting, prewash, main wash, and rinse occur. Subsequently, it is dewatered in presses, rollers, or special extractors and then transported to the dryer. Washing processes involve removal of soil and stains from fabrics through the series of baths in which soil is loosened from the fabrics, suspended in water, prevented from redepositing on the fabrics, and finally rinsed away. All these operations are handled fully automatically without any manual labor. This saves on labor, energy, water, and detergents.

Continuous batch washing machines and some washer-extractors are automatically fed with detergents and auxiliary agents such as bleaching and fabric softeners. Most common is the time-dependent dosing of stock solution. This is typically a 10% liquid preparation of powder detergent concentration in the wash liquor by conductivity measurement. The dosing of liquid detergents is not generally accepted due to poor performance; liquid detergents are generally less concentrated in actives. Each dosing system dictates the detergent requirements. Powder detergents need to be free flowing, readily soluble, dispersible, or capable of forming concentrated stock solutions. Solids blocks made in highly concentrated form are convenient. Hot water is injected into powder or solid detergent block to dissolve into stock solution and dosed by required detergent concentration by conductance measurement. Liquid detergents can be metered by an automatic pump and must be chemically and physically stable. Stable slurry and gel forms like the commercially available liquid automatic dishwashing detergents are also available. An important criterion of the industrial washing process is the use of steam. It enables heating the solutions to 200°F within a few minutes, resulting in substantially shortened washing time. In laundries, bleaching agents are applied as needed in addition to the detergents. Stains are removed by the chemical reaction of oxidation by bleaches such as chlorine or oxygen. Reducing bleach such as oxalic acid is also used to remove iron stains. Detergents and bleaching agents are adjusted depending on the washing processes, types of fabrics (cotton, synthetic fiber, fiber blends, etc.), color of fabrics, types of soils, and degree of soiling. Several review articles have appeared on laundry detergent formulations [57,58].

The same four basic factors as illustrated in ware washing involve and influence laundering performances: wash time, wash temperature, mechanical action, and chemical action. Generally, the longer the soiled fabric has contact with hot water and detergents in a washer, the better is the cleaning. The length of wash time needed depends on the soil loads and soil types. For heavily soiled or very dirty laundry, longer wash time is necessary. Normally, a wash control chart is prepared to run the wash wheel for the proper length of time. Like length of wash time, wash temperature is a critical factor for optimum cleaning. Depending on the type and level of soil on fabrics, different wash temperature may be required. For example, for a heavily soiled fabric, a higher wash temperature is preferred. However, for blood-stained hospital or operating room fabrics, cold water should be used first to flush out blood, then warmer water can be used. Fresh blood is set by hot water (>100°F). Mechanical action in the form of agitation is needed to scrub out the soil embedded in the fabrics. In a cylinder wash wheel machine, the wheel lifts and drops the fabrics in the washing solution. Overloading, like other washing situations, has negative effect for mechanical as well as chemical action. Chemical action involves all cleaning ingredients used in laundry, including water, detergents, bleach, softeners, and bactericidal and souring agents. OPLs frequently use dry bleaches because of easy and safe handling. The objective of the laundering is to provide linen that is hygienically clean and free of soil stains. Part of the laundering process includes removal and destruction of bacteria from the washed items. Hygienically clean linen or any washed item that is free from disease-causing bacteria is the standard for laundry. High-temperature washing and use of chlorine bleach can effectively kill bacteria. The bleaches generally contain buffers to aid in controlling pH and releasing the active species.

A broad range of detergents and washing agents have been developed in view of short washing times with low detergent concentrations and high standards for the wash quality, and these I&I detergents are quite different in composition than for household detergents.

Laundry detergents vary widely in compositions and particular uses and can be partial-built, complete-built, prewash, main wash, bleaching, or enzyme detergents. The liquid detergents can be structured or unstructured.

Partially built detergents are available as blends in powder or liquids that predominantly use only one class of active ingredients. They often contain, additionally, antiredeposition agents, optical brighteners, and stabilizers. Most widely used are blends of surfactants or alkalis; partially built detergents sometimes consist of only components or a simple mixture of several detergent components. Detergents based on surfactants are typically liquids, whereas alkali/builder based products may be formulated in either liquid or solid form. Typical solid form consists of solid builders, polyacrylates, soda ash, silicates, and alkalis (caustic soda or potash), and this can be diluted in liquid form with water. Liquid forms that are predominantly surfactant based and contain little or no builders or alkalis are not very suitable for I&I laundry cleaning.

Modern laundry detergents are usually completely built and they are highly alkaline, containing almost all the ingredients needed for the laundry except bleaching agents. Bleaching agents are desired and can be combined with liquid or solid detergents with chlorine or oxygen bleach. Builders, alkalis, silicates, surfactants, optical brighteners, and antiredepositing agents are all used. Phosphates and carbonates can be experimentally balanced, and both solid and powder can be produced. For a continuously operating machine, the use of built detergents can be advantageous due to easy handling of prepared, concentrated stock solution made from both powder and solid detergent. The completely built detergents have an advantage in that they can be readily dosed, but sometimes have the disadvantage of lower performance, although rarely.

A good number of test methods are used to evaluate the performance characteristics of laundry detergents. Typically three stages of testing are done during the product formulation phase: laboratory testing, practical evaluation, and field-test validation.

Laboratory soil removal tests are usually conducted using specially designed equipment such as Terg-o-tometers, Launder-o-meter, and the like. These are small machines that simulate laundry washing processes. These test methods can only provide a directional trend and should not be overemphasized. Terg-o-tometer testing is widely used and consists of a series of 1-L stainless steel cylinders; each equipped with a mechanical agitator. Artificially soiled test fabrics known as swatches are placed in the wash solution to wash under controlled conditions. A wide variety of soils, very specific to the product's positioning in the market, are applied to different kinds of fabrics like cotton, cotton/polyester blends, or polyester. The main types of soils used are particulate clays, human sebum, oils/fats, and bleachable stains, for example, mustard, tea, grass, red wine, and chocolate. Artificially soiled test swatches are also commercially available. The soiled fabrics are then washed under controlled wash conditions in Launder-o-meters or Terg-o-tometers at different temperature and water hardness conditions. Important wash parameters such as detergent concentration, agitation rate, washing time, water hardness, and washing temperature are considered. The detergency is evaluated by examining the washed fabrics by a visual rating by expert panels or by optical and physical instruments such as the Gardner Color difference. The soil removal efficacy is expressed by the change of reflection between the unwashed and washed soiled fabrics. In addition to soil removal, other performance criteria are also evaluated, particularly in household laundry care, for example, foaming behavior, soil redeposition, fabric softening, incrustation (insoluble Ca salts of soap scum and detergent residue deposits on fabrics), color loss, and dye transfer. Physical characteristics that may change during shipping and storage, affecting performance, are also evaluated. Physical characteristics include density, homogeneity, solubility, color, odor, caking, flow ability, and appearance. A practical washing assessment is conducted in commercial washing machines after satisfactory performance on the laboratory test. All variable parameters, such as water volume, water hardness, load size, cloth/liquor ratio, detergent concentration, temperature, and time, are taken into consideration during the evaluation processes. Finally, a field evaluation of the product on various aspects of cleaning is collected and analyzed.

Laundry detergents for fabric cleaning are complexly formulated, containing many different types of cleaning agents. Major ingredients are classified into four categories: surfactants, builders, bleaching agents, and auxiliary performance agents.

Surfactants are by far the most important cleaning components of laundry detergents. The physical, chemical, and phase stability aspects of surfactants greatly limit their uses in liquid detergents. In laundry detergents, surfactants contribute greatly to soil removal and wetting ability of the fabric surface, and assist in the dispersion and suspension of the washed soils. There is a wide variety of surfactants available and generally used in laundry applications. The cost, performance, and physical characteristics of the surfactants very much dictate the selection choice and their use concentrations in the product formulation. Anionic surfactants and NIs are most commonly used in laundry detergents. Cationic surfactants are also useful in laundry detergents, but their use is very limited in auxiliary products such as fabric softeners. Anionic surfactants such as LAS (sodium dodecylbenzenesulfonate), AES (sodium lauryl ether sulfate-3 EO) and NI such as AE (fatty alcohol ethoxylate) are predominantly used in laundry. Surfactants are used at lower concentration in I&I products compared to household laundry detergents.

LAS is generally made by sulfonating alkylbenzene, followed by neutralization by alkali or other base materials to suit needs. Use of $AlCl_3$ or HF catalyst and the reaction conditions used in the alkylation of benzene dictate the isomeric distribution of phenyl ring and alkyl chain. LAS with C_{12} alkyl chain is dominant, and the most important surfactant used in the laundry detergents because of low cost and better performance in solubility, detergency, and foaming properties. The alkyl group is typically a linear alkyl chain of C_{10}–C_{15}, with a phenyl group attached to one of the secondary carbons of the alkyl chain. Commercial LASs are mixtures of phenyl isomers and alkyl chain homologues. LAS provides a superior, cost-effective detergency, and is usually formulated with a builder due to their high sensitivity to hard water.

In structured liquid detergents, a longer alkyl chain is more desirable, whereas in unstructured liquid detergents, shorter alkyl chains ($\sim C_{11}$) are desirable for increased solubility. Potassium and amine salts are preferred to improve solubility and phase stability of the liquids. LAS has a disadvantage in liquid enzyme–based formulation due to enzyme destabilization.

AESs are anionic surfactants made by sulfating alcohol ethoxylates, and the degree of ethoxylation typically ranges from 1 to 4, but predominantly 2–3 moles of ethoxylation (EO) are used with both natural and synthetic alcohol sources. AES provides numerous benefits such as high solubility, very low sensitivity to water hardness, and high stability in liquid formulations. AES is friendlier to enzyme formulations and provide skin compatibility. Addition of a small amount of NaAES to LAS can improve detergency. AES provides excellent detergency on most soil stain categories and is widely used in hand dishwashing, liquid hand soap, and shampoo chemistry because of mildness to skin.

FASs, also known as alkyl sulfates (ASs), are anionic surfactants made from long alkyl chain alcohol sources by sulfation, and have long been used in laundry detergents in combination with LAS. ASs are primarily used in European laundry detergents as a substitute for LAS. The alkyl chain length of ASs ranges from C_{10} to C_{18}; however, tallow alcohol sulfate is commonly used. AS provides excellent detergency, and good foaming and solubility; SME, an anionic surfactant used specially in Japan, is made by sulfonation of fatty acid methyl esters derived from oleochemical sources. SME used in combination with LAS is less sensitive to water hardness and also acts as a hydrotrope.

Fatty acid soaps are now used only as minor ingredients, and function as defoamers in the washing machines. Soaps also aid in the cleaning process, but with hard water, they leave encrustation of soap scum on fabrics.

NIs in recent years became important in laundry detergent, due to lower wash temperature, and nonphosphate or low-phosphate detergents. Typically, the critical micelle concentration of NI when compared to anionic surfactants is very low, often lowered by a factor of 10, and therefore, NIs are used at relatively lower concentrations, and they show excellent soil removal, good dispersing, and soil antiredeposition effects. Ethoxylated alcohol surfactants with alkyl chain length C_{10}–C_{15} and 5–7 degrees of ethoxylation are widely used. Commercial alcohol ethoxylates are sold as Neodol™, Tergitol™, Alfonic™, and the like. The feed stocks are generally derived from natural sources, such as coconut oil, or synthetically prepared from petroleum stock. APG nonionic surfactants are also used in laundry detergents, along with other anionic and nonionic surfactants. APG with an alkyl chain length of C_{12}–C_{14} and a degree of polymerization of 1.4 is suitable for laundry applications. APG is particularly effective against fatty soils, and it has been found that enzyme stability can be improved with APG formulations. NIs provide superior tolerance for hard water ions, provide excellent cleaning benefits, and are commonly used with LAS. NIs provide excellent cleaning benefits, particularly on oily soils, and are more tolerant with enzyme chemistry. Polyhydroxy fatty acid-amides or glucoamides (also known as glucosamides) are currently used in major household dishwashing and laundry detergents. They exhibit excellent biodegradability. Glucoamides have been claimed to have superior cleaning efficacy for oily/greasy soils and skin mildness, to help in removing enzyme-sensitive soils, and to show good synergy with LAS. APGs like alkyl glucoamides are also mild and biodegradable, and are used in laundry products. Amine oxides, betaines, and other amphoteric surfactants have very limited use in major laundry detergents but have some use in specialty laundry detergents.

Builders are multifunctional components and are widely used in laundry detergents. The primary function of the builders is to soften water by tying up the water hardness ions such as Ca^{2+} and Mg^{2+}, thereby increasing detergent efficiency. Builders also provide alkalinity, soil suspension, dispersion, and antiredeposition. Alkaline builders provide peptizing action sometimes called deflocculation. This action refers to the breaking up of larger pieces of protein soil into smaller pieces, making them easier to disperse, suspend, and rinse away. Soil redeposition is a major problem in I&I laundry, because of the combination of high soil loading and lower bath-to-fabric ratio. Soil depositions on fabrics lead to graying. Because of their ability to adsorb onto soil and substrates, polyacrylate polymers can reduce soil redeposition by increasing the overall negative charge of the fabric/soil system. Builders can tie up the water hardness ions by sequestration (chelation), precipitation, or an ion-exchange mechanism, depending on the nature of builders. Water hardness ions such as Ca^{2+} and Mg^{2+} form soluble complexes by chelation or sequestration with phosphates, citrates, polyacrylates, and NTA, whereas insoluble precipitation occurs with alkaline carbonates. Zeolites tie up by an ion-exchange mechanism. Alkali metal tripolyphosphate is by far the most efficient builder; however, because of environmental concerns it is severely controlled and even banned in home laundry detergents in many countries. Phosphate-based consumer laundry detergents are very much nonexistent in North America and Europe. However, use of tripolyphosphate in I&I laundry detergents is yet to be regulated.

Alkali carbonates and silicates precipitate out Ca^{2+} ions as $CaCO_3$, and can leave insoluble deposits on clothes and washing machines. Organic builders, in spite of good sequestration capacity, have found limited use because of unfavorable cost-performance benefits. Citrates have replaced sodium TPP, and because of high solubility and lower effective pH, they make good builders in enzyme formulations. Polycarboxylate salts such as EDTA and NTA, in spite of their efficiency as chelators, are not widely used. NTA, because of its toxicity profile, has very limited use as a builder. Zeolite A, an insoluble builder, has also been used as a nonphosphate builder.

For specific applications, a variety of special agents for treatment of certain types of wash and soils are available. Detergents for laundry heavily soiled with fat and oil, and colored work clothes that are made of polyester/cotton blend fabrics, are predominantly formulated with specific nonionic surfactant combinations and a high concentration of alkalinity. Combination of alkali and phosphate blends with low surfactant concentration provides an easy stock solution preparation that is pumpable with automatic dosing. Emulsifying or wetting agents containing a blend of surfactants are occasionally used in continuous washing machines for fast wetting of the soiled laundry. These are also used as detergency boosters for laundry fabrics that are heavily soiled with oily and fatty materials.

10.5.3 AUXILIARY PERFORMANCE AGENTS

Auxiliary agents are widely used to enhance washing processes. They are bleaching agents, wetting or emulsifying agents, disinfecting agents, fabric softeners, optical brighteners, soil release agents, and dye transfer inhibitors.

Bleaches play a very significant role in I&I laundry detergent formulations. Bleaching action provides cleaning efficacy by whitening or lightening fabrics due to removal of colored stains. Bleaching agents help removing colored stains by destroying or modifying them into more soluble entities, and minimize gray or yellowish tint. Typical bleach-sensitive stains include coffee, tea, wines, fruits, vegetables, and chocolate. Bleaching also provides sanitation to the fabrics and equipment. Proper sanitation and hygiene is particularly important in hospital, nursing home, and health-care laundries. Detergents for disinfection of laundry such as in hotels, restaurants, and hospitals require chlorine bleaching in the final rinse cycle. Oxidizing bleaching agents are exclusively used for bleaching fabrics.

The two types of bleaches hypochlorite and peroxide have become dominant in laundry detergents. Hypochlorite bleach, although very effective, produces color fading and fabric damage, and is chemically difficult to formulate in liquid detergents due to its reaction with other organic materials and also its shorter shelf life. On the other hand, peroxide bleach is costly and not very effective; however, it causes only minimal color fading and damage to the fabric. I&I laundry products do not often contain bleach, whether chlorine or peroxide, directly in the formulations. Typically certain bleaches such as peroxide or chlorine bleach are added separately in the wash, because of the chemical instability in the formulations. However, a single product containing both detergents and bleaching agents is desirable, and is typically produced in solid powder or solid block form. Both the active oxygen and chlorine bleach sources can be used. Sometimes, encapsulated bleaches are used in I&I laundry detergents to prevent chemical degradation with the surfactants.

Hydrogen peroxides as active oxygen bleaches are widely used on large industrial bleaching operations such as textiles, woods, pulp, and paper industries; on the other hand, because of the chemical instability in liquid formulations, their use is limited and hydrogen peroxides are not generally formulated in liquid detergents. However, precursor compounds such as sodium perborate, persulfate, or percarbonate that generate peroxides in water are widely used. Peroxycarboxylic acids or peracids are by far more potent bleaching agents than the other peroxy agents are, especially at lower temperature. The peroxy acid delivered by reaction with a bleach activator and a source of hydrogen peroxide is widely used. The bleach activators react with hydroperoxide anion (OOH^-) and form the reactive organic peracid [R(C=O)OOH]. Well-known activators include tetraacetylethylenediamine (TAED), sodium nonanoyloxybenzene sulfonate (SNOBS), benzoyloxybenzene sulfonate (BOBS), pentacetyl glucose (PAG), tetraacetylglycoluril (TAGU), and glucosamide.

Hypochlorite bleaches provide both cleaning and sanitation in laundry, especially where it especially requires hygienic and sanitized conditions, such as in hotels, hospitals, and food services industries. Liquid sodium hypochlorite is the most common chlorine bleach used in detergents. Other compounds such as lithium, calcium hypochlorite, chlorine oxide solutions, chlorinated phosphates, sodium/potassium dichloroisicyanurate, or encapsulated materials are also used. Sodium hypochlorite solutions are generally made by reacting liquid chlorine with a solution of sodium hydroxide. Small amounts of free caustic or soda ash are typically added to buffer to a desired pH. The byproduct sodium chloride is not generally removed. Reducing bleaches handle some stains that are not removed by oxidation. Such stains are fewer in number; a common one is iron. Oxalic acid is the most common reducing agent used for iron stain removal. Reducing bleaching agents such as sodium bisulfate are also useful.

Oxygen bleach that needed high temperature for activation is added in the main wash, whereas chlorine bleach can be added in any of pre-, main, or rinse cycle. Hydrogen peroxide or sodium hydrogen sulfite is also used in the final cycle typically to remove the residual chlorine bleach, which tends to damage fabric, or yellowing during the drying cycle. Hospital and commercial laundries that process hospital wash are especially required to disinfect by a thermal process of washing at very high temperatures of 185–195°F for 10–15 min, or at lower-temperature rinse of 105–140°F with chlorine bleach or peracetic acid. About 80 ppm of chlorine bleach is considered adequate for disinfection treatment.

Residual detergents or alkalis that remain in the washed laundry tend to yellow the clothes on pressing or ironing. Souring agents or organic acids are commonly used to neutralize the residual alkaline materials. Typically organic acid such as formic, acetic, or powder alkali/ammonium salt of hexafluorosilicate is used to neutralize the residual detergents.

Fabric softeners are used in laundry to give a soft, pleasing feel to the fabrics. Softeners can also save valuable production time in minimizing flat work rolling, speed up extracting and drying, and reduce static electricity. However, overuse and excessive buildup of cationic softener will cause a reduction in water absorption in fabrics such as bath towels and diapers. This softener buildup also reduces the cleaning power of the detergents in the wash cycle and causes soap specks or grease balls on fabrics if softener is not flushed out properly. Fabric-softening agents used in the last rinse bath provide an antistatic effect on polyester/cotton blend fabrics. They also help in unloading in washer-extractor machines. Quaternary ammonium compounds are commonly used as fabric softeners. Addition of bacteriostat and fungistat are also applied during the last rinse to prevent recontamination during the finishing process. Starches or other stiffeners are no longer used, because of a wide variety of modern fabrics are available and used. Mildewcides such as quaternary ammonium compounds are also used to prevent growth of mildew.

Enzymes are becoming very important ingredients in home laundry detergent, because of their effectiveness in removing certain specific stains. However, in I&I laundry products their use is very limited because of temperature, short wash cycles, and highly alkaline detergent formulations. Most enzymes operate at optimum pH ranges from 9 to 11. Certain important ingredients such as chlorine bleach have detrimental effects on enzyme stability. Certain surfactants such as LAS cause enzyme degradation. Moreover, the enzyme stability in liquid formulations is short, and certain stabilizing agents are needed. Soil-specific enzymes, such as protease, lipase, amylase, mannose, and cellulase, are widely used in laundry detergents. Enzymes catalyze the hydrolysis of protein stains such as milk, egg, blood, grass, and excrement (protease); greasy, oily stains (lipase); and starchy food stains such as rice, spaghetti sauce, and gravy (amylase), and remove damaged cellulose microfibrils (cellulase) from cotton, making the faded and worn appearance into new, bright fabric.

Optical brighteners or fluorescent whitening agents (FWAs) are used in small quantity ($<1\%$) in virtually all laundry detergents. Fabrics, particularly cotton, appear yellowish after repeated wash, and in early days bluing agents were added to compensate. Today, with the help of FWAs, an optimum whiteness that has been considered a symbol of perfect clean laundry can be achieved. FWAs absorb invisible UV light from the sun or other light sources and reemit it as visible fluorescent blue light. This visible blue light offsets the yellowish hue from the fabrics and provides a whitening and brightening effect. A wide variety of FWA are known, available, and widely used [51]. Commonly used FWAs are stilbene, biphenylstilbene, coumarin/quinoline, and diphenylpyrazoline derivatives. Various substituent groups are added to the parent molecule to control solubility, substantivity, and overall performance of FWAs. Chlorine bleach resistant FWAs are distyrylbiphenyl and triazolylstilbene derivatives.

Soil release agents (SRAs) are generally added to laundry formulations to aid greasy/oily soil removal from polyester or polyester blend fabrics. SRAs modify the hydrophobic surface of the polyester and decrease the soil affinity toward oily soils. Typical SRAs are polymeric compounds with hydrophobic ethylene terephthalate and hydrophilic polyethylene oxide. Agents that inhibit the transfer of dyes from colored fabrics onto other washed items in the washing machines are also used. Polyvinylpyrrolidone, a water-soluble nonionic polymer, interacts with the water-soluble dyes to form complexes with less substantivity than the free dyes, and helps in preventing color transfer to the other fabrics. Antisoil-redeposition agents such as carboxymethyl cellulose are also incorporated in the laundry detergents or added separately to the washer. When present in the wash water, SRAs help prevent soils from depositing on the laundry load, and thereby help prevent a dulling effect that would build up during repeated washings.

The future trend will continue in automation of washing processes, including automatic dosing of detergent and auxiliary agents; use of continuous batch washing machines with counter flow will also increase, and pumpable, completely built detergent gel or slurry with automatic dosing may gain importance in the future. With increasing automation of I&I laundering processes, partially built, both structured and unstructured liquid detergents are achieving more commercial acceptance. These part-built liquid detergents are manufactured with relatively high active ingredients and can achieve even better cleaning efficacy with skillful formulation than completely built detergents.

Following are some formulation examples of I&I laundry detergents as shown in Tables 10.33 through 10.36. Laundry detergents are available in powder, solid block, liquid, and liquid gel/slurry.

TABLE 10.33
Completely Built Laundry Detergent

Ingredients	Solid Concentration (wt%)	Liquid Concentration (wt%)
Linear alkylbenzene sulfonate	0–3	0–2
Fatty acid soap	0–5	0–2
Polyethylene glycol ether	3–12	5–10
Sodium/potassium tripolyphosphate	8–17	10–15
Sodium carbonate	18–33	0–5
Sodium silicate	40–50	2–5
Sodium/potassium hydroxide	0–10	5–20
Optical brightener	0.1–0.5	0.1–0.5
Antiredeposition agent	0–2	0–2
Water	—	q.s.

TABLE 10.34
Partially Built Laundry Detergent

Ingredients	Liquid I Concentration (wt%)	Liquid II Concentration (wt%)	Solid Concentration (wt%)
Linear alkylbenzene sulfonate	0–12	—	—
Fatty acids soap	5–15	—	—
Polyethylene glycol ether	20–30	—	—
Na/K Tripolyphosphate	—	10–15	10–20
Sodium carbonate	—	0–5	15–30
Sodium silicate	—	10–20	30–40
Na/K Hydroxide	—	10–20	20–30
Optical brightener	0.1–0.5	0.1–0.5	0.1–0.5
Hydrotrope/solvent/coupling agent	10–20	10–20	—
Stabilizer	10–20	10–20	—
Antiredeposition agent	0–2	0–2	0–2
Water	q.s.	q.s.	—

TABLE 10.35
Nonphosphate Liquid Laundry Detergents

Ingredients	Structured Liquid Concentration (wt%)	Unstructured Liquid Concentration (wt%)
Sodium linear alkylbenzene sulfonate	0–35	0–20
Sodium AES	0–15	0–20
Ethoxylated alcohol	0–15	0–20
Sodium carbonate	0–30	—
Zeolite A	0–30	—
Sodium citrate	0	0–15
Optical brightener	0.1–0.5	0.1–0.5
Fatty acid soap	0–5	0–5
Hydrotrope/coupling agent	—	0–15
Buffering agent	—	0–5
Bleaching (oxygen, optional)	0–15	0–15
Enzymes (protease/cellulase/lipase, optional)	0–5	0–5
Bleaching activator (optional)	0–5	0–5
Water	q.s.	q.s.

TABLE 10.36
High-Alkaline Solid Laundry Detergent

Ingredients	Concentration (wt%)
Linear alkylbenzene sulfonate	10–30
Fatty acid soap	0–5
Sodium hydroxide	10–30
Sodium alcohol ether sulfate	5–15
Solid chlorine bleach	10–15
Sodium carbonate	5–20
Optical brightener	0.1–0.5
Sodium tripolyphosphate	5–20
Process binder (high-mol. wt. polyethylene glycol)	5–10

10.6 JANITORIAL CLEANERS

The largest and most diffuse I&I market is the janitorial segment, which uses a wide variety of products, including floor and wall cleaners, carpet shampoos, glass cleaners, toilet bowl cleaners, deodorants, microbial sanitizing products, grease cutters, and drain cleaners. The janitorial market for I&I cleaners will experience the most rapid growth through the twenty-first century.

10.6.1 FLOOR CLEANERS

A major portion of time, energy, and money is spent on cleaning and maintaining the overall appearance of floor surfaces in I&I environments. Floor care probably constitutes half or more of total housekeeping cost. Floor materials and their surface treatments vary widely. A wide variety of floor types exist in I&I establishments, and a number of materials are used in manufacturing of floor surfaces. The flooring types typically found in I&I environments can be grouped into four general categories: wood floor, resilient floor, carpet floor, and hard floor. The cleaning and maintenance of each type of floor is different, because their materials of construction and placements are different. Which soils are found on the floor surface and how they interact with each other, and whether any coating or finish has been applied to the surface, are some of the factors that need be considered before a cleaning formulation is developed. There is also a unique safety factor involved in floor cleaning. The floor must be safe to walk on, avoiding slip-and-fall accidents. Therefore, specific cleaning formulations that address the problems associated with each type of floor are necessary.

Wood floors are not very common in I&I settings compared to residential homes, but still exist in places like gymnasiums and restaurants. All wood floors are typically sealed with a penetrating sealer to protect and subsequently strengthen the wood fibers. The topcoat polishes are scrubbed, buffed, and recoated periodically as the traffic conditions warrant. The coating materials are typically urethane or epoxy types in water base. The hard wood floors require little or no maintenance except dust mopping and damp mopping using a neutral cleaner.

Resilient floors are typically vinyl, modified vinyl, and to a lesser extent asphalt, rubber, and linoleum. Resilient floors are so named because they are quiet and lessen fatigue underfoot. Resilient floors are typically cleaned with mild cleaners.

Carpet is one of the most commonly used flooring materials in every residential household, and is very common in many I&I places such as offices, hotels, schools, and hospitals. Carpet has the ability to perform the functions of many materials. Its overall acoustical, aesthetic, psychological, thermal insulation, safety, and low maintenance cost features make it very desirable. Different areas may need different types of commercial carpeting. Reception areas, aisles, open work areas, stairways, and elevators may require heavier carpet than lightly trafficked executive offices. Similarly, corridors, classrooms, and libraries need carpet to withstand heavier than average foot traffic. In general, an effective cleaning and maintenance preparation starts with proper selection and installation of carpet. The most effective cleaning of carpet requires detergency, agitation, and extraction. Materials used in carpet construction as well as soil types must be considered when selecting the detergent and cleaning method. The factors involved in selecting and maintaining industrial carpeting are fiber constructions, soil types, cleaners, and cleaning methods and equipment used. Many factors and issues need to be considered in selecting cleaning compounds. A neutral detergent will not emulsify soil as well as a slightly alkaline one. On the other hand, one with high alkalinity may strip dye from carpet and damage some fibers. Pile yarns, such as some polyester and acrylic fibers, tend to retain oily soils and require more rigorous treatment, including steam cleaning with hot water. Wool shags, however, require gentler treatment without over-wetting so that delicate construction is not damaged. All carpets are not the same; their makes are quite different. Retail grade carpets are made for residential installations and the normal wear and tear of an average family. Commercial grade carpet is a heavy-duty fabric produced of superior face and backing materials used in heavily trafficked areas. It features tighter construction and stronger backing, and provides long wear.

A great variety of dry and liquid substances can soil carpets. These soils can be classified into several groups: dry, water-based, and oil-based stains. Dry soils may include dust, lint, gravel, sand, hair, and ashes; water-based soils may include inks, coffee, soft drinks, milk, washable inks, and sugar syrup. The oily soils may include grease, tar, crayons, butter, or lipsticks, and stain soils are fruit and vegetable juices, grass, blood, ink, and coffee and tea stains. Soils can fall, or be tracked, spilled, or blown onto carpet. Mixture of the soils requires multiple cleaning procedures and adjustments. The quicker the cleaning process, the easier the soils can be removed and the less harm to the fibers. Traffic constantly forces soils deeper into the carpet fibers, and stains become more set and permanent with age. Ideally, carpets should be vacuumed every day to remove soil and restore the pile. In a hospital environment, the use of carpeting in conjunction with regular vacuuming and effective filtration provides an effective mechanism for limiting the spread of airborne contaminants. In hospitals and healthcare facilities, the carpet is treated with a permanent antimicrobial. This product permanently controls fungi growth, gram-positive and gram-negative bacteria, and odors caused by fungal action. However, antimicrobial efficacy is lost on subsequent cleanings and wear, and periodic replenishment is required. Since the antimicrobial agents often used are quaternary ammonium type cationic, they frequently interact with anionic cleaning agents, and their efficacy is diminished.

The choice of cleaning methods depends on soiling in each area of carpeting floor. Dry or absorbent powder method involves powder clay or other absorbent material that is saturated with a dry cleaning compound, chiefly a solvent. This compound is sprinkled or lightly brushed onto the carpet. The compound is then allowed to dry. While it is drying, the compound dissolves the oily soil, which in turn is soaked up by absorbent material. Removal of this compound by vacuuming takes the soil out. The yarn pad or bonnet method uses similarly absorbing material as in a wet mop, but is circular to fit under a floor machine and is usable on both sides. The detergent solution can be a standard carpet shampoo in standard dilution. It is sprayed onto the carpet ahead of the floor machine. The action of the pad forces the solution onto the fibers to remove the soils, and then the absorbent pad picks up the soils, leaving a relatively dry and clean carpet. The dry foam method involves use of a high-foaming detergent shampoo in special machines that generate foam, and brushing the foam onto carpet fibers. Some machines include a vacuum pickup of the foam, whereas others rely on the use of a separate wet vacuum to remove the foam. The foam penetrates a bit deeper into the pile than the absorbent powder, but also can leave a soil-attracting residue if the proper method is not used. The rotary brush or wet shampoo method is the best known and most aggressive. This technique uses a standard floor machine with a mounted solution tank, which releases solution as desired so that it flows through a fountain brush to the carpet while the brush is spinning. This method cleans deeper and better than dry methods. A wet vacuuming picks up the generated foam and the moisture including the soil, and is recommended after shampooing. The water extraction or steam cleaning method cleans deeper into the pile, and the absence of brushing action leaves the fibers with no distortion. Jets of low-foaming detergent solution are sprayed into the carpet with a special tool, which is also fitted with a suction that extracts the solution back out of the carpet. The solution carries the soils with it. The use of hot water increases the cleaning power and also the drying time. Some extraction systems employ special tooling that includes a brush that helps to loosen soils. Rotary shampoo and hot water extractor are used in exceptionally soiled carpet. This method combines the best of surface cleaning and deep cleaning. The action of the rotary floor machine and shampoo loosens and emulsifies soils and then the extractor follows to flush out the solution. Rug shampooing products are predominantly of two types. A foam-generating product is employed with rotary brush machines. A steam-cleaning product is employed with a wide variety of portable and truck-mounted machines designed essentially to inject hot water solutions of the cleaners onto the carpet and immediately vacuum up the cleaner solution and soils with the same equipment. The foam-generating products using brush machines also require a final vacuuming, which is accomplished with separate equipment.

As with carpet-cleaning methods, the types of cleaners used also depends on the nature of the fiber, the nap, types of traffic, and the amount and character of the soils. Overwetting of the carpet should be absolutely avoided to prevent shrinkage, discoloration, mildew and odor growth, and even seam splitting.

Sodium lauryl sulfate is the primary surfactant used for foam-generating products, since it dries as powder and is free flowing, thus easy to remove via vacuuming. Other synthetic detergents can be employed, for example, sarcosines, sarcosinates, AESs, and sulfosuccinates. Formula optimization must be balanced, and care must be exercised in avoiding sticky residues left in the carpet, which will promote faster resoiling tendencies. Since foaming is to be avoided in steam cleaning, low-foaming surfactants are exclusively used in steam cleaning products as well as prespotter products, which are sprayed on heavily soiled traffic lanes, or on troublesome soils. Other ingredients may include foam stabilizers, malodor counteractants, bacteriostats, optical brighteners, antisoil ingredients, alkalis, and perfumes. Auxiliary products such as soil guards or soil repellants (e.g., 3M's Scotchgard™, Dupont's Stain Master™) are either used on fibers during carpet manufacturing or sprayed onto carpet during maintenance procedures.

Hard floors are very common in I&I establishments. They typically consist of concrete, terrazzo (a mosaic floor of marble or granite pieces), ceramic tile, quarry tile, brick, and natural stone such as marble, slate, or granite. Concrete surfaces can be found in many areas, each with different traffic conditions, from industrial plants to school corridors, from automobile showrooms to loading docks. Quarry tiles are very common and can be found in places such as restaurant, restroom, or bathroom floors. Typically, quarry tile is made primarily of silica and clay, and is baked at high temperature. It becomes polished from constant footsteps; cart movements, sliding boxes, or soils build up particularly in a restaurant environment. Terrazzo or marble floors can be found in office lobby areas. The washing, coating, and maintenance processes very much depend on the type and frequency of traffic. Light to medium traffic areas may only require a dust mopping and damp mopping with a neutral cleaner. For heavy traffic areas, it may require highly alkaline or acidic industrial cleaners.

Some floor surfaces are inherently slippery, and the presence of foreign substances such as spilled foods, grease, oil, or water makes them even worse. Over time the combination of wear and tear with greases and soils results in a smooth surface with a polymerized grease layer. Kitchen floor soil is made of fats, proteins, calcium, fatty acids, and other components. Susceptible areas are entrances, restrooms, loading docks, and restaurants. Also, water on polished marble floors in bathrooms and tiled surfaces near swimming pools presents a serious slip problem. Floor restoration that involves elaborate floor stripping, etching, and cleaning is the only way to improve traction. Floor treatments such as slip-resistant coatings help in improving the traction and slip resistant, and a number of water-base products, synthetic resins, and paint-on/travel-on finishes are commercially available.

Slips and falls may appear to be simple trivial accidents, but they result in thousands of deaths and cost billions of dollars in direct and indirect cost [59]. According to statistics compiled by the National Safety Council, falls are the second leading cause of accidental deaths. Over 40% of the dollars spent on workers compensation in the U.S. food service industry are due to the results of slips and falls. Annual expense from slips and falls is about $12,000 per restaurant for an average of 3–4 accidents per year. In 1988, for example, more than 12,000 people died from accidental falls. In public areas such as hotels, motels, and restaurants, slips and falls occur more frequently than any other accidents. Slips and falls can result in serious injuries, especially to the head and back. The floor surface is the single most important factor contributing to slips and falls. The slip-fall relationship between the floor surface and the floor coating is also an important consideration, as it relates to liability and worker's compensation, especially in the fast food industry, where a floor can be wet or greasy.

The slips and falls hazard very much depends on the traction or slip resistance of the flooring materials. The tendency of falls and slips can be correlated with the static coefficient of friction (SCOF).

A SCOF is a ratio of sliding force (horizontal) that is required to move one surface over another to the total vertical force applied to two surfaces in contact. In simpler terms, it is an indicator of the grabs, traction, or friction present between two surfaces in contact. A minimum of 0.50 or higher is recommended for adequate slip resistance for most travel surfaces that are dry, as higher SCOF increases the traction, and therefore reduces the possibility of slips and falls. Flooring products used for commercial jobs must have a SCOF of 0.50, as determined through testing that utilizes a leather sensor and a clean, dry, level walkway surface. Leather is used for testing for SCOF, because it is usually the most slippery shoe sole material. American Society for Testing and Materials (ASTM) committee standards establish test methods for SCOF measurements of ceramic tile, polish-coated floor, painted surfaces, and tiles with shoe sole and heel materials. Historically, Underwriters Laboratories used the James Machine, a nonportable laboratory instrument, to measure SCOF, but it does not address on-site field testing that provides data corresponding to conditions concerning actual installed flooring products. The slip-resistance test is generally performed with the NBS-Brungraber Slip Tester, equipped with a synthetic rubber sensor. This portable James Machine is a standard means of measuring the SCOF that correlates with the slip resistance of floor surfaces. The SCOF varies considerably for different types of floors and the type of materials that come in contact with the floor, as well as how environmental conditions affect it. The SCOF helps in quantifying a floor's slip resistance and is used in floor-design and specification. It is also measured by using a slip meter such as the horizontal pull slip meter. The portable testers that use leather sensors simulate walking pressure, giving lower SCOF.

The Brungraber equipment is commonly used to measure the SCOF of quarry tiles, before and after treating the floor with grease by an ASTM Method F1677-96 [60]. The SCOF measurements are done for at least three conditions: dry or wet, greasy, and greasy and wet. The SCOF value decreases as the floor becomes more slippery; therefore, it increases the slips and falls. The American National Standard Institute (ANSI) has not established a minimum SCOF above which a floor surface is considered to be a nonhazardous walkway surface. So, a product meeting the 0.50 SCOF requirements using this method offers great credibility as a slip-resistant product in a dry condition. Typically, wet conditions reduce the traction and decrease the slip resistance or SCOF. There have been several industry and government studies that have addressed the appropriate SCOF threshold for slip resistance for wet floors. As reported by the ASTM Committee D-21 in ASTM D-2047, SCOF of not <0.50 traditionally has been recognized as indicating a nonhazardous walkway surface [61]. However, based on other studies, ASTM Committee D-21 suggested that a SCOF of 0.50 might be a conservative threshold and most people, walking normal strides, would be unlikely to slip on surfaces for which the value is $>0.30–0.35$. Floor surfaces with SCOF below 0.30–0.35 are considered slippery by this test.

Floor cleaning requires the most effort, since gravitation and shoe traffic deposits the most soil. Hard surface floor-finish actually adds friction at the same time, making it easier to clean and helping to prevent staining. Various mechanical devices are known and used to increase the SCOF of the flooring. Ecolab has developed a new floor treatment system called Airon Process [62]. Ecolab's Airon process restores SCOF through a technique that is superior to acid etching. This mechanical method involves a sandblasting type process that restores worn and slippery quarry tile flooring to its original traction and increases SCOF. This mechanical Airon restoration process makes quarry tile floor more slip-resistant. This process is applied with a surface renewal unit that combines jet-powered air and small particles to remove a finite layer of the tile surface. This leaves a slightly roughened surface of the harder silica portion for improved traction. The process lasts about 18 months to 2 years before further treatment is necessary. With acid etching with hydrofluoric acid, the floor is restored to its original traction, but it lasts for only a short period, and damages tile and grout. Use of hydrofluoric acid is also hazardous. With acid etching, a microscopically, roughened surface tile is produced. Acid usually dissolves away the harder silica portion of the tiles, leaving pits on the tile surfaces.

Floor strippers are periodically used to clean hard-to remove soils, and occasionally stripping is done before finishing or coating the floors. Strippers are cleaners that may be made acidic or neutral, and ammoniated or nonammoniated, based on water-soluble solvents. Both the solvent and ammoniated strippers are either soap or detergent based. Alkaline strippers may have pH from 10 to 13. All stripper products are employed with abrasive scrubbing pads or brushes that also effect mechanical removal. A functional stripper must have the following properties: easily and completely removes the floor finish film, relatively low foaming, nondamaging to floor materials, capable of stripping at an economical dilution, suspends and emulsifies soils for easy removal by rinsing or wet vacuuming, easily rinsed, and effective in hard water. Floor maintenance should be done on a daily basis by dust mopping with a treated dust mop, and possibly also by damp mopping with a neutral cleaner. Spray buffing of finishes or dry buffing of floor may be performed as the traffic conditions and their effects dictate. Spray buffing involves the mist spraying of a special spray product or a diluted floor finish into the floor immediately ahead of the buffing machine.

As hard floors are different, different flooring materials are used for different I&I settings. The type of soils and soil loads are also quite different; therefore, the cleaning compounds and methods used are also different. The floor cleaners can be formulated alkaline, acidic, or neutral pH. However, floor cleaners widely used in the I&I arena are either alkaline or acidic, and could be both, switching alternately.

Acid floor cleaning compositions are widely employed to improve the coefficient of static friction of floors, especially quarry tiles, in environments conducive to the buildup of slippery-when-wet films, for example, fast food/quick service restaurants [63,64]. A synergistic combination of week and strong acids is employed in the formulations. These compositions are useful in particular for avoiding the occurrence of, for removing, and for preventing the return of slippery-when-wet films. The soil film is predominantly composed of Ca and Mg salts of polymerized fats and fatty derivatives. The film appears to be made up of chemically combined water hardness minerals and polymerized grease of animal and vegetable fats. The divalent Mg^{2+} and Ca^{2+} can cross-link carboxylate group present in the fatty moiety and can also attach the polymerized film to the tile. The cross-linking also occurs via C=C double bond, and the polymerized films may be due to bonding of cohesive and adhesive properties. This wet film is comprised of animal/vegetable fats and fatty derivatives, including their polymerized materials, and water hardness minerals from water, and ceramic tile flooring and organic film forming materials. Food service establishments have been plagued by an incessant slippery-when-wet condition of the flooring, which is caused primarily by an undesirable film that forms on ceramic (quarry) tile flooring, and it is extremely difficult to remove. This wax-like, shiny, transparent film resists removal by conventional floor-cleaning products. The detergent-resistant, polymerized grease and certain underlying white film are undesirable not only from an aesthetic viewpoint, but more importantly because floors having this film exhibit greatly increased slipperiness when wet. This results in both serious accidents and increased accident insurance premiums. Liquid hydrofluoric acid (3–4%) solution is used to clean quarry tiles, but it is an exceptionally hazardous chemical.

Alkaline floor cleaners are also widely used. The floor cleaner compositions are either acidic or alkaline, and use a wide variety of surfactants. Floor cleaner formulations typically contain surfactants, chelating agents, acid or alkalinity sources, hydrotropes, and special cleaning agents such as bleach or solvents. A number of surfactants are available for floor cleaner. Alkali metal or amine salts of linear alkylbenzene sulfonate (sodium dodecylbenzene sulfonate), AES (sodium lauryl sulfate-3EO), alcohol sulfate (sodium lauryl sulfate), alkanolamide (cocamide diethanolamine), alkylphenol ethoxylate with a wide variety alkyl groups and degrees of ethoxylation (nonylphenol ethoxylate-9 EO), alcohol ethoxylates with a wide variety alkyl group and degrees of ethoxylation (alkyl C_{12}–C_{16} ethoxylate-6 EO, Neodol 25–7, etc.), and APG (Glucopon™ 625) are all used. APG is particularly useful for dispersing and emulsifying of fine wax particulate for floor care products. For alkaline floor cleaners, a host of alkalinity sources from soda ash, caustic alkali, metasilicates, and alkanolamines are used. For acid cleaners, organic acids such as citric, phosphoric, aliphatic, and aromatic acids are widely used. Chelating agent or builders such as EDTA-Na_4, polyphosphates, and commonly used coupling agents or hydrotropes are also used. Bleaching agents such as chlorine bleach sources, liquid ammonia or ammonium hydroxide, and special organic solvents such as butyl cellosolve or butyl carbitol are also used.

Some examples of various types of floor cleaners are shown in Tables 10.37 through 10.44.

10.6.2 ALL-PURPOSE HARD SURFACE CLEANERS

In the cleaning industry, a hard surface is considered to be one that is cleaned *in situ*; it cannot be removed and washed in a tub or a basin [65]. Hard surface cleaners are common cleaning products that are designed to remove soils from hard surfaces. This type of cleaner includes all-purpose cleaners, kitchen cleaners, bathroom cleaners, wall cleaners, concrete cleaners, metal cleaners, equipment cleaners, and the like. Consumers do most of these cleaning by hand in the household. In I&I establishments, although most of these tasks are also done by hand, some machine operations are increasingly available. Hard surface cleaning involves such tasks as cleaning of countertops, bathtubs, mirrors, windows, bathroom fittings, and sinks. Hard surface cleaners are fairly alkaline, all-purpose cleaners are neutral or low alkaline, and toilet bowl cleaners are generally acidic. Toilet bowl cleaners, being acidic, are discussed under acidic cleaners in Section 10.9. The pH of most all-purpose cleaners is between 8 and 12. Generally, this is the best range for grease-cutting alkalinity to help the surfactant and solvent system in removing soil. A higher alkalinity pH can damage certain surfaces and irritate skin.

TABLE 10.37
Acidic Floor Strippers

Ingredients	Floor Strippers, Liquid Two-Step Concentration (wt%)	Floor Strippers, Liquid One-Step Concentration (wt%)	Floor Strippers, Powder Concentrate Concentration (wt%)
Citric acid, weak acid	12	9.2	15–45
Phosphoric acid, strong acid	2	1.5	1–8
Monosodium phosphate buffer	20	15.3	50.5
Sodium acid pyrophosphate buffer	0.5	0.4	1.5
Sodium xylenesulfonate hydrotrope	2	5.2	0.2–2
Nonylphenol ethoxylate: 9.5 EO surfactant	1	3.5	1–5
Sodium chloride filler	4	3	4–18
Sodium TPP sequestrant	0.5	—	0.1–3
Isopropyl alcohol	—	0.5	—
Dodecylbenzene sulfonic acid surfactant	—	2.9	—
Triethanolamine	—	1.4	—
Coco fatty acid alkanolamide	—	1.7	—
Water	q.s.	q.s.	—
pH	1.95	2.27	—

Source: Adapted from Cockrell, J. R., Jr. and Thekkekandam, J.T., U.S. Patent 4749508, Kay Chemical Co., 1988; Cockrell, J. R., Jr. and Thekkekandam, J. T., U.S. Patent 4877459, Kay Chemical Co., 1989.

TABLE 10.38
Acidic Floor Cleaners

Ingredients	Liquid Cleaner Concentration (wt%)	Liquid Cleaner Concentration (wt%)	Powder Cleaner Concentration (wt%)
Citric acid, weak acid	8.5	6–10	10–20
Sulfamic acid, strong acid	—	—	0.5–1.5
Phosphoric acid, strong acid	1.9	1.5–2.5	—
Monosodium phosphate buffer	13.3	8–18	—
Sodium acid pyrophosphate buffer	—	—	20–45
Sodium xylenesulfonate hydrotrope	10.7	6–13	0.2–2
Ethoxylated nonylphenol 9.5 EO surfactant	2.9	2–5	3
Sodium chloride filler	0.8	0.6–1.1	15–16
Silica drying agent	—	—	0.5
Isopropyl alcohol	2	1.5–2.5	—
Dodecylbenzene sulfonic acid surfactant	18.3	16–26	20 (Na salt)
Triethanolamine	5.7	6–10	—
Coco fatty acid alkanolamide	1.7	1.7	12 (Monoethanolamine salt)
Sodium hydroxide	1.1	1–2	—
Water	q.s.	q.s.	—
pH	2.32	—	—

Source: Adapted from Cockrell, J. R., Jr. and Thekkekandam, J. T., U.S. Patent 4749508, Kay Chemical Co., 1988; Cockrell, J. R., Jr. and Thekkekandam, J. T., U.S. Patent 4877459, Kay Chemical Co., 1989.

TABLE 10.39
Alkaline Floor Cleaners

Ingredients	Liquid Cleaner Concentration (wt%)	Liquid Cleaner Concentration (wt%)	Powder Cleaner Concentration (wt%)
Citric acid	1	1–5	1–5
Sodium xylenesulfonate hydrotrope	0–8	0–10	—
Ethoxylated nonylphenol 9.5 EO surfactant	2	2–8	2–10
Dodecylbenzene sulfonic acid surfactant	10	10–20	10–20
Alkanolamine	10	10–20	10–20
Sodium hydroxide	0–1	0–3	0–3
Water	q.s.	q.s.	—

Some important criteria are considered in formulating all-purpose hard surface cleaners. The product is formulated as ready to use, such that it can be packed in a container that is fitted with a spray pump, or as an aerosol for easy dispensing and treatment. Alternatively, a concentrated formulation is made that can be diluted for ready-to-use concentration. The formulation can be capable of cleaning a variety of surfaces, such as glass, wood, porcelain, vinyl, marble/granite, and painted

TABLE 10.40
Floor and Wall Cleaners

Ingredients	Floor/Wall Degreaser Concentration (wt%)	Floor/Wall Degreaser Concentration (wt%)
Phosphoric acid	3–6	—
Tetra potassium pyrophosphate	—	2–6
Quaternary ammonium chloride	—	0–4
Potassium hydroxide	10–20	0–4
EDTA-Na_4	10–20	2–10
Sodium xylenesulfonate	10–20	0–10
Ethoxylated alcohol	2–6	0–4
Ethoxylated nonylphenol 9.5 EO	2–6	2–8
Sodium metasilicate	0–2	0–4
Water	q.s.	q.s.

TABLE 10.41
Rug Cleaner/Graffiti Remover

Ingredients	Rug Cleaner Concentration (wt%)	Graffiti Remover Concentration (wt%)	Graffiti Remover Concentration (wt%)
Isopropyl alcohol	—	—	15–25
Diethylene glycol methyl ether	—	—	20–40
Dipropylene glycol methyl ether	—	25–35	—
Pine oil	—	10–15	—
Low-foaming anionic surfactant (Dowfax 2A1)	5–10	—	—
Triethanolamine	6–14	—	—
Propylene glycol methyl ether	2–6	40–50	40–60
Potassium oleate	1–2	—	—
Water	q.s.	Solvents may also be used	q.s.

TABLE 10.42
Carpet Cleaner/Carpet Steam Cleaner/Carpet Shampoo

Ingredients	Carpet Cleaner Concentration (wt%)	Carpet Steam Cleaner Concentration (wt%)	Carpet Shampoo Concentration (wt%)
Sodium TPP	25–30	—	5–8
Sodium carbonate	15–20	—	—
Sodium metasilicate	25–30	6–10	—
Potassium silicate 29%	—	—	20–25
Betaine surfactant	2–4	—	—
Ethoxylated alcohol C_{12}–C_{15} 12 EO	—	3–5	—
Sodium sulfate	q.s.	—	—
Optical brightener	0–0.2	—	—
Trisodium phosphate	—	—	2–5
Phosphate ester anionic sufactant	—	—	2–4
Hydrotrope-Na xylenesulfonate or other	—	6–10	2–5
Alkylphenol ethoxylate C_8 8 EO	—	4–6	—
Water	—	q.s.	q.s.

TABLE 10.43
Wax Stripper Formulation

Ingredients	Wax Stripper Concentration (wt%)	Grease Cutting Wax Stripper Concentration (wt%)
Alkanolamide–coco diethanolamine	6–10	—
Alcohol ethoxylate	2–4	2–6
Monoethanolamine	4–8	6–10
Trisodium phosphate	20–25	0–5
Sodium hydroxide (50%)	—	5–8
EDTA-Na_4	—	1–4

TABLE 10.44
General Formulation Guideline for Floor Care Products

Ingredient Categories	Ingredients	Concentration (wt%)
Wax component including emulsifier	Carnauba wax	1–2 0.3–0.6
Surfactants	Alkyl sulfate, alkyl polyglucoside, alkyl polyethylene glycol ether	2–5 2–5
Additives	Fragrances colorants	<1
Solvent	Water	q.s.

Source: Adapted from Sajic, B., Ryklin, I., and Frank, B., *Household and Personal Products Industry (HAAPI)*, 35(4), 94–100, 1998.

surfaces without having any adverse effect. Further, the product should not leave any stain, streak, or marks and should be easily removed or left on the surface without rinsing. The product should contain low or nonfoaming surfactant and should be mild and skin compatible.

A wide variety of surfactants including anionic and nonionic are widely used as shown in Table 10.45. Builder salts, such as phosphates, EDTA-Na_4, soda ash, and citrates, are also used. Certain special ingredients such as ammonia or pine oil are product specific and are widely used. Alkaline sources are added to the formulations, and they are available from caustic alkali, alkanolamines, silicates, and phosphates. Many hard surface cleaners contain some solvents; typically they are alcohol, glycol ethers, or *d*-limonene. Certain operations need abrasive actions, where certain soft or friable abrasive materials are preferable. Calcium carbonate, laponite clay, silica (SiO_2), alumina (Al_2O_3), and titania (TiO_2) are widely used as abrasive agents.

Some formulation examples of typical hard surface cleaners are provided in Tables 10.46 through 10.48.

10.6.3 GLASS CLEANERS

Glass cleaners are typically formulated with a low level of ingredients, because they are intended for light-duty cleaning. These products are formulated with sufficient ingredients to remove light window soils, such as dust, water spots, and fingerprints. These products are not intended for heavy-duty cleaning. The major requirements for glass cleaners are that they deliver minimum cleaning, leaving no streaks, stains, or residues that would be visible on transparent surfaces. For these reasons, quick-evaporating or volatile ingredients are desired in glass cleaners. As a general trend, glass

TABLE 10.45
Liquid All-Purpose Cleaners Formulation Guide

Ingredients	Examples	Concentration (wt%)
Anionic surfactant	Alkylbenzene sulfonate, paraffin sulfonate, secondary alkanesulfonate, soap, ethoxylated alcohol sulfate, alcohol-sulfate, dialkyldiphenylether disulfonate	0–40
Nonionic surfactant	Ethoxylated phenol, ethoxylated alcohol, amine oxide, alkanolamide, alkyl polyglucoside, alkyl polyalkylene glycol ether	0–40
Builder	Phosphate, carbonate, bicarbonate, silicate, citrate, gluconate, polyacrylate, EDTA-salt, phosphonate	0–15
Solvent	Alcohol, alcohol glycol ether, pine oil, *d*-limonene	1–60
Alkalinity	Sodium/potassium hydroxide, alkanol-amine, ammonia, magnesium hydroxide	0–15
Coupling agent or hydrotrope	Sodium xylenesulfonate, sodium cumene sulfonate, dialkyldiphenylether disulfonate	0–15
Disinfectant	Hypochlorite bleach source, pine oil, quaternary ammonium chloride	0–15
Special additive	Polyethylene glycol, polyacrylate, polyvinyl pyrrolidone	0–15
Filler	Water	q.s.

TABLE 10.46
Liquid Abrasive Cleaners

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Calcium carbonate	50	—
Silica	—	50
Polyacrylate thickener/stabilizer Acusol 820 (30%)	1–2	1–3
Bentonite clay thickener	1–3	0–3
Tetrapotassium pyrophosphate (60%)	0–3	3–5
Nonylphenol ethoxylate 10 EO	0.25–1.00	0.25–0.50
Sodium hydroxide (50%)	0–0.50	0–1.00

TABLE 10.47
Liquid All-Purpose Hard Surface Cleaners

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Tetrapotassium pyrophosphate	3–5	2
Sodium metasilicate	1–3	1
Sodium xylenesulfonate	3–5	3
Ethylene glycol butyl ether	4–8	4
Pine oil	0.25–0.50	0.25
Alkyl ethoxylate-C_{12}–C_{13} 6.5 EO	4–6	4
Alkyl ethoxylate-C_{12}–C_{13} 3.5 EO	2–4	2
Water	q.s.	q.s.

TABLE 10.48
Heavy-Duty Concrete Cleaners

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Tetrapotassium pyrophosphate	8–12	10
Sodium metasilicate	5–10	5
Sodium hydroxide (50%)	2–6	2
Ethylene glycol butyl ether	5–10	5
Phosphate ester	5–10	5
Nonylphenol ethoxylate 9.5 EO	5–10	5
Water	q.s.	q.s.

cleaners are formulated with more solvent content and with less surfactant. Since window soils are light, grease-cutting solvents such as pine oil or *d*-limonene are not generally used. Generally low molecular weight alcohols that are volatile are used in the glass cleaner formulations. Amphoteric and nonionic surfactants that give less streaking have advantages. Alkanolamines and carbamates are used as an alkalinity source. Ammonium salts of surfactants or builders are better suited for glass cleaners, as they provide lubricity during wiping stages. General glass cleaning formulation guidelines and some formulation examples are given in Tables 10.49 and 10.50. A microemulsion composition of graffiti remover that also removes marking ink and crayons marks from coated or uncoated surfaces was patented [66], as shown in Table 10.51.

10.6.4 BATHROOM CLEANERS

Bathroom cleaners are specially formulated with attention to specific soil and cleaning problems associated with bathrooms, such as hard water deposits, soap, lime soap scum, fatty deposits, human skin, hair debris, and fabric fiber. Both moderately alkaline and highly acidic bathroom cleaners are available. Bathroom cleaners are formulated with higher builder concentration to combat water hardness ions that contribute significantly to making the bathroom soils tougher to remove. Many bathroom cleaners use quaternary type disinfectant, which puts some constraint in using anionic surfactant. However, nonionic surfactants are usually used in such cases. Acid cleaners are advantageous in that they work more efficiently in combating soap scum. Acid cleaners can hydrolyze the soap scum to more soluble fatty acids for easy removal. Acid cleaners also break some bridging between soils and receptive surfaces. Acid cleaners are more effective in dissolving hard water spots, stains, rusts, and calcium/magnesium encrustation. Oxalic acid is

TABLE 10.49
Spray Glass Cleaners Formulation Guide

Ingredients	Examples	Concentration (wt%)
Anionic surfactant	Alkylbenzene sulfonate, paraffin sulfonate, olefin sulfonate, secondary alkane sulfonate, alkyl sulfonate, dialkyldiphenylether disulfonate	0–3
Nonionic surfactant	Ethoxylated phenol, ethoxylated alcohol, amine oxide, alkanolamide, carbamates, alkyl polyglycoside	0–5
Amphoteric surfactant	Betaines, sulfobetaines	0–10
Builder	Carbonate, silicate, citrate, polyacrylate, EDTA-salt, phosphonate	0–4
Solvent	Glycol ether, low-molecular weight alcohol (ethanol, isopropanol)	1–50
Alkalinity	Ammonia, alkanolamine, sodium hydroxide	0–5
Antistreaking agent, antifogging agent	Polyethylene glycol, Polyvinyl alcohols, silanes, ethoxylated silicones	0–1
Filler	Water	q.s.

TABLE 10.50
Window Glass Cleaners

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)	IV Concentration (wt%)
Butyl cellosolve	2–3	3–4	1–2	2–4
Isopropyl alcohol	5–7	4–6	8–12	20–30
Aqueous ammonia	1	1	0.25–0.5	0.25–0.5
Nonylphenol ethoxylate	—	—	0.15–0.25	0.15–0.25
Sodium lauryl sulfate	0 .5	0.5	0.5	—
Ethoxylated alcohol	—	0.4	0.5	0.4
Water	q.s.	q.s.	q.s.	q.s.

especially effective to remove rust and copper stains. Acid cleaners are generally formulated with pH ranging from 2.5 to 5.0. Acid cleaners also have their share of disadvantages. Many bathroom fixtures, cement grout materials, and enameled objects such as bathtubs or shower stalls are sensitive to acids, and can be damaged by weakly acidic products of a pH value of 4.5 or lower. Neutral or weakly alkaline cleaners are used in such cases. Formulation chemistry is very much similar to all-purpose hard surface cleaners. Many bathroom cleaners use amphoteric, amide nonionic, ethoxylated alcohol sulfates. Often difficulties are encountered in cleaning vertical bathroom surfaces because products are thin and do not cling. In those circumstances, a thick foamy product or a product with added thickener in the formulation could be used. This will increase residence time of the cleaner on vertical surfaces [67]. A formulation guideline for bathroom cleaners is given in Table 10.52.

TABLE 10.51
Graffiti and Marking Materials Remover

Ingredients	Concentration (wt%)	Concentration (wt%)	
Terpene compounds	10–20	Solvenol	14.3
Pyrrolidone compound	10–20	*N*-Methyl pyrrolidone	14.3
Surfactants	10–15	Neodol 91-2.5	6.2
		Neodol 91-6	6.2
Solvent	10–15	Hexylene glycol	5.1
		Propylene glycol monomethyl ether	7.2
Cationic surfactant	1–5	Exxon Q-17-2	1.6
Water	q.s.		45.1
pH	2–12		

Source: Adapted from Purcell, K., Hawes, C. L., Harry, D. R., Jr., and Lacosse, G. E., U.S. Patent 5691289, Kay Chemical Co., 1997.

TABLE 10.52
Spray Bathroom Cleaners Formulation Guide

Ingredients	Examples	Acid Cleaner Concentration (wt%)	Alkaline Cleaner Concentration (wt%)
Anionic surfactant	Alkylbenzene sulfonate, paraffin sulfonate, soap, ethoxylated alcohol sulfate, alcohol ether sulfate, dialkyldiphenylether disulfonate	0–8	0–5
Nonionic surfactant	Ethoxylated phenol, ethoxylated alcohol, amine oxide, alkanolamide, carbamates	0–5	0–8
Amphoteric surfactant	Betaines, sulfobetaines	0–5	0–5
Builder	Carbonate, citrate, polyacrylate, EDTA salt, phosphonate	0–2	0–2
Solvent	Glycol ether, low molecular weight alcohol	0–15	0–15
Alkalinity	Sodium/potassium hydroxide, alkanolamine	0	0–5
Acid compound	Phosphoric acid, sulfamic acid, acetic acid, citric acid, dicarboxylic acid, oxalic acid	0.5–10	0
Disinfectant	Hypochlorite bleach source, quaternary ammonium chloride	0–5	0–5
Filler	Water	—	q.s.

10.7 DEGREASERS AND HEAVY-DUTY DEGREASERS

Degreasers are generally defined as cleaning agents that can effectively remove grease and oily soils from any substrate. In an I&I setting, unlike household degreasing tasks, a wide variety of substrates, and different types of greasy and oily soils are encountered, and the degree of soil load and nature of degreasing tasks are quite different. In some tasks, an ordinary degreaser is used, but in some cases a much stronger heavy-duty degreaser is needed to do the job. In industrial plants or factories, for example, degreasing may involve heavy-duty cleaning of engines or industrial equipment; on the other hand, in the institutional setting, it could involve a simple degreasing of tables or countertops, or simple window cleaning. Since individual cleaning tasks are quite different, the degreasers can be classified as simple degreasers or heavy-duty degreasers depending on the degree of soil load or nature of soils.

There are many kinds of degreasing products: alkaline-based, hydrocarbon solvent–based, chlorinated solvents, water-soluble, and vapor degreasers. Specialization also exists in the solvent cleaner; in the degreaser area, one finds cold solvent degreasers designed to degrease electrical equipment such as generators, condensers, coils, and regulators. There are water-rinsable degreasers designed to degrease equipment or areas where higher levels of oil are present, such as engine blocks or plant warehouse concrete floors. Cleaner is sprayed on the surface and rinsed off with water, at which time an emulsion forms, carrying away cleaner and oils with it.

Water-soluble solvent degreasers range from simple general-purpose degreasers to specialized foam clean degreasers or clinging foam used to clean meat-processing equipment. Solvent cleaners are based on hydrocarbon, glycol ethers and emulsifiers. They may include perchloroethylene, trichloroethane, trichloroethelyne, methylene chloride, high aromatics, mineral spirits, and kerosene. Toxicity and environmental considerations are causing gradually cessation of the use of one or more solvents. Use of chlorinated hydrocarbon solvents is very limited or nonexistent because of potential toxicity, hazard, and health reasons. Solvent cleaners are used widely both for general degreasing and a number of specific purposes, such as cleaning engines, aircraft tail assemblies, landing gear, diesel locomotives, cabs, bodies and gear boxes, the undercoating of trucks, and heavy construction equipment. They are extremely useful in degreasing concrete driveways, around loading platforms, drive-through walks, bus berths, in passenger-loading areas, firehouse floors, and machine shops areas with heavy staining due to leakage of lubricants.

Fryers are typically used for frying fish, chicken, or French fries in restaurants. The basic soil is oil and fat, with some meat, fish, or potato, in part burnt-on or carbonized. Owing to the burnt-on or carbonized nature of the soils, a heavy-duty alkaline degreaser is used for cleaning. Generally, a restaurant fryer is boiled with water at 165°F and heavy-duty degreaser for several hours, drained, rinsed, and scrubbed to remove difficult soil [68]. Finally the fryer is washed with acid to neutralize any alkaline residue.

Nonionic surfactants such as alcohol ethoxylates, alkylphenol ethoxylates, ethoxylated phosphate esters of alcohol, and phenols are widely used in heavy-duty degreaser formulations. Moderate alkalinity is generally used in degreasing formulations. Sodium/potassium silicates, alkali metal hydroxides, metasilicates, alkanolamines, and triethanolamines are typically used as alkalinity sources. Builder salts also play an important role in degreasing formulations, but are used in relatively lower concentrations. Widely used common builder salts such as EDTA-Na_4, sodium TPP, sodium/potassium pyrophosphate, trisodium phosphate, and citrate are commonly used. Formulations containing water-soluble solvents, such as ethylene and propylene glycol, glycol ethers, and higher alcohol are used as solvent cleaners. Butyl carbitol and butyl cellosolve are widely used as solvents.

Typical examples of various formulations for degreasers and heavy-duty degreasers are shown in Tables 10.53 through 10.56.

A heavy-duty degreaser cleaning composition that is environmentally friendly, free of phosphate, and free of organic solvent yet highly effective has been formulated with the nonphosphate builder tetrasodium ethylenediaminetetraacetate, potassium carbonate as both builder and buffering agent, alkali metal hydroxide, nonionic surfactant Neodol® 1-5 (C_{11} primary alcohol ethoxylated with 5 moles of ethylene oxide), and hydrotroping agent sodium xylenesulfonate [69], as shown in Table 10.56. The heavy-duty degreaser cleaning composition uses reduced alkalinity, has reduced corrosion properties, and is very effective in removing grease and oil from surfaces.

TABLE 10.53
Heavy-Duty Cleaner/Degreaser

Ingredients	Solvent Degreaser Concentration (wt%)	Heavy-Duty Degreaser Concentration (wt%)
Nonylphenol ethoxylate 9 EO or ethoxylated alcohol 9 EO	2–6	2–3
Ethoxylated phosphate ester of phenol or alcohol	10–14	4–8
Triethanolamine	—	2–4
Alkanolamides, monoethanolamine or diethanolamine of coco/other fatty acid	—	1
Sodium TPP or EDTA-Na_4	4–6	2–5
Sodium metasilicate		1–5
Glycol ether solvent (butyl cellosolve/butyl carbitol)	10–15	10–15
Hydrotrope-sodium xylenesulfonate	q.s.	q.s.
Kerosene or mineral spirit	8–10	—
Water	q.s.	q.s.

TABLE 10.54
Engine Degreaser-Cleaner/Engine Room Cleaner-Degreaser

Ingredients	Engine Degreaser Concentration (wt%)	Engine Room Degreaser Concentration (wt%)
Sodium LAS	5–8	—
Kerosene	—	40–50
Tetrapotassium pyrophosphate	5–10	—
Tall oil (fatty acid)	—	30–40
Sodium metasilicate	6–10	—
Di- or tripropylene glycol methyl ether	1–5	5–15
Triethanolamine	—	4–6
Pine oil	—	1–2
Water	q.s.	q.s.

TABLE 10.55
General-Purpose Spray Degreaser

Ingredients	Concentrated Degreaser Concentration (wt%)	Spray Degreaser Concentration (wt%)
Disodium cocoamphodipropionate	—	3–5
Sodium TPP or EDTA-Na_4	6–10	1–4
Ethoxylated nonylphenol 9 EO	8–10	—
Phosphoric acid	4–6	—
Sodium metasilicate	0–3	2–5
Sodium phosphate	—	1–3
Tall oil fatty acid	—	1–3
Potassium hydroxide	10–15	1–3
Propylene glycol methyl ether	0–5	8–10
Water	q.s.	q.s.

TABLE 10.56
Phosphate-Free and Solvent-Free Heavy-Duty Degreaser Composition

Ingredients	Nonphosphated Concentrated Degreaser Concentration (wt%)	Phosphated Concentrated Degreaser Concentration (wt%)
EDTA-Na_4 (30%)	20	13.65
Phosphoric acid (75%)	—	4.52
Potassium Carbonate	15	—
Ethoxylated C_{11} alcohol 5 EO (Neodol 1-5)	4	4
Surfonic L12-6	—	2.03
Neodol 91-2.5	—	2.03
Sodium xylenesulfonate	15.10	10
Sodium metasilicate · $5H_2O$	—	0.42
Potassium hydroxide (47%)	13.39	1
Water	50	48.86
Drive-through cleaning test at 0.5% v/v numerical rating; lower number means better cleaning	2.48	1.33

Source: Adapted from Ahmed, F. U., U.S. Patent 6156716, Kay Chemical Co. (Ecolab), 2000.

10.8 DISINFECTANTS AND SANITIZERS

Disinfectants and sanitizers play an important role in I&I cleaners on the market. Industrial and institutional sanitation entails the maintenance of essential cleanliness, order, and safety in the environment. To provide and maintain a clean and healthy environment, and employee comfort and safety, a sanitation program is essential. There are many elements of cleaning and sanitation tasks: floor cleaning and maintenance, structural cleaning, and maintenance of facilities, including offices, dormitories, restaurants, restrooms, lockers, dressing rooms, and lounges. It includes also machines and equipment cleaning, controlling insects and pests, collection and disposal of garbage and product waste, and care of exterior areas. Furthermore, it includes parking, roadway, walkways, landscaping, and maintenance of safe working conditions and maintenance of facilities to sustain hygienic conditions. This covers overall sanitary maintenance and workers' own sanitation program, including hand washing and sanitation. The importance of proper hand washing and sanitizing by workers in a food service establishment, hospitals, restaurants, day care centers, and the like cannot be overestimated nor overemphasized. Pathogenic bacteria can be found on the hands after using the restroom, handling raw foods, changing diapers, or touching soiled surfaces. Hand washing with antimicrobial soap and sanitizer is vital to prevent the transfer of these pathogenic bacteria to any other media or persons or to prepare food items that will be served to the dining guests. The importance of hand washing by workers and other aspects are covered in Section 10.4.2.

Formulation of disinfectant cleaners and sanitizers is dictated to some extent by regulatory requirements. All disinfectants and sanitizers must be properly registered with the U.S. Environmental Protection Agency (EPA), and with each state where the products are being used and sold. Residual cleaners must also comply with U.S. FDA requirements. The USDA regulates hand-washing soaps that are used in food-processing and services industry such as in meat- and poultry-processing industries. Cleaning and sanitation products that are intended for use in slaughtering and processing plants operate under USDA regulations. Poultry, meat, shell egg grading, and egg inspection programs are controlled by the USDA. Food-processing plants, whether they are poultry, meat, or fish, fall under jurisdiction of the USDA. These are generally inspected areas and must follow strict sanitation procedures. Cleaning products intended for use in the plants operate under U.S. Department of

Commerce (USDC) guidelines. Similarly, the USDC National Marine Fisheries Service controls fishery product inspection programs. Thus, all disinfectants and sanitizer products must be formally authorized under specific restrictions, such as specific usage.

Soil in itself is not a cause of cross-infection. But soils serve as a refuge for disease-causing bacteria. Detergents are needed to break down the soils and permit the disinfectants to contact and kill the organisms. When a disinfectant is combined with a detergent, it is the role of the detergent to disperse and remove soil from a surface, and thereby enable the detergent to reach and destroy any microbial contamination that may lie beneath the dirt barrier.

A wide variety of disinfectant active ingredients (antimicrobial agents) are commercially known and widely used in cleaning products, as listed in Table 10.57 [70]. An excellent overview of disinfectants in general is given in the *Encyclopedia of Chemical Technology* [71].

Although phenols, chlorophenols, alcohols, hypochlorites, and iodophors are used as active biocide agents against certain strains of bacteria in some applications, formulations with quaternary ammonium compounds as the active biocide ingredients account for the majority of all I&I sanitizers and disinfectant products. A variety of known quaternary ammonium compounds are effective, but the quaternary compound of choice is dialkyl dimethyl ammonium chloride.

Disinfectant active ingredients (quaternaries, bleaches, phenolics, iodophors, etc.) can be formulated with other detergents and detergent additives to combine the germ-killing ability of the basic disinfectant with cleaners to clean and disinfect or sanitize in a single-step procedure. An optimized and balanced formulation with surfactants, detergent builders, and antimicrobial agents is required to provide the best possible cleaning properties. Combination of disinfectants and detergent

TABLE 10.57
Different Types of Antimicrobial Agents Used in Cleaners and Sanitizers

Type	Examples
Quaternary ammonium compounds (quats)	Benzyl dimethyl alkyl ammonium chloride, dialkyl dimethyl ammonium chloride lauryl pyridinium chloride, cetyl pyridinium chloride, benzalkonium chloride
Biguanides	Polyhexamethylene biguanide
Organic acids	Lactic acid, alkyl fatty acids ($<C_{12}$), dodecylbenzene sulfonic acid, salicylic acid, glycolic acid, benzoic acid
Chlorhexidine	Chlorhexidine gluconate/acetate
Organic amines	Fatty alkyl 1,3-diaminopropane
Amphoterics	*N*-Fatty alkyl β-aminopropionate, *N*-hydroxyethyl-*N*-carboxymethyl fatty acid sodium salt of amidoethylamine
Alcohols	Ethyl alcohol, propyl alcohol, benzyl alcohol, pine oil
Oxidizing agents	Sodium hypochlorite (liquid chlorine bleach), chlorine dioxide, hypochlorous acid, trichloro- and dichloroisocyanuric acids and their salts, sodium perborate and activator, peroxy acid (per acid), magnesium salt of peroxy phthalic acid, oxygen bleach generated from ozone
Aldehydes	Formaldehyde, glyoxal, glutaraldehyde, polyaldehyde (polyacrolein), aldehyde-amine condensation products, aldehyde-glycol condensation products, bronopol
Phenols, chlorophenols, and their derivatives	*o*-Phenyl phenol, *o*-benzyl-*p*-chlorophenol, *p*-chloro-*m*-xylenol, *o, p, p′*-trichloro-*o′*-hydroxydiphenyl ether (Triclosan)
Iodophors concentrate	Nonylphenoxypoly(ethyleneoxy) ethanol–iodine complex, ethoxylated nonyl phenol–iodine complex, polyvinyl pyrrolidone–iodine complex
Isothiazolones	5-Chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one (Kathon)

components is a challenging science. All detergents and disinfectants are designed to work at a certain pH, and should be compatible for optimum activity. Phenolic disinfectants function best in a pH range of 6–7, and are not compatible with cationic surfactants and some nonionic surfactants. They are generally formulated with anionic surfactants and fatty acid soaps. They are sensitive to hard water and precipitate Ca and Mg ions when diluted. Phenolics may cause odor, skin irritation, and environment waste disposal problems. Phenolic compounds may not be used for sanitizing equipment that is used in food handling. The synthetic phenol products that were used in early days have been replaced by derivatized phenolic type compounds, which exhibit broader ranges of germicidal effectiveness.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Agents ⇒			Iodophors			Phenols			Quaternaries (Quats)					
Effective pH ⇒			3.5			6–7			9–10					

Quaternary ammonium compounds are combined with nonionic surfactants, alkalis, and sequestrates to achieve a variety of disinfectants and sanitizers, which may be used in hospitals, and food-handling areas, where germ-free surfaces are desired. The quaternaries are capable of combating a wide variety of gram-negative and gram-positive bacteria, fungi, and viruses. Some quaternaries are approved by the FDA as final rinse sanitizers at levels of 200 ppm, and do not require a final potable water rinse. The quaternaries are not compatible with anionic surfactants, and work best as disinfectants in the range of 9–10 pH. Anionic surfactant inactivates the disaffection action by reacting with these cationic compounds. Since good detergency and antibacterial efficacy of quaternaries occur in this alkaline pH range, the resultant sanitizers/surfactants combined cleaners deliver the best activity of both ingredients. Common chelating/sequestering agents, such as STTP and EDTA-Na_4, can boost the efficacy of quaternary compounds. Quaternaries do not contribute to the objectionable odor problems of phenolics, and often they counteract foreign odors. Hard water can inactivate the germicidal properties of quaternaries. Nonionic surfactants also can inactivate the disinfecting ability of quaternaries. Sometimes combinations of quaternaries and other sanitizers such as alcohol are effectively used. Although many new members of quaternaries such as isomeric and polyquaternary ammonium compounds have surfaced, the dominant force in disinfectant and sanitizer formulations is derived from the optimally formulated products using the existing quaternaries. Sometimes two or more antibacterial/antimicrobial agents combined provide synergistic efficacy. For example, a combination of iodine complex such as iodophors and quaternary ammonium compounds gives the optimum benefit. The quaternaries are relatively lower cost and effective against bacteria and viruses.

Iodophors, which are typically surfactant–iodine complexes, are effective broad-spectrum germicides as long as their pH is acidic. The term iodophor is applied to any product in which a surfactant or polymer acts as carrier and solubilizing agent for iodine and enhances the bactericidal activity of iodine, reducing vapor pressure and odor. Staining is almost nonexistent, and wide dilution is possible with iodophors. Iodophor containing detergent additives must maintain a pH level of ~3.5 to attain maximum activity. Iodophors have varied activity, but typically have 20–24% of available iodine. Iodophors are used in detergent sanitizers and germicidal cleaners, as well as surgical scrub soaps containing 0.5–2.0% of available iodine. Iodophors are sanitizing or germicidal cleaners used to clean and sanitize lightly soiled surfaces, for example, hospital equipment, walls, bed pans, clinical thermometers, and surgical instruments, typically having 100–150 ppm iodine at pH 4.5 or lower. An acid buffer is employed to stabilize the iodine content. Citric acid, phosphoric acid, or glycolic acids are generally used. Iodophor cleaners and sanitizers may be used in many food-oriented areas. Some surfactants that are widely used in iodophor complexes are ethoxylated alcohol, for example, nonylphenoxy poly(ethelyneoxy) ethanol and α-(*p*-nonylphenyl)-ω-hydroxy poly(oxyethelyne). Foaming iodophors are good for hand cleaning and nonrinse application for surfaces in contact with food where foaming is desirable, and are also used as disinfectants in hospitals, food plants, and farms. The low toxicity of iodophors makes this type of sanitizer more desirable. The acid iodophor may damage terrazzo tile flooring and some metals.

Isothiazolones (Kathon™ CG/ICP) are highly effective and versatile preservatives, and are used to prevent the growth of bacteria and fungi, including yeast and molds.

Environmental concerns and local regulations often dictate the use of specific sanitizers in a particular geographic location. Owing to safety concerns, the use of formaldehyde in USA has declined, in contrast to Europe, where formaldehyde and glyoxal are widely used in formulations for hard surface care products and hospital instrument disinfection. Alcohol sanitizers are primarily used in waterless hand wipes, and hand sanitizers and disinfectants. The antimicrobial action wears off when the volatile alcohol evaporates from hands or substrates. Alcohol sanitizers are not strong biocides. The most commonly used alcohol as a disinfectant is pine oil that is obtained from pitch soaking of pinewood by steam distillation or solvent extraction. It consists mainly of isomeric tertiary and secondary, cyclic terpene alcohol, and has a turpentine-like odor. Pine sol is predominantly used in household consumer products.

The broadest spectrum disinfection at a very low price is delivered by hypochlorite bleach. Because of its chemical reactions and incompatibility, most common nonionic and some anionic surfactants cannot be formulated with chlorine bleach. The surfactants that are commonly used with NaOCl are tertiary amine oxides, soaps, alkyl sulfates, and alkyldiphenylethersulfonates. Amine oxides can interact with anionic surfactants at certain ionic strength to produce a viscous product and with chlorine bleach, a thickened, viscous product can be made. Certain cleaning and sanitation applications may need thickened products for vertical clinging or increased contact time, such as for cleaning bathroom tiles and walls, and bleach-stable thickeners such as clay or polycarboxylic thickeners are widely used for these special formulations [67]. There is widespread interest in nonchlorine bleach sanitizers due to increased environmental concerns. Oxygen bleach generated from perborate-activated compounds or peracids are some examples; however, the peracid bleaching disinfectants are not quite effective as their hypochlorite counterparts.

The soils encountered in food-processing establishments are diverse in nature and require different cleaning and sanitation. There are a variety of categories of food service industries, including food processing, food canning, restaurants, cafeterias, and hotels, and their individual cleaning requirements are different. The food-processing industry includes fluid milk, meat/poultry slaughtering and processing, and food canning. Food service establishments include full service restaurants, fast food, and quick service restaurants.

In a fluid milk plant, the soils encountered consist mainly of the constituents of milk and inorganic salts and other impurities from water. Equipment may also be soiled with bacteria, molds, mildews, yeast growth, and foreign airborne soils. All fluid milk plant cleaners typically are alkaline products. Hard water forms insoluble films or "milk stones" that are easily removed by chelating agents added as a separate component in a CIP alkaline wash program. Dairy and other food service industries CIP systems assure process-ready surfaces to the highest standards. Milk stones, fats, and proteins entrapped in the film serve as a growth media for bacteria. Some of the milk stones of inorganic salts are removed by an acid rinse. Typical raw milk is composed of 3.5–5% fats, 3.3–3.8% proteins (primarily casein), 4.7–5% lactose, and 0.7–0.9% minerals, and the remaining 85–88% is water. A three-step washing procedure is followed in cleaning. Warm wash with chlorinated alkaline (1000–1500 ppm of NaOH) detergent with chelating agents is used, followed by an acid rinse (pH 4–5), and sanitation is the last step. High-temperature short-time pasteurizing units and homogenizers, milk transfer lines, and storage tanks usually contain baked-on fats and proteins soils, along with Ca deposits. Generally, acid wash, followed by a heavy-duty alkaline wash, is used to clean these soiled substrates. A foam suppressant is typically added to the cleaning agents, as milk protein generates foam.

The meat and poultry industry has several types of plants such as slaughtering plants and processing plants, that includes cooking, curing, and smoking. Proper sanitation programs are essential in eliminating or minimizing bacteria from the processing environment and equipment. The USDA governs the use of direct and indirect food additives in the meat- and poultry-processing facilities, and also regulates the sanitation procedure and inspection programs in the meat/poultry industry. Freshly slaughtered and dressed meat has very few microorganisms on the surface or interior; however, as the carcass is subjected to handling, processing, and moving, or cut into smaller pieces, the number of microorganism increases. Blood is the primary soil, composed of plasma, protein, serum, red cells, white cells, and platelets. Blood is more easily removed in prerinse with warm water (<105°F) to avoid clotting and setting. A chlorinated, built alkaline detergent is effective in peptizing protein soils, and is typically used. Fat is a predominant soil in slaughtering and processing plants. Initially, a hot water prerinse is used to melt away the fat, and a detergent that emulsifies the fat and breaks down the protein soils is widely used. Acid rinse, followed by chlorine bleach sanitation, is the final step of cleaning. Typically, at least 500 ppm of chlorine bleach is used for sanitation after general cleaning and washing. Cutting boards where meat fats, proteins, and bloods could hide in small cracks and crevices are usually cleaned either by soaking in chlorine bleach tanks or by spraying a thickened bleach followed by washing with hot water [72].

In institutional settings, disinfection and sanitation also play a very important role. In food preparation and service industries such as restaurants and cafeterias, employees are required by law to wash and sanitize their hands before handling any food. Equipment, cooking and serving utensils, and service dishes are usually washed and sanitized before use. There are typically three steps involved: wash, rinse, and sanitize. Towels, rags, and wipes are also washed and sanitized after use. Similar restrictions and requirements are applied in healthcare establishments, nursing homes, hospitals, and daycare centers.

The U.S. Occupational Safety and Health Administration (OSHA) has a stringent requirement covering hand washing to protect workers against blood-borne diseases. Employers must supply conventional hand-washing materials or where running water is not available, alternatives such as water-free sanitizers, (e.g., alcohol gels) and antiseptic hand cleaners.

The local government regulates disinfectant-testing protocols; for example, the EPA sets the rules and procedures for disinfectants. A typical test for disinfection efficacy for both disinfectant compounds and cleaning formulations is the dilution test. The test consists of treating a use dilution of cleaning solution with a specific organism, followed by incubation. Disinfection of the cleaning product is determined by the number of surviving microorganism at the end of the incubation period. U.S. regulations specify three different levels of disinfection claims, as well as a sanitation claim depending on the organisms used in the test method [66].

Although the disinfectants and sanitizers category is growing steadily (~4.5 to 5% annually), increased regulatory issues will demand more efficacious products, and changes in customers' requirements are creating exciting opportunities for new technologies and formulation improvement. The quaternaries will continue to provide optimum performance in the next generation of cleaning formulations. The demands for veridical products that are effective against viruses have been increasing all over the world and will continue to do so.

Some examples of disinfectants and sanitizers that are typically used in I&I establishments are shown in Tables 10.58 through 10.65.

TABLE 10.58
Food Plant/Dairy Detergent/Sanitizer (Powder)

Ingredients	Concentration (wt%)
Sodium TPP	30–40
Sodium metasilicate	5–10
Sodium LAS	5
Sodium dichloroisocyanurate	5–8
Sodium sulfate/chloride (filler)	q.s.

TABLE 10.59
General-Purpose Sanitizer (Powder)

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sodium dichloroisocyanurate	25	28	34
Sodium TPP	10	—	—
Sodium sulfate (filler)	65	42	66
Sodium dihydrogen phosphate	—	30	—

TABLE 10.60
General-Purpose Sanitizer

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sodium dichloroisocyanurate	6	18	12
Sodium TPP	30	25	15
Sodium carbonate	—	25	15
Sodium metasilicate	5	—	3
Anionic surfactant	5	3	2
Sodium chloride (filler)	q.s.	q.s.	q.s.

TABLE 10.61
General-Purpose Sanitizer (Powder)

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sodium dichloroisocyanurate	7	20	7
Sodium TPP	58	60	—
Sodium sulfate (filler)	20	—	57
Sodium carbonate	10	20	16
Sodium citrate	—	—	20
Nonylphenol ethoxylate-11	5	—	—

TABLE 10.62
Sanitizing or Germicidal Cleaner/Rinse

Ingredient	Cleaner Concentration (wt%)	Rinse Concentration (wt%)	Sanitizer Concentration (wt%)
Iodophor–nonylphenoxypoly (etheneoxy) ethanol-iodine complex	9	4	9
Phosphoric acid	8	4	1
Surfactant, Igepal CO-880	5	5	5
Water	q.s.	q.s.	q.s.
Available iodine/ppm	1.75%/17,500	0.8%/8,000	1.75%/17,500

TABLE 10.63
Disinfectant/Cleaner/Deodorant

Ingredients	Disinfectant Concentration (wt%)	Disinfectant/ Deodorant Concentration (wt%)	Disinfectant/ Cleaner/ Sanitizer Concentration (wt%)
Quaternary ammonium chloride alkyl (C_{12},C_{14},C_{16}) dimethyl benzyl ammonium chloride	4	2	22
Thickener	0.5	0.25	0.25
Isopropyl alcohol	8	3	1
Essential oil	0.5	—	0.25
Pine oil	—	4–20	—
Water	q.s.	q.s.	q.s.

TABLE 10.64
Germicidal Cleaner/Pine Oil Cleaner/CIP Cleaner

Ingredients	Pine Oil Cleaner Concentration (wt%)	CIP Cleaner Concentration (wt%)	Germicidal Cleaner Concentration (wt%)
Alkyl dimethyl benzyl ammonium chloride (quat)	12	5–10	1
Pine oil	24	—	—
Sodium TPP	—	2–8	—
Sodium carbonate	—	3–10	—
Nonylphenol ethoxylate-11	—	3–8	—
Water/inert materials	q.s.	q.s.	q.s.

TABLE 10.65
Milk Stone/Milk Can Cleaner

Ingredients	Milk Stone Remover Concentration (wt%)	Milk Can Cleaner Concentration (wt%)
Phosphoric acid	30–50	—
Nonionic surfactant	1–3	2–5
Water	q.s.	—
Sodium TPP	—	30–50
Trisodium phosphate	—	15–20
Sodium sesquicarbonate	—	20–25
Sodium metasilicate	—	20–40
Sodium dichloroisocyanurate	—	2–5
Sodium carbonate	—	q.s.

10.9 MISCELLANEOUS SPECIALTY CLEANERS

10.9.1 Transportation Cleaners

Transportation cleaning involving cleaning of cars and trucks has evolved into a very specialized and important market in the I&I cleaning industry. A wide variety of transportation cleaning formulations are available, from acidic to highly alkaline cleaners; many are built products. The acid cleaners may contain certain varieties of acids, from hydrofluoric to phosphoric, which are used as brighteners. High-foaming cleaners primarily based on anionic surfactants are mainly used on painted surfaces to minimize chemical attack and corrosion. Low-foam cleaners based on either anionic or nonionic surfactants are used primarily for cleaning the inside of tanks, where the soils could cause excessive foam. The traffic soil film is composed of a complex material, widely varying in composition and very much depending on geographic location and climatic condition in which the vehicle traveled. Generally, it is composed of earth soils, such as sand, clay, Ca, Mg, Fe salts, carbon black, soot from exhaust emissions, and rubber particulate from tires. A combination of anionic and nonionic surfactants or cationic and nonionic surfactants cleaner formulations are frequently used to remove the traffic film soils without brushing. Builders, sequestrants, and chelants are also used to aid in cleaning in hard water as in all other cleaners. Corrosion inhibitors such as silicates, phosphates, and buffering agents are widely used to inhibit attack and retardation on truck metals that are typically galvanized and polished aluminum and brass. Care must also be taken in cleaning to avoid damaging rubber and Plexiglas™, so solvents and high-alkaline formulations are avoided. The ideal product should be biodegradable, safe to use, safe to materials, and able to disperse and emulsify traffic soils. Some typical formulation examples are shown in Tables 10.66 through 10.68.

10.9.2 ACID CLEANERS

Acid Cleaners are used with extreme caution. Bowl cleaners are generally acidic in nature, and are available in powder, preferred solid block or liquid form. The function of toilet cleaners is to remove effectively fecal soils, lime and rust deposits, and urinary calculus from commodes and urinals.

TABLE 10.66
Car Wash/Truck Wash Cleaners

Ingredients	I Car Wash Concentration (wt%)	II Car Wash Concentration (wt%)	I Truck Wash Concentration (wt%)	II Truck Wash Concentration (wt%)
Potassium pyrophosphate	15–20	10–15	—	—
Trisodium phosphate	—	—	10–15	5–10
Sodium metasilicate	—	—	30–35	20–25
Sodium silicate	4–6	—	—	—
Potassium silicate	—	2–5	—	—
Nonionic surfactant, ethoxylated alcohol	5–7	3–5	6–10	4–6
Anionic surfactant	—	—	5–10	6–8
Filler	Water, q.s.	Water, q.s.	Na_2SO_4, q.s.	Na_2SO_4, q.s.

TABLE 10.67
Car Wash Cleaners

Ingredients	Powder Concentration (wt%)	Liquid Concentration (wt%)
Sodium TPP	35–50	—
Potassium pyrophosphate	—	15–20
Sodium metasilicate	6–10	—
Potassium silicate, liquid	—	4–10
Nonionic surfactants	4–6	4–8
Anionic surfactant	10–15	—
Coupling agent, hydrotrope	—	10–15
Filler	Na_2SO_4, q.s.	Water, q.s.

TABLE 10.68
Aluminum Truck Body Cleaner/Brightener

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Phosphoric acid	35–40	10–15	40–50
Nonionic surfactant	5–10	4–6	2–4
Butoxyethanol	—	—	10–20
Sodium hydrogen bifluoride	1–2	—	—
Hydrofluoric acid	—	10–15	—
Water	q.s.	q.s.	q.s.

TABLE 10.69
Bowl Cleaners Formulation Guideline

Ingredients	Examples	Concentration (wt%)
Nonionic surfactants	Ethoxylated alcohol, alkylphenol ethoxylated, alkyl polyglucoside, alkyl polyethylene glycol ether	2–15
Anionic surfactants	Alkyl benzene sulfonate, paraffin sulfonate, alkylsulfate, secondary alkanesulfonate, ethoxylated alcohol sulfate	0–5
Acid sources	Phosphoric acid, citric acid, oxalic acid, acetic acid, formic acid, lactic acid, hydrochloric acid	0.5–15
Quaternary biocides	Alkyl benzyl dimethyl ammonium chloride	0–4
Bleaching agents	Persulfate salts, hydrogen peroxide, peracetic acid	0–15
Thickeners	Amine oxides, acid thickeners, cellulose gums, polyacrylic acid	0–2
Abrasive	Silica, alumina, calcite	0–1
Filler	Water, salts	q.s.

In the past, products made with hydrochloric and phosphoric acids in combination with surfactants were used to remove toilet soils. But safety and ecological reasons very much precluded these types of formulations. A wide variety of inorganic and organic acids are used; however, organic acids bring multifunctional benefits. The use of oxalic acid is particularly good for removing rust. Nonionic or low-foaming anionic surfactants are preferred in toilet bowl cleaners. A wide variety of thickeners, including acid thickener and polyacrylate thickeners, are known and used. A general formulation outline for toilet bowl cleaner is shown in Table 10.69. Weak acids, such as citric acid and oxalic acid, are used in damp wiping of bathroom fixtures, such as bronze trim and nonstreak wash for stainless steel. Properly buffered phosphoric acid is effectively used in cleaning exterior aluminum trim; diluted HCl sold as “Muriatic” or Plumber’s Acid is widely used in removing lime encrustation in the interior cleaning of piping and processing equipment, and also in cleaning cement mortars. Germicidal agents, such as quaternary ammonium compounds, are typically added to acid bowl cleaners. Bathroom cleaners are used in the form of liquid and foam pumps or aerosol packs. Bathroom cleaners are generally acidic products, although care must be taken to ensure that damage to sensitive enamels is avoided. A pH range of 3–5 is recommended for bathroom cleaners. The most common soils in bathrooms are greasy soils, lime soap residues, hairs, fibers, and lime residues of water hardness. A wide variety of surfactants can be used, as shown in Table 10.70 through 10.72. An important factor that must be considered in formulating bathroom cleaners is the avoidance of environmental stress cracking in components made of plastic, including handles, bathtubs, fittings, and shower holders. By interacting with various ingredients present in the bathroom cleaners, plastic can develop environmental stress cracks.

TABLE 10.70
Bathroom Cleaner Formulation Guidelines

Ingredient Categories	Examples	Concentration (wt%)
Nonionic surfactants	Ethoxylated alcohol, alkylphenol ethoxylated, alkyl polyglucoside, alkyl polyethylene glycol ether	1–5
Anionic surfactants	Alkyl benzene sulfonate, paraffin sulfonate, alkylsulfate, secondary alkanesulfonate, ethoxylated alcohol sulfate	1–5
Builder salt	Citrate	0.5–2
Acids	Citric acid, acetic acid, lactic acid, dicarboxylic acid	3–8
Solvents	Alcohols, glycols	2–10
Additives	Fragrances, colorants, preservatives	<1
Water	—	q.s.

TABLE 10.71
Acid Bowl Cleaners

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Thickener			
Organic-xanthan gum	0.5	—	—
Inorganic clay-Veegum	1.0	—	—
Acid thickener	—	3	4
EDTA-Na_4	1–4	—	—
Phosphoric acid	—	2	13
Hydrochloric acid	20	—	—
Dowicil™ 75	—	0.1–0.5	0.1–0.5
Benzalkonium chloride	1–2	—	—
Surfactant	1–2	1–2	1–2
Water	q.s.	q.s.	q.s.

TABLE 10.72
Acid Scale Remover

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Nonylphenol ethoxylate 9 EO	—	3
Oleyl amine ethoxylate 2 EO	3	—
Citric acid	—	13
Sulfamic acid	13	—
Modified polyurethane thickener Acusol 880 (35%)	6	6
Water	q.s.	q.s.

10.9.3 Oven/Broiler Cleaners and Pretreatment Compositions

Oven cleaners are basically thickened products with caustic alkali. The cleaner is spread or sprayed onto the oven surface to be cleaned, and then the oven is warmed, after which the mixture of cleaners and soils to be removed are scraped, wiped, or flushed off. In household oven cleaning, this type of cleaning task is very typical. However, the removal of baked-on and burnt-on organic food deposits from surfaces of cooking equipment is a considerable problem, and poses a very challenging cleaning task, especially in restaurants, where ovens and broilers are used to cook large amounts of food, and the resulting soil levels are high. The surface of ovens, broilers, and other cooking equipment is heavily soiled by baked-on organic food deposits. The food soiling matter deposited on these surfaces typically consists of a complex mixture of natural fats and other organic deposits from cooking of food. When heated at oven or broiler temperatures, this soil may be converted into a polymeric mass in which part of the organic material may also be carbonized.

Oven cleaners offer a variety of formulation choices from low alkaline to very high alkaline products. Alkali metal phosphates combined with an amine component and surfactants, abrasives, and thickening agents are used. In contrast to oven cleaners, oven pretreatment methods and compositions that are applied to oven surfaces prior to soiling and then removed afterward are also known [73–76]. These food-safe compositions are made from ingredients generally recognized as safe, and typically contain an inorganic thickener (clay thickener) and alkaline water-soluble organic salt. The composition forms a food-safe coating, which adheres to all portions of an oven surface, are shown Table 10.73. After soiling, the films and accompanying spattered food soils are easily removed by water or an aqueous solution. An interesting low-temperature, low-pH oven cleaner is described, where the action of a trans-esterification between the fatty soil and a poly alcohol, catalyzed by alkali bicarbonate, and assisted by a mixture of organic acids salts, yielded an eutectic mixture as shown in Table 10.74 [77]. An NPE-based formula of oven/grill cleaner is shown in Table 10.75.

10.9.4 Clean-in-Place Cleaners

Cleaning in the food-processing or food services industry is generally done by the CIP method. Cleaning solution with sanitizer is circulated through the process equipment, pipelines, milking equipment, or dairy product dispensing equipment without dismantling. It is important to remove residual soil and mineral salts from the interior tank, pipeline, and process equipment surfaces. The Federal and State Milk Sanitation Program as administered by FDA regulates dairy products.

TABLE 10.73
Oven/Broiler Pretreatment Composition

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Clay-Veegum HS	2.11	2.65	2.65
Polydimethylsiloxane	—	—	6.1
Potassium phosphate	8.76	4.5	4.5
Potassium chloride	5.26	—	
Sodium tripolyphosphate	2.62	1.4	1.4
Soybean oil	12.31	—	6.1
Hydroxypropylmethyl cellulose	—	0.07	0.07
Water	q.s.	—	q.s.

Source: Adapted from Harry, D. R., Jr., U.S. Patent 5480493, Kay Chemical Co. (Ecolab), 1996; Harry, D. R., Jr., U.S. Patent 5662998, Kay Chemical Co. (Ecolab), 1997; Harry, D. R., Jr., U.S. Patent 5389138, Kay Chemical Co. (Ecolab), 1995; Schoenholz, D., Peterson, A. W., and Northup, M. A., Jr., U.S. Patent 4193886, Church & Dwight, 1980.

TABLE 10.74
Low-Temperature Oven Cleaner

Ingredients	Concentration (wt%)
Sorbitol	2–5
Alkali metal bicarbonate	0.1–4
Eutectic mixture: sodium acetate/ lithium acetate/potassium acetate	1–5
Thickening agent	q.s.
Abrasive	q.s.
Surfactant	q.s.
Water	To 100

Source: Cockrell, J. R., Jr., U.S. Patent 5137793, Kay Chemical Co., 1992.

TABLE 10.75
Oven/Grill Cleaners

Ingredients	I Oven Cleaner Concentration (wt%)	II Grill Cleaner Concentration (wt%)	III Oven Cleaner Concentration (wt%)
Nonylphenol ethoxylate 10 EO	0.5	0.5	1–2
Sodium hydroxide (50%)	10	20	30–40
Polymer stabilizer/thickener Acusol 820 (30%)	3.75	4.25	—
Sodium gluconate	—	—	2–4
Propylene glycol	—	—	4–6
Butyl cellosolve	—	—	4–6
Alkali surfactant	—	—	8–12
Water	q.s.	q.s.	q.s.

A major concern is that the soil may nourish the growing microorganisms that present potential health problems. Liquid CIP cleaners are preferred, because they are easy to use in the automated cleaning systems. Traditionally, alkali hydroxides, alkali TPP, low molecular weight polyacrylates with nonfoaming or very low-foaming surfactants, and sanitizing agents such as chlorine bleach make up the CIP cleaning composition. Polyacrylates prevent scale formation on equipment and slow the accumulation of protein and fats on surfaces [78].

The technology of cleaning in the food process industry has traditionally been empirical. For example, most dairies employ the CIP method, involving the flushing of contaminated equipment surfaces with cleaning solution(s). For example, the equipment is rinsed with lukewarm (110–120°F) water, followed by a hot wash using a chlorinated alkaline detergent at 160–170°F, and lastly a cold acidic rinse using a mineral acid based composition such as phosphoric acid, sulfuric acid, and nitric acid based compositions. In addition to milk fat, milk also contains various soluble minerals, such as calcium, and proteins, such as casein and whey. Milk proteins at elevated temperatures tend to denature and tenaciously adhere to surface in layers. These layers of denatured milk protein are difficult to remove. The soluble minerals can combine with milk proteins to form scaling, also known as milk stone. Milk stone generally is insoluble in ordinary tap water and alkaline systems, but is soluble under acidic conditions. Conventionally, acidic solutions of mineral acids and organic acids have been used to remove these scales.

Even if the milk fat, milk protein, and milk stone are removed from a surface, residual microorganisms may still be present on the surface. Therefore, some sanitization of the surface needs to be performed to reduce the level of microorganism populations to safe levels established by public health ordinances or levels proven acceptable by practice. A sanitized surface is, by EPA regulation, a consequence of an initial cleaning treatment followed with a sanitizing treatment resulting in a reduction in population of at least 99.999% (a 5-$\log_{10}$ reduction) for a given microorganism. For a product to be certified under European Standard Method EN 1040 as a disinfectant or antiseptic, the product must demonstrate at least a 99.999% reduction (10^5 reductions) of *Pseudomonas aeruginosa* (ATCC 15442, CIP 103467) and *Staph. aureus* (ATCC 6538, CIP 483) at 20°C for 5 min contact time at the product's recommended use concentration. Similarly, for a product to be certified under European Standard Method EN 1276 as a sanitizer for food contact surfaces, the product must demonstrate at least a 99.999% reduction (10^5 reductions) in viable counts of *P. aeruginosa* (ATCC 15442, CIP 103467), *E. coli* (ATCC 6538, CIP 54127), *Enterococcus hirae* (ATCC 10541, CIP 5855), and *Staph. aureus* (ATCC 6538, CIP 483) at 20°C for 5 min contact time at the product's recommended use concentration under simulated clean conditions (0.30 g/L bovine albumin) or dirty conditions (3 g/L bovine albumin) [50].

The presence of residual food soil can inhibit sanitizing treatments by acting as a physical barrier that shields microorganisms lying within the soil layer from the biocide, or by inactivating sanitizing treatments by direct chemical interaction. A complete cleaning process must address all three cleansing elements (cleaning, sanitizing, and descaling) to provide a hygienic environment for all food-processing surfaces, especially milk-processing surfaces.

Hypochlorite or chlorine bleaches are effective in degrading protein by oxidative cleavage and hydrolysis of the peptide bond. However, the use of chlorinated detergent solutions in the food-processing industry is not problem-free. Corrosion is a constant concern, as is the degradation of polymeric gaskets, hoses, and appliances. Available chlorine concentrations must initially be at least 75 ppm, and preferably at least 100 ppm for an optimum removal of protein film [79]. At concentrations of <50 ppm of available chlorine, protein soils buildup is worsened by formation of insoluble, adhesive chloro-proteins [79]. Typically, chlorinated alkaline detergent in both liquid and powder forms is widely used, which will clean and sanitize the food processing surface at the same time, followed by an acid wash to remove lime scale or milk stone. Powder, liquid, slurry, and solid blocks are commercially available for CIP cleaners, and they are typically highly alkaline with chlorine bleach. Acid-type CIP cleaners are rarely seen on the market, because acid cleaners are not efficient in cleaning food soils such milk fat and milk proteins. An acid-type liquid CIP cleaner formulation with antibacterial agents that would clean, sanitize, and descale as in the all-in-one type is disclosed in Table 10.76 [80]. Some typical CIP formulations are shown in Tables 10.77 through 10.79. An enzymatic solid block CIP cleaner formulation is shown in Table 10.77 [79].

10.9.5 DRAIN CLEANERS

I&I drain-cleaning products are formulated differently than the household drain cleaners. The effluents collected in the drain of households are totally different than in I&I establishments. For example, typical household drains may contain kitchen food items such as leftover food residues, grease, and fats, and bathroom effluents such as soap scum and human hair. These solids slowly deposit in the drain, and as a result slow down drainage of the effluents and can ultimately clog the drains. On the other hand, an institutional drain such as in restaurants or bars may contain grease, fats, and other food residues including sugar-based soft drinks and alcoholic beverages. Detergent effluents from various cleaning tasks including floor cleaning also goes through the drains. Likewise, these effluents over time can modify themselves, and can deposit in the drainpipes, leading ultimately to slowing down and clogging the drains.

Mechanical water jetting and rotor rooting are often used in both household and I&I settings to clean up drain blockage and restore drains. But these methods require outside help and are expensive.

TABLE 10.76
Acidic Liquid All-in-One CIP Cleaner

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Deionized water	21.85	25.85	26.35
Acetic acid	1	1	1
Duomeen SV (soya alkyl-1,3-propyldiamine)	0.15	0.15	0.15
Propylene glycol	3	3	3
Plurafac LF 303	1.5	1.5	1.5
Citric acid	3	3	3
Phosphoric acid (75%)	35	35	35
Sodium xylenesulfonate (40%)	30	30	30
Emory 658	3	1	1
Plurafac 18B-45	1.5	1.5	1.5
Glycolic acid	—	3	2.5
pH	0.74	0.74	0.74
Cleaning performance, 60°C/8 min	97%	97%	97%
Germicidal kill data (AOAC test 960.09): *E. coli* and *Staph. Aureus*	>7 log reduction	>7 log reduction	>7 log reduction

Source: Adapted from Ahmed, F. U. and Traistaru, N. C., U.S. Patent Application 2006/0035808 A1, DeLaval (West Agro Inc.), 2006.

TABLE 10.77
Enzymatic Solid Block Clean-in-Place Cleaner

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Protease enzyme (Purafect 4000L	5	5	5
Alcohol alkoxylates, nonionic surfactant sulfonic LF41	—	10.7	25
Dry milk	5	—	—
Deionized water	15	—	27.50
Propylene glycol	—	1	4.25
Potassium cumene sulfonate (potassium naxonate)	—	—	12.25
Triethanolamine	—	—	26
Borax, $Na_2B_4O_6$	35	30	—
Dense soda ash (sodium carbonate)	—	29	—
Sucrose	10	10	—
Polyacrylic acid (50%)	—	10	—
Sodium sulfate	30	—	—
Sodium metabisulfate	—	1	—
Potassium hydroxide (45%)	—	4	—

Source: Adapted from Wei, J. G., McSherry, D., and Cords, B. R., World Patent WO 99/47631, Ecolab Inc., 1999.

TABLE 10.78
Acidic Enzymatic Liquid All-In-One CIP Cleaner

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Deionized water	74	73	73
Sulfamic acid	5	5	5
Bronopol	2	—	0
Anhydrous citric acid	5	5	10
Phosphoric acid (75%)	15	15	15
Glutaraldehyde (50%)	—	2	2
Triton DF-12 (nonionic surfactant)	—	1	—
Acid protease enzyme (validase AFP 1000 SAPU/L)	6	6	6
pH (0.5% solution)	2.45	2.54	2.66
Cleaning performance (0.5% usage concentration), 60°C/8 min 400 ppm hard water	92%	96%	100%

Source: Adapted from Ahmed, F. U. and Traistaru, N. C., U.S. Patent Application 2006/0035808 A1, DeLaval (West Agro Inc.), 2006.

TABLE 10.79
Chlorinated Liquid Nonphosphate Food Process Cleaner

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Low-molecular weight polyacrylate dispersant, Acusol 445N (45%)	9	—
Low-molecular weight polyacrylate dispersant, Acusol 505N (45%)	—	8.6
Sodium hydroxide (50%)	20	20
Sodium silicate (2:1, 44%)	1.5	1.5
Sodium hypochlorite (12%)	16.7	16.7

Source: Adapted from *Acusol Detergent Polymers for Food Process Cleaner*, Formulation FC-318, Rohm & Hass Company, Philadelphia, PA, May 1995.

Various chemical formulations for drain treatments in both household and I&I establishments are available and mostly contain highly corrosive and toxic chemicals. Typical drain cleaners contain very highly alkaline or highly acidic or bleaching materials that are dangerous and require special handling due to their corrosiveness. Sodium hydroxide, sodium silicate, sodium metasilicate, sulfuric acid, hydrochloric acid, and chlorine bleach are widely used. Some enzymatic or bacterial culture compositions made for treating drains are also on the market in both segments. These compositions additionally contain thickeners and surfactants. Depending on the nature of the compositions and special ingredients used in the formulations, pH of the products is adjusted accordingly. In restaurants, quick service restaurants, or bars where carbonated beverages or alcoholic beverages are served, a microbial or bacterial cellulose is produced from biosynthesis of sugar chemistry with *Acetobacter* bacteria, microorganisms that thrive in sugar- or alcohol-enriched acetic environment. Microbial cellulose is spongy, floppy material that grows and deposits in the sugar-enriched drains, and ultimately slows down and clogs the drains. A method to treat such drains with an enzymatic chemical composition has been developed and patented [81–84]. Some typical I&I drain-cleaning compositions are shown in Tables 10.80 through 10.82.

TABLE 10.80
Liquid Drain Cleaner Composition

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sodium hydroxide (50%)	50	10–15	20
Alkyl alcohol ethoxylate or alkylphenol ethoxylate	1	—	—
Phosphate ester	—	3–7	8
m-Pyrol-*N*-methyl-2-pyrrolidone	—	2–4	5–8
Water	q.s.	q.s.	q.s.

TABLE 10.81
Biological Drain Treatments

Ingredients	I Concentration (wt%)	II Concentration (wt%)
Bacterial cultures	10–20	15–20
Organic thickener	1–5	2–3
Alkyl alcohol ethoxylate or alkylphenol ethoxylate	1–3	2–3
Water	q.s.	q.s.

TABLE 10.82
Powder Enzymatic Drain Cleaner

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Sulfamic acid	40	20	—
Citric acid	—	20	40
Sodium bicarbonate	0	40	40
Sodium carbonate	5	5	5
Sodium dodecyl benzene sulfonate	10	10	10
Carbopol thickener	1	1	1
Bacterial cellulase	4	4	4

Source: Adapted from Ahmed, F. U. and Traistaru, N. C., U.S. Patent Application 2006/0035808 A1, DeLaval (West Agro Inc.), 2006; Ahmed, F. U., Goldschmidt J. E., and LaCossee G. E., U.S. Patent 5783537, Kay Chemical Co. (Ecolab), 1998; Ahmed, F. U., Goldschmidt, J. E., and LaCossee, G. E, International Patent WO 9732960 A1, Kay Chemical Co. (Ecolab), 1997; Ahmed, F. U., Goldschmidt, J. E., and LaCossee, G. E, U.S. Patent 5975095, Kay Chemical Co. (Ecolab), 1999; Ahmed, F. U., Goldschmidt, J. E., and LaCossee, G. E., U.S. Patent 6020293, Kay Chemical Co. (Ecolab), 2000.

10.10 TEAT DIP APPLICATIONS FOR DAIRY ANIMALS

Bovine mastitis is the single most costly disease affecting the dairy industry. Annual economic losses due to mastitis is approximately $185 per dairy animal. This amounts to approximately $1.7 billion annually for the entire U.S. market or ~10% of total milk sales, with about two-thirds of this loss is due to reduced milk production from infected cows [85–87]. Mastitis is a bacterial infection of the mammary gland that causes inflammation and is always a potentially serious infection. It results when various species of bacteria enter the gland through the streak canal. If they are successful in gaining a foothold, they can colonize the gland, producing infection and inflammation. In dairy cows, mastitis typically results from microorganisms, usually bacteria that invade the udder, multiply in the delicate mastitis-producing tissues, and synthesize toxins, a byproduct of bacterial metabolism. The characteristic features of inflammation are swelling, heat, redness, pain, and disturbed function. More than 80 species of microorganisms have been identified as causal agents; approximately 95% of mastitis is caused by four pathogens: *Staph. aureus, Streptococcus agalactiae, Streptococcus dysagalactiae*, and *Streptococcus uberis.* Mastitis-causing pathogens fall into two categories, namely, contagious and environmental. Contagious bacteria, such as *Staph. aureus* and *S. agalactiae*, primarily colonize host tissue sites, such as mammary glands, teat canals, and teat skin lesions, and are spread from one infected cow to another during the milking process through contact between the animals and dairy equipment that may carry a source of mastitis pathogens. The second type of mastitis is environmental mastitis, which is caused by contamination of surfaces within the animal's surroundings from sources such as cow feces, soil, plant material, bedding, water, and like materials from the barnyard environment and barn interior. Such pathogens often include streptococci, enterococci, and coliform organisms such as *E. coli, S. uberis, Klebsiella,* and others that are commonly present within the cow's surroundings. Such contamination occurs as the animal moves through its environment. This distinction has practical importance because different dairy herd maintenance measures are needed to control different groups of microorganisms. Management of dairy herds focuses on treatment of both established mastitis and prevention of new intramammary infections. Therapy and hygiene are the two fundamental components of an effective mastitis control protocol. Each is applied in concert, and each operates independently. In a typical operation of a dairy herd, the herd is brought into a milking station (parlor), and the udder is washed to remove the dirt and barrier film. Udder teats are washed, cleaned, sanitized with a predip, milked, and treated with a barrier teat dip having antibacterial properties to protect teats from mastitis between milking.

To reduce mastitis, commercial teat dips have been developed that are usually administered to the teat by dipping or spraying the teat prior to milking, as well as after milking after removing the milking cup. Contagious mastitis is almost controlled using germicidal postmilking teat dips; such germicidal dips kill bacteria that are introduced onto the surface of the animal from milking machines and milking workers' hands. Teat dips applied subsequent to milking may form a thick film or barrier that remains on the teat until the next milking, which is generally 8–12 h later.

Commercially available teat dips have been divided into two primary categories, namely nonbarrier and barrier dips. Product types include: postdips, predips, post- or predip concentrates, foaming dips, winter dips, and versions for spraying. General knowledge and disclosures of teat dip technology are widely published [88–90].

Table 10.83 shows some of the performance requirements for the main classes of teat dip [88]. It should be noted that teat conditioning is extremely important for all types of postmilking dips, whereas for predips or udder washes it is somewhat less important because of the shorter contact time.

To reduce mastitis, commercial teat dips have been developed containing a variety of antimicrobial agents, including iodophors (iodine complexes), free iodine, quaternary ammonium compounds, chlorhexidine compounds (gluconates, acetates, etc.), oxidizing chlorine-releasing compounds (e.g., alkali hypochlorites and many organic and inorganic precursors), oxidizing peroxy compounds (hydrogen peroxides, peracids), protonated carboxylic acids, acid anionic surfactants (e.g., alkylarylsulfonic acid), and chlorine dioxide (generated from acidification of alkali chlorite). Table 10.84 shows world teat dip disinfectant market share based on common germicidal agents [84]. Although there are some general trends in various germicides on teat conditioning, the major results are formulation dependent; some exceptions may be use of strong oxidizers such as sodium hypochlorite (chlorine bleach), which cannot be preformulated with

TABLE 10.83
Preferred Characteristics of Teat Dips

Attributes/Properties	Predip	Postdip	Postdip Barrier	Postdip Concentrate
Germicidal broad spectrum	Critical	Critical	Critical	Critical
Speed of kill	Critical	Important	Important	Important
Nonirritating	Desirable	Critical	Critical	Critical
Promotes healing (added emollient)	Beneficial	Desirable–critical	Desirable–critical	Desirable–critical
Good wetting	Critical	Desirable	Desirable	Desirable
Viscosity	Low	Low–moderate	High	Low–moderate
Germicide stability	Critical	Critical	Critical	Critical, concentrated and ready to use
Physical stability	Critical	Critical	Critical	Critical, concentrated and ready to use
Residual efficacy	Unwanted	Desirable	Critical	Desirable
Persistent physical/chemical	Unwanted	Desirable	Critical	Desirable
Detergency	Desirable	Not important	Not important	Not important
Milk residue	Critical	Critical	Critical	Critical

Source: Adapted from Hemling, T. C., *Proceedings of the British Mastitis Conferences*, Institute for Animal Health/Milk Development Council, Brockworth, pp. 1–14, 2000.

TABLE 10.84
Teat Disinfectants Estimated Market Share

Germicide	Type	USA	Americas and Pacific	Europe[a]
Iodine	Oxidative	70	60–70	45
Chlorhexidine	Nonoxidative	10	10	25
Hydrogen peroxide	Oxidative	7–8	4–5	5
Chlorine dioxide	Oxidative	7	4–5	5
Chlorine bleach (NaOCl)	Oxidative	4	10–15[b]	5
DDBSA Dodecylbenzenesulfonic acid	Nonoxidative	1–2	1–2	10
Lauricidin	Nonoxidative	1–2	1–2	—
Nisin	Nonoxidative	1–2	<1	—
Others	—	—	—	5

[a] UK, Iodine=60–65%, DDBSA=5%

[b] Brazil 50%,

Source: Adapted from Hemling, T. C., *Proceedings of the British Mastitis Conferences*, Institute for Animal Health/Milk Development Council, Brockworth, pp. 1–14, 2000.

oxidizable emollients such as glycerin, sorbitol, and propylene glycol, and certain germicides that require a low acidic pH (≤ 3) for effective germicidal activity. Iodine is the most common germicide used in the teat dips in worldwide market, and it commends nearly 70% of the market share of teat dip products, as shown in Table 10.84. With over 100 iodine-based teat dips available in USA and probably more than 500 globally, their compositions are widely varied. Iodine levels in teat dips vary from 500 (0.05%) to 10,000 ppm (1%), and other formulation ingredients are also widely varied. Iodine teat dips are very effective at reducing the spread of bovine mastitis. The concentrations of various active ingredients used in teat dip applications are formulation specific and widely varied; concentrations of certain antibacterial agents found in typical topical teat dip products are: chlorhexidine (0.35–0.55%), chlorhexidine gluconate (0.4–0.5% with 6–10% glycerin); iodine (0.05–0.25% with 0.75% glycerin; 1% with 10% glycerin, lanolin, and polyvinylpyrrolidone [PVP]; 0.5% with 1% glycerin, 0.55% lanolin, and 0.5% aloe vera); linear dodecylbenzene sulfonic acid (DDBSA) (1.94%); caprylic acid and capric acid mixture (1.25%); quaternary ammonium compounds (0.5%); sodium chlorite acidified with inorganic and organic acid to generate chlorine dioxide (0.64–0.7% with 2.64–2.90% lactic acid; 0.64% with 3% mandelic acid; 0.25% with 1.67% phosphoric acid; 0.32% with 0.27% DDBSA, 1.32% lactic acid, 2.5% glycerin); iodophors (0.10–0.25%); Bronopol (0.5–1%); and isocyanuric acid as a source of hypochlorite (0.5–1%).

Acidified sodium chlorite disinfectant is often referred to as a chlorine dioxide generating system, and results in a product of sodium chlorite when treated with organic and inorganic acid, which activates $NaClO_2$ and generates chlorous acid ($HClO_2$) that converts into a chlorine dioxide germicide. A wide variety of mineral and organic acids, such as lactic acid, citric acid, mandelic acid, DDBSA, and phosphoric acid are reacted with sodium chlorite to generate gaseous chlorine dioxide. It is noted that the use of α-hydroxy organic acids, such as lactic acid and mandelic acid, are preferably used. When DDBSA is used as an activator for $NaClO_2$, it also provides residual germicide after gaseous ClO_2 evaporates off. DDBSA-based teat dips have been found to significantly reduce intramammary infections by contagious pathogens.

Iodine is not very soluble in water, exhibiting about 300 ppm of water solubility at ambient temperature. Additional solubilizers are used to increase the solubility. The effectiveness of iodine germicides has little dependence on the iodine concentration. It has been reported that the efficacy of iodine teat dips is greatly affected by the concentration of free iodine in the product [91]. Free iodine is a measure of the concentration of uncomplexed or molecular iodine as shown in Equation 10.1 [92]:

$$I_3^- \text{ (Complexed Iodine)} \longrightarrow I_2 \text{ (Free Iodine)} + I^- \tag{10.1}$$

A wide variety of ingredients can complex iodine. Nonionic surfactants are also commonly used to form iodine complex, and these complex mixtures are generally referred to as iodophors. Equation 10.2 shows the typical equilibrium for an iodophor.

$$\text{Surfactant: } I_3^- \text{ (Complexed Iodophor)} \longrightarrow \text{Surfactant} + I_2 \text{ (Free Iodine)} + I^- \tag{10.2}$$

Typical iodine-based teat dips may contain 5–8 ppm of free iodine; however 12–16 ppm of free iodine is optimum. A broad range of NIs may be utilized: nonylphenol ethoxylates, alcohol ethoxylates, alcohol alkylates, sorbitan ester ethoxylates, ethoxylated alkylpolyglucosides, alkyl ether carboxylates, and ethylene oxide–propylene oxide copolymers. Many of these are also used as detergents to remove oily soils from hard surfaces. This same property can lead to removal of natural protective oil in teat skin. PVP is widely used to solubilize and complex iodine for use in many topical germicidal applications including teat dips. PVP is also used in barrier teat dips where it can form a physical film or barrier and is very compatible with bovine skin chemistry. Use of surfactants improves the spreading characteristic of disinfectant solution, due to lowering of surface tension and their ability to penetrate cracks, crevices, cavities, and films or barriers of organic material.

In the treatment and prevention of mastitis, use of protective coatings such as a prophylactic physical barrier or film from organic materials has long been practiced. Materials may be simply film barriers formed on the skin surface to prevent contact between vulnerable tissues and the environment, or coating compositions that are actively antimicrobial and prevent the incidence of infection in the animal through the presence of an active biocide in the coating. The barrier type materials simply prevent direct contact between the skin and contagious materials. Barrier type materials rarely contain antibacterial agents; the combination of effective germicidal materials with film forming or a barrier dip formulation would provide the potential for controlling both contagious and environmental mastitis infections. A wide variety of organic materials are found to be effective for forming a film barrier in teat dip formulations. These film agents are typically polymeric organic material such as PVP, polyvinyl alcohols (PVAs), and other vinyl polymers; protein hydrolyzate; natural and synthetic gums; cellulose derivatives; and acrylic polymer lattices. The latex and PVA form a flexible film on the skin that can be peeled off after moistening the area.

Skin-conditioning agents are usually added to teat dips to mitigate any adverse effect of other skin-unfriendly ingredients in the teat dips and lower pH, which is often necessary to provide effective germicidal properties or conditioning benefits to address harsh weather or the effects of milking machines. Skin-conditioning agents are either moisturizers, also known as humectants, or moisture barriers. Moisturizers are additives that attract moistures to the outer layers of the skin to keep it soft and supple. Common moisturizers either used alone or in combination include glycerin, propylene glycol, sorbitol, and aloe vera gel, and range from 2 to 10% in the formulation. Generally all moisturizers are high in hydroxyl group content, which attracts and bind moisture. Glycerin has a 1.35 times higher moisture binding capacity than propylene glycol and four times the capacity of sorbitol. A high glycerin level in teat dips leaves a tacky film, whereas sorbitol leaves a much drier film on teats. For iodine teat dips, high concentrations of glycerin are difficult to formulate, and a combination of propylene glycol and glycerin is widely used. Moisture barriers are also skin-conditioning agents, and function by creating a barrier to prevent loss or evaporation of moisture from the skin. The functional properties of moisture barriers are determined by measuring transepidermal water loss. Typical moisture barriers are oily materials such as lanolin, lanolin derivatives such as ethoxylated material, mineral oil, and petrolatum. Mineral oil and petrolatum are occasionally used in udder cream, and are seldom used in aqueous teat dips because of their poor solubility. Viscosity of teat dips plays an important role, depending on product form. The viscosity of common commercial teat dips varies from 1 to 5 cP water thin predips for spray type products to much more viscous 300–1000 cP barrier postdip products. Postdip formulations with viscosity range of 5–50 cP are also on the market. Viscosity and product rheology of post teat dips are so designed based on specific viscosity modifiers to provide good adherence to skin and provide vertical clinging to teats with no dripping. Increased viscosity teat dips will provide longer adherence on teats to protect skin as conditioners with increased layer thickness, and on the other hand, in adverse cold weather conditions in harsh winter, may prolong evaporation and cause increased chapping, frost bite, or teat end freezing. Teat conditioning depends on amount of emollients, pH of the teat dips, and other skin-conditioning agents. A study shows that in a comparison between two iodine teat dips with identical, mild surfactants but differing in level of glycerin emollient at 2% versus 8%, teat conditioning scores for teat skin and teat end are significantly higher with 8% glycerin [93]. A similar teat-conditioning trial compared a teat dip with 10% glycerin, a chlorine dioxide teat dip, and a chlorine teat dip with 10% glycerin, and again 10% glycerin alone provided the best teat condition, followed by chlorine dioxide with glycerin, and lowest score was for the chlorine dioxide based teat dip [94].

Teat dips are regulated as drug products by the Center for Veterinary Medicine, part of the FDA, which requires that manufacturers list their products with the agency. Since teat dips are topically applied antiseptics, they are regarded as over-the-counter drugs, and are regulated as such. Teat dips manufacturing follows the current Good Manufacturing Process. The FDA does not require manufacturers to submit efficacy data. However, recommended protocol for determining efficacy of a postmilking barrier teat dip based on reduction of naturally occurring new intramammary infections follows the guidelines of the National Mastitis Council (NMC) protocol developed by the NMC Research Committee in 1997.

Teat dip compositions and formulations are widely varied, and commercial products are generally separated based on active germicidal agents. Iodine germicide based teat dips are the market leader and command 60–70% of the worldwide market, as shown in Table 10.84. The other minor teat dips command the rest of the market share, and are roughly equally distributed among chlorhexidine, chlorine dioxide, and hydrogen peroxide germicides. Typically, standard teat dip formulations contain <1% germicide, <1% thickener (0.5% optimum for barrier dips), teat conditioners other than moisturizers <1%, emollients 5–10%, wetting agents/surfactants <1%, film/barrier agents for barrier postdips 1–5%, buffering agents <5%, pH-controlling agents <2%, choice of dyes, and water carrier. Examples of some typical iodine, iodophors, chlorine dioxide, and other germicides are shown in Tables 10.85 through 10.89. The estimated U.S. market for teat dips is $114 million according to a market survey conducted by Kline Co., and the Canadian teat dip market is $10 million. The worldwide teat dip market is not well defined.

TABLE 10.85
Iodine Teat Postdip Barrier Formulation

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Water	90.55	88.29	87.76
Acid blue #9 dye	Trace	Trace	Trace
Xanthan gum	0.45	0.45	0.40
Elvanol 90–50 (polyvinyl alcohol, 99% hydrolyzed)	4	4	4
Sorbitol	5	5	5
NPE-I2 (nonylphenol ethoxylate 12 EO) Iodophor[a]	—	2.26	2.26

[a] Triiodine complex premix (contains 57% iodine and 20% iodide).

Source: Adapted from Foret, C. and Hemling, T. C., U.S. Patent 5916581, West Agro (DeLaval Inc.), 1999.

TABLE 10.86
Iodine Teat Postdip Barrier Formulation

Ingredients	I Concentration (wt%)	II Ingredients	III Concentration (wt%)
Film forming agent	0.25–0.6	Natrosol 250 KR, Pluronic P105	0.625, 3.0
Germicidal agent (iodine)	0.10–0.75	Iodine	0.50
Complexing agent: iodine	2:1–12:1	Hydrogen iodide	0.18
Iodine:Iodide	1:015–1:0.6	Sodium iodate	0.02
Emollients	2–12	Glycerin	6
Wetting agents	0.01–0.5	Sodium dioctylsulfosuccinate	0.10
Thicker	0.01–0.3	Keltrol	0.20
Buffer agent for pH control	4.5–6.5	Citric acid sodium hydroxide (50%)	0.30, 0.14
Water	q.s.	q.s.	q.s.
Viscosity	100–800 cP	—	—

Source: Adapted from Foret, C. and Hemling, T. C., U.S. Patent 5916581, West Agro (DeLaval Inc.), 1999.

TABLE 10.87
Chlorine Dioxide Teat Dip Composition: Two-Part System (Base and Acid Activator)[a]

Ingredients	Part A: Base Concentration (wt%) pH = 12.3	Part B (I): Acid Activator Concentration (wt%) pH = 2.9	Part B (II): Acid Activator Concentration (wt%) pH = 2.9
Sodium chlorite (25%)	50	—	—
Deionized water	50	—	—
Glycerin (96%)	—	5	5
Isopropanol (99%)	—	2	—
Nonanoic acid (Pelargonic acid)	—	1.5	—
Lactic acid (88%)	—	2.95	2.95
Dodecyl benzene sulfonic acid (97%)	—	—	2
Xanthan gum (Keltrol® K5C151)	—	0.30	0.30
Deionized water	—	60.76	78.14
Potassium benzoate	—	0.20	0.20
Potassium hydroxide (45%)	—	0.29	1.41
Sodium octane sulfonate	—	17	—
ELVANOL® Premix (10%)[b]	—	10	10

[a] Ninety-three grams of base (Part A) is mixed with 3376 g of activator (Part B) to give 0.32% of ClO_2 with viscosity of ~304 cP.

[b] The premix is 10% aqueous solution of ELVANOL 90–50, which is a grade of polyvinyl alcohol.

Source: Adapted from McSherry, D. D. and Richter, F. L., U.S. Patent 6699510 B2, Ecolab Inc., 2004.

TABLE 10.88
Two-Part Chlorine Dioxide Teat Dip Composition: 1:1 v/v (Part A Acid Activator, Part B Base)

Ingredients	I Part A: Acid Activator Concentration (wt%)	I Part B: $NaClO_2$ Base Concentration (wt%)	II Part A: Acid Activator Concentration (wt%)	II Part B: $NaClO_2$ Base Concentration (wt%)
Malic acid	2	—	5	—
Polyacrylamide	1	—	0.75	—
Isopropyl alcohol	25	—	15	—
Sulfuric acid, 1N	—	—	2	—
Poloxamer 188	—	—	0.62	—
Sodium benzoate	0.04	—	0.0.04	—
Deionized water	q.s.	—	q.s.	—
Sodium chlorite	—	0.80	—	1
Polyacrylamide	—	1	—	0.75
Octylphenoxy polyoxyethylene 12 EO	—	—	—	0.45
Triton X-100	—	0.45	—	—
Polyethylene glycol	—	—	—	0.30
Tetrasodium edetate	—	—	—	0.19
Isopropyl alcohol	—	25	—	15
Deionized water	—	q.s.	—	q.s.

Source: Adapted from McSherry, D. D. and Richter, F. L., U.S. Patent 6699510 B2, Ecolab Inc., 2004.

TABLE 10.89
Noniodine Barrier Teat Dip Composition

Ingredients	I Concentration (wt%)	II Concentration (wt%)	III Concentration (wt%)
Water	87.40	80.28	—
Xanthan gum (Novaxan D/ADM)	0.40	0.40	0.40
Polyvinylpyrrolidone K-30	0.80	0.40	—
Salicylic acid	0.50	0.50	0.90
Allantoin	0.10	0.10	0.10
Glycerin	—	10	10
Isopropyl alcohol	3	—	—
Lactic acid (88%) USP (ADM Co.)	4	4	4
Benzyl alcohol	1	1	1
PEG-7-glycerylcocoate (Cetiol HE)	0.50	0.50	0.50
EO/PO/EO block copolymer (Pluronic P105)	0.50	0.50	0.50
Sodium dioctylsulfosuccinate (75%)	0.15	0.15	0.15
Polysorbate 80 (Tween 80)	0.50	0.50	0.50
Sodium hydroxide (0.50%)	1.25	1.25	1.25
pH	3.50	3.50	3.50
AOAC germicidal kill test 960.09 (20°C, 30 s contact time) on *E. coli* and *Staph. aureus*	7.80–8.00 $\log_{10}$ reduction	—	—

Source: Adapted from Ahmed, F. U., Traistaru, N. C., and Hemling, T. C., U.S. 2007/0027119 A1 and World Patent Application WO 2007/0016067 A2, DeLaval (West Agro) Inc., 2007; McSherry, D. D. and Richter, F. L., U.S. Patent 6699510 B2, Ecolab Inc., 2004.

10.11 FUTURE TRENDS

The I&I cleaners market is very dynamic and is evolving rapidly. Newer products are developed and marketed quickly as the demands for specific needs are realized. Newer I&I products are probably commanding ~20 to 30% of total business.

A major formula change is the move away from solvents to aqueous based I&I cleaners. *Butyl type* solvents are contained in some floor strippers, all-purpose degreasers, and heavy-duty cleaners, because they are very effective as grease cutters. Many industry observers, however, believe that butyl solvents will eventually be phased out. Mildness is also an important issue in the I&I cleaning products. An increased need in keeping places like hospitals and nursing homes clean has brought about demand for milder surfactants. This trend will continue as the population of 70–75-year-olds doubles in the beginning of the twenty-first century. There is also an increased concern for safety of workers handling the I&I cleaners. This results in a move to a safer formulation, such as those using less corrosive sodium hydroxide, and less solvents and greater use of aqueous surfactants to improve worker safety. The phasing out of chlorinated and chlorofluorocarbon solvents in industrial cleaners is helping in development of more safe solvents, safe chemicals, and solvent-free products for I&I applications. Although the peroxide bleach generated from various sources is not expected to replace commonly used chlorine bleach (NaOCl) completely in the future, it does bring a number of advantages, such as enhanced fabric protection, compatibility with colored textiles, and prevention of spots due to some chlorhexidine-containing disinfectants used in hospital laundry.

A cleaning product that is mild and good for the environment and still offers performance is the ideal choice. NPEs constitute the largest volume of surfactant used in I&I cleaners, but because of increasing environmental concerns, their use will be significantly less in the future.

In I&I product formulations, existing products with NPEs are being reformulated with NPE performance-comparable surfactants and ingredients. Recently, a study conducted on diethanolamine and its alkanolamide derivatives showed some carcinogenic properties on laboratory animal, and there are some growing concerns on using these materials in any cleaning products. Ethoxylated alcohols are much favored because of their excellent hard surface cleaning power, effectiveness in hard water, and skin compatibility. Linear alkylbenzene sulfonates, the leading surfactant used in household consumer products, are only used in relatively minor quantities in I&I cleaners. Various new raw materials that fit the bill of the future thrust are now available. An expanded line of APG (Glucopon) surfactant is available for use in household and I&I cleaning products. These surfactants are derived from natural raw materials, such as glucose from corn and fatty alcohol from coconut and palm-kernel oils. These surfactants give formulations flexibility by offering more opportunities. The APG concentrates can be used in dishwashing, laundry, hand soap, and all-purpose hard surface cleaners as a primary or cosurfactant. They offer high foaming, exceptional mildness, and strong interaction with anionic surfactants. Rhone-Poulenc introduced a new generation of amphoteric surfactants such as glycine-based amphoacetate amphoterics (Miranol Ultra™ and Excel™) for personal care and I&I cleaning products. These amphoteric surfactants are well known to reduce skin irritation and provide rich creamy foam.

There is a trend in the industry to reduce water and lower wash temperature (low-temperature laundry and ware washing), as mandated by the U.S. Department of Energy, which requires reformulation of detergent, making them effective at low water volume and low temperature. In consumer laundry detergent products, horizontal load washing machines, which use less water and less detergent, are now commercially available. Cold water laundry detergents for household use are also now available. The advent of less water and cold temperature laundry wash and in possible automatic dishwashing applications in the consumer segment will definitely influence development of similar products in I&I applications.

Cleaning formulations are often impacted by a drive to be global, and this trend continues toward designing global products where possible. Serving customers all over the world demands the development of products that meet the stringent requirements of particular geographic locations. Customers want proactive programs with innovative R&D, and often dictate formulation developments and regulatory demands that address their direct needs and help target future products. I&I cleaner manufacturers must find alternative ways to differentiate themselves; this often means providing extra services to keep the customer base happy. Trends continue in developing multipurpose, value-added, concentrated products that can be diluted on-site rather than specialized items in the I&I segment. The search for new surfactants and other detergent ingredients that are multifunctional, effective, and mild will continue.

Solid detergent in the form of tablet or block is spreading to I&I applications and gaining popularity because of safety and convenience. The solid products continue to grow faster than powders or liquids. The solid block detergents developed and aggressively marketed by Ecolab Inc. have well taken over in the institutional ware-washing and some commercial laundry operations. Solid detergents, for example, are made by a variety of methods. In one area, molten caustic soda or slurry of detergent formula is prepared and poured into containers. As the STPP in the formula changes to STTP hexahydrate, the slurry solidifies. The solid detergents are readily soluble in hot water with correct dosing for each wash load as determined by controlling the amount of water injected into the dispenser, in the more advanced models, by measuring conductivity of the detergent solution formed. To avoid mix-up and use of the wrong detergent for a specific use, solid block with specific shapes designed for a particular application that would fit only in the particular shaped-dispenser are now common in some I&I applications. The search for revised cleaning formulations without or with reduced solvents and reduction in volatile organic compounds (VOCs) may be the number one consideration in I&I cleaners now and will be for the foreseeable future. Another trend is a sales and advertising emphasis of environmental and safety aspects of I&I cleaners. I&I cleaner manufacturers often emphasize the biodegradability of the products that are phosphate free, although phosphates are exempt from most bans in I&I applications. The phosphate content, which is relatively low due to the soft water used in I&I cleaning, will be further reduced. Biodegradable cleaning agents such as zeolite A, citrates, polycarboxylates (polyacrylates), and soda ash will be used as phosphate substitutes. There will be increased use of more ecological and operator-friendly products, and continued focus on multifunctional attributes. There has been a growing concern for environmentally unfriendly ingredients in household consumer products (e.g., phosphate), and now we are seeing similar concern expressed in the I&I arena. There are concerns and uncertainty about the impact strong environmental emphasis by government. Institutional healthcare is growing very steadily because of an increasingly older population, and is emerging as the fifth segment in the I&I category after janitorial, food service, laundry, and industrial. There is a growing tendency to use building service contractors rather than in-house staff for cleaning and maintaining institutional buildings, even including supermarkets. This will also influence future product development.

Ultra–high-speed floor care systems show continuing growth, because they reduce labor, the single most expensive element in floor care, estimated at 90–95% of the total cost. For example, some industry experts estimate a job can be done by a 2000 rpm floor machine in one-tenth of the time taken by a 175 rpm machine. Recent developments, such as to make such machines wider to cover more floor area at one pass, will again save labor. The automation of equipment will continue to reduce labor; there will be more highly automated scrubbing machines, and larger and faster burnishes to accomplish floor care faster and better. Robot type equipment, either wire-driven from the floor or radio-controlled, will be popularly introduced in the next 10 years for a large, relatively unobstructed area. Robot-type cleaning systems such as vacuuming and floor cleaning are now available on the household market. One supervisor may be able to watch four or five such robots do the cleaning, rather than watching four or five people.

Use of newer flooring materials is also increasing in I&I arena. One of the reasons for the growth of natural stone is that it is easy to maintain. An important consideration in stone care is the need to clean the surface of the new floor well and then to protect it with impregnators and sealers. If this one-time, long-term protection is not done initially, the floor will absorb water and other liquids, stain, and exhibit abrasion. As the popularity of natural stone floor has risen, a need for setting standards for its care has been recognized. Chemical maintenance procedures and developing standards for the care of mineral flooring, which includes marble, terrazzo, and granite, also have to be developed.

Safety is the hallmark of the twenty-first century, as predicted by floor care industry experts. Along with selecting products that will reduce labor and maintenance cycle, the distributors will be looking for products they can market as posing no threat to the environment or to workers. There will be a stronger impact for workers' safety by OSHA in buying and dispensing I&I cleaners, in particular increasing concern about the disposal of 55 gal. drums and 5 gal. pails. There is a demand to recycle and reduce packaging waste, and recycling of drums is now common. Equipment and machines require surface cleaning and sanitation especially in the food and health industries. Cleaning materials must be very functional, not corrode or damage surfaces, and retain surface characteristics. Stainless steel is the best noncoated metal surface for durability and ease of cleaning. Aluminum surfaces pose problems because of the corrosive effects of acids and alkalis, spotting and streaking from drying. Increased use of detergent bags in a dispenser and solid capsule dispensing will greatly reduce the amount of plastic waste in landfills. The desire for safe products and customers' sensitivity to product safety have become enhanced by transportation labeling, material safety data sheets, disposal criteria, and workers' health and safety regulations. The ever-increasing concern about the spread of disease is causing some turbulence. There is great interest in very effective and efficient disinfectants and sanitizers. Commercial laundries heavily rely on a variety of cleaning agents to assure that linens are hygienically clean. Cost control and system efficiency with very effective sanitation and cleaning programs will be a key driver for developing these types of cleaners. The outlook for disinfectants and detergent sanitizers is taking a different turn. The higher costs associated with registration fees and prohibitive costs for developing new actives have led to higher dependency on optimizing formula rather than individual ingredients. Technological challenges continue in providing maximum biocide efficacy and performance properties while minimizing ecological impact. In the future, hygienic requirements will become more important in all I&I establishments, especially in healthcare, food preparation, and the food services industry. A renewed challenge lies with formulators to use an existing, registered active ingredient and provide legitimate differentiation. The trend toward the automation of washing processes including the dosing of detergents and auxiliary agents will continue to grow in the future. Use of continuous batch washing machines with counter-flow system will increase. An ideal product will be a single detergent that delivers all the needed functionality of auxiliary-cleaning agents. For example, a laundry detergent should be a fully loaded product containing optical brightener, fabric softener, and bleaching agents. A ware-washing detergent may contain bleaching agents and rinse-aids together. Automatic dispensing and dosing systems will need to be perfected. Pumpable, completely built detergent paste or slurry may gain importance in the future. Generally, the concentrated products will gain more and more ground because of savings on shipping and storage space. A tougher regulatory climate, phasing out of some widely used I&I solvents, and customer demands for milder, more concentrated products will dictate the product formulation in I&I cleaners in the future. It is an exciting time to everyone in the I&I cleaning industry called on to meet the future demands and challenges.

Mild, *green*, and clean are the thrust of future research and development efforts in the I&I Cleaners market. The three topics are among the most important current and future trends. There is a move toward ingredients that are environmentally friendly, biodegradable, or derived from renewable resources due to customer demand for *green* products. But regardless of whether it is a fast food restaurant, nursing home, or high school, nearly all users of I&I products are beginning to show an interest in environmentally friendly products both in the United States and around the world, even as a clear-cut definition of green has yet to be developed. There is a great deal of interest in sustainability in I&I products.

What are "*green*" and "*green chemistry*"? There have been a lot talks, conferences, and movements all over the world, especially in Europe, about *green*. A clear-cut definition of green and green chemistry is evolving rapidly. Green chemistry is defined as the "design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances" in an article published recently in *Inform* [96]. The approach is outlined in the 12 principles of green chemistry:

1. Prevent waste
2. Design safer chemicals and products
3. Design less hazardous chemical syntheses
4. Use renewable feed stocks
5. Use catalysts, not stoichiometric reagents (stoichiometry calculates the exact quantities of substances that enter into, and are produced by, chemical reactions)
6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible
7. Maximize atom economy: Design methods to maximize the incorporation of all materials used in the process into the final product
8. Use safer solvents and reaction conditions
9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

There are many institutions like the Green Chemistry Institute at the American Chemical Society, and GreenBlue, a nonprofit organization founded in 2002 in Charlottesville, VA. GreenBlue certifies and maintains an online database of I&I cleaning product ingredient chemicals and provides verified information about the environmental and human health attributes of listed ingredients in the database CleanGredients™. GreenBlue helps formulators to identify better "design for the environment" ingredients, and helps suppliers to showcase better ingredients; the database includes information on more than 70 surfactants supplied by major manufacturers such as Akzo Nobel, BASF, Uniqema, and Tomah Products. The U.S. EPA's Design for the Environment Formulator Program (EPA DfE) is one of the EPA's premier partnership programs, working with individual industry sectors to compare and improve the performance, human health and environment risks, and costs of existing and alternative products, processes, and practices. Products created from CleanGredients could be fast-tracked for recognition by the EPA DfE program, or could facilitate certification to ecolabels such as the Canadian EcoLogo™.

Legislators in Europe and other parts of the world are not waiting either. They have banned or heavily restricted use of hundreds of toxic substances in recent years. The proposed Registration, Evaluation, and Authorization of Chemicals (REACH) initiative would require chemicals and chemical producers to register most chemicals that are widely used. There is enormous interest in also *green cleaning*. I&I customers want green cleaners; I&I manufacturers must satisfy multiple stakeholders, including governments, distributors, customers, and users. But even as regulations rise and demands for green cleaning increase, the cost for chemicals continues to run at ~5 to 15% of total I&I costs. The generally accepted cost breakdown for I&I detergent applications are: labor, 50%; water and energy, 40%; capital investment, 5%; and chemicals, 5%. Clearly, chemicals make up only a small fraction of overall I&I costs. Yet, I&I marketers must address cost issues if they hope to maintain customers and attract new business. Although marketers agree that green cleaning is a trend that runs across all I&I product categories, they remained mixed on what segment of the products should be emphasized during the coming years. Manufacturers are focusing on floor care, for both carpets and hard surfaces, and a few have recently introduced systems with good stain resistance and durability to help customers keep labor costs in check. Surface treatments with chemicals such as coating fabrics with antibacterial agents and soil-repelling fluorocarbons are showing up in household consumer products, and the trend soon will spill over into I&I cleaners.

Demand for environmentally friendly products may continue to grow, but successful marketers will combine green ideas with value. Besides wrestling with costs, nearly every I&I company is rolling out a new line of environmentally friendly cleaners. Corn, soy, and sugar are ingredients found in some of today's industrial and institutional cleaners. Most people probably don't think of floor strippers as environmentally friendly, but more government groups and school systems have issued a green mandate. Ecolab, JohnsonDiversey, and other marketers are now filling the need for environmentally friendly products that still do the job when it comes to finishing floors, cleaning hard surfaces, and sanitizing surfaces. In fact, nearly every finished product company is focusing on going green as a No. 1 priority.

Presently green cleaners account for ~5 to 10% of the State Industrial market, but once the critical mass of customers gain confidence that the products really work, sales of green cleaners will take off dramatically. In probability, the I&I market may convert almost entirely to green cleaners. Major I&I detergents manufacturers sell product-specific dispensers, which protect workers from contact with concentrated chemical, minimize packaging waste, and guarantee correct product dose rates. Two growth areas that fall under the green umbrella are lower VOCs and organic-based solvents. Many companies recently rolled out an entire line of low-VOC cleaning products for floor care, all-purpose cleaning, and several other categories. It is a myth that a product must either be green or effective. Recently, Zep celebrated its 70th anniversary by rolling out Zep 70, a penetrate type product and lubricant based on soy. Organic-based solvents and lubricants have become a basic part of the environmental equation. Environmentally friendly soy-based products can be petroleum-free and VOC-compliant, and they can actually work more effectively.

Green chemistry will continue to grow and grow rapidly. Ecolab already offers 37 Green Seal®-approved cleaners, strippers, floor cleaners, degreasers, and finishes. The stripper is an interesting product in that it does a great job at pH 7. Green Seal, founded in 1989, provides science-based environmental certification standards that are credible, transparent, and essential in an increasingly educated and competitive marketplace. Other players have rolled out green cleaners of their own as well. Envirox is a relatively new player in I&I space, but its "H2Orange2" is already making significant gains in school systems, which are often the most receptive customers for green cleaners.

Meanwhile, Spartan continues to expand its bio offerings, which are based on corn and soy. Spartan's seven-item product line includes glass cleaners, restroom cleaners, multipurpose cleaners, and foaming hand cleaners. Another element of Spartan's environmental initiative was the rollout of a cleaner designed specifically for waterless urinals. Water conservation is becoming a major issue in the United States. Recently JohnsonDiversey announced that its Healthy High Performance Cleaning System is the first cleaning system to achieve certifications from the GreenGuard® Environmental Institute, an industry-independent, third-party organization founded in 2001. According to Johnson Diversey, its products and tools were tested and certified based on GreenGuard low-emitting product certifications, including GreenGuard for Children and Schools. GreenGuard is complementary with environmentally preferable product certifications, such as Green Seal®. This is because it goes beyond products and actually looks at how the cleaning process affects indoor air quality. Just using Green Seal-certified products is not enough, because the products can be misused and impact indoor air quality. The GreenGuard Environmental Institute oversees the certification program to improve public health and quality of life through programs that improve indoor air; it has noted that most people spend 90% of their time indoors.

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11 Applications of Amphoterics-Based Formulations

David Floyd (Editing/Compiling: Uri Zoller)

CONTENTS

11.1 INTRODUCTION

Amphoteric surfactants comprise a broad range of compounds that, depending on pH or in-use conditions, display noionic, cationic, or even anionic tendencies; their charge changes as a function of the pH value of the formulation in which they are used. Betaines, imidazoline-derived amphoacetates, alkyl amino propionates, and glycinates are generally included in this category. They are generally regarded as mild surfactants, but this is not a simple matter and may not always be true; when they build complexes in combination with anionic surfactants, these complexes are milder than the individual surfactants [1]. Amphoteric surfactants have the ability to reduce the surface tension of water, as do all other surfactants. The reduction of surface tension depends on the pH of the solution. At pH 6, close to the isoelectric point of most amphoteric surfactants, the net charge of the molecule is zero, which allows for closer packing of surfactant molecules at the interface and produces a great reduction of surface tension.

Amphoterics are excellent foamers and foam stabilizers under a variety of conditions. Their foamability is essentially insensitive to water hardness. Capitalizing on these properties, amphoterics were among the many specialty surfactants commercialized after World War II [2]. Since then, these surfactants have been used in personal care products because of their unsurpassed mildness and low eye-sting properties. Today, most mild skin cleansers and shampoos contain an amphoteric surfactant as a major component.

The variety and range of amphoteric surfactant types are quite large. The following are the characteristic properties that amphoteric surfactants have in common [3]:

- Lime soap dispersancy and hard water tolerance
- Hydrolytic stability over broad acidic and alkali pH ranges
- Water solubility and wetting characteristics
- Compatibility with cationic, anionic, and nonionic surfactants
- Foam enhancement
- Viscosity enhancement
- Irritation reduction in combination with anionic surfactants
- Emulsification
- Good detergency in hard water
- Mild toxicology profile

Importantly, stability and performance at acidic and alkaline pH extremes are a signature characteristic of these surfactants. Thus, for example, commercial amphoterics such as dihydroxyethyl alkyl glycinate are considered to be excellent thickeners for strongly alkaline oven as well as acid toilet bowl cleaners. Amine oxides enjoy similar properties. Resistance to both acids and bases make them suitable for use in products such as hypochlorite and phosphoric acid hard surface cleaners, hair dyes, corrosion inhibitors, and printing inks [4].

11.2 CLASSES OF AMPHOTERIC SURFACTANTS

Amphoteric surfactants can be subdivided into three major classes:

1. Acyl/dialkyl ethylenediamines and derivatives
2. *N*-alkylamino acids
3. Miscellaneous products:
   a. Betaines
   b. Amine oxides

The classical types of amphoteric surfactants are presented in Figure 11.1 [5].

The most important shampoo hair conditioners are the alkyl amido alkyl amines. As a rule, they are complex mixtures derived from the reaction of alkyl-substituted imidazolines with chloroacetic acid or ethyl acrylate [6]. They have undergone a number of name changes and were originally known as amphoglycinates and amphopropionates; the glycinates subsequently were renamed acetates. The current names reflect the identity of the cation, which is generally sodium. Typical representatives are referenced in the CTFA dictionary as disodium lauroamphodiacetate or sodium caproamphopropionate. Similar to the acylated protein derivatives, these amphoteric surfactants exhibit detergency. They are compatible with anionic detergents and reportedly form complex salts with anionics. These complexes reportedly do not sting the eyes and are employed in baby shampoos. These amphoterics in combination with anionic detergents leave the hair conditioned after rinsing.

11.2.1 ACYL/DIALKYL ETHYLENEDIAMINES AND DERIVATIVES

The amphoteric compounds in this group originally were viewed as heterocyclic derivatives of imidazolines.

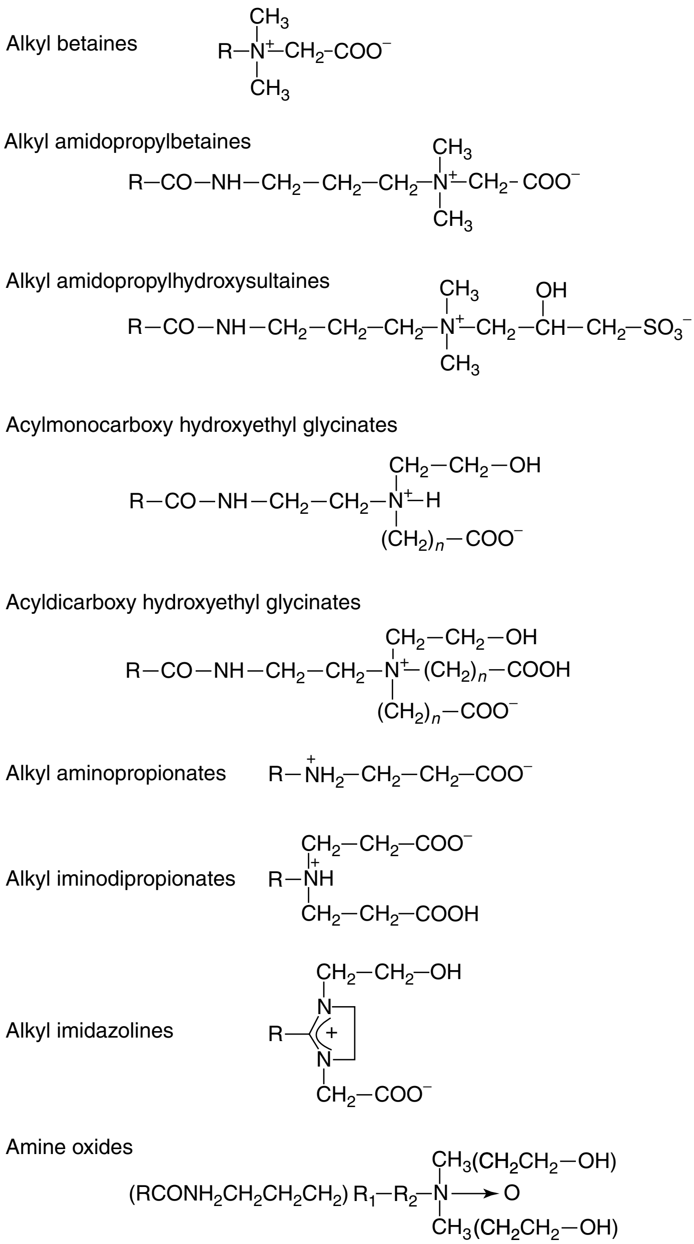


FIGURE 11.1 Main types of amphoteric surfactants.

11.2.1.1 Amphoacetates

These surfactants are well established as extremely mild surfactants [7]. They are referenced in the CTFA dictionary as sodium coco (or lauryl) amphoacetate and disodium coco (or lauryl) amphodiacetate. Amphoterics are widely used in mild, tear-free shampoos and sensitive skin cleansers due to their favorable surfactant properties, low irritation profile, and irritation-mollifying properties [8]. Amphoacetates or diacetates are excellent foaming agents, even in hard water, and they exhibit compatibility with all other types of surfactants.

The market launch of the Johnson & Johnson No More Tears shampoo containing Miranol's amphoteric surfactant in the early 1960s proved to be the beginning of worldwide use of these products. Over the years, through extensive use and testing, a number of desirable properties of these products were recognized. These properties include low toxicity; biodegradability; good surface activity; hydrotroping ability; compatibility with other types of surfactants; excellent foaming and foam stabilization, particularly in the presence of oil and sebum; free rinsing; hard water compatibility; low irritation; and the ability to reduce the irritation from more aggressively formulated systems.

11.2.1.2 Amino Propionates

Amino propionates are preferably produced by the addition of methyl acrylate on primary fatty amines. Depending on the amount of acrylate added, mono- and diadducts are obtained in varying ratios [9], primarily, by the heating of carbonate-free alkyl amine with 1.1 mole of methyl acrylate at 100°C in an autoclave for several hours. This is followed by removal of the unreacted acrylate by vacuum distillation, and hydrolysis of the ester adduct with either alkali or acid.

11.2.1.3 Carboxy Amphoterics

Carboxy amphoteric surfactants based on fatty alkyl imidazolines (*imidazolinium* surfactants) make up a large part of the amphoteric surfactants. Materials of this surfactant class are based on the imidazolines obtained by the condensation of fatty acids or their esters with aminoethyl ethanol amine.

11.2.1.4 Acyl/Dialkyl Ethylenediamine Applications

The most important products of this group are the coco derivatives; cocoamphoglycinate, cocoamphocarboxyglycinate, cocoamphopropionate, and cocoamphocarboxypropionate. In former times, these were referred to as imidazoline derivatives, but chemical studies have shown that the imidazoline structure hydrolyzes completely during the production process.

The glycinates and propionates have good skin compatibilities and show some conditioning properties in shampoo application. They are excellent foamers, but the foam is not very stable in hard water. When combined with anionics, they synergistically reduce the irritancy [10]. In the U.S. market, the glycinates and propionates are widely used, whereas in Europe the betaines are more often selected. The glycinates and propionates are generally regarded as milder than the betaines. Betaines give better cleansing, foam volume, and viscosity response than do the glycinates and propionates.

Amphoteric surfactants, such as acyl β-aminopropionates, for example, sodium lauriminodipropionate, also function as detergents, but they have somewhat different chemical structures and properties.

These materials are generally less irritating than other classes of surfactants. Therefore, they are typically used as primary detergents in *mild* formulations, such as baby shampoos. Other common uses are as primary and secondary detergents (see, for example, Figures 11.2a and 11.2b).

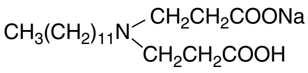
The mono- or dipropionate amphoterics, also known as salt-free amphoterics, are rarely used in mild shampoos. They are more commonly used in high-alkaline cleaners because of their stability in caustic solutions [11].

In the U.S. market, three traditional amphoterics are used in most mild shampoos: disodium cocoamphodiacetate, sodium lauroamphoacetate, and disodium lauroamphodiacetate. The eye irritation properties of these three surfactants were compared under identical conditions, with solutions of each surfactant prepared at four active levels: 5, 10, 15, and 25%. After the pH was adjusted to 7.0, the solutions were evaluated according to the Draize method [12,13].

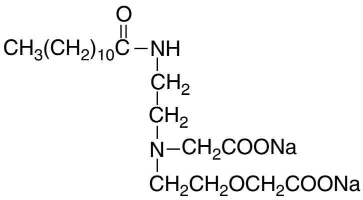
The structures of the acetate- and propionate-based amphoterics are illustrated in Figure 11.3.

11.2.2 *N*-ALKYLAMINO ACIDS

Most of the *N*-alkylamino acids are alkyl derivatives of β-alanine or of β-*N*(2-carboxyethyl)-alanine. Only a few of them exhibit structures analogous to those of the natural α-amino acids.



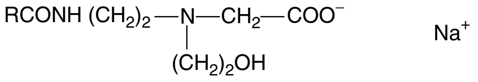
(a) Sodium lauriminodipropionate



(b) Disodium lauroamphodiacetate

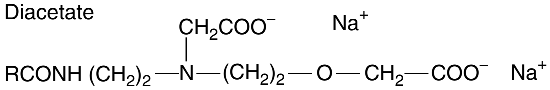
FIGURE 11.2 Examples of amphoterics (of class 4).

Monoacetate



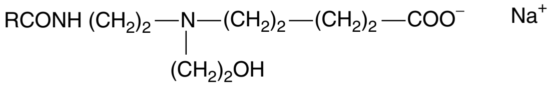
$$\mathrm{RCONH\,(CH_2)_2{-}\underset{\underset{\displaystyle (CH_2)_2OH}{|}}{N}{-}CH_2{-}COO^-\quad Na^+}$$

Diacetate



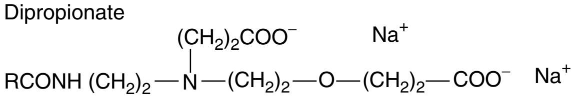
$$\mathrm{RCONH\,(CH_2)_2{-}\overset{\overset{\displaystyle CH_2COO^-\;\;Na^+}{|}}{N}{-}(CH_2)_2{-}O{-}CH_2{-}COO^-\quad Na^+}$$

Monopropionate



$$\mathrm{RCONH\,(CH_2)_2{-}\underset{\underset{\displaystyle (CH_2)_2OH}{|}}{N}{-}(CH_2)_2{-}(CH_2)_2{-}COO^-\quad Na^+}$$

Dipropionate



$$\mathrm{RCONH\,(CH_2)_2{-}\overset{\overset{\displaystyle (CH_2)_2COO^-\;\;Na^+}{|}}{N}{-}(CH_2)_2{-}O{-}(CH_2)_2{-}COO^-\quad Na^+}$$

FIGURE 11.3 Acetate- and propionate-based amphoterics.

The compounds in this group are available as the free carboxylic acids or more commonly as the corresponding sodium salts. When fully neutralized with alkali, these substances behave as amines. Only when the pH is adjusted to about 6 do they exhibit their zwitterionic character.

The sodium salts of the alkylamino acids possess high water solubility. The zwitterionic forms, especially those of the alkylaminopropionic acids, are not as water-soluble as the iminopropionates.

Although these amino acids and their salts are available as solids, they are also distributed in solution form. The alkylamino acids foam copiously in the alkaline or neutral pH range. At low pHs, they behave as cationics and lose their foaming power. In their zwitterionic forms, they are substantive to hair and find use in all types of hair products.

They are not hydrolyzed by acids or bases, exhibit excellent stability under normal use in cosmetics, and also can be used as emulsifying agents.

11.2.3 MISCELLANEOUS AMPHOTERICS

11.2.3.1 Betaines

The betaines are different in their behavior compared with other amphoterics, in that they cannot be forced to assume anionic active behavior, through an increase in the pH value [14]. Figure 11.4 shows the structure of a representative widely used amphoteric betaine:

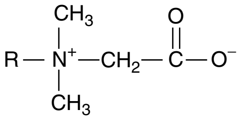
Betaines, for example, cocamidopropyl betaine, or the less complex lauryl betaine, are very water soluble over a wide pH range. They not only act as foam boosters in the presence of the common detergents, but also provide an important second conditioning effect to hair, due to their presumed substantivity. In addition, the betaines help to increase the viscosity of aqueous surfactants and exhibit low eye and skin toxicity.

The alkylamidopropyl betaines, as a rule, are compatible with the anionic detergents over a wide range of concentration. The simpler alkyl betaines show some incompatibilities with alkyl sulfates at concentrations at which the betaine's concentration is about one half that of sodium lauryl sulfate [15–17]. The nature of these incompatibilities is largely dependent on the nature of anionic species present. The pH of the system also plays a role in compatibility. At the pHs normally encountered in shampoos, a competitive reaction occurs between the presumed zwitterionic inner salt and the complex salt formation from the interaction of the anionic detergent with the quaternary nitrogen.

11.2.3.1.1 Alkyl Betaines

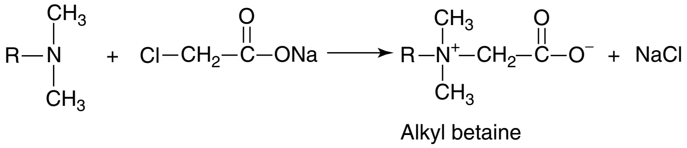
Alkyl betaines may be considered to be [2] homologues of betaines, for example, trimethyl ammonium acetate. Commercial betaines are usually 30% active products, containing ~6% sodium chloride, which is a byproduct of their production (Figure 11.5). The sodium chloride is left in the resulting aqueous solution, as it does not interfere with most applications. In fact, sodium chloride is desirable to build viscosity in ready-to-use preparations, such as shampoos. For special applications, the salt contents can be reduced either by using solvents, or separating the salt via remembrance-based process. Depending on the pH, the alkyl betaines can be cationic or anionic surfactants. At pH values between 5 and 7, which are typical for shampoos or shower baths, they form ionic complexes in combination with anionic surfactants such as either sulfates or fatty alcohol sulfates. These complexes are poorly soluble in water, but the presence of excess anionic surfactant or betaine aids solubilization. The improvement of the skin compatibility of an anionic formulation due to the addition of betaine is partly based on the reduction in the overall activity. A side effect is the increase in the size of the micelles and consequently, an increase in the viscosity. This principle is often used for thickening of a formulation, especially in the case of formulas based on ether sulfates.

Betaines can improve the foaming of a formulation, particularly the structure of the foam, which becomes finer and more creamy. On the other hand, a 1:1 complex of anionic surfactant and



$$R-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_2-\overset{\overset{O}{\|}}{C}-O^-$$

FIGURE 11.4 Structure of amphoteric surfactants.



$$R-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}} + Cl-CH_2-\overset{\overset{O}{\|}}{C}-ONa \longrightarrow R-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_2-\overset{\overset{O}{\|}}{C}-O^- + NaCl$$

FIGURE 11.5 The synthesis of commercial betaines.

betaine shows poor foaming and poor solubility in water. In conditioning shampoos, betaines support the effect of polymeric quaternaries, which impart good manageability and body to the hair.

11.2.3.1.2 Alkyl Amido Betaines

Alkyl amido betaines are the most common of the betaine types. They have become the most important type of secondary surfactant, specially cocamidopropyl betaine (CAPB) [18]. It can also be referred to as coco fatty acid amidopropyl betaine [19]. Thus, combining primary surfactants with CAPB reduces skin and mucus membrane irritation [20,21], improves the conditioning properties of hair shampoos [22,23], and produces a pleasant, smooth skin feel. Formulas that include CAPB thicken more easily, develop better foam, and give a better cleansing performance than formulas without CAPB [24].

The uses of CAPB in efficacious, mild dishwashing liquids and oral hygiene products are the latest examples of CAPB's versatility. Its excellent toxicological profile, which has been documented by many investigations and reports in the past few years, is one reason for its success in dentifrice products [25].

11.2.3.1.3 Flowable CAPB Concentrates

Most marketed CAPB solutions contain ~30% active matter. This is, primarily, because aqueous betaine solutions form viscous, gel-like phases at slightly higher concentrations. In contrast to the situation for surfactants like lauryl ether sulfates, fluid mesophases consisting of CAPB, NaCl, and water do not exist at higher concentrations. The critical concentrations above which nonflowable gel phases are formed partly depend on the length of the fatty acid alkyl chains.

Numerous attempts have been made to obtain flowable betaine solutions with increased active matter, in some cases by adding other surfactants [25–27], adding solvents, or using additional salts not normally contained in betaine solutions, such as sodium citrate, trimethylglycine (natural betaine), methanaminium, 1-carboxy-*N*,*N*,*N*-trimethyl- (inner salt) [28], or nitrilotriacetate.

A relatively simple way to obtain more highly concentrated betaine solutions is to adjust the free fatty acid content. By adding small amounts of fatty acid to the betaine with the amidoamine solution, betaine contents of 34–36% and detergent-active substances, including fatty acids, of 36–38% are attainable. Such betaine solutions are microbiologically stable and do not require preservatives [29].

By spray-drying aqueous betaine solutions, it is possible to obtain highly concentrated betaine products, typically consisting of 80–85% fatty acid amidopropyl betaine, 13–15% sodium chloride, and 0.3–3.0% water. Spray-drying typically uses betaines with low C_8/C_{10} alkyl components (J. Venzmer, personal communication, 1996).

11.2.3.1.4 Imidazolinium Betaines

Imidazolinium betaines were initially described by Mannheimer, who obtained them from the reaction of fatty alkyl imidazolines with sodium chloroacetate [30,31].

The classic preparation method of sulfo betaines utilizes the conversion of tertiary amines with propane sultone. Hydroxy sulfo betaines amino oxides are obtained from tertiary amines and chloro hydroxypropane sulfonic acid [32–34].

Amine oxides are produced by oxidation of tertiary alkyl amines, for example, dimethyl or ethoxylated amines, with hydrogen peroxide. They are excellent foamers, so that in combination with anionics, small amounts can act as foam boosters and can improve the foam structure. Like betaines, they are good thickeners for anionic surfactants. In addition, amine oxides are good conditioning agents in hair rinses. They are commercially available as 30–50% aqueous solutions.

Amino oxides are widely used in hard surface cleaners for their ability to suspend heavy soils and grimes. They are often combined with sodium alkyl sulfonates and nonionics. The foam-boosting properties of amine oxides have been widely reported and are well known in the industry [15,16,35].

The oxidation of tertiary amines with hydrogen peroxide provides a large group of nonionic surfactants. They are sometimes classified as cationics, since they are claimed to exist in a protonated form at low pHs. In cosmetics and shampoos, the pH is near neutrality, and amine oxides more likely act as nonionics. They stabilize foam primarily in moderately acidic systems. Cocamine oxide, for example, is one of the preferred foam-boosting ingredients for shampoos. Like the betaines, the amine oxides reportedly are mild surfactants that have the ability to condition hair [36]. They have been used in bath foams for their ability to foam and in mild facial cleansers because of their ability to release lipids and pigments from the skin.

Amine oxides have also found a role in emulsification. A prior publication makes note of the use of amine oxides as emulsifiers and lists many useful characteristics that make them attractive in cosmetic formulations [37]. They are reported to be extremely mild in skin and eye irritation tests and disclose a synergistic counter irritancy when blended with other ingredients. In addition, amine oxides are known to impart lubricity and emollience to skin surfaces in acidic emulsions [38].

The stearyl amine oxide has been used as a primary emulsifier for many years. It has been generally acknowledged that amine oxides other than the stearyl derivative could also be used as cosmetic emulsifiers; indeed lauryl, cetyl, and myristyl derivatives are excellent emulsifiers in their own right. Unlike anionic and cationic emulsifiers, these amine oxides can be used as secondary emulsifiers in normal two-phase cosmetic systems.

A unique advantage of amine oxides is their ability to be formulated with quaternary preservatives without inhibition of the cationic. Although there are other nonionic emulsifiers that can be used in cosmetic emulsions compatible with quaternary emulsions, very frequently the preservative activity of the quat is inhibited by the nonionics. Not only are the amine oxides not inhibited by the quats, but by themselves being slightly cationic at acid pHs, they actually enhance the preservative action of quaternaries.

11.3 TARGETED APPLICATIONS: UPDATED

Even though applications for amphoteric surfactants are well known and documented, new applications and refinements in the art continue to be developed. A search of U.S. patents between 1991 and 1997 reveals a wide range of current consumer, pharmaceutical, and industrial uses for betaines, amine oxides, and all other amphoteric surfactants. A review of over 500 patents yielded 260 industry-specific application patent references. Of these, ~31% referred to household, industrial, and institutional markets, 22% pertained to personal care applications, 13% applied to oral care or pharmaceutical products, and 33% could be categorized as industrial applications. Examples include metal working, mining, photographic processes, paper, and textile treatments. This list is not meant to be all-encompassing, but rather to provide a good survey of the contemporary art. Results of this survey are tabulated in Table 11.1.

11.3.1 CONSUMER APPLICATIONS

11.3.1.1 Hard Surface Cleaners

Hard surface cleaners, household, industrial, and institutional detergents, and laundry detergents continue to account for a significant preparation of amphoteric and amine oxide use.

For example, detergent compositions containing a hydrocarbamidoalkylene-betaine in combination with at least one cosurfactant can offer excellent removal of grease soils and also offer superior filming and antistreaking properties in hard surface cleaners [39]. Similarly, short-chain amphocarboxylates, when incorporated into formulas that do not contain large amounts of builders, are also claimed to offer improved filming or antistreaking properties and good cleaning in glass cleaner formulas [40].

A related application is the car wash market, for example, the use of a cocodimethyl betaine as a mild foaming agent for car wash compounds dispensed in commercial equipment [41] and an amine oxide, as the coupling solvent, in environmentally friendly natural fatty acid–based emulsions that are used as auto spray waxes and drying aids in automatic car washes [42].

TABLE 11.1
U.S. Patent Citations 1991–1997: Application of Amphoteric Surfactants

Consumer or I&I	**Betaines**	**Amphoteric (other)**	**Amine Oxides**
Detergent, undifferentiated liquids	15	4	7
Hard surface cleaners	12	14	5
Light-duty liquids, including dishwashing	3	2	3
Fabric and laundry cleaners	5	5	7
Shampoos	3	7	1
Skin cleansers and gels	6	6	0
Hair treatment products and dyes	2	18	3
Cosmetic and skin products	2	9	0
Oral care and food	4	9	3
Pharmaceutical and clinical	6	10	2
Industrial and Agricultural			
Agricultural products	1		
Metallurgy	4	6	0
Photography	3	6	0
Inks	3	0	3
Magnetic recording devices	2	1	0
Corrosion inhibitors	1	1	1
Mining and well treatment	0	6	0
Paper	0	6	0
Flame retardants	0	3	0
Electronics	0	5	0
Latex and rubber	0	8	0
Leather and textile processing	0	4	0
Cellulose processing	0	0	13
Waste treatment	0	3	0
Biocides	1	2	2
Fiberglass	0	1	0

Performance criteria for light-duty liquid dish wash detergents include mildness, good foam, good detergency, and grease removal ability over a range of water hardness conditions. In these systems, an optimal efficacy using a three-component formula consisting of an amido amine oxide, an anionic surfactant, and a nonionic surfactant has been reported [43–44]. Selected betaines and amine oxides, as the cosurfactants of choice, have been suggested for ensuring mildness in other dish detergent systems [43], as has employing an anionic surfactant and a nonionic polyhydroxyamide in combination with an amine oxide to achieve mildness, cleansing, and sudsing [44].

Other hard surface applications rely on amphoteric and amine oxide surfactants to enhance viscosity in highly acidic or alkaline formulas. Some liquid toilet bowl cleaners, for instance, are formulated within a pH range of 2–4 [45]. Also, amphoteric surfactants and amine oxides have been demonstrated to provide good gelation and stability in compounds containing peracetic acid [46].

Likewise, thickened aqueous hypochlorite compositions rely on these surfactants to accomplish the same purpose at alkaline pH levels of 11 or higher [47]. Desired viscosity for such formulas may range from 150 to 3000 cP. This would not only permit easy dispensing, but provides good coating action necessary for cleaning toilet bowls, bathroom tiles, and shower walls [48]. Effective viscosity control is also necessary to suspend abrasives found in scouring cleansers. Finally, the choice of the particular amphoteric surfactant is an important factor in the preparation of *low solvent* hard surface cleaners [49–50].

11.3.1.2 Laundry Products

Although amine oxides are widely used in fabric detergents, other materials, such as betaines, continue to be evaluated by mass market producers. Thus, a patent assigned to Lever Brothers Company describes new fabric-conditioning compounds that provide effective softening and static control, derived from glycerol and betaine [51]. A patent assigned to Colgate-Palmolive Co. reports that amphoteric surfactants, such as sodium carboxymethyl tallow propylamine, contribute to fabric cleansing and softening when incorporated into aqueous systems with polyethoxylated fatty alcohols, inorganic builders, and bentonite [52]. Systems using amphoteric surfactants in lipase-containing laundry detergents have also been developed [53].

Amine oxides can also be found in enzyme-containing detergent formulations, where they enhance formula stability [54].

There is evidence that sequestration rates of certain zeolites, such as zeolite A, can be enhanced by incorporating *N*-tetradecyldimethylamine oxide and related species. The increased sequestration imparted by the amine oxide synergy is claimed to make zeolite A more suitable for use as a detergent builder in anionic surfactant-based formulas [55].

Other recent uses for amine oxides include applications in solid detergents. For example, solid amine oxides can be prepared by mixing maleic acid and amine oxide in a 1:1 molar ratio, at a pH of one unit or greater below the pKa of the amine oxide. This maleic acid amine oxide salt can be readily dried and then blended into granular detergents. This salt dissolves readily in water at 25°C and at a pH above the pKa of the amine oxide [56].

11.3.1.3 Sanitizers and Disinfectants

Owing to their compatibility with cationic biocides, amphoteric and amine oxide surfactants continue to be used widely in the development and formulation of disinfectants and sanitizers for personal care, household, industrial, and institutional markets. For instance, substituted imidazoline amphoteric surfactants, in combination with didecyl dimethyl ammonium chloride, have been found to display unexpected synergistic irritation reduction compared to formulas with alkyl dimethyl benzyl ammonium chlorides [57]. Also, imidazoline derivatives and betaines are known to impart moderate cleansing without causing skin roughness, stickiness, or irritating reactions with cationic disinfectants [58]. Amphoteric surfactants are also suitable for use in antimicrobial medications requiring subcutaneous, cutaneous, or mucosal membrane administration [36].

11.3.1.4 Personal Care Cleansers and Shampoos

The use of betaines, amine oxides, and imidazoline-derived amphoteric surfactants in foaming systems is not surprisingly high. Examples include shampoos, hair tint treatments, permanent waves, antidandruff preparations, hair revitalizing tonics, shower gels, facial cleansers, foam baths, and closely related formulations. Performance claims include mildness, improved lathering, cleansing/oil removal, suspending or viscosity stabilizing, and functional enhancement of actives such as hair dyes [59–63].

As noted before, amine oxides can be easily adapted for use in solid systems, including their use in bar soaps. Amine oxide computability with water-sensitive systems is accomplished by reacting the tertiary amine with aqueous hydrogen peroxide, using liquid polyethylene glycol as the sole organic solvent [64].

11.3.1.5 Cosmetics

Broad pH surfactant compatibility characteristics have contributed to greater usage of amphoteric surfactants in a variety of leave-on cosmetic and skin treatment products. These include alpha hydroxy acid treatment creams, skin desquamation aids, cleansing gels, and massage creams. Excellent skin feel and moisturization, coupled with long-term stability of active components, are some requirements that must be met when developing such *new generation* beauty aids [65–70].

Amphoterics can also be used to stabilize emulsions by immobilizing the oil droplets in a network to retard or prevent coalescences [71–72].

11.3.1.6 Oral Care Products

As the line between therapeutic cosmetics, *cosmeceuticals*, and drugs becomes more vague, the use of amphoteric surfactants in the development of products evaluated through clinical trials is likely to increase. This is especially true concerning the use of amphoteric surfactants in the oral care industry.

Toothpastes contain foaming agents that impart a pleasant mouth feel during use. This foam also helps create a suspension of abrasive ingredients, thereby improving cleaning efficacy. Sodium lauryl sulfate is typically used for this purpose [73]. The use of betaine as a surfactant alternative to sodium lauryl sulfate is not yet widespread in the North American market. However, commercial products are now available internationally. Clinical studies describing use of betaine in oral care applications have been published, and major producers, such as Procter & Gamble and Colgate, have been awarded patents in this area. It has been shown experimentally in a toothpaste study that sodium lauryl sulfate significantly increased the incidence of desquamation of oral mucosa compared with cocamidopropyl betaine. Less toxic detergents, such as cocamidopropyl betaine were, therefore, found to be desirable in oral care products [74]. Similarly, a preparation of a toothpaste containing a betaine surfactant, such as cocamidopropyl betaine, was claimed to retard, or stop, the proliferation of plaque, which is detrimental to oral health [74]. Cocamidopropyl betaine, as a cationic compatible with surfactant, was also used in the preparation of another antiplaque composition, utilizing *bis*-biguanide as an antimicrobial active [75]. Similar plaque control claims were made with respect to a composition based on a blend of C_{10}—C_{18} alkyl *N*-sulfobetaine and C_{10}—C_{18} alkyl *N,N*-dihydroxylethylamine oxide [76].

11.3.2 PHARMACEUTICAL INDUSTRY APPLICATIONS

Most recent patent references to amphoteric surfactants and amine oxides in the pharmaceutical industry involve the development of new diagnostic test methods, such as immunochemical assays and improved genetic diagnostic methods. In these applications, selective use of amphoteric surfactants has been shown to enhance the sensitivity of detection [77–79].

11.3.3 OTHER INDUSTRIAL APPLICATIONS

The use of amphoteric surfactants in heavy industry is a broad topic, encompassing such varied applications as oil well and mining fluids, fire-fighting foams, printing inks, wastewater effluent recovery aids, leather softeners, electroplating bath additives, and corrosion inhibitors [54,80–87]; with respect to amine oxides, there are also numerous references to the production of cellulose films and fibers [88–92]. Clearly, developments involving amphoteric surfactants in these sectors will, ultimately, have an impact on their consumption and availability in consumer markets and elsewhere.

11.4 CONCLUSION

Amphoteric surfactants are a class of chemicals whose functionality and utility to the industry is showing definite growth. As a class of surfactants, they are safe, both functional and with low irritation potentials for consumer products and, consequently, are finding increased use in personal products. The wide range of chemistries that are encompassed by this class of surfactant afford product development chemists the opportunity to tailor the performance of their products for specific applications. This is evident by the broad range of industries interested in these technologies.

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12 Detergents in Agrochemical and Pesticide Applications

Robert L. Hill

CONTENTS

12.1 INTRODUCTION

Throughout history, significant challenges have always existed for those growing agricultural products as food and fiber. Cooperative weather delivering water as needed and in the proper amounts without flooding, hail or wind to damage the crop can be a factor for success or failure. Competition from undesirable plants, insect attacks, and plant diseases can also take their toll on the ultimate yield of the planted crop now as in ancient times. Farming practices today have allowed some control of the factors influencing crop production. Irrigation offers some control over weather conditions with regard to delivering water at needed times. Modern agricultural products and practices have allowed effective control of many weeds, insects, and plant diseases, but even with all the assistance modern technology provides, farming is still a very risky venture for the grower. Applying and delivering the various products used in modern agriculture to the site of action is a daunting task. The use of detergents and surfactants in agricultural products is virtually universal. Detergents and surfactants are also occasionally used in manufacturing the active ingredient, and are almost always used in formulating and applying pesticides.

This review of detergents in agrochemicals and pesticide formulations and applications will use a broad definition of detergents. The classic definition of detergents as a subset of surfactants will be expanded here to include all surface active agents. As surface modifiers, their use in pesticide formulations is critical. Very few pesticides are used without some type of surface active agent in the manufacture of the active ingredient (AI), in the formulated end use product, or as an adjuvant added at the time of dilution and application. The manufacturers, formulators, and applicators involved in modern agriculture make use of most of the advances in both active ingredients and surfactant formulation, and application aids maximizing crop production. This review will discuss some of the factors that affect herbicide, insecticide, and fungicide applications. A discussion of the different types of pesticide formulations will summarize how the type of formulation can affect the application of the active ingredient. Methods of application and some of the equipment used in the applications are discussed. Finally, the impact of physical properties of the formulations and how they affect applications will be summarized.

12.2 PESTICIDE TYPES AND APPLICATIONS

Pesticides, consumer products, and drugs have many similarities. The formulation is intended to deliver an active or beneficial ingredient to a general target area, where it migrates to a specific biological site to elicit a biological effect. Agricultural products are unique when compared to drugs or consumer products. Drugs and consumer products are usually used as formulated and packaged. Most pesticides are formulated as a concentrate and then diluted in water or, occasionally, an oil for application. This dilution step assures an even, accurate application at a lower AI concentration over the large surface areas of a field. The concentrate is formulated with surfactant to keep the formulation stable under storage conditions, as well as to improve dilution and AI coverage.

The importance of surfactants for pesticides from manufacture of the AI through formulation, dilution, application, plant uptake, metabolism, and breakdown cannot be overemphasized. The use of surfactants is discussed in more detail below, but the impact surfactants have in most aspects of pesticide formulation, application, and delivery to the active site is summarized in Figure 12.1. Surfactants can make processing of AIs into formulations more efficient by lubrication in grinding, through surface wetting, by dispersing small AI particles, or aiding the dissolution of the AI. Surfactants aid in the dilution of formulated pesticides by efficiently mixing water and organic components together into diluted emulsions or suspensions. Surfactants are important in producing controlled delivery or encapsulated formulations. At the plant level, wetting of the plant surface, adsorption and absorption of the AI, as well as distribution through the plant can all be

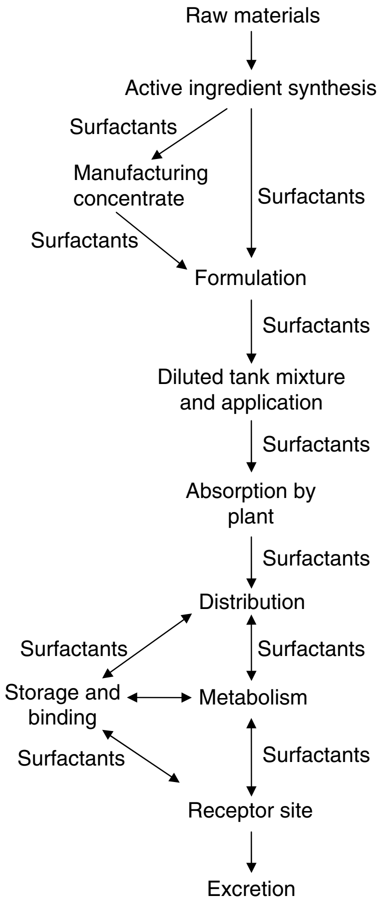

FIGURE 12.1 Schematic diagram of the production, formulation, application, and distribution of an active ingredient within a plant. Surfactants are used in the processes or activities indicated by the word **Surfactants**. The formulation and delivery processes are usually aided by surfactants. After delivery to the plant, surfactants often continue to function as penetration enhancers, and in some cases aid the movement of AI within the plant.

impacted by surfactant selection. Surfactants can be used to produce enhanced delivery systems such as nanoemulsions and microcapsules. Even AI metabolism, environmental movement, and degradation can be impacted by surfactants.

The three major classes of pesticides are herbicides, insecticides, and fungicides. The formulation required to deliver each pest control agent may be any one of several types. The physical properties of the AI and the route of delivery to elicit the biological response generally determine the formulation type. Efficient formulation development emphasizes working with the AI's physical properties rather than attempting to overcome them. If the AI is a low-melting solid or liquid, formulation types may include an emulsion concentrate for a liquid formulation, and a granule or wettable powder composed of a carrier loaded with the AI for solid formulations. In some cases, a specific formulation type may be desired for safety, environmental impact, or packaging needs. Extensive testing is then conducted to determine if the AI can be produced as that formulation type without compromising delivery and biological effect. The biological effects that are sought reflect the type of pest that is encountered.

Selectivity and rate reduction have been the main areas of improvement for modern agricultural products. Application rates historically were high, in the pounds per acre range (kilogram/hectare). Early applications were simply the act of scattering the chemical on the field or crop. With the discovery of 2,4-dichlorophenoxyacetic acid (2,4-D) and later the grass herbicides such as trifluralin, broad leaf weeds could be selectively removed from grass-type crops, or weedy grasses inhibited from growing among broad leafed crops. Occasional overapplication resulted in crop injury and loss in yield. Application of insufficient AI or spotty application resulted in poor control. Improvements in formulations and application methods have minimized these adverse issues. Adjuvants, often tank mixed surfactants, oils, or polymers, have aided application effectiveness. Even with the difficulties of application and selectivity, significant increases in yields were achieved. Modern agriculture is truly a marvel of efficiency, with yields increasing more than fivefold since the 1940s. Much more food and fiber are obtained from less land today with a significant reduction in labor.

With the passage of time, improved chemistry, selectivity, and application methods have resulted in the ability to target specific weeds in crops. Selective control of insects without adversely impacting beneficial insect populations has become possible with the newer and more specific AIs. The rates of applications have been greatly reduced down to the ounce or fraction of an ounce per acre (gram/hectare) rate. With this reduction in rate, precise and effective application of the AI is critical. The AI must be applied to the target crop and stay on target with minimal material lost. With the continuing advances in agricultural product AIs, surface active agents play an ever increasing role in AI delivery to the target.

12.2.1 HERBICIDE APPLICATIONS

Weeds are defined as plants growing where they are not wanted. Weeds damage crops by competing for food, water, and sunlight at the expense of the planted crop. Early methods of effective weed control included burning, cultivation (hoeing and tilling), grazing by animals, selective flooding, seed selection (the first attempts at hybrid development), cleaning of seed to remove unwanted seeds or debris, and equipment sanitation. Undesirable plants produce tremendous seed pressure, with many of the seeds ultimately germinating and competing with the crop for food, water, and sunlight. In one Nebraska study, more than 20 million velvet leaf seeds per acre were found in the top 8 in. of soil [1]. Several broad leaf herbicides provide effective control for this aggressive weed. Johnson grass is a very damaging weed in crops [2]. A single plant can produce up to 80,000 seeds, and 212 ft of root rhizomes per season [3]. Tillage can spread this plant by breaking up the rhizome segments. Johnson grass has been known to reduce corn yields from over 100 bushels per acre to <20. Severe infestations have resulted in complete crop failures. Chemical herbicides are the only way to deal effectively with a weed like this.

Different application methods are shown below and will be developed in more detail in the discussion of the formulation types developed for each application method. Preemergent application of herbicidal chemicals can be accomplished before planting by spraying the surface of the field with the diluted herbicide solution just prior to chisel plowing, disking, or cultivating the field. This permits even application of the herbicide to the soil surface, and the applied herbicide can then be incorporated into the soil. Another application to dormant fields is achieved by spreading coated fertilizer granules after harvest or during the dormant season (Figure 12.2). Herbicide applications can be performed at planting by banding the specific herbicide or broadcast spraying the herbicide while the planter is moving through the field (Figure 12.3). One of the most common application methods is foliar treatment after the crop has emerged from the soil (Figure 12.4). Surfactants are used in the formulation and application of herbicides to move the AI in the soil, and for coverage on the plant surfaces and penetration into the plant tissues.

The first effective synthetic herbicide was 2,4-D, discovered in the mid-1940s. The first formulations were emulsions diluted in water and applied by broadcast sprays. Initial application rates in the 1950s were up to 75–150 lb acre against some weeds. These applications were performed

FIGURE 12.2 Preemergent granular fertilizer application using Terra Gator 9203 Floater equipment. An Air Spreader is used to disperse the fertilizer. (Photo courtesy of AGCO Corporation. With permission.)

FIGURE 12.3 Incorporation of a diluted liquid product (fertilizer or pesticide) using a Terra Gator 9105. (Photo courtesy of AGCO Corporation. With permission.)

using ground application equipment as shown in Figure 12.4, using the typical dilution in water and broadcast spraying of the area to be treated. Recognition that this herbicide alone could not control all weeds led to abandoning the highest rates and targeting specific weed species. Improvements in activity of the molecular forms of 2,4-D, such as formation of esters and salts and the use

FIGURE 12.4 Postemergent application of a diluted product by a John Deere 4720 Sprayer. (Photo courtesy of the John Deere Company. With permission.)

of surfactants as adjuvants for delivery and in formulations, have reduced the application rate to 0.5–2 lb acre (0.6–2.3 Kg/Ha). Newer, more specifically targeted herbicides are now delivered in the range of a few ounces per acre (g/Ha), and additional improvements in application methods, as well as improved activity, are being developed.

12.2.2 INSECTICIDE APPLICATIONS

Insect damage can also severely reduce yields, and various products are needed to control these insects. Insecticides most often function by killing the insect or inhibiting insect growth and maturation. Pheromones act by disrupting mating behavior. Many of the same attributes required by the herbicide formulations, for example, ease of application, coverage of the leaves, and penetration of the plant tissues, are also desired in insecticide formulations. These properties include adherence to the target such as a plant leaf, rainfastness so rain water does not wash off the applied material, plant penetration, and translocation of the AI to the site of action. Direct contact with the target insect may be desirable, but this is often difficult. Application of insecticides are most often direct foliar applications to the plant, using ground application methods as in Figure 12.4 or aerial application equipment as shown in Figures 12.5 and 12.6. Soil application or band application at planting is often used if there are damaging nematodes or larval stages of insects that can destroy the seed or new plant shoot after the plant emerges from the seed or soil. An alternative method of insecticide application is coating the seed with the insecticide or an insecticide and fungicide mixture.

FIGURE 12.5 Postemergent helicopter application. (Photo courtesy of the Spray Drift Taskforce. With permission.)

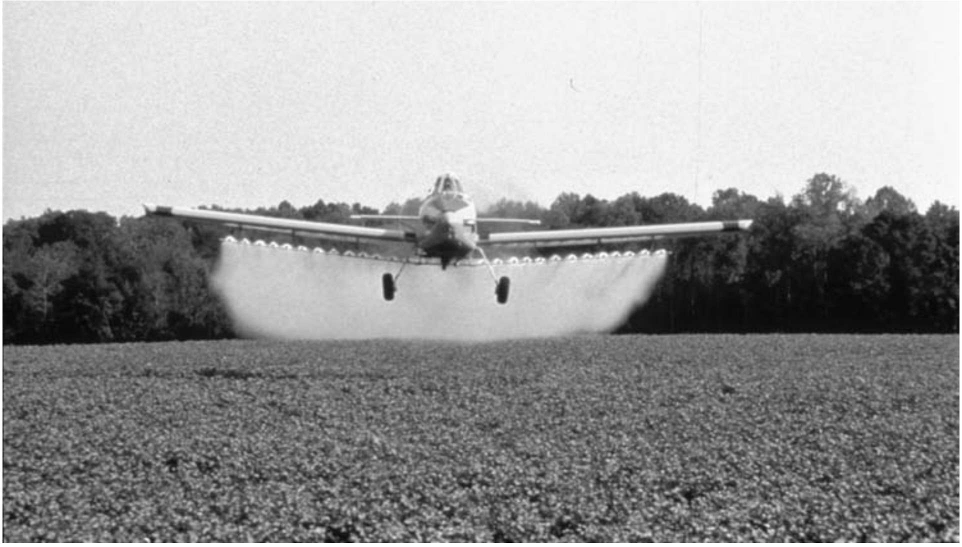

FIGURE 12.6 Postemergent aerial application. Note that the spray boom extends only two-thirds the length of the wing to avoid wing tip vortices. (Photo courtesy of the Spray Drift Taskforce. With permission.)

This protects the seed during storage, and in some cases controls insects for a short time after the plant emerges from the seed.

New technologies have been developed that can be used to attract insects to a solid bait. Solid baits can be scattered on the soil surface using ground or aerial equipment to control grubs or beetles that can move to the bait. Other baits that control insects at later stages of plant growth are applied as bait granules scattered over a crop canopy that attracts the insect to the toxicant. Liquid baits are also used and applied aerially or using ground application to attract the insects to the bait, where the insects feed on the bait and ingest a toxic level of the insecticide.

Insecticides have undergone developments similar to herbicides. Original insect control patterns ranged from turning poultry into a field to eat the insects to the use of very toxic, naturally occurring compounds such as arsenic as control measures. Synthetic chemistry produced DDT, a very effective, potent broad-spectrum insecticide. This compound was used extensively globally, but is so broad spectrum that beneficial insects were killed as well as the pests. Another detriment was the environmental persistence of the compound. Once DDT entered the food chain, it was bioaccumulated from one animal to another until it concentrated at the top of the food chain. This was first observed through adverse influences on bird reproduction. Other, safer insecticides have since been developed. Today, the relatively benign naturally produced endotoxin produced by *Bacillus thuringiensis* (Bt) is used as an insecticide, and very selective insecticides such as spinosad have been found that will kill particular pest species, but do not adversely impact beneficial insect species. Pyrethroids, both natural and synthetic, have also been used in areas formerly treated with more persistent and broad-spectrum insecticides.

Urban pest products control pests in and around homes, buildings, and offices. Attributes acceptable for field applications are very different from those required for products used to control urban pests. Desirable attributes for these products include nonodorous and nonstaining formulations with residual control. Contact activity for roaches is an example of a product that requires special formulation techniques and surfactants to effectively deliver the AI. Baits for roaches and rodents have also been developed and are now routinely used.

A final example of an urban pest formulation with unusual needs is a slow-acting termiticide. The AI is consumed by termites from a bait station and taken back to the termite colony. The sharing of food within the termite colony is utilized to spread the AI throughout the colony. This results in elimination of the entire termite colony. In this case, the AI and formulation components must be well dispersed throughout the bait, with no repellency exhibited by the termites.

12.2.3 FUNGICIDE APPLICATIONS

Most plant diseases can be controlled by selecting the appropriate fungicide. These materials ideally would both prevent infection and cure already infected plants. Some modern fungicides are able to cure an existing disease (curative) as well as protect the plant from infection. Others are only able to provide a curative effect, with little protection. Some compounds can only prevent infection before it occurs. Certain fungicides act as barrier compounds. For these fungicides, coverage of possible infection routes is critical. Surfactants that encourage distribution are important in formulating these products. Some molecules have a systemic effect that protects plants from attack. The ability of surfactants to encourage penetration and distribution on and within the plant tissues becomes extremely important in formulating all types of fungicides, because the products are never applied to the actual target, which is the fungal spore or the infective fungal pathogen.

Fungicides are generally applied postemergent to the crop canopy. Application methods depend on the type of crop and density of the drop foliage. If the foliage is sparse, such as in early applications to vineyards prior to or just after leaf emergence, normal field equipment is often used with drop sprayers to coat the plant stems, buds, shoots, and newly emerged leaves. An example of this type of equipment is shown in Figure 12.7. After the canopy develops, more force is required to move the larger plant leaves, and an air blast sprayer is often used (Figure 12.8).

Some fungicides are used in seed treatments. Seeds are protected from pathogens during storage, and some products may protect newly emerged shoots from initial infections by pathogens. Application of the fungicide to seeds is performed in seed tumblers or other applicators that use small volumes of concentrated fungicide or insecticide fungicide mixtures. These mixtures are usually a suspension concentrate. The seeds are often coated with different polymers, lubricants, or other coatings, then dried and packaged.

FIGURE 12.7 Vineyard application using a wraparound sprayer. (Photo courtesy of the Spray Drift Taskforce. With permission.)

FIGURE 12.8 Air blast application to a vineyard. (Photo courtesy of the Spray Drift Taskforce. With permission.)

12.3 FORMULATIONS USED IN AGRICULTURAL APPLICATIONS

Pesticide formulations span a wide range of formulation types and application methods. Formulation components are varied to modify specific physical properties for the delivery of the wide variety of active ingredients. Surfactants obviously modify surface and solution properties of the active ingredients, and are routinely used in the formulation process.

The largest volumes of pest control agents are applied as aqueous dilutions of concentrates, which are then sprayed on the target to control target pests. These pests can be of many different types, including the weeds, insects, and plant pathogens described earlier. The major component of the diluted formulation is almost always water. Acreages treated can contain food or fiber crops, ornamental and specialty crops such as lawns or landscaping plants, rail or highway rights of way, and forests. Surfactants are used in formulations for wetting surfaces, dispersing and suspending the AI, photo protection of the AI, as penetration enhancers, and as antifoam to reduce foaming of surfactants required in application equipment.

Noncrop uses for pesticides include pest control in living quarters and protecting structures from infestation or attack. These last two examples reflect a direct beneficial impact of pesticides on human health and comfort. The economic effects of wood rot and insect attack on structures demonstrate the benefits of controlling these wood-destroying pests in homes and other structures. The health and safety issues are obvious. Replacement and repair costs for damaged structures must also be included in the benefits of pesticides to society.

All pesticides sold in any given country must undergo approval by regulatory agencies within that country. The AI must pass an extensive battery of toxicological and environmental testing. The final formulation that delivers the AI to the marketplace must exhibit no toxicological effects during testing. Two of the major agencies are the Environmental Protection Agency (EPA) in the United States and the Organization for Economic Cooperation and Development (OECD) in Europe. Each country may also have specific registration requirements for the sale and application of pesticides within its borders. Regulations can differ significantly for different countries, and regulatory cost becomes an important consideration. If the size is not sufficient for a particular market, some products may not be registered in those countries. The OECD and EPA, in conjunction with other regulatory agencies, are striving for global harmonization of the regulatory process. This will ensure that a product registration granted in one of the participating countries will be recognized in other countries.

Any ingredient that does not exert the biological effect of the AI is considered an inert ingredient by the EPA. All inert ingredients (such as surfactants or surfactant blended with other nonactive ingredients, solvents, fillers, and other additives) used in agricultural products in the United States must be approved for that use by the EPA, which means that the toxicological properties of the inert ingredients have been investigated. The surfactants used to formulate and apply the different pesticides fall into this inert category. Previous volumes of *The Handbook of Detergents* have summarized the general classes of surfactants used in other industries. These same surfactants are used in agricultural products, and the reader is referred to the previous works for names, structures, and characteristics [4–6].

The major types of formulations used in agriculture today reflect the history as well as the future of modern agricultural practices. The types of formulations can be broken down into three major types: gasses, liquids, and solids, with a subgroup of these last two, combinations of solids and liquids. The oldest products were solutions of metal ions such as arsenic or copper salts or dispersions of inorganic compounds like sulfur. With the advent of organic chemistry, compounds that affected specific plant, insect, and fungal biochemical pathways were discovered. Further selectivity has been achieved by optimizing the AI and formulation based on the specific biochemistry of the target organism.

12.3.1 GASEOUS FORMULATIONS

The two gaseous AIs in use today are methyl bromide and sulfuryl fluoride. 1,3-Dichloropropylene is also discussed here due to this liquid's very high vapor pressure and the use of 1,3-dichloropropylene as a fumigant. Methyl bromide is used as a fumigant for rodents and insects in stored grain, and injected into the soil for the control of nematodes, weed seeds, fungi, and insects. Neither product utilizes surfactants in their delivery or application. A mixture of methyl bromide with chloropicrin, a liquid with high vapor pressure, is used both as a second AI to control target pests, as well as chloropicrin acting as a warning agent to mix with the colorless, odorless methyl bromide. Methyl bromide is under regulatory limitations as an ozone depletion catalyst, with its use scheduled for elimination in the United States starting in 2001. According to the Montreal Protocol, use in developed countries was to cease in 2005 and in developing countries in 2015. The target dates have not been met, and the exact elimination dates are still in question. Sulfuryl fluoride is a product that can replace methyl bromide with a safer environmental profile. Sulfuryl fluoride is used for fumigation of rodent and insect infestations in dwellings, structures, vehicles, and in grain storage facilities. A building is tented, the gas is pumped into the enclosed structure at the appropriate concentration, and after treatment, the gasses are removed and the building ventilated. 1,3-Dichloropropylene mixed with chloropicrin, a liquid formulation with a very high vapor pressure, is also used for soil fumigation. This product is usually mixed with water and injected into the soil to kill nematodes and fungi. 1,3-Dichloropropylene can also replace methyl bromide with a better environmental profile.

12.3.2 Liquid Formulations

Liquid formulations are the simplest types of formulations to produce. They are well liked by users, easy to use, and simple to measure volumetrically or by weight. Liquids dilute easily, rapidly, and in all proportions with no premixing needed. Detriments include: the level of AI loading may be low, increasing the cost of transportation; the possibility of metal corrosion or materials incompatibility due to solvents; and the effectiveness of container rinse-out for container disposal or return.

12.3.2.1 Solution Concentrates

The simplest type of formulation is a solution obtained by dissolving an AI into water. A method to produce this simple formulation is to chemically modify the AI into a water-soluble molecule without loss of activity. The active ingredient (usually present at ~20–50%) is simply dissolved in water with surfactants for wetting (3–10%), an antifreeze agent such as propylene glycol (5–10%), and possibly a water-miscible solvent to increase the solubility of the AI. Surfactants often include nonionic wetting agents, which have historically been nonylphenol ethoxylates. These particular surfactants have come under scrutiny recently as endocrine mimics, and consequently, their continued use in agricultural formulations is in question at this time (see Section 12.3). The system may be buffered to maintain stability of the AI for pH-sensitive molecules. A surfactant is usually tank-mixed with the AI solution concentrate to assure surface wetting on application. The added surfactant assures spreading of the AI solution on the leaf surface and helps to avoid recoil (bounce off) of the spray droplets.

2,4-D amine salts are another example of an AI that is often delivered as a solution. Final formulations usually include some pH adjustment to maintain the AI in the amine state, and often some sequestering agent to prevent Mg and Ca precipitation of the 2,4-D acid in hard water regions and to assure effective delivery of the AI to the crop.

Glyphosate, a herbicide, is one example of a water-soluble amine salt of an AI acid that is usually delivered as a solution. Stabilizers and surfactants are combined in the formulation for effective application. The surfactant of choice, in fact critical for activity, is a tallow amine ethoxylate. This surfactant appears to be involved with translocation of the glyphosate across the leaf cuticle so the AI can be moved through the plant to the roots [7]. Example aqueous solution formulations are shown in Table 12.1.

12.3.2.2 Emulsifiable Concentrate

Emulsion concentrates (ECs) are one of the oldest formulation types for agricultural pesticides. Even today, ECs are a prevalent delivery system. As liquid formulations, with physical properties similar to the aqueous solution concentrates, these formulations are easy to use, transport, and mix,

TABLE 12.1
Example Solution Formulations

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
2,4-D Amine solution		
Active ingredient	2,4-D Amine	20–45
Surfactant	Phosphate ester	2–10
Chelant	EDTA	0.1–2
Solvent	Water	53–80
Glyphosate solution		
Glyphosate	Glyphosate isopropylamine	10–40
Surfactant	Quaternary alkylamine	5–15
Solvent	Water	55–85

Note: The AI is dissolved in water or the active acid is neutralized with the amine in water, and the remaining ingredients are added after dissolution of the AI.

and can be measured volumetrically for dilution. The EC is usually dispersed and diluted in water. Emulsions are kinetically rather than thermodynamically stable systems. When diluted, the emulsion must be stable for the length of time required for application to the crop. One aid to emulsion stability during application is the agitation equipment being used. Occasionally an EC is diluted with an organic solvent for application. Additional surfactant may be tank mixed at the time of application to aid in penetration or impart some other desired characteristic. An EC formulation is well suited for active ingredients that are liquid, waxy, or low-melting solids. Economics related to manufacture and shipping dictate that the AI be delivered as concentrated as possible. Historically, the xylene range aromatic solvents were very effective for many AI molecules. Solvents that have a safer environmental profile including higher flash points have gained popularity and replaced the xylenes [8,9].

ECs are easy to use, but caution must be exercised with these formulations due to a few safety concerns. The combination of surfactant and AI could cause significant ocular irritation if the concentrate is accidentally splashed into the eye. As with any organic liquid, the potential for accidental aspiration exists, and is one of the important safety issues in using ECs. The solvent and AI mixture may exhibit toxicity if ingested, and the solvents used may be flammable. Recently, issues related to limiting volatile organic carbon (VOC) emissions have become important in considering EC formulations. Many existing products containing solvent are being reformulated to reduce or minimize solvents to meet new VOC limits. Phytotoxicity toward the crop is a possibility for some solvent and surfactant mixtures. This potential for crop damage must be evaluated when formulating an EC, especially if the intended crop is sensitive to the solvents and surfactants.

An emulsion concentrate is made by dissolving the active ingredient in a solvent and adding a surfactant package. Thus, the solubility of the AI determines the solvent selected. The solvents used are common and usually inexpensive. Solvents used include nonpolar hydrocarbons, xylene or higher boiling aromatics and polyaromatics, and odorless kerosene. More polar, water-miscible solvents are sometimes added to the emulsion concentrate to increase the solubility of AI. In the United States and Europe, there has been a general trend toward the use of higher flash point solvents for ECs. This is in response to the desire for products that are safer to transport, warehouse, and use.

The surfactants used in ECs are usually a balanced pair of anionic and nonionic matched to the solvent and AI combination. The selection of the surfactant pair is critical for performance and bloom in the wide range of water hardness conditions found around the world, and a broad range of water temperatures from ~8 to 30°C. Performance refers to formation of a stable emulsion that can be easily applied. Bloom is the rapid and complete emulsification in water with minimal agitation. The diluted EC forms an emulsion with emulsion droplets in the range of 0.1–10 μm. A typical EC formulation composition is shown in Table 12.2.

12.3.2.3 Microemulsion

Microemulsions are a special type of EC. These systems are thermodynamically stable mixtures with microemulsion particle sizes of <0.1 μm. These systems form clear dispersions when diluted, and are stable over wide temperature ranges. Microemulsions often exhibit enhanced biological activity. Microemulsion systems usually require high levels of surfactant blends (10–40%) with solvent and often a cosolvent. [10,11]. The higher loading of surfactant with the solvent and cosolvent means microemulsions can only be formulated at relatively low levels of AI, which adds to the expense of these systems. These formulations are economical in systems that maintain their activity at high dilutions, such as insecticides and fungicides. An example of a microemulsion system developed for some insecticides is shown in Table 12.3.

TABLE 12.2
Example Emulsion Concentrate Formulation

2,4-D Ester Emulsion Concentrate

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Active ingredient	2,4-D Butoxyethyl ester	20–50
Surfactant	Calcium dodecylbenzene sulfonate	3–10
Cosurfactant	Castor oil ethoxylate 40 EO	2–5
Solvent	Aromatic 150	45–75

Note: The active ingredient is dissolved in the solvents, with the surfactants added after dissolution of the AI.

TABLE 12.3
Example Microemulsion Formulation

Pyrethroid Emulsion Concentrate

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Active ingredient	Synthetic pyrethroid	10–30
Surfactant	PO-EO block copolymer	5–15
Cosurfactant	Castor oil ethoxylate 40 EO	5–10
Solvent	*N*-Octyl pyrrolidone	45–75
Cosolvent	*N*-Methyl pyrrolidone	5–25

Note: The active ingredient is dissolved in the solvents, with the surfactants added after dissolution of the AI.

12.3.2.4 Suspension Concentrate

A suspension concentrate (SC) is formed by milling a solid AI in a carrier fluid. A solubility of 100 ppm or less in the carrier fluid is desirable to assure crystal growth due to Ostwald ripening is minimized. For most SC systems, the carrier fluid is water. These formulation types have the same advantages of other liquid formulations in ease of use, volumetric measurement, and rapid dispersion when diluted. Since the carrier fluid is usually water, SCs exhibit reduced flammability and lower phytotoxicity. SCs are generally nonstaining and have minimal odor. Reduced human toxicity and irritation as well as reduced phytotoxicity relative to an EC are additional benefits of SCs [12–14].

Milling the AI to a particle size of 0.1–10 μm in the carrier fluid is usually performed in a ball mill or other high-shear milling process. Wetting and dispersing agents are added to prevent agglomeration during and after milling. Multiple modes of stabilization of the dispersion are utilized depending on the types of wetting agents and dispersants used. These include charge stabilization, steric stabilization, or a combination of both. Wetting agents and dispersants commonly used include sodium lignosulfonate, sodium naphthalene sulfonate formaldehyde condensates, aliphatic alcohol ethoxylates, tristyrlphenol ethoxylates and esters, ethylene oxide and propylene oxide block copolymers, and various polymeric surfactants. Milling is usually performed with the dispersants and surfactants in the milling chamber to assure complete coverage and mixing of the surface active agents with the newly created AI surfaces. Because these formulations are composed of particles suspended in liquid, gravity is responsible for separation due to settling. Rheology modifiers are included to overcome these settling tendencies. The substances used include swelling clays such as montmorillonite clays, modified synthetic clays often mixed with polymers to give synergistic rheological responses, cellulose gums, and polysaccharides. These last two naturally derived rheology modifiers usually require inclusion of an antimicrobial agent to protect the gums and polysaccharides from microbial degradation. Table 12.4 shows a typical formulation composition for an SC.

Typical formulations of SCs utilize AIs at 20–50% ground or milled to a small particle size, wetting and dispersing agents at 5–10%, an antifreeze agent such as propylene glycol at 5–10% for aqueous suspensions, and polymeric or clay rheology modifiers at 0.1–2%, with the carrier fluid completing the SC. The inclusion of the antifreeze brings up an important point. Aqueous SCs must be protected from freezing. Freezing these systems often breaks down the dispersion- and rheology-modifying systems and aggregation of the AI can occur. Another aggregation or crystal growth

TABLE 12.4
Example Suspension Concentrate Formulation

Imidacloprid Suspension Concentrate

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Active ingredient	Imidacloprid	20–50
Surfactant	Sodium lauryl sulfate	2–10
Dispersant	Sodium lignin Sulfonate	5–15
Antifoam	Silicone antifoam	0.1–1
Antifreeze	Propylene glycol	5–15
pH adjust	Organic acid or base	0–1
Thickener	Xanthan gum	0.1–0.5
Rheology aid	Microcrystalline cellulose or sodium silicate	0.1–0.4
Carrier	Water	45–75

Note: The active ingredient is milled with the surfactants and dispersants, with the remaining ingredients added after milling is almost completed.

phenomena that must be prevented in these systems is Ostwald ripening. Both these phenomena prevent even distribution of the AI, and can cause significant problems with the application of the AI through a typical agricultural spray system.

12.3.2.5 Suspoemulsion (Suspension Emulsion)

Suspoemulsion (SE), a recent formulation development, is a combination of a suspension and an emulsion or emulsifiable concentrate in a single formulation. A review of SEs is available [15,16]. The development of formulations of this type requires optimization of many variables, and often requires long development times. The insoluble active is milled to a small particle size similar to an SC, and the low-melting solid, liquid, or emulsifiable AI is formulated as an emulsion or EC in an organic phase. The dispersant for the SC and the emulsion package for the EC must be well matched for SE stability. These types of formulations usually have an extended development time, due to the complexity of the formulation, the narrow window of composition for a stable system, significant possibility of flocculation of the AIs, and the long storage stability times required to verify stability. Another major issue for an SE is the possibility of AI or inert ingredient instability due to hydrolysis when the carrier fluid is water. The advantages of an SE are volumetric measuring, low or no flammability, significant reduction in skin and eye irritation potential, and ease of mixing and dispersing on dilution. A formulation for an SE is shown in Table 12.5.

Inert ingredient selection and process condition control are very important in the production of a stable SE. The component phases, the suspension concentrate, and the EC are usually manufactured separately, and the two combined with vigorous stirring to form the SE. Surfactant and dispersant selection for use in SEs are very important [17–19]. The ideal candidates are surfactants or surfactant classes that are compatible with both the aqueous and oil phases of the formulation. Incompatibilities and flocculation can occur if the dispersant is desorbed from the particulate

TABLE 12.5
Example Suspoemulsion Formulation

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Aqueous phase		
Active ingredient 1	Imidacloprid	10–30
Surfactant	Alkylether ethoxylate or alkylglucoside	1–5
Dispersant	Sodium lignin sulfonate	2–8
Antifoam	Silicone antifoam	0.1–1
Antifreeze	Propylene glycol	0–5
pH adjust	Organic acid or base	0–1
Thickener	Xanthan gum	0.1–0.5
Rheology aid	Microcrystalline cellulose	0.1–0.3
Carrier	Water	10–30
Organic phase		
Active ingredient 2	Chlorpyrifos	10–30
Surfactanat	Phosphate ester surfactant	1–5
Cosurfactant	Alkyl ether ethoxylate or alkylglucoside	1–5
Solvent	Aromatic 150	10–30

Note: The aqueous and organic phases are prepared separately and mixed together under high shear.

surface through replacement by the surfactant. Dispersants used include the ethoxylated comb and block-type copolymers, alkylglucoside surfactants, modified lignosulfonates, and latex dispersions. Surfactants used include sodium alkyl aryl sulfonate, butyl polyalkylene oxide, nonylphenol ethoxylates, polymeric surfactants, graft copolymers, latexes, and polyvinyl alcohol. With the variety of systems described above, the task of defining a system with adequate stability for each phase of the SE is a daunting task. Finding optimized blends of surfactants and dispersants that will stabilize the mixtures is a significant challenge.

12.3.3 SOLID FORMULATIONS

Solid formulations have a few definite advantages over the liquid formulations. They are generally solvent-free. The current drive to reduce VOCs creates a definite advantage for solid formulations in some parts of the world. Solid formulations can be easily swept or vacuumed up if spilled. The packaging for granules is often simple kraft paper, plastic- or foil-lined paper, or plastic bags. The bags are usually minimally contaminated with AI, and quite easy to discard or incinerate.

12.3.3.1 Granule

Granule delivery systems are quite old. They are produced by loading inert carriers, generally in the size range of 250–1000 μm, with AI. Granule formulations are generally loaded with AI at concentrations of 1–40%. The granules are often spread over a field before planting occurs or applied to existing crops such as orchards, vineyards, or turf applications. The granules may be incorporated in the soil, where they release the AI. Other granule types may disintegrate in the soil or on the surface, releasing the AI into the soil. Granules are often made from liquid or low-melting solids sprayed onto the solid carrier. Higher-melting solids can be formulated by dissolving the AI in a suitable solvent, and then spraying the mixture onto the granules or using a suspension concentrate with a coating polymer to avoid abrasive loss of AI from the granule surface. The granule carrier may be inorganic, such as fertilizer blends, clays, talcs, other minerals, silicon, synthetic silicas, carbonates, and silicates, or organic, such as ground corn cobs, grains, rice hulls, walnut shells, or wood [20]. Table 12.6 shows a typical granule formulation for an AI loaded on a carrier.

Sorptive capacity of the carrier is important, especially if higher loadings of AI are desired. Some carriers, such as silica sand, are nonabsorptive and will only carry the AI on the surface when applied with a sticking polymer such as polyvinyl pyrrolidone. Others, such as precipitated silicas, some clays, and many of the organic carriers, are quite porous and will hold large amounts of the melted AI or solvent-dissolved AI. Stability of the AI on the granule is obviously a concern. Spreading the AI over the large surface area of the carrier can increase AI degradation. Many carriers have acidic, basic, or catalytic sites on their surfaces, and these active or reactive sites on the carrier may interact with the AI to cause decomposition. In these cases, a deactivating material is often used to block the reactive sites. These materials can be solvents, surfactants, or other coating or reactive chemicals that impact the reactive site.

TABLE 12.6
Example Granule Formulation

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Inorganic carrier	Urea fertilizer	99.5
Active ingredient	Dithiopyr	0.5

Note: The active ingredient is melted and sprayed onto the fertilizer granules. Alternatively, a formulated AI concentrate can be sprayed onto the fertilizer granules at low rates.

Newer developments for granular formulations have been the addition of coating agents. These coating chemicals, such as resins and polymers, are used to coat the surface of the granule. The effect of these polymers, resins, or waxes is to control the release rate of AI from the granules. The method of these coatings is to act as a protective layer that is slowly eroded or dissolved away to release the active ingredients on the granules. Multiple layers of coatings can be built up to prepare a granule that will deliver somewhat of a controlled release of the active ingredient.

12.3.3.2 Wettable Powder

A wettable powder is produced by mechanically grinding a water-insoluble active ingredient in a ball mill, sand mill, pin mill, or air mill to produce a powder usually of 1–10 μm in size. Care must be exercised during milling due to the potential for a dust explosion. The technical AI is usually milled with a dry surfactant blend and dispersant, so when the AI is dispersed in water, the powder will wet into the water and disperse without clumping. Typical surfactants include sodium dodecylbenzene sulfonate, sodium lauryl sulfate, sodium dioctyl sulfosuccinate, aliphatic alcohol ethoxylates, and nonylphenol ethoxylates. Dispersants include sodium lignosulfonates, other modified lignosulfonates, and sodium naphthalene sulfonate formaldehyde condensates. Polycarboxylate surfactants are often used as codispersants with the lignosulfonates. Wettable powders (WPs) can have very high loadings of AI, from 25 to 90%. After the AI, dispersants, and wetters, the remainder of the formulation is a filler, such as silica, clays, or other inert components. The fillers can also help to prevent fusing of the AI particles during milling [21,22]. An example WP formulation is shown in Table 12.7.

Wettable powders are made even more convenient and safer by limiting worker exposure to the AI via water-soluble packaging, usually films of polyvinyl alcohol (PVA). The water-soluble packets make preparation of the tank mix easy, since each is designed to treat a specific number of acres at a particular dilution. The water is added to the spray tank, and the number of packets is added to achieve the final concentration desired. These packets minimize the potential for worker exposure to the AI. There are a few drawbacks to the water-soluble packaging. The most significant is that the PVA does not always dissolve completely. In hard water or water containing significant amounts of ionic components such as liquid fertilizer, a favorite diluent for many applicators or farmers, the PVA often remains in globules, which will plug spray nozzles. In the worst cases, the PVA sachets may not dissolve at all [23,24].

12.3.3.3 Water-Dispersible Granule

One of the major detriments to wettable powders is the dustiness of these formulations. Many WP formulations have been granulated into water-dispersible granules (WGs) for easier handling and to reduce the danger of dust. WGs also have the benefits of easy flowability and easily measured

TABLE 12.7
Example Wettable Powder Formulation

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Active ingredient	Pronamide	40–90
Surfactant	Sodium lauryl sulfate	1–5
Dispersant	Sodium lignin sulfonate	1–5
Antifoam	Fatty acid soap	0–1
Filler	Barden clay	5–55

Note: The dry active ingredient is milled with the dry surfactants and filler with a high-energy mill such as an air mill.

TABLE 12.8
Example Water-Dispersible Granule Formulation

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Active ingredient	Isoxaben	20–60
Surfactant	Sodium lauryl sulfate	2–5
Dispersant	Naphthalene sulfonate condensate	3–15
Antifoam	Sodium tallowate	0.1–1
Binder	Starch	5–20
Filler	Barden Clay	25–65

Note: The dry active ingredient is mixed with the remaining components and milled with a high-energy mill to achieve the desired particle size. The milled mixture is then mixed with a small amount of water to form a paste for extrusion through a low-pressure extruder, and the resulting granules are dried often in an air stream or fluid bed dryer.

volumes for dosing. WGs manufactured from WPs usually contain additional components. Sometimes fillers are needed to decrease the concentration of AI, and usually binders and disintegrants are included in the formulation. Production of a WG from a WP increases cost, since an additional granulation step is involved. AIs with very high activity and high value will tolerate the additional processing costs for the final product. New products are more frequently developed as WGs, rather than converting older commodity type products to these more convenient product forms.

An example WG formulation is shown in Table 12.8. Fillers such as kaolin clays or precipitated silicas are used to dilute the AI and maintain a constant level of AI in the formulation. Fillers are generally mixed with the AI, and the two milled together to achieve intimate mixing and consistent particle size for these two components.

Wetting agents function in two ways in WGs, wetting of the surface of the granule and wicking of the water into the granule. These physical processes cause initial breakup of the granule and dispersion of the AI. Common wetting agents are usually surfactants such as sodium lauryl sulfate, sodium dioctyl sulfosuccinate, alkyl phenol ethoxylates, and aliphatic alcohol ethoxylates. Wetting agents function through surface tension reduction. Generally, the lower-molecular weight surfactants make better, faster wetting agents, since migration to the surface is a critical aspect for surfactant efficiency.

Lignosulfonates and naphthalene sulfonates have been very important dispersants in WG formulations. Lignosulfonates have also been shown to exert binding effects on granule formation. Additional surfactants have been shown to aid lignosulfonates in wetting and dispersion without adversely impacting granule properties. Ethylene oxide–propylene oxide surfactants are one class of surfactants that was found to aid lignosulfonates in pan and extrusion granulation processes [25]. Selection of the correct lignosulfonate as combination dispersant and binder greatly enhances formation, redispersion, and disintegration of a WG. Techniques have been developed to determine acceptable dispersants for WGs [26].

Granulation requires the use of binders to form the granules, and make them harder and less likely to fracture. Water-soluble polymers, such as polyvinylpyrrolidone and starches or other polysaccharides, are commonly used to increase the adhesion between particles. Water-soluble binders are used to produce rapid and complete breakup back to the primary particle size. Some surfactants and polymers can also act as binders, especially for mechanical granulation techniques.

Disintegrants encourage the rapid breakup of the granules back to their primary particle size. The compounds used are often highly water-soluble polymers and inorganic salts. Disintegrants generally absorb water quickly, swell, and break the particles apart. Cross-linked polyvinylpyrrolidones are very effective for this type of granule disintegration. Effervescence can be added to the granule, which also speeds up particle breakup.

Production of the WG can be accomplished by several methods. Among the oldest is pan granulation. The powdered formulation is slowly fed onto a slanted rotating pan, and the binder solution is sprayed onto the powder as it slides and rolls around on the rotating pan. Granules are formed, and their size increases. The manufacture of acceptable granules depends on many variables, and this process is very much an art [27].

Spray drying is a method used to form small granules from droplets of solutions or suspensions. A concentrated dispersion is atomized into a stream of hot air. The solvent, generally water, is flashed off, and the resulting particle collected. Introduction of warm air in both the top and bottom of the spray drier generates a fluidized bed that forces the fine particles and dusts back up into the liquid stream. The particles tend be somewhat sticky, and multiple particles agglomerate, forming larger granules.

Fluid bed granulation is another method used for granule formation. This batch process utilizes a current of air, keeping particles suspended in a fluidized region, while the binder is sprayed onto the particles, encouraging agglomeration. Granulation and drying can be carried out in the same process. Fluidized beds have also been incorporated after spray drying to agglomerate the powder exiting a spray dryer.

Low-pressure extrusion is being used more frequently in agricultural formulations. Twin screw extruders and basket extruders have been used quite extensively. The dry powder and other formulation components are thoroughly mixed with the binder. The resulting wet cake is forced out of dies to form the granule. Surfactants are included as lubricants during processing, and dispersants and wetters are included for granule performance. The granule is then dried in a fluid bed to complete the granulation process.

WG formulations are becoming more popular as pesticide formulations. The VOC issue is circumvented, since no solvents are used. The newer highly active AIs are often formulated as WGs. This trend is expected to continue in the future.

12.3.3.4 Emulsifiable Granules

Emulsifiable granules have been developed by some of the raw material suppliers to the agricultural products industry within the past few years. These products utilize water-soluble or dispersible polymers such as starch, lignins, polymers, or other water-soluble carrier dispersant molecules with the active ingredient to form an emulsion system. The emulsion system is then spray dried to drive off the water, producing small granules that will redisperse when mixed with water. The key to this type of system is to match the polymer and active ingredient to produce a stable emulsion system in the aqueous phase prior to spray drying, and then have the spray dried product redisperse quickly and well when diluted in water.

12.3.3.5 Baits

Baits are solid, gelled, or liquid formulations that incorporate an attractive food for the target species, usually an insect or rodent. Rodenticides usually use coated grains or other foods. The AI that is coated on the grain bait is usually an SC or EC that will be adsorbed or absorbed by the food bait. Binders are often organic polymers such as polyvinylpyrrolidone or polysaccharides and starch.

Insects are more specific regarding their desires. Termites ingest wood or paper products as food sources. Baits for termites are usually treated wood chips, sawdust, or paper. Again, solutions, ECs, or SCs are usually the form of the AI used in preparing the baits. The AI is sprayed onto or mixed with the bait material, and then formed into a shape in a press or mold. Repellent adhesives and binders must be avoided, and these materials are prescreened for repellency prior to use in the bait.

Ant baits are generally one of three types of foods. Ants are attracted to sugar, protein, and oils, depending on ant species and time of year. Baits are made of the individual foods or a mixture of them. Baits often use low levels of AI dissolved in a solvent such as a vegetable oil on a bait substrate with

TABLE 12.9
Example Ant Bait Formulation

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Active ingredient	Chlorpyrifos	0.1–5
Solvent	Vegetable oil	1–10
Antioxidant	Butylated hydroxy toluene	0.1–1
Carrier	Ground corn cob	85–99

Note: The active ingredient is dissolved in the solvent with the antioxidant and is sprayed on the carrier.

the addition of an attractant to form the complete bait. Recently, sugar baits and gelled sugar baits have become available [28–30]. Table 12.9 shows an example of ant bait applied to an inert carrier.

12.3.4 RECENT FORMULATION IMPROVEMENTS

Current trends in agricultural arenas are reduced risk AIs, lower application rates, safer environmental characteristics of the AIs and formulations, and more specific biological performance, all achieved with reduced net cost to the end user. Formulations have been developed to meet particular needs, often achieving many of these objectives. The goal of many of these formulations has included increased safety, boosting initial or residual activity, and limiting environmental risk by limiting movement of the pesticide, while reducing production costs.

12.3.4.1 Capsule Suspension

The added expense of formulating an AI as a microcapsule must result in significant improvements in active ingredient delivery to justify the added cost. The reasons for encapsulating an AI are varied. Controlled release of the AI is achieved by encapsulation, since the AI must migrate through the capsule wall to exert a biological effect. Safety is often increased by reducing the amount of AI available to elicit a toxicological effect. Reduced leaching of the AI into the environment can be achieved by tying up the AI into a microcapsule that is substantive to the soil. Improved delivery to the target can be achieved as well by reducing environmental degradation such as photochemical breakdown, improving rainfastness of the formulation, and reducing evaporative losses into the air. One benefit for some AIs is a reduction in odor of a formulation by encapsulating the odor bodies.

Microencapsulation is achieved by several methods [31]. Interfacial polymerization is one of the widely used techniques. This encapsulation method utilizes an AI emulsified as an oil in water emulsion with the AI in the oil phase. The AI may be a liquid; dissolved in an organic, water-immiscible solvent; or melted into a liquid state. Reactive surfactants are often used to form a stable emulsion for cross-linking. A surface-active monomer, usually polymeric in nature for cross-linking, is dissolved or dispersed so it will reside predominantly at the water–organic solvent interface. A second cross-linking reactive monomer is added to the aqueous phase, and the shell wall forming reaction occurs at the oil–water interface. Careful selection of the components, concentrations, rates of cross-linking, and amount of shear during the cross-linking can help determine the size of the capsule and the thickness of the capsule wall. The resulting capsular suspension must then be further formulated with dispersants and wetters to stabilize and keep the microcapsules in suspension to produce a final formulation. The water-soluble cross-linking monomers are often polyfunctional amines. Commonly used oil-soluble monomers are polyfunctional isocyanates (to produce polyurea capsules) or acid chlorides (producing polyamide capsules). Other classes of polymers can be used as well to form polysulfonamide, polyurethane, or polyepoxide shells.

Interfacial coacervation has been successfully used for many types of microcapsules. Stabilization of the emulsion phase with surfactant is an important step in this process. The surfactants used have included lignin sulfonates, other sulfonated polymeric surfactants, and vinylpyrrolidone co- and terpolymers. Increased photo stabilization of the AI, apparently due to light-absorbing properties of the polymers used, has been an added benefit observed for some encapsulated formulations.

Other encapsulations utilize more or less similar methods for the formation of the capsule wall. Complex coacervation utilizes the reaction of an anionic water-soluble polymer with a cationic material to form the shell wall that separates from the solution. As the coacervate separates from the solution, it will tend to coat suspended particles with a protective shell. The shell wall is then hardened with a cross-linking agent. *In situ* polymerization is used to form urea formaldehyde or melamine formaldehyde shells by using heat to cross-link the monomers forming the shell wall. Interfacial polymerization with isocyanates via hydrolysis is another method to form a shell wall at an organic–water interface. In this case, water acts to hydrolyze some of the polyisocyanate to an amine, which cross-links to form the polyurea microcapsule wall.

After the formation of the microcapsule, the resulting material must be formulated for delivery. The microcapsules have to be dispersed in a formulation or they can settle into a hard cake. The dispersants used are the lignosulfonates used in some of the encapsulation processes. Some vinylpyrrolidones have also shown benefits in maintaining disperse states in the final formulations. Table 12.10 shows an example of a microencapsulated formulation in an aqueous suspension.

TABLE 12.10
Example Microcapsule Formulation

Ingredient	Example Ingredient	Concentration (%) (wt/wt)
Aqueous phase		
Catalyst	Ethylenediamine	0.1–3
Antifoam	Silicone antifoam	0.1–1
Antifreeze	Propylene glycol	0–5
Thickener	Xanthan gum	0.1–0.5
Rheology aid	Microcrystalline cellulose	0.1–0.3
Carrier	Water	10–30
Organic phase		
Active ingredient	Chlorpyrifos	10–30
Surfactanat	Phosphate ester surfactant	0–5
Cosurfactant	Alkyl ether ethoxylate or alkylglucoside	0–5
Reactive monomer	Polymethylene polyphenyl isocyanate	0.5–5
Solvent	Aromatic 150	10–30

Note: The AI is dissolved in the organic phase with the surfactants and polyurea capsule monomer. The organic phase is mixed with water under high shear to form the desired droplet size, and the polymerization of the capsule wall is achieved with the addition of the cross-linking catalyst. After formation of the capsule, the remaining ingredients are added to stabilize the resulting capsule suspension.

In some cases, the formed microcapsules have been dried or spray dried into a powder or granule. These systems can then be treated as wettable powders or water-dispersible granules in the finished formulation, with the wetters and dispersants added in the drying step.

12.3.4.2 Nanosuspensions and Emulsions

Nanosuspensions have been developed in recent years that take advantage of the smaller droplet size, in some cases producing an enhanced biological effect. One method is to produce an emulsion system using surfactants that will form liquid crystal structures at an oil–water interface. These systems are then homogenized under high shear to produce droplets in the size range of 100–500 nm. These types of systems have occasionally demonstrated activity different than that observed in a traditional emulsion. One added advantage of this newer emulsion system is the replacement of most or all of the organic solvent in the EC with water in the nanoemulsion. Similar types of systems are under development for SC-type systems. These systems are more difficult to produce, because the small particles of suspension must be produced by either a precipitation process or very intense milling to produce particles in the nanometer size range. Economical nano-SCs have not yet been introduced into the marketplace, but they are being researched.

12.4 PESTICIDE APPLICATIONS

The different formulation types discussed above are used with and without additional components for a variety of agricultural applications. Various surface active ingredients are frequently added to boost performance. The major considerations are effective delivery of the tank mixture, which may be a mixture of formulations that are not completely compatible with each other. Selection of the AI is of paramount importance to achieve control of the pest, but the formulation or formulations to be applied must be considered as well. Tank mixtures and the requirement of a particular physical effect may require additional modifications of the physical properties of the original formulation, due to specific circumstances or application methods. This is often where an adjuvant or additive to modify a specific physical property enters the picture. The goal of all application methods is to effectively apply the appropriate chemical or chemicals to control the pests attacking the planted crop. Minimizing the number of trips through a field is desirable, because labor, physical damage to the crop, equipment wear and tear, and fuel all need to be minimized. Application of multiple AIs is often made with a single pass through the fields by tank mixing compatible chemicals or by combining multiple applications through the use of multiple pieces of equipment and products.

12.4.1 Seed Treatments

Seeds are often treated with a fungicide or an insecticide to protect the seed from fungal or insect attack during storage. Seed treatments are also a very effective method for direct application of a systemic insecticide or fungicide to a plant. The AI is delivered directly to the site of plant growth and can protect the young plant with minimal waste [32]. A few insecticides, both systemic and local protectants for nematode or grub protection, have also been delivered via seed treatments.

Treatments are generally applied to the seed as an AI suspended in a liquid either as an aqueous suspension or solvent-based suspension. In some cases, the formulation is not robust enough to withstand the rigors of seed treatment. In those cases, or to boost desired effects, surfactants may be added to aid in wetting the seed surface and adherence of the AI. Dispersants may also be added to keep the AI evenly distributed during the application process. Water-soluble polymers are frequently used for a final coating on treated seeds to improve handling and storage characteristics. These polymers seal the treatments on the seed surface and aid in the passage of the seed through the planting equipment.

12.4.2 PREPLANT APPLICATIONS

Preplant applications are made to the soil or crop stubble before or during planting. Combining selected herbicides and insecticides to control weeds and soil insects with fertilizer applications is common. Granular products are often used for these applications, and they are often applied the winter before planting or very early in the spring. If a material has to be incorporated into the soil, it is usually applied during or just before disking the field. In some cases, incorporated materials are applied during the crop-seeding operation. One method is to band apply the product, such as an insecticide or herbicide directly in the region of the seed bed. This assures the protective chemical is placed exactly where needed to protect the seed and very young plant after germination. Some equipment used to apply aqueous formulations at the time of planting is shown in Figure 12.9. Other types of equipment can be used to apply granular formulations at the time of planting.

12.4.3 POSTEMERGENT APPLICATIONS

Postemergent application is the most common method for agricultural pesticide application (Figure 12.4). Application to the emerged plant allows delivery to the regions of the plant that will benefit through the application in the case of insecticides and fungicides. Postemergent herbicides are applied to crops that are tolerant to the herbicide while the weeds are controlled. One very commonly used application method is a tank mix of the pesticide with foliar absorbed nutrients. This permits controlling the pest while feeding the crop.

Selected adjuvants are used to aid in delivering the pesticide. Herbicides usually benefit from a surface tension reduction and penetration enhancer. Adjuvants are from the three classes of surfactants: nonionic alkyl polyethylene oxide alcohols, organosilicones, and anionic surfactants such as

FIGURE 12.9 Planting seed with the incorporation of a diluted product using a John Deere 1770 NT Planter, showing the seed boxes above the planting heads and the liquid tanks containing the diluted treatment. (Photo courtesy of the John Deere Company. With permission.)

the alkyl alcohol sulfonate; for glyphosate, tallow amine ethoxylate is also used as a wetter. Many times, the liquid fertilizer acts as a penetration enhancer. Other penetration enhancers include vegetable, methylated vegetable, or paraffinic oils with anionic/nonionic surfactant packages for emulsifying the oil. Polymeric adjuvants are often used as sticking and rainfastness aids. These are often the polyvinyl alcohols, polyacrylamides, alkylated vinylpyrrolidones, and vinylpyrrolidone–vinyl acetate copolymers. Polymers are sometimes added to tank mixtures to aid in the reduction of spray drift by inhibiting the generation of very small droplets during application. Spray drift will be addressed in greater detail later.

Insecticides and fungicides are usually applied postemergent, when the insect or disease is present. The application characteristics and tank mix additives used for herbicides are very similar to those for insecticides and fungicides. As often as possible, pesticides and fertilizers are applied simultaneously to avoid multiple trips through the fields.

12.4.4 CHEMIGATION

Chemigation is the application of pesticides through an irrigation system. Many compounds are applied via the irrigation water. A pesticide concentrate is injected and diluted into the water stream of an irrigation system, and then pumped through piping and nozzles onto the field (Figure 12.10). The dilution factors are very high. This dilution generally means the surfactants are stripped from the pesticide matrix, and highly diluted pesticide is applied to the crop. The movement of water and pesticide through the pipes and nozzles keeps the pesticide droplets suspended and isolated, preventing coalescence into pools of pesticide that would result in uneven application. Fungicides and insecticides are the products most often applied via chemigation.

Chemigation occasionally requires additional additives to assure complete dispersion of the AI in the chemigation injection system. Aids to application via chemigation may include slight dilution of the concentrated pesticide in a crop oil or crop oil concentrate. The added oil and surfactant

FIGURE 12.10 Chemigation application of a pesticide. This application is using drop nozzles. An end gun, which results in significant spray drift, is not in use here. (Photo courtesy of the Spray Drift Taskforce. With permission.)

reduces viscosity of the pesticide concentrate, and the surfactants often aid in the rapid formation of a diluted emulsion.

Chemigation application systems always include precautionary systems to prevent the backflow of the pesticide into the irrigation well or source of irrigation water. The concentrated pesticide is usually mixed into the chemigation water via an inline injection/dilution system. After formation of that diluted emulsion or solution, the surfactants will often dissolve into the water, leaving the oil droplet behind moving through the chemigation piping. Assuming the droplet maintains sufficient velocity through the piping to prevent settling or creaming, even application is assured [33].

12.4.5 Preharvest

Pesticides are not usually applied close to harvest due to preharvest interval restrictions for most pesticides. Crop modifiers, however, are applied, such as defoliants to sugar beets prior to digging the beets and desiccants to cotton to aid the picking of the fibers. These products usually utilize some of the wetting and spreading surfactants to aid distribution of the products.

12.4.6 Postharvest

Postharvest pesticide applications are usually restricted to fungicides to protect the stored grains, vegetables, and fruit from mold and mildew, insecticides to prevent insects attacking the stored grains, and rodenticides to prevent rat and mouse depredation. Fungicide application utilizes the same wetting and spreading surfactants already discussed. Fumigants do not utilize any surfactants, and rodenticides utilize the usual coating or bait components already discussed.

12.4.7 Nonagricultural Pest Control Applications

Pest control in and around buildings, both residential and commercial, is generally for insect or rodent control. In warm, moist climates, in older buildings, and in major metropolitan areas, cockroaches and other insects can be a significant pest issue. Adverse health effects are attributable to these insects due to the spread of disease and the allergic sensitization effects of these insects. Control has historically been through crack and crevice treatment with an insecticide formulated as an emulsion or microemulsion. These emulsions are of the traditional type. The AI is dissolved in a solvent, such as an aromatic blend, and a surfactant package, often a blend of an anionic surfactant, such as calcium dodecylbenzene sulfonate, and a nonionic surfactant for emulsification. Newer formulations have taken advantage of behavior patterns of cockroaches and applied microencapsulated insecticide in areas where the insect will contact the treatment. The microcapsules are a specific size range and are picked up by the leg and body hairs of the roaches. These are spread to other roaches by contact and ingested during grooming with a lethal dose delivered via this grooming.

Rodent control is generally performed using baits containing toxins. Baits are prepared using a stable food source such as grain coated with the toxin or a paste bait with the toxin incorporated in the bait matrix. Toxins are impregnated or incorporated in the bait matrix via solubility in a solvent, which is taken up by the bait matrix or through the use of a suspension of the toxicant that can be dispersed and incorporated in the bait matrix. Concentration of AI in baits is often very low, on the order of 0.01–1% AI. Most toxicants used in baits are very potent toward the target species.

12.5 SURFACTANT IMPACT ON APPLICATIONS

Surfactants have significant impact on the application of pesticides beyond the effects in the formulation. Since the formulations are generally diluted, the surfactants must function well in the dilution process, with rapid dispersion into the diluting liquid, which is usually water. During the application process, the diluted product must be applied to the desired area with minimal drift or movement off the target site. The droplets of spray should hit the target and stay on the surface as efficiently as possible. Finally, the applied pesticide should stay on the target without degrading too fast for effective control or moving off the target with rainwater. The discussions below will touch on the effects of surfactants on these areas.

12.5.1 SPRAY DRIFT

The EPA requested data regarding spray drift to support existing and proposed registrations. In 1990, a consortium of 38 agricultural chemical companies was formed to respond to this data request. Data were generated to support the registration of ~2000 existing products and provide data for the registration of future products from the Spray Drift Task Force (SDTF) member companies. Additional companies have joined the Task Force, so now almost all companies are represented. The studies were designed and conducted through consultation, and at times, direct involvement with scientists at universities, research institutions, and the EPA. Field-collected data was generated for aerial, ground hydraulic, ground air blast, and chemigation applications.

The data generated in these studies, including laboratory and field applications, were generated under good laboratory practices to assure that they would comply with existing EPA submission requirements. The data generated resulted in computer models that predict drift based on physical parameters. As expected, the droplet size was the most important factor in drift. Thus, factors that have the most impact on droplet size are the equipment generating the droplet and controlling the size of individual droplets. Weather conditions such as temperature and wind speed can also have a significant impact on spray drift.

The parameters affecting spray drift are slightly different depending on the application method. For aerial applications, the largest contributor to drift is droplet size. Aircraft position relative to the target area will affect drift, and is controlled by the pilot. This spray swath adjustment is dependent on cross winds and height of application. Spray drift minimization can also be impacted by the physical setup of the aircraft. Spray boom length should not approach the ends of the wings, to avoid vortices during application. Wind speed and direction must also be closely monitored during application, since these parameters can significantly affect spray drift. Finally, physical properties of the spray solutions have a minor impact on spray drift. Dynamic surface tension is the physical parameter with the most significant affect on droplet size, with spray solution elongational viscosity contributing a minor component.

The factors affecting spray drift in chemigation applications were found to be the sprinkler height, wind speed, and whether end guns were used to reach edges of the fields. The use of end guns significantly increased drift.

Air blast applications found much lower levels of drift than expected. This is due to high application volumes, comprised of larger-volume drops that settle out rapidly. The high volume also results in lower application concentrations. Most small drops generated are captured by the foliage of the treated plants. The larger drops generated do not have sufficient momentum to move off site significantly. Finally, the effects of wind on drift in air blast applications are greatly moderated by the foliage.

Ground hydraulic applications, probably the most often used application method, were found to be impacted by the spray nozzle height, droplet size, and wind speed. Keeping the spray nozzle as close to the target plants as possible greatly reduces spray drift. Selecting the appropriate nozzle to produce the desired droplet size also will minimize drift. Monitoring meteorological conditions to avoid spraying under windy conditions will minimize spray drift as well.

The data generated by the SDTF are owned by the member companies. The data has been submitted to the EPA, and is currently under regulatory review. Many pieces of the data have been published in various journals and presented at symposia. Additional information is available from the contract administrator for the SDTF in the form of brochures and presentations describing the tests and results for aerial, air blast, chemigation, and ground application of pesticides [34].

Surfactants that impact the dynamic surface tension of the pesticide can impact spray drift. Generally, these are included within the formulation rather than tank mixed at application.

The lower dynamic surface tensions appear to aid the formation of larger droplets during atomization of the pesticide. This physical effect reduces spray drift. The use of surfactants that rapidly move to the interfaces produces lower dynamic surface tensions over the time frame of droplet generation for the test nozzles (5–50 ms). These surfactants are often the lower-molecular weight anionic and nonionic surfactants commonly used in the formulation of pesticides.

12.5.2 Recoil and Bounce

A sprayed droplet hitting a leaf can result in one of two actions. Either the droplet will hit the leaf and spread to form a layer on the leaf, or the droplet will strike the leaf and recoil to bounce off. Surfactants can have an impact on this behavior, and the dynamic surface tension of the droplet can aid in reducing droplet bounce. The dynamic surface tension is important, since the concentration of surfactants above the critical micelle concentration of the surfactant is the important parameter in determining recoil. Small droplets are retained better than larger droplets, and droplets with surface tensions significantly less than water will also be retained better [35,36].

Retention was found to be related to the ethylene oxide (EO) content for primary alcohols of a particular alkyl chain (e.g., C_8–C_{12}). The more hydrophilic (higher EO) surfactants were found to perform better as deposition agents than the more hydrophobic surfactants. Similarly, the size and shape of the hydrophobic moieties are important. Bulky, highly branched head groups, ethoxylated secondary alcohols, ethoxylated tertiary tallow amines with two ethoxylated tails, and sugars all appear to be efficient as deposition aids [37].

12.5.3 Adjuvants and Tank Mix Additives

Tank mix additives are often added to pesticide formulations prior to application. These adjuvants have been described briefly in the sections above as related to individual applications, and will be discussed in more detail here. The reasons for the use of one or more of the multitude of additives available are varied. Effects on absorption, buffering efficacy, uptake, penetration, rainfastness, mobility, and translocation are all reported in the literature. Physical modifications of the spray application or pattern with drift reduction, droplet size changes, evaporation modification, wetting, and spreading have also been identified. Safening (changing the metabolism rate of a herbicide), as well as antagonism with another applied AI, have also been reported. There are over 1000 possible additives and adjuvants that could be used with a product. No individual researcher or company could possibly investigate all possible combinations with a registered product. Manufacturers often include surfactants with adjuvantal effects in their formulations. The companies may also recommend specific adjuvants and additives as possible tank mix additives in their product labels that have been tested and shown to be effective. Extreme care must be taken by the applicator in selecting an adjuvant, since the potential exists to adversely affect the AI, interfere with or change application parameters, or severely restrict the availability of the AI to the targeted pest. However, the possibility also exists that an untested adjuvant may be found that will significantly boost activity or reduce the rate needed to control the targeted pests.

Adjuvants are most often used with herbicides, but they are also used with selected insecticides and fungicides. The adjuvants commonly in use include surfactants, oils, solvents, polymers, foams, salts, and photo protectants, as well as combinations of these components. Adjuvants for herbicides delivered from water dilutions are most commonly nonionic surfactants and crop oil concentrates. Nonionic surfactants are added for wetting of the leaf surfaces, and the crop oil concentrates are added as penetration enhancers. Organosilicone surfactants have been shown to enhance the availability of several pesticides. The silicone surfactants reduce the surface tension below 20 dyne/cm and are often referred to as super wetting surfactants.

Fertilizer additives can often enhance the uptake of herbicides. In some cases, specific salts such as ammonium sulfate, diammonium sulfate or ammonium nitrate can boost the activity of the specific herbicide. These materials often increase the absorption of the herbicide into the plants. In some cases, they act as pH modifiers for the tank mixture.

Oils, such as crop oil and crop oil concentrates, or solvents such as *N*-alkyl pyrrolidones, can have a significant impact on pesticide uptake. The oils can aid in solubilizing the leaf cuticle as an aid to penetration, and also aid the solubilization of the AI and distribution into plant leaf waxes. The polar alkyl pyrrolidone-based solvents often act as solvents for the pesticide, thus aiding leaf penetration as do the paraffinic and vegetable oils and the methylated seed oils. Mixtures of these solvents with surfactants and vinylpyrrolidone copolymers can act as wetters, stickers, and penetration-enhancers, increasing the rate of penetration of the pesticide as well as limiting wash off of the pesticide by dew or rain [38].

High-molecular weight polymers can have an effect on spray drift by increasing droplet size if the polymer is not physically degraded by mechanical action in the spray tank pumps. Newer nonpolymeric drift control aids have also been developed that change the rheological properties of the tank mixture. Many additional types of adjuvants are used commonly. Those presented above are only a few examples.

12.5.4 Degradation and Metabolism After Application

Degradation and metabolism are the means by which pesticides are removed from the environment. Metabolism of the pesticide is often enhanced by rapid uptake by the target organism and completion of biochemical pathways. The various surfactants in the formulation or adjuvants that are tank mixed to promote uptake can have a significant impact on metabolism. Aids to translocation to the active site or areas of degradation will also have an impact on metabolism of the AI.

Photochemical degradation is usually the first degradation pathway observed for an AI. The photo protectants that are used will inhibit photochemical events for awhile, but these are usually degraded or overcome in time with AI decomposition resulting. The photochemical events occur on both the plant surfaces and the soil surface. Some photochemical events occur in water as well.

Off-target movement due to spray drift or ground water runoff is often the greatest concern for pesticide usage. This is especially true for movement to or in ground water. Various materials are added to formulations to prevent or limit movement into water. Most materials added to control leaching and movement in the soil are polymeric materials that do not move themselves but have affinity for the pesticide. Lingins, activated charcoal, and synthetic polymers all have been shown to reduce leaching [39]. Surfactants, especially at high rates, can adversely impact pesticide movement in soil by solubilizing AI that would otherwise bind with soil clays or organics [40].

12.6 SUMMARY

The use of surfactants in pesticides is truly universal. A wetter, dispersant, physical property modifier, or surface active polymer is always present in both the concentrated formulation and the application solutions. Surfactants and polymers are even used in the manufacture of the AI in a few cases. The only formulations that do not use some form of surfactant are the gasses used for fumigation of soil, structures, stored grain, and occasionally, granules that have the melted or solubilized active ingredient sprayed onto the granular carrier. Formulated materials utilize surfactants as dispersants, wetting agents, emulsifiers, disintegrants, rheology aids, and stabilizers. At the tank mixture level, many different surfactants are added to the formulated materials to optimize delivery or activity for specific crops or pests. Modern agriculture could not function without the surface-modifying properties of detergents. Application methods are varied. They range from the baits placed individually to granules spread over fields or crops, to sprays applied over the coverage area. Application equipment spans an enormous range of application volumes, and is reflected in hand application, backpack sprayers, tank trucks with spray nozzles or granule application equipment, tractor-pulled application equipment for both liquids and solids, large-scale floaters used by commercial applicators also for liquids or solids, helicopters and fixed wing aircraft applying both liquids and solids, and railroad tank cars equipped with pumps and spray nozzles or solid applicators. All applications are intended to apply a particular concentration of active ingredient to a specific target surface area. This application rate is critical to assure control of the target pests without damaging nontarget species.

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13 Application of Surfactants in Lubricants and Fuels

Tze-Chi Jao and Charles A. Passut

CONTENTS

13.1 INTRODUCTION

Many applications of surfactants in lubricants and fuels have a common purpose, namely to reduce or prevent the formation of deposits by the degradation products of lubricants and fuels. In lubricant applications, surfactants serve in various roles. In crankcase oils, surfactants reduce and prevent sludge formation and deposit formation in pistons, cylinders, and valve train systems [1]. They also reduce and prevent sludge formation in the reservoirs of transmission fluids, gear oils, and industrial oils, and keep parts clean by prevention of deposit formation on metal parts. In addition, they provide friction control in friction interfaces as in automatic transmissions.

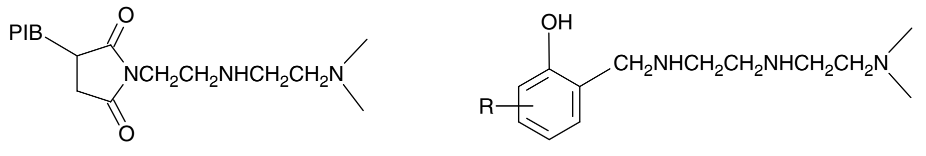
Surfactants are used in fuel applications to prevent fuel injector deposits, intake valve and exhaust valve deposits, combustion chamber deposits [2,3], injector deposits of direct gasoline injector systems [4,5] and high-pressure diesel injector systems [6], and low-temperature intake valve deposits [7].

13.2 APPLICATIONS OF SURFACTANTS IN LUBRICANTS

13.2.1 ENGINE OILS

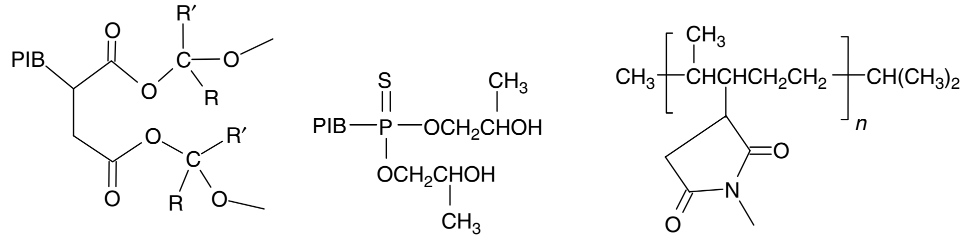
Two types of surfactants are used in engine oil applications. One is ashless dispersants, and the other is metallic detergents. Typical ashless dispersants, as described in Chapter 15 of Part D (Formulations) of the *Handbook of Detergents* [8], include succinimides, Mannich condensates, esters, phosphonates, functionalized ethylene-propylene copolymers, and others. Their molecular structures are shown in Figure 13.1.

Dispersants are used to control sludge, which is formed when engine temperatures are low. Such operation is often encountered in stop-and-go city driving or during engine idle conditions.



Polyisobutenylsuccinimide (PIB-succinimide)

Polyaminomethylalkylphenol (PIB-Mannich)



Polyisobutenylsuccinate ester (PIB-succinate)

bis-Hydroxypropyl alkenylphosphonate

Functionalized ethylene-propylene copolymer through maleic anhydride grafting

FIGURE 13.1 Dispersant molecules commonly used in engine oils.

The situation is particularly prevalent in cold weather. Under these conditions, the combustion process is often not completed, generating a large amount of unburned fuels and partially oxidized hydrocarbons, which include ketone, aldehyde, and carboxylate compounds of ill-defined molecular structures. These materials often find their way along with combustion products such as sulfuric acid, NOx and water as blow-by gases into the crankcase and contaminate the lubricant. As the limit of maximum sulfur level in the fuel is reduced, the amount of sulfuric acid compared with NOx becomes less significant. From this mixture, a reaction leads to the formation of resins. These are complex mixtures of high molecular weight polar materials containing nitro-, hydroxyl-, and carbonyl-functional groups, and sludge. It involves the reaction of fuel and fuel-derived unsaturated hydrocarbons, such as olefins and diolefins, with NOx and oxygen to form a class of compounds called nitro-nitrates [9]. The polymerization apparently involves an *Aldo-type* condensation reaction, by which carbonyl compounds react to form polymeric species of varying sizes [10].

Further heating of the complex mixtures will result in the precipitation of oil-insoluble resins. In higher-temperature lubrication, most often found in super-highway driving by passenger cars or heavy-duty trucks, the lubricant temperature can exceed 150°C. The oxidation of lubricant and fuel involves a different type of reaction, termed *nitro-oxidation*. The oxidized products in this case contain predominantly organic nitrate [10]. Such oxidized products, if allowed to polymerize, will also form insoluble resin. Such resin can plate out on various engine parts, such as valve lifters, piston and rings, as varnish, which may cause troublesome adhesion of parts or interference with tolerances. Besides dispersants, detergents are also believed to be capable of dispersing such resinous materials. At some point, the intermediate resinous materials can interact with water, strong acids, and unburned fuel to form water-in-oil emulsions. In used diesel engine oils, such emulsions can be stabilized or thickened by the presence of soot. Sludge is the colloidal phase that separates from crankcase oil. Sludge is often found in the more stagnant regions of the engine, or is deposited in places critical to oil supply and distribution, such as the piston rings and the oil screen in the sump.

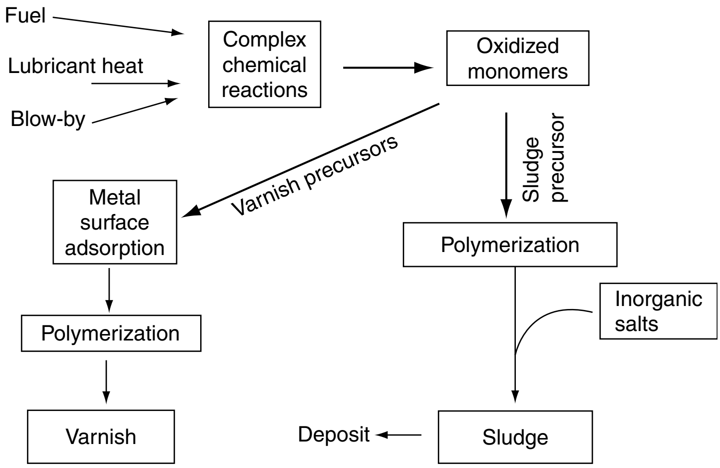


FIGURE 13.2 Sludge and varnish formation.

If sludge is not properly dispersed, the flow of oil through the engine system will be diminished, which could cause a catastrophic problem. Sludge and varnish formation processes are shown in Figure 13.2.

It is noted that the step involving inorganic salts for the formation of sludge was most prominent before the 1970s, when leaded fuel was used. In today's sludge, inorganic salts are almost nonexistent. The chemistry of sludge discussed so far was established in the 1960s. Since then, engine design changes coupled with alteration in fuel composition have given rise to a slightly different sludge called *black sludge*. The problems surfaced in 1984 and 1985. The most serious problems surfaced in Germany. The black sludge deposits were usually found on the cooler inner surfaces of the engine and in particular, tended to accumulate initially in engine top cover or on the top of the cylinder head (valve deck). Engine malfunctions and in extreme cases, total engine failure sometimes resulted from accumulation of these deposits, the most serious engine damage usually arising from blockage of the oil pump pick-up screen [11]. The formation of black sludge is shown to be sensitive to the nature and rate of blow-by gases [12]. Contrary to the earlier sludge discussion, the oxidized products involved were not found to contain any organic nitrate or nitro compounds. A different type of dispersant is needed to disperse this type of sludge. Nevertheless, existing crankcase dispersant chemistry is capable of handling this type of sludge. The mechanism by which dispersants are used to disperse sludge can be found in Part D of the *Handbook of Detergents* [8]. In general, higher-molecular weight dispersants are more effective in dispersing sludge. Among the various types of dispersants, succinimide dispersants are preferred in most of the applications. However, succinate (ester) dispersant is required for certain lubrication conditions. One way to measure the effectiveness of dispersants is to evaluate fully formulated engine oil in a Sequence VG sludge test (ASTM D 6593) in an engine following a specified test condition. An example of the test results is shown in Figure 13.3.

Commonly used metallic detergents in engine oils are sulfonates, phenates, salicylates, and others. Example of these three types of metallic detergents are shown in Figure 13.4.

Detergents function in lubricants mainly in high temperature lubrication to reduce engine deposits, particularly in the ring belt area of pistons. They work by suspending contaminants in oil and by neutralizing acidic materials that are combustion byproducts of the fuel and oxidation degradation products of the lubricant. Though metallic detergents are used in both passenger gasoline engine motor oils and heavy-duty diesel engine oils, their role in heavy-duty diesel engine oils is more critical, since lubrication in the ring-belt zone of the diesel engine is typically run at higher temperatures. The chemistry of deposit formation in high-temperature lubrication and

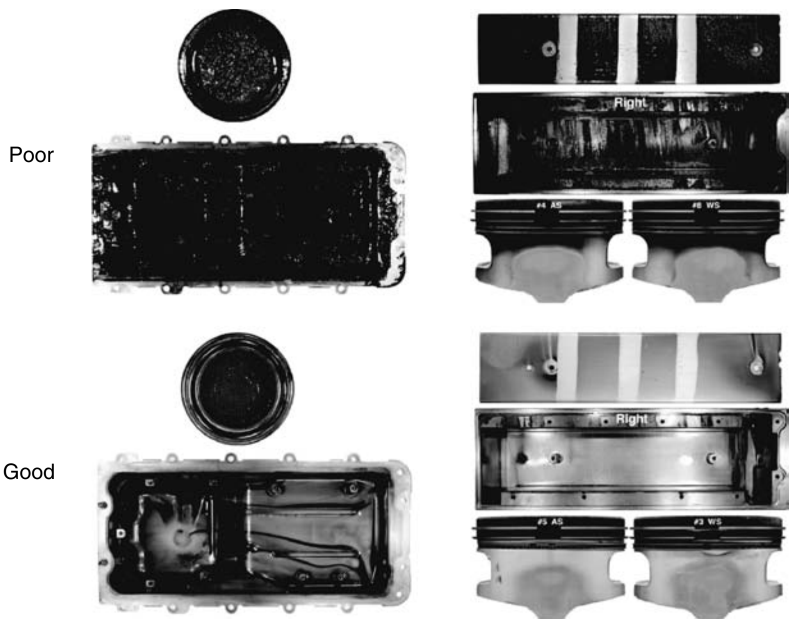
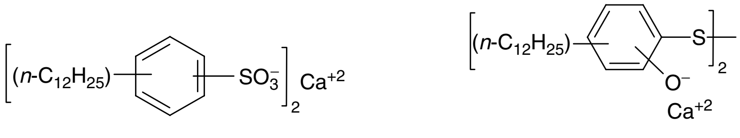
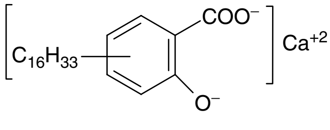


FIGURE 13.3 Comparison of passing and failing oils in the Sequence VG engine test.



Calcium didodecylbenzene sulfonate

Calcium dodecylphenolate



Calcium hexadecylsalicylate

FIGURE 13.4 Example of metallic detergents used in engine oils.

related problems have been extensively investigated by Kreuz [13]. One of the major contaminants is soot, which is a partial combustion product and may be viewed as condensed fuel hydrocarbon fragments, from which the hydrogen atoms have been largely stripped. Soot exists as soot particles and contains ~1% hydrogen, along with small but significant amounts of oxygen and sulfur. These particles have been shown to be spheroidal and of 20–50 nm in diameter [14]. Soot particles have high surface energy and are strongly attracted to each other, forming chain- or clump-type aggregates. The second major source of contaminants is resins, which are oxygenated fragments derived from a complex mixture of large hydrocarbon molecules in the C_{15}–C_{50} range. Resins may arise both from partial combustion products of the fuel and from thermo-oxidative degradation of lubricants.

Regardless of the source of the resins, their formation involves basically an oxidation reaction mechanism that produces peroxides as intermediate species. In the presence of sulfuric acid, the intermediate peroxides catalytically convert to carbonyls, which polymerize to form oil-insoluble resins. Such oxidative degradation is particularly severe in the ring-belt area of the piston, where the temperature can reach 260–320°C in diesel engines and 200–260°C in gasoline engines.

Depending on the relative amount of soot and resins present in the ring-belt area, the deposit pattern will vary. At low soot levels, resins that are partly insoluble in the oil will plate out on the piston surface as *amber lacquer.* At higher soot levels, resin-coated soot will be formed and the deposit on the piston surface becomes *black lacquer.* As the soot concentration increases, the deposit will not only be darker, but will also increase until the supply of resin eventually becomes depleted, and a regime of soot-coated resin particles emerges [13]. Such undispersed agglomerates have little tendency to adhere to metal surfaces as lacquer, but can accumulate as deposit in regions of compaction, as in groove filling behind the piston rings.

Whereas the effect of soot is to draw the resins out of oil solution, the detergents act to increase their dispersibility. They achieve this by attracting their polar ends to such polar materials, whereas their long hydrocarbon tails act as *fenders* to prevent these particles from agglomerating, adsorbing on soot and plating out on metal surfaces. The mechanism of soot dispersion by metallic detergents is illustrated in Part D of Ref. 8. Though ashless dispersants have similar ability to disperse soot-coated resin particles or resin-coated soot particles, the deposits on the crown land area and in the top ring groove are effectively reduced by a certain level of nonoverbased detergent present in the lubricant. This unique function of detergents to keep the piston ring belt area clean distinguishes them from dispersants as the additives for high-temperature lubrication.

A method to measure the effectiveness of metallic detergents is to run a fully formulated engine oil containing the specific metallic detergents in a Caterpillar IK single-piston diesel engine test, which is ASTM D 6750. A comparison of good and poor detergent performances is shown in Figure 13.5.

Some metallic detergents, such as sulfonates, in particular the overbased sulfonates, function as a rust inhibitor by forming a film through adsorption of surfactant molecules or neutralizing the acidic materials, preventing them from attacking the metal surfaces. Acidic materials are commonly produced by incomplete combustion of fuels or oil oxidation.

The other surface-active chemical components include antiwear additives, friction modifiers, and antifoam additives [15]. The functions of these other lubricant additives, as their names imply, are quite different from these two surfactants. For example, antiwear additives, such as zinc dialkyldithiophosphates, are used to prevent wear on engine parts; friction modifiers, such as glycerol monooleate, are used to reduce boundary friction in engine operation to improve fuel economy; antifoam additives such as polymethylsiloxane are used to inhibit foam formation. Excessive foam formation in lubricants can cause inadequate oil supply to certain parts of the engine and a high rate of oil loss.

FIGURE 13.5 Comparison between good and poor detergent performances in a Caterpillar diesel engine test.

13.2.2 AUTOMATIC TRANSMISSION FLUIDS

A large portion of passenger cars produced today are equipped with automatic transmissions. This is particularly true in the North American market. More than 95% of passenger cars sold in North America have automatic transmissions, and a similar situation is also true for cars made in Japan and Korea. The percentage of cars equipped with automatic transmissions made in Europe, though not as high as in North America, Japan, or Korea, is growing rapidly. Thus there is always a volume of automatic transmission fluids required to lubricate these cars.

Metallic detergents and ashless dispersants are also used to formulate automatic transmission fluids (ATFs) [16]. However, the additive packages used in ATF products are often more complex, with more additive components. Similar to the metallic detergents used in engine oils, various sulfonates, phenates, and salicylates of either neutral or overbased materials are commonly employed for ATF formulations. The neutral or overbased detergents are used to neutralize acids that may form through oxidation of the fluid, preventing acidic materials from chemically attacking the metal surfaces. It is noteworthy that neutral detergents that are made for lubricant applications are usually slightly basic, so they are not completely neutral. The soap portion of the detergent operates by dispersing fluid degradation products and preventing the deposit of these materials on active surfaces. The rust/corrosion and deposit preventative actions keep the transmission parts clean. Unlike for applications of surfactants for engine oils, there is no industrial standardized detergency rig test, such as Caterpillar 1K to rate diesel piston cleanliness, to determine the detergency performance of ATFs.

Though ashless dispersants made by Mannich condensation reaction, functionalized ethylene-propylene dispersants, and succinate ester dispersants can be used in ATF formulations, succinimide dispersants are more commonly used. The dispersants used in ATFs have similar chemistries as those described in engine oil applications, except in most cases the molecular weights of the polyisobutyl hydrocarbon chain of the dispersants used in ATFs are lower. Furthermore, the dispersant molecules are reacted with boric acid and caped with additional antiwear chemistries.

One of the roles of dispersants in ATFs is to suspend sludge [16]. Unlike the sludge formed in engine oils, the sludge commonly found in aged ATFs is the product of thermal decomposition and oxidation products. If the sludge is not properly suspended in oil, it can fill up the *holes* in the porous surface of the friction materials. The plugging of these holes can significantly change the shift characteristics of the clutches. The role of dispersants discussed so far concerns engine part cleanliness.

Besides keeping automatic transmission parts clean, metallic detergents and ashless dispersants also play an important role in helping to achieve a proper balance in the frictional characteristics of automatic torque converter clutches and shift clutches. Two important basic features of frictional characteristics are required in an automatic transmission: antishudder and torque capacity [17]. These two parameters often require a very complex balance of the various additive components used in ATFs. In general, to prevent shudder in automatic transmissions, a positive slope of the friction versus sliding speed curve (or the μ-v curve) is often required [18]. Achieving a positive μ-v curve can be readily attained by adding friction modifiers; however, this is often accompanied by lowering the friction level or torque capacity. To raise the friction level and maintain the positive μ-v slope, metallic detergents and ashless dispersants are often employed [19].

The ATF chemistry required to achieve a positive μ-v curve to prevent shudder and maintain a sufficiently high friction level to provide adequate torque capacity will depend on the chemistry of the friction materials and the type of materials used to construct the transmission clutches [20]. A typical transmission clutch uses a cellulosic friction material in combination with steel plates. Other friction materials like carbon fiber are also used. Instead of steel plates, aluminum, copper, bronze, tin, and other metallic materials can also be used. In addition to these materials, plastic, nylon, and a variety of elastomeric sealant materials are used to construct other components of the automatic transmission. More recently, ATFs are required to be compatible with electronic circuitry and sensors [21]. Thus, changes in transmission design and materials have a direct effect on the performance of an ATF. Such changes naturally will influence the choices and levels of detergents and dispersants for their applications in ATFs.

13.2.3 GEAR OILS

As in engine oils and ATFs, metallic detergents like sulfonates, phenates, and salicylates of both neutral and overbased materials are used in gear oils [22]. The purpose of using detergents in gear oils is similar to their use in engine oils and ATFs, namely to keep metal surfaces clean of deposits. These additives neutralize organic acids from lubricant oxidation and associate with precursors that form sludge and varnish. This has the overall effect of keeping metal surfaces free of deposits. Consequently, the manner in which detergents react with oxidation products can result in prolonging the use of gear lubricants and maintaining working gear boxes.

The ashless dispersants used in gear oils have the same chemistry as those used in engine oils and ATFs. The main purpose of dispersants in gear oils is to keep insoluble contaminants in the bulk lubricant. The main source of the insoluble materials is oxidation degradation products of lubricants [22]. Dispersants interact with precursors of insolubles by adsorbing onto the precursors through hydrogen bonds. The presence of long hydrocarbon chains in the dispersant molecules helps in suspending the precursors of insolubles in the bulk oil. Despite the fact that gear oil approved for use will have an adequate antioxidant system in the oil to reduce oxidation to a controllable level, as the gear oil ages a certain amount of insoluble contaminants or sludge will always be present. If these insoluble materials were not properly dispersed by dispersants, unacceptable deposits or varnish would appear. Detergents are often found to complement the performance of dispersants in reducing deposits and varnish. Standard industrial bench tests or rig tests are available for evaluation of gear cleanliness. The test to be used for gear oil approval will depend on the region where the original equipment manufacturer (OEM) is located. In North America, the L-60-1 rig test is used to evaluate the sludge and varnish performance of the gear oil on the metal surface of a spur gear. Figure 13.6 shows a good and poor control of sludge and varnish on the L-60-1 test. In Europe, there are CEC-48 Part A and Part B tests; Part A is used by French OEM to approve gear oils, whereas Part B, which is a glassware test, is used by German OEMs. In Japan, a glassware bench test named *ISOT* is used.

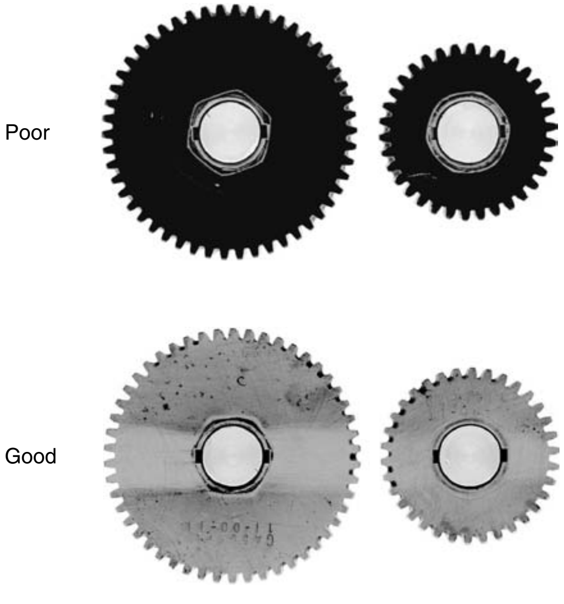


FIGURE 13.6 Comparison of good and poor L-60-1 test results.

13.2.4 Industrial Oils

Industrial lubricants include metalworking lubricants, industrial greases, industrial lubricants, transformer oils, hydraulic oils, refrigeration oils, turbine oils, compressor oils, rock drill lubricants, paper machine oils, way lubricants, and railway journal box oils. The required additive package for each of these industrial oils is different depending on its specific application. Unlike lubricants used in automotive lubrication, industrial lubricants typically do not use metallic detergents and ashless dispersants as additives to keep metal surfaces clean and prevent insoluble materials from formation of deposits on metal surfaces [23]. However, in recent years the use of overbased detergents to supplement performance of the antiwear additive zinc dialkyl dithiophosphate has been reported [24].

However, metallic detergents, such as calcium sulfonate, are often used as rust inhibitors to prevent or reduce rusting on the metal parts. Moisture due to machine operating conditions, for example in circulating systems of steam turbines, steel mills, and paper machines, may be present either as free water or as entrainment in the lubricant. Rust inhibitors function by formation of a protective oil film on the surfaces [25]; the film effectively separates the water from the metal surfaces.

The metallic detergents used in engine oils are also used in industrial oils as emulsifiers and demulsifiers. In most lubrication applications, emulsification is an undesirable characteristic. In some specific types of usage, however, lubricants are purposely compounded with emulsifying agents. In the case of fire-resistant hydraulic fluids, water-in-oil emulsions are desired. In this case the primary function of the fluid is still lubrication; the water incorporated in the fluids serves primarily to decrease the flammability of the oil. These products are safer for use in mines and other locations where low flammability is needed for safety reasons. On the other hand, in the metalworking area, such as cutting and grinding of metals, the key function of the fluid is for cooling. In this case, oil-in-water emulsions are desired.

Metallic sulfonates, such as sodium sulfonate, are often used as emulsifiers in both water-in-oil and oil-in-water emulsions. Other emulsifiers used include ethylene oxide condensation products and derivatives of polyhydroxy alcohols such as sorbitol and sulfosuccinates for water-in-oil emulsions. For oil-in-water emulsions, soaps of fatty acids, rosins, or naphthenic acids are often used as emulsifiers. In either application, the role of emulsifiers is to change the interfacial tension at the water and oil interface. In cases where emulsification with water is undesirable, demulsifiers are used. Frequently, the demulsifiers are heavy metal soaps, such as alkaline earth sulfonates. These surfactants function by lowering emulsion stability.

13.3 APPLICATIONS OF SURFACTANTS IN FUELS

13.3.1 Gasoline Engine Fuels

The most important role of today's gasoline additive package is to clean engine deposits and to keep it clean. Detergents are a major component of the fuel additive package. An extensive review on the engine deposit formation mechanisms and the detergent chemistry required to prevent or reduce engine deposits due to fuels has been written by Kalghatgi [2]. There are three types of engine deposits caused by fuels, namely fuel system deposits, intake valve deposits (IVDs), and combustion chamber deposits (CCDs). The deposit formation mechanisms among these three types of deposits are different. The detergent chemistries required to control these three types of deposits are also different.

Fuel system deposits occur in fuel-metering devices. In the chronological order of the deposit problems discovered, the three commonly observed fuel system deposits are carburetor deposits, port fuel injector (PFI) deposits, and direct injection gasoline (DIG) injector deposits. In automotive engine history, carburetors were used as the fuel-metering device in gasoline engines up until around 1990. Since then, the PFI system has predominantly been used as the fuel-metering device due to its ability to improve combustion efficiency and reduce emissions. Around 2000, the DIG injector system was introduced to the automotive industry. Typical deposits on PFI, DIG injector, and combustion chamber are shown in Figure 13.7.

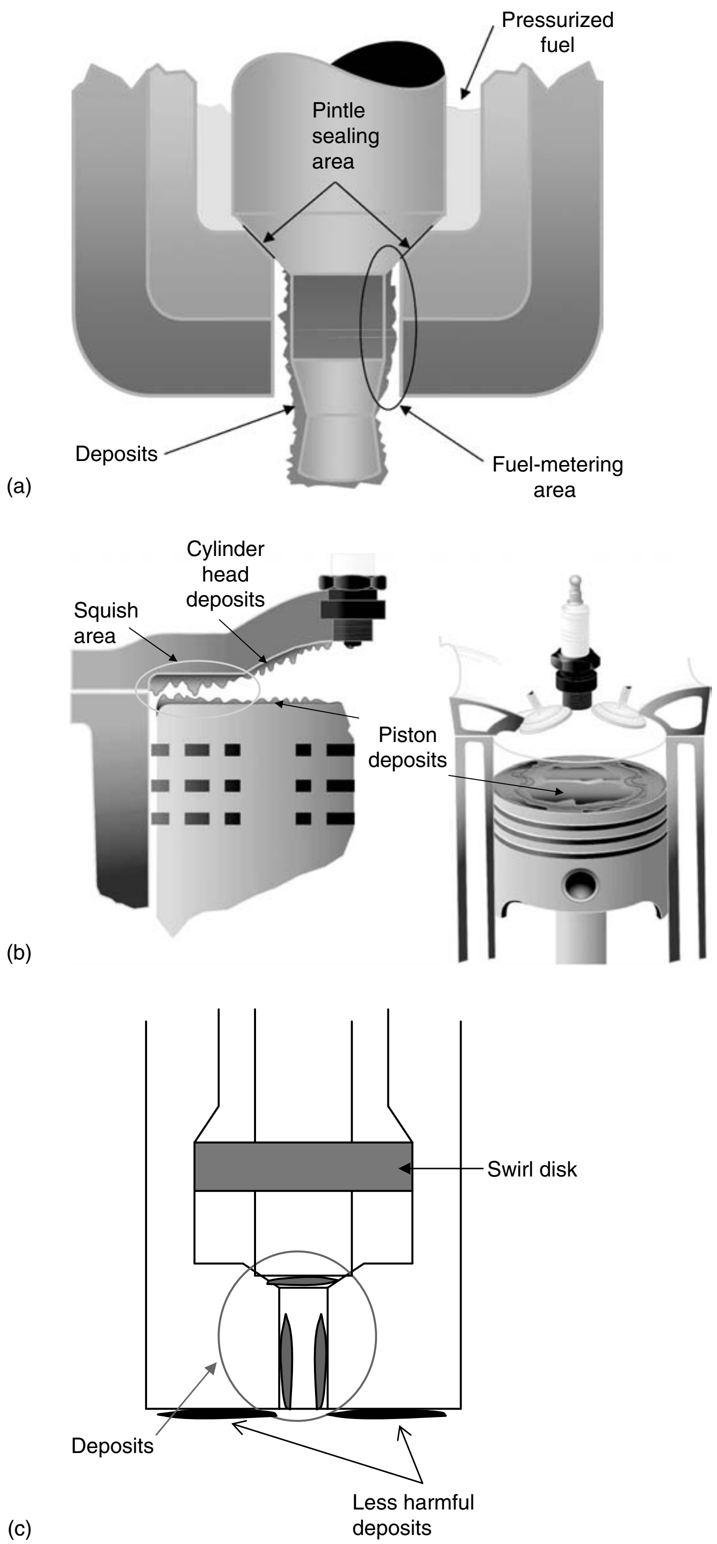


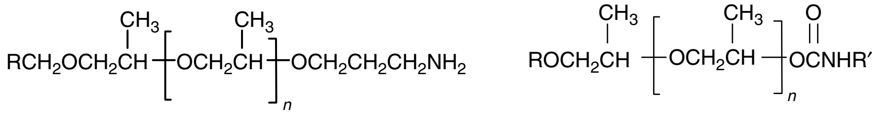
FIGURE 13.7 Deposits seen on (a) a port fuel injector (pintle cross section), (b) a combustion chamber, and (c) a DIG injector.

Initially, DIG technology promised about a third less carbon dioxide emissions than comparable conventional PFIs [26,27]. The large carbon dioxide reduction prediction was based on a 10–15% improvement in fuel consumption when operating in the homogeneous mode, and up to 35% when operating in the lean stratified mode. In addition, the DIG operation platform facilitates up to a 10% power increase for the same fuel burned in the equivalent PFI configuration. However, today only a fraction of the original potential benefit of DIG technology has been realized. As a result, the implementation of DIG technology for fuel systems is slower than expected. For example, in the United States <1% of automobiles use DIG technology; in Europe and Japan the percentage is considerably higher. This means even today the great majority of fuel systems use port fuel injection systems.

PFI and DIG injector deposits, if allowed to form, can increase emissions, cause engines to lose power and driveability, and decrease fuel economy [2,5,27]. IVDs can result in octane requirement increase (ORI) in some engines, increase NOx emissions, and also cause power loss; CCDs can produce ORI in almost all engines, increase certain emissions, like hydrocarbon (HC) and NOx, and change ignition timing [2]. Thus these types of deposits seriously affect the engine operation and need to be carefully controlled.

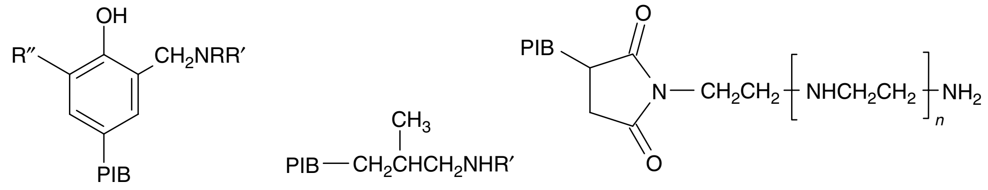
Commonly used detergents to control port fuel injector deposits, intake valve deposits, and combustion chamber deposits include polyether amines, polyisobutylene (PIB)-Mannichs, PIB-amines, and PIB-succinimides [2,3,28]. The typical chemical structures of these detergents are shown in Figure 13.8. The effectiveness of each of these four detergents to prevent and reduce deposits is different for the three types of deposits [28–31]. Polyether amines in general are excellent to control combustion chamber deposits, but less effective to control intake valve deposits and PFI injector deposits. Both PIB amines and PIB-Mannichs are very effective to prevent intake valve deposits, slightly less effective to prevent PFI deposits, and only moderately effective to prevent combustion chamber deposits. PIB-succinimides are moderately effective against PFI deposits, but relatively ineffective to reduce IVDs, and even less effective to reduce combustion chamber deposits. It is common industry knowledge that detergents that are effective in preventing or cleaning up PFI deposits are usually found to be equally effective against DIG injector deposits. It is also true that detergents good for PFI deposit control are effective against carburetor deposits and can be used at significantly lower levels [2].

Detergents are usually used with carrier fluids, which are high boiling point, thermally stable solvents. Examples of carrier fluids include polyols and high molecular weight mineral base oils. The mechanism by which deposits are reduced in fuel and intake systems is commonly believed to be effected by forming a thin hydrocarbon film through the detergents' polar head adhering on the



Polyether amine 1 (R can be aromatic or alkyl)

Polyether amine 2 (R can be aromatic or alkyl; R′ can be alkyl or alkyl amine)



PIB-Mannich PIB-amine PIB-succinimide

FIGURE 13.8 Detergents commonly used in gasoline fuels.

metal surface. However, it is also believed that at higher detergent levels, deposits can be cleaned up by dissolving the soluble part of the deposit, which binds the deposit to the metal surface [2]. Beside the detergent approach to reduce or remove CCD to prevent the ORI issue, there are other methods to remedy ORI, for example, the use of fuel additives to modify the thermal property of the CCD.

13.3.2 Diesel Fuels

Diesel pumps and injectors are intricate metering devices that control the quality of fuel delivered to a diesel engine in correct proportions over the full range of operating conditions. Two general types of injectors are in use; the pintle, or indirect-type injector (IDI), or the hole-type direct injector (DI). Pintle nozzles are used in precombustion and turbulence chamber engines, primarily for use in diesel-powered automobiles or light trucks. Direct injection is primarily used in heavy-duty trucks and other heavy-duty diesel equipment. Figure 13.9 shows the likely locations of deposit buildup in IDI and DI injectors.

Varnish-like deposits tend to accumulate at the throat of the pintle for the IDI, and on the injector needle for the DI; these deposits result in poor spray patterns of fuel into the combustion chamber, as well as irregular fuel flow. Deposit buildup is more noticeable with pintle than with direct injection injectors.

Some of the detergents used in gasoline fuels are also used in diesel fuels. These include polyether amine carbamates and PIB-succinimides. The detergents that are effective in gasoline fuels are not necessarily effective in diesel fuels. The reverse is also true. For example, PIB-Mannich works well in gasoline to control port fuel and DIG injector deposits, but it is not as effective in controlling diesel fuel injector. It is believed that injector tip temperature plays a role. The injector tip temperatures in PFI, DIG, and diesel fuel injectors are found to be around 100, 150 [4], and 450°C [6], respectively. The different performance can be attributed to thermal stability. In addition, chemical compounds derived from asparagine have been used as detergents to control diesel injector deposits. A typical chemical structure for detergents derived from asparagine is illustrated in Figure 13.10. In general, the three most often used detergents for diesel fuels to control injector

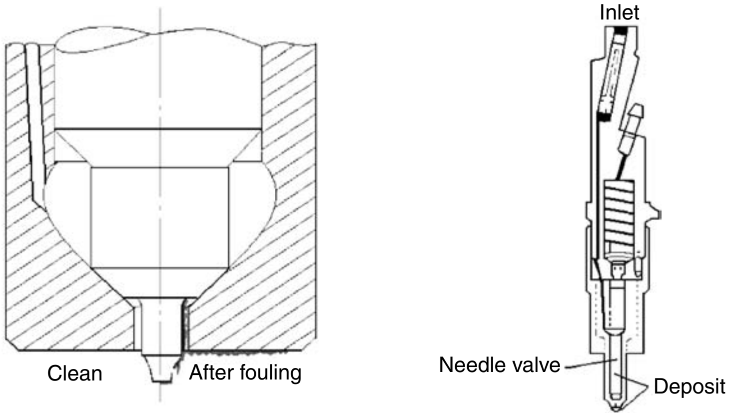
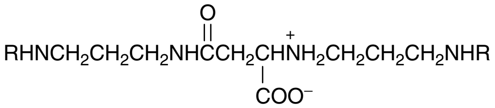


FIGURE 13.9 Indirect and direct injectors used in diesel engines.



$$RHNCH_2CH_2CH_2NH\overset{\overset{\displaystyle O}{\|}}{C}CH_2\underset{\underset{\displaystyle COO^-}{|}}{C}H\overset{+}{N}H_2CH_2CH_2CH_2NHR$$

FIGURE 13.10 Typical chemical structure of asparagines derivative.

deposits are PIB-succinimides, polyether amine carbamates, and asparagines derivatives. They are very active in keeping injectors clean, and also show some activity in removing preexistent deposits.

The chemical behavior of detergents is complex. In addition to functioning as surfactants, they also are antioxidants and acid neutralizing agents. As a surfactant they lay down a surface-active film on a clean metal surface and, in this manner, prevent the buildup of deposits (or gums) that may form from the fuel [32]. Additionally, once a deposit forms on the metal surface, the antioxidant and stabilizing (acid-neutralizing) activity of the additive tends to reduce further buildup. These multifunctional additives also offer metal corrosion and high-temperature oxidation protection in fuels.

There are no uniform testing procedures for injector additives, and a variety of tests have been reported [33]. One of the tests uses a commercially available naturally aspirated 3.9-L 4-cylinder Cummins engine with direct fuel injection. Use of effective detergents in this engine resulted in reduced smoke levels and improved fuel economy compared to measurements done on the same engine using untreated fuel or fuel treated with ineffective detergent [6].

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14 Polymeric Surfactants and Their Applications: Steric, Emulsion, and Suspension Stabilization

Tharwat Tadros, Bart Levecke, and Karl Booten

CONTENTS

14.1 INTRODUCTION

Surfactants (amphipathic molecules consisting of hydrophobic and hydrophilic portions) are essential materials for preparation of many industrial systems, of which we mention dyestuffs, paper coatings, inks, agrochemicals, pharmaceuticals, personal care products, ceramics, and detergents. One of the most important applications of surfactants is in the preparation of oil-in-water (o/w) and water-in-oil (w/o) emulsions. In this case, the hydrophobic portion of the surfactant molecule should adsorb *strongly* at the o/w interface or it becomes dissolved in the oil phase, leaving the hydrophilic components in the aqueous medium, whereby they become strongly solvated by the water molecules. This configuration provides an effective repulsive force, usually referred to as steric stabilization. A convenient method for selection of surfactants is based on the relative proportions of the hydrophilic and hydrophobic groups, that is, the hydrophilic–lipophilic balance (HLB) introduced by Griffin [1,2]. For o/w emulsions, one chooses surfactants with an HLB number in the range 8–18 (depending on the nature of the oil), whereas for w/o emulsions an HLB number in the range 3–6 is usually the case.

The other major application of surfactants is for the preparation of solid/liquid dispersions (usually referred to as suspensions). There are generally two methods for preparation of suspensions, referred to as the condensation and dispersion methods. In the first case, one starts with molecular units and builds up the particles by a process of nucleation and growth. A typical example is the preparation of polymer lattices. In this case, the monomer (such as styrene or methylmethacrylate) is emulsified in water using an anionic or nonionic surfactant (such as sodium dodecyl sulfate or alcohol ethoxylate). An initiator such as potassium persulfate is added, and when the temperature of the system is increased, initiation occurs, resulting in the formation of latex (polystyrene or polymethylmethacrylate). In the dispersion methods, preformed particles (usually powders) are dispersed in an aqueous solution containing a surfactant. The latter is essential for adequate wetting of the powder (both external and internal surfaces of the powder aggregates and agglomerates must be wetted) [3]. This is followed by dispersion of the powder using high-speed stirrers, and finally the dispersion is *milled* to reduce the particle size to the appropriate range.

In all the above processes, the surfactant has to satisfy the following criteria. For emulsions, the surfactant should be efficient in reducing the interfacial tension at the o/w interface to a low value (this results in reduction of the energy required for emulsification). Usually, the lower the interfacial tension, the smaller the droplets that are produced. In addition, the surfactant should reduce any coalescence during emulsification by enhancing the Gibbs–Marangoni effect [3]. Owing to the incomplete adsorption of the surfactant during emulsification (as a result of the continuous production of a new surface), an interfacial tension gradient results. This interfacial tension gradient promotes diffusion of surfactant molecules from the bulk to the interface. These molecules carry solvent molecules with them, resulting in stabilization of the liquid film between the droplets. This phenomenon of liquid flow as a result of interfacial tension gradients is referred to as the Marangoni effect [3], and this stabilizes the emulsion against coalescence during emulsification.

Once the emulsion is produced, the emulsifier has to provide stability against three main processes, namely flocculation, Ostwald ripening, and coalescence. Flocculation is reduced or eliminated by providing a strong repulsive force (electrostatic or steric repulsion). Ostwald ripening results from the difference in solubility between small and large droplets. The surfactant reduces Ostwald ripening by reducing the interfacial tension and enhancing the Gibbs elasticity [3]. Coalescence during storage is reduced by stabilization of the liquid film between the droplets. Additional effects that may contribute to the reduction of coalescence are interfacial viscosity and elasticity [3]. These effects usually arise from the film rigidity produced by polymers and proteins.

For suspensions, the surfactant has also to satisfy a number of criteria; some of them are similar to those described above for emulsions. The surfactant has to be a good wetting and dispersing agent. It has also to enhance stabilization against flocculation, and it should also reduce Ostwald ripening.

Most of the above criteria for stability are best served by using a polymeric surfactant. In particular, molecules of the A-B, A-B-A blocks and BA_n grafts (see the following) are the most efficient for stabilization of emulsions and suspensions. In this case, the B chain (referred to as the *anchoring* chain) is chosen to be highly insoluble in the medium and with a high affinity to the surface in the case of suspensions or soluble in the oil in the case of emulsions. The A chain is chosen to be highly soluble in the medium and strongly solvated by its molecules. These block and graft copolymers are ideal for preparation of concentrated emulsions and suspensions, which are needed in many industrial applications.

In this overview, the first section will on general classification of polymeric surfactants. This is followed by a section on preparation of polymeric surfactants, with particular reference to sugar-based molecules. This is followed by a discussion of their solution properties. The next section will be devoted to the adsorption of polymeric surfactants at the solid/liquid (S/L) interface, whereby a summary will be given to some of the theoretical treatments and the methods that may be applied for studying polymeric surfactant adsorption and its conformation at the S/L interface. The same principles may be applied to the adsorption of polymeric surfactants at the L/L interface, although theoretical treatments of this problem are not as developed as those for the S/L interface. The next section will be devoted to the principles involved in stabilization of emulsions and suspensions using polymeric surfactants, that is, the general theory of steric stabilization. Two sections will be devoted to describe the use of polymeric surfactants for stabilization of suspensions and emulsions. Finally, a section will be devoted to the application of polymeric surfactants for preparation of stable water-in-oil-in-water (w/o/w) multiple emulsions, which have attracted considerable attention in recent years for application in personal care products [3] and agrochemical formulations.

14.2 GENERAL CLASSIFICATION OF POLYMERIC SURFACTANTS

Perhaps the simplest type of a polymeric surfactant is a homopolymer, which is formed from the same repeating units, such as poly(ethylene oxide) or poly(vinyl pyrrolidone). These homopolymers have little surface activity at the o/w interface, since the homopolymer segments (ethylene oxide or vinylpyrrolidone) are highly water soluble and have little affinity to the interface. However, such homopolymers may adsorb significantly at the S/L interface. Even if the adsorption energy per monomer segment to the surface is small (fraction of kT, where k is the Boltzmann constant and T is the absolute temperature), the total adsorption energy per molecule may be sufficient to overcome the unfavorable entropy loss of the molecule at the S/L interface.

Clearly, homopolymers are not the most suitable emulsifiers or dispersants. A small variant is to use polymers that contain specific groups that have high affinity to the surface. This is exemplified by partially hydrolyzed poly(vinyl acetate) (PVAc), technically referred to as poly(vinyl alcohol) (PVA). The polymer is prepared by partial hydrolysis of PVAc, leaving some residual vinyl acetate groups. Most commercially available PVA molecules contain 4–12% acetate groups. These acetate groups, which are hydrophobic, give the molecule its amphipathic character. On a hydrophobic surface, such as polystyrene, the polymer adsorbs with preferential attachment of the acetate groups on the surface, leaving the more hydrophilic vinyl alcohol segments dangling in the aqueous medium. These partially hydrolyzed PVA molecules also exhibit surface activity at the o/w interface [3].

The most convenient polymeric surfactants are those of the block and graft copolymer type. A block copolymer is a linear arrangement of blocks of variable monomer composition. The nomenclature for a diblock is poly-A-block-poly-B, and for a triblock it is poly-A-block-poly-B-poly-A. One of the most widely used triblock polymeric surfactants are the *Pluronics* (BASF, Germany) or *Synperonic PE* (ICI, U.K.), which consists of two poly-A blocks of poly(ethylene oxide) (PEO) and one block of poly(propylene oxide) (PPO). Several chain lengths of PEO and PPO are available. More recently, triblocks of PPO-PEO-PPO (inverse Pluronics) became available for some specific applications.

The above polymeric triblocks can be applied as emulsifiers or dispersants, whereby the assumption is made that the hydrophobic PPO chain resides at the hydrophobic surface, leaving the two PEO chains dangling in aqueous solution and hence providing steric repulsion.

Although the above triblock polymeric surfactants have been widely used in various applications in emulsions and suspensions, some doubt has arisen on how effective these can be. It is generally accepted that the PPO chain is not sufficiently hydrophobic to provide a strong *anchor* to a hydrophobic surface or to an oil droplet. Indeed, the reason for the surface activity of the PEO-PPO-PEO triblock copolymers at the o/w interface may stem from a process of *rejection* anchoring of the PPO chain, since it is not soluble both in oil and water.

Several other di- and triblock copolymers have been synthesized, although these are of limited commercial availability. Typical examples are diblocks of polystyrene-block-polyvinyl alcohol, triblocks of poly(methyl methacrylate)-block poly(ethylene oxide)-block poly(methyl methacrylate), diblocks of polystyrene block-polyethylene oxide, and triblocks of polyethylene oxide-block polystyrene-polyethylene oxide [4].

An alternative (and perhaps more efficient) polymeric surfactant is the amphipathic graft copolymer consisting of a polymeric backbone B (polystyrene or polymethylmethacrylate) and several A chains (*teeth*) such as polyethylene oxide [4]. This graft copolymer is sometimes referred to as a *comb* stabilizer. This copolymer is usually prepared by grafting a macromonomer such methoxy polyethylene oxide methacrylate with polymethylmethacrylate. The *grafting onto* technique has also been used to synthesize polystyrene-polyethylene oxide graft copolymers.

14.2.1 SYNTHESIS OF POLYMERIC SURFACTANTS

14.2.1.1 Block Copolymers

A number of approaches can be applied for the synthesis of block copolymers [4]. One method uses an active end group on one polymer to initiate the polymerization of another monomer to produce an A-B block. Alternatively, one can have active sites on both ends of the polymer, initiating the reaction for formation of an A-B-A triblock. The active end groups can be created by free radicals, anions, Ziegler catalysts, or cations. Another method involves the reaction between two functional groups each at the end of a different polymer chain. In this reaction, the two segments of the block copolymer with appropriate functional end groups are synthesized separately, and the block copolymer is then formed by coupling these two segments. This type of synthesis resembles a condensation reaction. A third method is the so-called postpolymerization method. This technique involves polymerization of a parent polymer with subsequent modification to form the desired block. A fourth (theoretically possible) method is the simultaneous polymerization of two or more appropriate monomers. However, this method is not easy, since one has to find monomers whose reactivity ratios are such as to create blockiness and formation of the required amphipathic copolymer.

Polymerization by free radical mechanism can be carried out in two stages. First a polymeric initiator is synthesized that can be activated in the second stage to initiate the polymerization of the second monomer. Di- and trifunctional initiators have been used to prepare di- and triblock copolymers. A large number of azo- and peroxy-type initiators are commercially available. However, this method of synthesis of block copolymers suffers from the disadvantage of the simultaneous formation of homopolymers. For synthesis of well-defined copolymers anionic polymerization is the most widely used technique. It provides a *living* anion for propagation of the monomer, and no termination is needed, unless desired. The main problem with anionic polymerization is the rigid conditions required, that is, high vacuum, inert atmosphere, low temperatures, and high purity of the monomers and solvent used. Thus, production of block copolymers using this method on a commercial scale can be expensive. Most of the block copolymers synthesized using anionic polymerization have been obtained in research laboratories. Typical block copolymers using this method are those based on polystyrene (B block) and polyethylene oxide (A block).

14.2.1.2 Graft Copolymers

Three methods can be applied for the synthesis of graft copolymers [4]: (i) the macromonomer method, which involves copolymerization of a monomer with a low-molecular weight prepolymer containing a double bond; (ii) the *grafting onto* method, which consists of reacting functional end groups of a prepolymer with reactive groups along the chain of another polymer; and (iii) the *grafting from* method, which involves the propagation of a monomer from active sites along the chain of a polymer.

An example of the macromonomer method is the preparation of graft copolymers of PEO by the free radical polymerization of vinyl acetate in the presence of PEO. The growing vinyl acetate radical would abstract a hydrogen atom from the PEO chain, creating a radical at this site. The newly created radical would then polymerize vinyl acetate to form a branch on the chain. The rather randomly occurring chain transfer reaction would form a graft copolymer of PEO and poly(vinyl acetate).

An example of the *grafting onto* technique is the synthesis of polymethylmethacrylate (PMMA)-graft PEO copolymers. A potassium alkoxide of PEO is grafted onto PMMA by the attack of the alkoxide on the carbonyl group of PMMA with the elimination of the methoxide ion. Fractionation of the crude graft copolymer indicated that the grafting reaction is random with one PEO chain per 10–170 methylmethacrylate units.

An example of the *grafting from* technique is the synthesis of poly(*p*-methyl styrene) (PMSt)-poly(*N*-vinylpyrrolidone) (PVP). The backbone PMSt is obtained by radical polymerization of Mst in the presence of *n*-hexadecyl mercaptan in toluene, with azobisdiisobutyronitrile (AIBN) as initiator at 60°C. Using *N*-bromosuccinic acid and benzoyl peroxide as initiator, the polymer is partially brominated to form the sodium salt of 3-mercaptopropionic acid to displace the bromo group. The graft copolymer is produced when *N*-vinylpyrrolidone is polymerized in the presence of the mercapto derivative of PMSt using AIBN as initiator.

Recently, graft copolymers based on polysaccharides [5–7] have been developed for stabilization of disperse systems. Among the most useful graft copolymers are those based on inulin that is obtained from chicory roots. It is a linear polyfructose chain with a glucose end. When extracted from chicory roots, inulin has a wide range of chain lengths ranging from 2 to 65 fructose units. It is fractionated to obtain a molecule with narrow molecular weight distribution with a degree of polymerization >23, and this is commercially available as INUTEC® N25. The latter molecule is used to prepare a series of graft copolymers by random grafting of alkyl chains (using alky isocyanate) on the inulin backbone. The first molecule of this series is INUTEC® SP1 (ORAFTI, Belgium), which is obtained by random grafting of C_{12} alkyl chains. It has an average molecular weight of ~5000 Da, and its structure is given in Figure 14.1. The molecule is schematically illustrated in Figure 14.2, which shows the hydrophilic polyfructose chain (backbone) and the randomly attached alky chains.

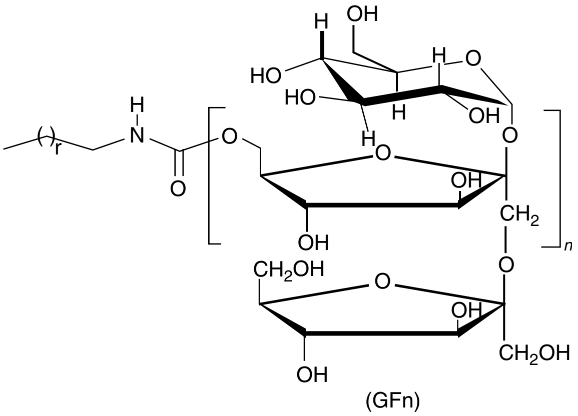

FIGURE 14.1 Structure of INUTEC SP1.

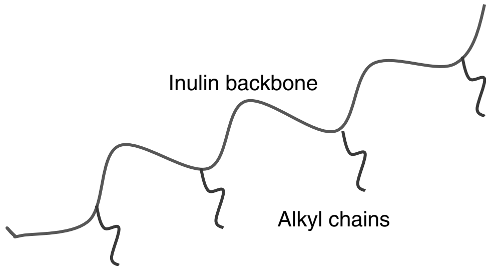

FIGURE 14.2 Schematic representation of INUTEC SP1 polymeric surfactant.

The main advantages of INUTEC SP1 as a stabilizer for disperse systems are

1. Strong adsorption to the particle or droplet by multipoint attachment with several alkyl chains. This ensures lack of desorption and displacement of the molecule from the interface.
2. Strong hydration of the linear polyfructose chains both in water and in the presence of high electrolyte concentrations and high temperatures. This ensures effective steric stabilization (see the following).

14.3 SOLUTION PROPERTIES OF POLYMERIC SURFACTANTS

To understand the solution behavior of polymeric surfactants of the block and graft types, it is essential to consider the solution properties of the more simple homopolymers. The solution behavior of polymers in solution has been considered in the thermodynamic treatment of Flory [8] and Huggins, usually referred to as the Flory–Huggins theory. This theory considers the free energy of mixing of pure polymer with pure solvent, ΔG_{mix}, in terms of two contributions, namely the enthalpy of mixing, ΔH_{mix}, and the entropy of mixing, ΔS_{mix}, that is, using the second law of thermodynamics,

$$\Delta G_{mix} = \Delta H_{mix} - T\,\Delta S_{mix} \tag{14.1}$$

Assuming that the polymer chain adopts a configuration on a lattice (provided by solvent molecules), and considering that the mixing is *random*, then the entropy of mixing ΔS_{mix} is given by the following expression:

$$\Delta S_{mix} = -k\,[n_1 \ln \phi_1 + n_2 \ln \phi_2] \tag{14.2}$$

where k is the Boltzmann constant, n_1 is the number of solvent molecules with a volume fraction ϕ_1, and n_2 is the number of polymer molecules with a volume fraction ϕ_2.

The enthalpy of mixing, ΔH_{mix}, is given by the expression:

$$\Delta H_{mix} = n_1 \phi_2 \chi kT \tag{14.3}$$

where χ is a dimensionless interaction parameter and χkT expresses the difference in energy of a solvent molecule in pure solvent compared to its immersion in pure polymer. χ is usually referred to as the Flory–Huggins interaction parameter.

Combining Equations 14.1 through 14.3, one obtains

$$\Delta G_{mix} = kT\,[n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2] \tag{14.4}$$

The mixing of a pure solvent with a polymer solution creates an osmotic pressure, π, which can be expressed in terms of the polymer concentration C_2 and the volume fraction of the polymer,

$$\frac{\pi}{C_2} = RT\left[\frac{1}{M_2} + \left(\frac{v_2^2}{V_1}\right)\left(\frac{1}{2} - \chi\right)C_2 + \cdots\right] \tag{14.5}$$

where v_2 is the partial specific volume of the polymer ($v_2 = V_2/M_2$) and V_1 is the molar volume of the solvent.

The second term in Equation 14.7 is the second virial coefficient B_2, that is,

$$\frac{\pi}{C_2} = RT\left[\frac{1}{M_2} + B_2 + \cdots\right] \tag{14.6}$$

$$B_2 = \left(\frac{v_2^2}{V_1}\right)\left(\frac{1}{2} - \chi\right) \tag{14.7}$$

Note that $B_2 = 0$ when $\chi = 1/2$, that is, the polymer behaves ideally in mixing with the solvent. This condition was termed by Flory [8] as the θ-point. Under these conditions, the polymer chains in solution have no repulsion or attraction, or they adopt their unperturbed dimension. Clearly when $\chi < 1/2$, B_2 is positive, and mixing is nonideal, leading to positive deviation (repulsion); this occurs when the polymer chains are in *good* solvent conditions. In contrast, when $\chi > 1/2$, B_2 is negative and mixing is nonideal, leading to negative deviation (attraction); this occurs when the polymer chains are in *poor* solvent conditions (precipitation of the polymer may occur under these conditions). Since the polymer solvency depends on temperature, one can also define a θ-temperature at which $\chi = 1/2$.

The function $[(1/2) - \chi]$ can also be expressed in terms of two mixing parameters, an enthalpy parameter κ_1 and an entropy parameter ψ_1, that is,

$$\left(\frac{1}{2} - \chi\right) = \kappa_1 - \Psi_1 \tag{14.8}$$

The θ-temperature can also be defined in terms of κ_1 and ψ_1,

$$\theta = \frac{\kappa_1 T}{\Psi_1} \tag{14.9}$$

Alternatively, one can write

$$\left(\frac{1}{2} - \chi\right) = \Psi_1\left(1 - \frac{\theta}{T}\right) \tag{14.10}$$

Although the Flory–Huggins theory is sound in principle, several experimental results cannot be accounted for. For example, it was found that the χ parameter depends on the polymer concentration in solution. Most serious is the fact that many polymer solutions (such as PEO) show phase separation on heating, when the theory predicts that it should happen only on cooling.

The solution properties of copolymers are much more complicated. This is due to the fact that the two copolymer components A and B behave differently in different solvents. Only when the two components are both soluble in the same solvent do they exhibit similar solution properties. This is the case for example for a nonpolar copolymer in a nonpolar solvent. It should also be emphasized that the Flory–Huggins theory was developed for ideal linear polymers. Indeed, with branched polymers consisting of high monomer density (e.g., star branched polymers), the θ-temperature depends on the length of the arms, and is in general lower than that of a linear polymer with the same molecular weight.

Another complication arises from specific interaction with the solvent, for example, hydrogen bonding between polymer and solvent molecules (e.g., with PEO and PVA in water). Also, aggregation in solution (lack of complete dissolution) may present another problem.

One of the most useful parameters for characterizing the conformation of a polymer in solution is the root-mean-square end-to-end length $\langle r^2\rangle^{1/2}$, which represents a configuration character r as the distance from one end group to the other on a chain molecule. Another useful parameter is the radius of gyration $\langle s^2\rangle^{1/2}$, which is a measure of the effective size of a polymer molecule (it is the root-mean-square distance of the elements of the chain from its center of gravity).

For linear polymers,

$$\left\langle s^2\right\rangle^{1/2} = \frac{\left\langle r^2\right\rangle^{1/2}}{6^{1/2}} \tag{14.11}$$

The radius of gyration of a polymer in solution can be determined from light-scattering measurements.

As mentioned above, dilute solutions of copolymers in solvents that are good for both components exhibit similar behaviour to homopolymer chains. However, in a selective solvent, whereby the medium is a good solvent for one component, say A, and a poor solvent for the second component B, one part of the amphipathic block or graft separates as a distinct phase, whereas the other stays in solution. The insoluble portion of the amphipathic copolymer will aggregate reversibly to form micelles. It is believed that the polymeric micelles are spherical [4]. The critical micelle concentration of these block and graft copolymers is usually very low.

Several methods may be applied to obtain the micellar size and shape of block and graft copolymers, of which light scattering, small angle x-ray, and neutron scattering are probably the most direct. Dynamic light scattering (photon correlation spectroscopy) can also be applied to obtain the hydrodynamic radius of the micelle. This technique is relatively easy to perform, when compared with static light scattering, since it does not require rigorous preparation of the samples.

14.4 ADSORPTION AND CONFORMATION OF POLYMERIC SURFACTANTS AT INTERFACES

Understanding the adsorption and conformation of polymeric surfactants at interfaces is key to knowing how these molecules act as stabilizers. Most basic ideas on adsorption and conformation of polymers have been developed for the solid/liquid interface [9–17]. As mentioned above, the same concepts may be applied to the liquid/liquid interface, with some modification, whereby some parts of the molecule may reside within the oil phase, rather than simply staying at the interface. Such modification does not alter the basic concepts, particularly when one deals with stabilization by these molecules.

The process of polymer adsorption involves a number of various interactions that must be separately considered. Three main interactions must be taken into account, namely the interaction of the solvent molecules with the surface (or oil in the case of o/w emulsions), which needs to be displaced for the polymer segments to adsorb; the interaction between the chains and the solvent; and the interaction between the polymer and the surface. Apart from knowing these interactions, one of the most fundamental considerations is the conformation of the polymer molecule at the interface. These molecules adopt various conformations, depending on their structure. The simplest case to consider is that of a homopolymer that consists of identical segments (e.g., PEO), which shows a sequence of loops, trains, and tails, as is illustrated in Figure 14.3a. It should be mentioned at this stage that for such a polymer to adsorb, the reduction in entropy of the chain as it approaches the interface must be compensated by an energy of adsorption between the segments and the surface. In other words, the chain segments must have a minimum adsorption energy, χ^s; otherwise, no adsorption occurs. With polymers that are highly water soluble, such as PEO, the interaction energy with the surface may be too small for adsorption to occur, and if this takes place, the whole molecule may not be strongly adsorbed to the surface. For this reason, many commercially available polymers that are described as homopolymers, such as PVA, contain some hydrophobic groups or

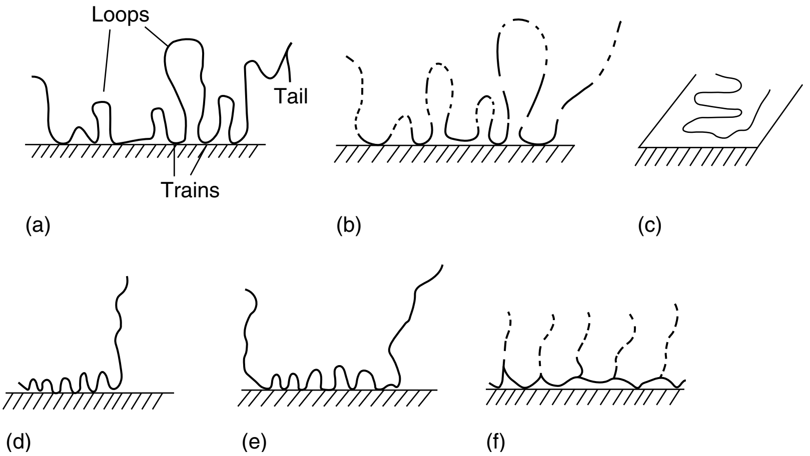

FIGURE 14.3 Various conformations of polymeric surfactants adsorbed on a plane surface: (a) Random conformation of loops-trains-tails (homopolymer); (b) preferential adsorption of *short blocks*; (c) chain lying flat on the surface; (d) A-B block copolymer with loop-train configuration of B and long tail of A; (e) A-B-A block as in d; and (f) BA_n graft with backbone B forming small loops and several tails of A (*teeth*).

short blocks (vinyl acetate in the case of PVA) that ensure their adsorption to hydrophobic surfaces. This is illustrated in Figure 14.3b. Clearly, if all the segments have a high affinity to the surface, the whole molecule may lie flat on the surface, as illustrated in Figure 14.3c. This situation is rarely the case, since the molecule will have very low solubility in the continuous medium.

The most favorable structures for polymeric surfactants are those represented in Figures 14.3d through 14.3f, referred to as block and graft copolymers. The molecules shown in Figure 14.3d is an A-B block, consisting of a B chain that has a high affinity to the surface (or soluble in the oil phase), referred to as the *anchoring* chain and an A chain that has very low affinity to the surface and is strongly solvated by the medium. As will be discussed in the section on stabilization, this is the most convenient structure, since the forces that ensure strong adsorption are opposite to those that ensure stability. A variance on the structure shown in Figure 14.3d is the A-B-A block copolymer shown in Figure 14.3e. In this case, the anchor chain B contains two stabilizing chains (tails). Another variance is that shown in Figure 14.3f, which is described as a graft copolymer (*comb* type structure) with one B chain and several A chains (tails or *teeth*).

It is clear from the above description of polymer configurations that for full characterization of the process of polymer adsorption, it is necessary to know the following parameters, namely the amount of polymer adsorbed per unit area of the surface, Γ (mole/m^2 or mg/m^2), the fraction of segments in close contact with the surface, p, and the distribution of polymer segments, $\rho(z)$, from the surface toward the bulk solution. It is essential to know how far the segments extend into solution, that is, the adsorbed layer thickness δ. It is important to know how these parameters change with polymer coverage (concentration), the structure of the polymer, and its molecular weight. It is also essential to know how these parameters change with the environment, such as solvency of the medium for the chains and temperature.

Several theories exist that describe the process of polymer adsorption, which have been developed using either a statistical mechanical approach or quasi-lattice models. In the statistical mechanical approach, the polymer is considered to consist of three types of structures with different energy states, trains, loops, and tails [10–12]. The structures close to the surface (trains) are adsorbed with an internal partition function determined by short range forces between the segment and surface (assigned an adsorption energy per segment χ^s). The segments in loops and tails are considered to have an internal partition function equivalent to that of segments in bulk solution, and these are assigned a segment-solvent interaction parameter χ (Flory–Huggins interaction parameter).

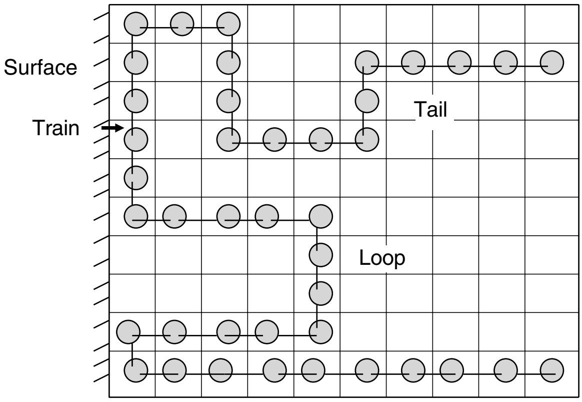

FIGURE 14.4 Schematic representation of a polymer molecule adsorbing on a flat surface. A quasi-crystalline lattice is depicted with segments filling layers that are parallel to the surface (random mixing of segments and solvent molecules in each layer is assumed).

By equating the chemical potential of the macromolecule in the adsorbed state and in bulk solution, the adsorption isotherm can be determined. In the earlier theories, the case of an isolated chain on the surface (low coverage) was considered, but later the theories were modified to take into account the lateral interaction between the chains, that is, at high coverage.

The quasi-lattice model was developed by Roe [13] and by Scheutjens and Fleer [14–16]. The basis of the procedure was to describe all chain conformations as step-weighted random walks on a quasi-crystalline lattice that extends in parallel layers away from the surface. This is illustrated in Figure 14.4, which shows a possible conformation of a polymer molecule at a surface.

The partition function was written in terms of number of chain configurations, which were treated as connected sequences of segments. In each layer, random mixing (Bragg-William or mean field approximation) between segments and solvent molecules was assumed. Each step in the random walk was assigned a weighting factor p_i that was considered to consist of three contributions, namely the adsorption energy χ^s, the configurational entropy of mixing, and the segment–solvent interaction parameter χ.

The above theories gave a number of predictions for polymeric surfactant adsorption, which are summarized as follows. As the number of segments in the chain increases from low (with few segments) to high (large number of segments) values, the adsorption isotherm changes from a Langmuirian type (characteristic for surfactant adsorption) to a high-affinity type. In the latter case, the first addition of polymer chains to the solution results in their virtual complete adsorption. Adsorption in this case is described as being *irreversible*, that is, the equilibrium between adsorbed and free polymer is shifted toward the surface. This explains the strong anchoring of the polymer chains to the surface. As the solvency of the medium for the chains decreases, the amount of polymer adsorbed increases. This explains the relatively *weaker* adsorption of homopolymers that are highly solvated by the medium. It is now clear from these theories why block and graft copolymers are preferred for stabilization of dispersions. The poor solubility of the anchor chain B in the medium and its strong affinity to the surface ensure the strong adsorption of the molecule. In contrast, the high solubility of the stabilizing chain A ensures effective steric stabilization. Another prediction from the theories is that the higher the molecular weight of the polymer, the higher the amount of adsorption, when the latter is expressed in mg/m^2. The bound fraction, p, increases with increase of the adsorption energy, χ^s, but it decreases with increase in surface coverage and increase of the molecular weight of the polymer. The segment density distribution, $\rho(z)$, and the adsorbed layer thickness δ, increase with increase of the molecular weight of the polymer. They also increase with increase of solvency of the medium for the chains.

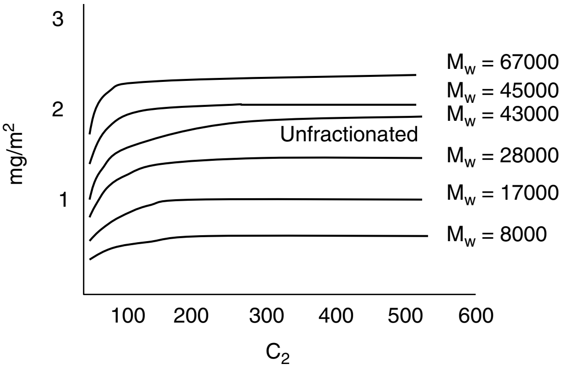

FIGURE 14.5 Adsorption isotherms of PVA with different molecular weights on polystyrene latex at 25°C.

Several experimental methods can be applied to study adsorption and conformation of polymers at interfaces. The amount of polymer adsorbed, Γ, can be directly determined by equilibrating a known amount of the disperse phase (particles or droplets) with a polymer solution of known concentration, C_1. When the system reaches equilibrium (that may take hours or even days with high-molecular weight polymers), the disperse phase is separated (by filtration or centrifugation), and the equilibrium concentration of the polymer, C_2, is determined using a suitable analytical method. From C_1 and C_2 and the amount of disperse phase m and its surface area A (m^2/g^1, which may be obtained from a knowledge of the particle size distribution), Γ can be calculated, that is,

$$\Gamma = \frac{C_1 - C_2}{mA} \tag{14.12}$$

As an illustration, Figure 14.5 shows the adsorption isotherms at 25°C for PVA (containing 12% acetate groups) on polystyrene latex [18]. The figure shows the high-affinity isotherms for the polymers and the increase in adsorption of the polymer with increase of the molecular weight. Similar isotherms are expected for the adsorption of the polymer on oil droplets. However, in the latter case it is not possible to obtain the full isotherm, since to produce the emulsion one requires a minimum amount of polymer. In addition, the surface area of the emulsion has to be determined at each point from the droplet size distribution.

As expected from theory, it was also shown that the adsorption of PVA increases with decrease of solvency of the medium for the chains [19], obtained either by increasing the temperature or addition of electrolytes such as KCl or Na_2SO_4.

The polymer bound fraction, p, can be directly determined using spectroscopic methods such as NMR. The method depends on the reduction in the mobility of the segments that are in close contact with the surface. By using a pulsed NMR technique, one can estimate p. An indirect method for estimation of p is to use microcalorimetry. Basically one compares the enthalpy of adsorption per molecule with that per segment [9]. The latter may be obtained by using small molecules of similar structure to a polymer segment.

Several methods may be used to determine the adsorbed layer thickness, δ. Most of the methods depend on measuring the hydrodynamic radius of the particles with and without the adsorbed polymer layer. For example, one may measure the relative viscosity, η_r, of a dispersion with an adsorbed polymer layer. Assuming that the particles behave as hard spheres (when δ is small compared with the particle radius R) of noninteracting units (low volume fraction of the disperse phase), η_r can be related to the effective volume fraction, ϕ_{eff}, by the Einstein equation,

$$\eta_r = 1 + 2.5\,\phi_{eff} \tag{14.13}$$

From ϕ_{eff} and ϕ (the core volume fraction), the adsorbed layer thickness, δ_h, can be calculated using the equation,

$$\phi_{eff} = \phi\left[1 + \frac{\delta_h}{R}\right]^3 \tag{14.14}$$

To apply the above method one should use a dispersion with monodisperse particles with a radius that is not much larger than δ_h. This limits the method for direct use with emulsions, which are polydisperse and with relatively large radii. However, small model particles of polystyrene may be used, and the assumption is made that the polymer conformation at the interface is similar to that at the o/w interface.

Another method for determining δ_h is to apply dynamic (quasi-elastic) light scattering, referred to as photon correlation spectroscopy. By measuring the intensity fluctuation of scattered light (using a laser) by the particles, as a result of their Brownian diffusion, one can determine the diffusion coefficient, D, of the particles [9]. It is also necessary to use small particles in this case (which show Brownian motion), with a radius that is not much larger than δ_h. From D, the hydrodynamic radius R_h of the particles can be obtained using the Stokes–Einstein equation,

$$D = \frac{kT}{6\pi\eta R_h} \tag{14.15}$$

By carrying out the measurements in the presence and absence of polymer layers, one can obtain δ_h. In the presence of an adsorbed polymer layer, the hydrodynamic radius is the sum of the core radius and the adsorbed layer thickness, whereas in the absence of the polymer layer, R_h is simply the core radius. Again, as with the viscosity technique, this method cannot be directly applied to emulsions, which are polydisperse and with a radius that is large for significant Brownian motion.

14.5 INTERACTION BETWEEN PARTICLES (DROPLETS) CONTAINING ADSORBED POLYMER LAYERS (STERIC STABILIZATION)

When two particles or droplets containing adsorbed polymer layers (with an adsorbed layer thickness δ) approach to a distance of separation h whereby these layers begin to overlap, that is, when $h < 2\delta$, repulsion occurs as a result of two main effects [20]. The first repulsive force arises from the unfavorable mixing of the polymer layers when these are present in a good solvent (i.e., the chains are strongly solvated by the medium). The unfavorable mixing of polymer solutions in good solvent conditions was considered by Flory and Krigbaum [21], whose theory was applied to the present case of interparticle interaction. A schematic representation of the mixing of polymer layers on close approach is shown in Figure 14.6, which shows the situation when two particles with polymer layers are forced to approach to a distance h that is less than 2δ, forming an overlap region with a volume element dV. Before overlap, the chains have layers and a volume fraction ϕ_2, and the solvent has a chemical potential μ_1^{α}. In the overlap region, the volume fraction of the chains is ϕ_2', which is higher than ϕ_2, and the solvent has a chemical potential μ_1^{β}, which is lower than μ_1^{α}. This is equivalent to an increase in the osmotic pressure in the overlap region. As a result, solvent diffuses from the bulk to the overlap region, and the two particles or droplets are separated, that is, this results in strong repulsion. The latter is referred to as mixing or osmotic repulsion.

Using the Flory–Krigbaum theory [21], one can calculate the free energy of mixing, G_{mix}, due to this unfavorable overlap, that is,

$$\frac{G_{mix}}{kT} = \frac{4\pi}{3V_1}\phi_2^2 N_{av}\left(\frac{1}{2} - \chi\right)\left(\delta - \frac{h}{2}\right)^2\left(3R + 2\delta + \frac{h}{2}\right) \tag{14.16}$$

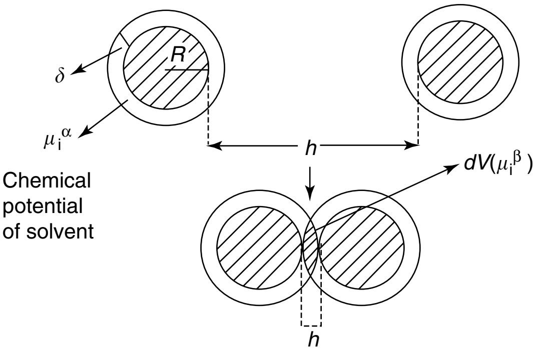

FIGURE 14.6 Schematic representation of polymer layer overlap.

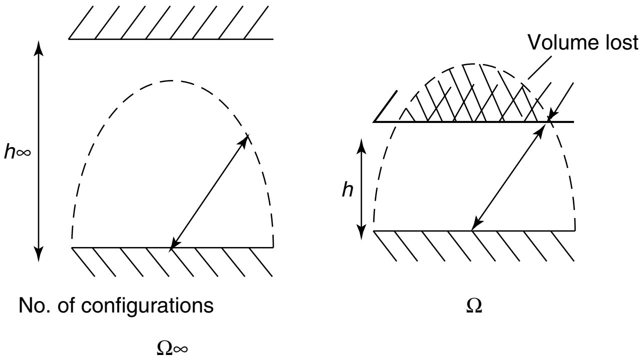

FIGURE 14.7 Schematic representation of entropy loss on approach of a second particle.

where k is the Boltzmann constant, T is the absolute temperature, V_1 is the molar volume of the solvent, and N_{av} is the Avogadros's constant.

It is clear from Equation 14.18 that when the Flory–Huggins interaction parameter, χ, is <0.5, that is, the chains are in good solvent conditions, G_{mix} is positive, and the interaction is repulsive and increases very rapidly with decreasing h, when the latter is lower than 2δ. This explains why polymeric surfactants such as Hypermer CG6 (a graft copolymer of polymethylmethacrylate backbone and PEO side chains, produced by ICI) are ideal for stabilizing dispersions in aqueous media. For stabilization of dispersions in nonaqueous media, such as w/o emulsions, the stabilizing chains have to be soluble in the oil phase (normally a hydrocarbon). In this case, polyhydroxystearic acid (PHS) chains are ideal. A polymeric surfactant such as Aralcel P135 (an ABA block copolymer of PHS-PEO-PHS produced by ICI) is an ideal w/o emulsifier.

Equation 14.18 also shows that when $\chi > 0.5$, that is, when the solvency of the medium for the chains becomes poor, G_{mix} is negative, and the interaction becomes attractive. The condition $\chi = 0.5$ is referred to as θ-solvent, and this denotes the onset of change of repulsion to attraction. Thus, to ensure steric stabilization by the above mechanism, one has to ensure that the chains are kept in better than a θ-solvent.

The second repulsive force arises from the loss of configurational entropy when the chains overlap [20]. This is schematically illustrated in Figure 14.7, whereby the polymer chain is represented by a simple rod with one attachment point to the surface. When the two surfaces are separated at infinite distance, each chain will have a number of configurations, Ω_∞, that are determined by the volume of the hemisphere swept by the rod. When the two surfaces approach to a distance h that is smaller then the radius of the hemisphere swept by the rod, the volume available to the chains

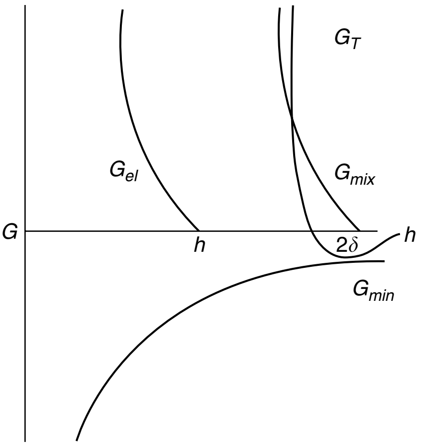

FIGURE 14.8 Energy–distance curves for sterically stabilized dispersions.

becomes smaller, and this results in a reduction in the configurational entropy to a value Ω (i.e., less than Ω_∞). This results in strong repulsion; the effect is referred to as entropic, volume restriction, or elastic repulsion, and is given by the following expression:

$$G_{el} = 2\,\nu \ln \frac{\Omega}{\Omega_\infty} \tag{14.17}$$

where ν is the number of polymer chains per unit area of the surface. It should be mentioned that G_{el} is always repulsive, and it becomes very high on considerable overlap of the polymer chains.

Plots of G_{mix} and G_{el} versus h are illustrated in Figure 14.8. This figure shows that G_{mix} increases very rapidly with decrease of h as soon as h becomes smaller than 2δ (and $\chi < 0.5$). G_{el} also increases very rapidly with decrease of h on further overlap. Combination of G_{mix}, G_{el}, and G_A (the van der Waals attraction) results in the total G_T–h curve shown in Figure 14.8. This curve shows a minimum (G_{min}) at $h \sim 2\delta$, but when $h < 2\delta$, G_T increases very rapidly with further decrease in h. The depth of the minimum, G_{min}, depends on the adsorbed layer thickness. With increase of δ, G_{min} decreases and at sufficiently high values of δ (of the order of 5–10 nm), it reaches small values (fraction of kT units). This shows that with sterically stabilized dispersions, there is only weak attraction at relatively long distances of separation, which in most cases is overcome by the Brownian diffusion. Thus, one can say that the net interaction is repulsive, and this ensures the long-term stability of the dispersion.

From the above discussion, one can summarize the main criteria for effective steric stabilization. First, there should be enough polymer to ensure complete coverage of the surface by the chains. This will prevent any attraction between the bare patches or bridging by the polymer chains (which can adsorb simultaneously on more than one particle). Second, the chains must be strongly adsorbed (*anchored*) to the surface. This prevents any displacement on close approach. In this respect, block and graft copolymers containing an anchoring chain (such as polystyrene or PMMA to hydrophobic surfaces) are the best stabilizers. In some cases, strong adsorption may be achieved by a phenomenon referred to as rejection anchoring. If the B chain is insoluble in the medium (water or oil), it can adsorb by this rejection mechanism. This situation applies to PPO, which is insoluble in water and in most oils. This explains the use of block copolymers of the PEO-PPO-PEO as emulsifiers.

The third criteria for effective steric stabilization is to ensure that the stabilizing chain A remains in good solvent conditions at all times and under all conditions. As discussed earlier, for systems where water is the continuous medium, PEO is the most suitable A chain(s). The polymer chain is highly soluble in water, and remains solvated up to high temperatures. It can also tolerate reasonable amounts of electrolyte. For dispersions, where the continuous medium is a hydrocarbon oil (e.g., w/o emulsions), polyhydroxystearic acid is the most suitable A chain(s).

The last criterion for effective steric stabilization is to have a sufficiently thick adsorbed layer to avoid any weak flocculation. This is particularly important for concentrated dispersions. As discussed previously, a value of δ of the order of 5–10 nm is usually sufficient. Hence, the side PEO chains need to have a molecular weight of the order of 1000–2000. With most graft copolymers, these side chains are extended, and they provide a sufficiently thick layer.

14.6 USE OF POLYMERIC SURFACTANTS FOR STABILIZATION OF EMULSIONS

Polymeric surfactants are ideal for stabilization of both (o/w) and (w/o) emulsions against flocculation, Ostwald ripening, and coalescence. The stabilization against flocculation was discussed in detail in the previous section, which showed that using A-B, A-B-A, or BA_n copolymers can overcome flocculation by proper choice of the B (anchor chain) and A (stabilizing chains). To ensure absence of flocculation, the χ parameter should be maintained at a value <0.5 under all conditions of storage of the emulsion. Both PEO and polyfructose chains can be used for this purpose in water. With PEO, flocculation can also be maintained at moderate electrolyte concentrations. For much higher electrolyte concentrations, the PEO chains may undergo dehydration, and χ may reach a value of 0.5 and higher, under which conditions strong flocculation (sometimes referred to as incipient flocculation) may occur. This problem may be overcome using polyfructose chains, as for example the case with inulin carbamates (INUTEC SP1) that can tolerate much higher salt concentrations when compared with PEO. To confirm the above hypothesis, we have recently investigated emulsion stability in the presence of high salt concentrations using INUTEC SP1 [22]. Oil-in-water emulsions of Isopar M (an isoparaffinic oil) were prepared using 2% (based on the oil phase) INUTEC SP1 surfactant (based on INUTEC N25, with a degree of polymerization >23). This polymeric surfactant is commercially available (Orafti, Tienen, Belgium). These emulsions were prepared in water, 0.5, 1, and 2 mol/dm^3 NaCl and 0.5, 1, and 2 mol/dm^3 $MgSO_4$. No emulsions containing NaCl showed any strong flocculation or coalescence up to 50°C for 1 year storage. The same result was obtained with $MgSO_4$ up to 1 mol/dm^3. This stability in such high electrolyte concentrations was not observed with polymeric surfactants containing PEO as the stabilizing chain.

The difference in stabilization between inulin-based and PEO-based surfactants can be accounted for in terms of the effect on the χ parameter. With both inulin and PEO in water, the χ parameter is maintained below 0.5 up to 100°C.

However in the presence of electrolyte, inulin and PEO show different behavior. With PEO, the cloud point becomes below 60°C when the NaCl concentration exceeds 2 mol/dm^3 NaCl and 0.5 mol/dm^3 $MgSO_4$. With inulin, no cloud point could be measured up to 4 mol/dm^3 NaCl or 1 mol/dm^3 $MgSO_4$. This indicates that the inulin chain (polyfructose) retains its hydration to much higher temperature and electrolyte concentrations when compared to the PEO chains, and this is probably the reason for the high stability obtained when using inulin carbamates as emulsion stabilizers.

Generally speaking, the cloud point is related to the χ parameter. When χ exceeds 0.5, dehydration of the chain will take place, and the chain–chain interaction leads to cloudiness. The cloud point depends on both the polymer concentration and as well as the molecular weight; with increase in the molecular weight and concentration, the cloud point decreases. With PEO at 2 mol/dm^3, the cloud point at 5% is ~60°C, and if the concentration in the polymer layer will reach for example 20%, the cloud point will be lower than 50°C. Thus, for emulsion stabilizers based on PEO, the stability against flocculation could not be maintained at 2 mol/dm^3 NaCl. With $MgSO_4$, the situation is even worse; at 5% PEO ($M_w = 4000$), the cloud point is lower than room temperature at 1 mol/dm^3 $MgSO_4$, and hence instability will be more serious with this electrolyte. However, for inulin-based emulsifiers, no cloud point was observed up to 4 mol/dm^3 NaCl and a temperature of 100°C. One would expect stable emulsions at temperatures exceeding 50° up to 4 mol/dm^3 NaCl. With

$MgSO_4$, stability could be maintained at high temperatures up to 1 mol/dm^3. Thus, these cloud point measurements give conclusive evidence of the unique behavior of polymeric surfactants based on inulin. The polyfructose chain remains hydrated up to high temperatures and in the presence of high electrolyte concentrations. Thus, by adequate design of the polymeric surfactant, one can achieve very high stability for the emulsions.

Another polymeric surfactant that is very effective for stabilization of w/o emulsions is the A-B-A block of PHS-PEO-PHS (Arlacel P135 commercially available by UNIQEMA, Wilton, U.K.). Thus, this polymeric surfactant [23] is a polyester-polyether-polyester ABA block. The head group is B PEO, whereas the two tails are poly(12-hydroxystearic acid). A schematic representation of the molecule is shown below. The weight average molecular weight M_w of the molecule is 6809 g/mol^1, whereas the number average M_n is 3499 g/mol^1 (i.e., the polymer is polysdisperse with $M_w/M_n = 1.94$). It has an HLB of 5–6, which makes it suitable for a w/o emulsion. The molecule is soluble in hydrocarbon oils, and it produces lamellar liquid crystals even at low concentrations. X-ray diffraction measurements showed a thickness of 17.3 nm for the bilayers, which implies an adsorbed layer thickness at the w/o interface in the region of 9 nm. Surface pressure measurement at the o/w interface using a Langmuir trough showed that on compression of the molecule, a surface pressure in the region of 50 mNm^{-1} could be obtained, indicating a very interfacial tension at the w/o interface. This makes this polymeric surfactant an ideal candidate for preparation of w/o emulsions. Indeed, w/o emulsions containing more than 80% water could be prepared, and these emulsions were relatively fluid. The droplet size of the resulting emulsion was quite small (in the region of 200 nm), and these emulsions were very stable against any flocculation or coalescence. In addition, due to the small droplet size, creaming was insignificant.

14.7 POLYMERIC SURFACTANTS FOR STABILIZATION OF SUSPENSIONS

To illustrate the use of polymeric surfactants for stabilization of suspensions, two graft copolymers were used to investigate the stability of dispersions of polystyrene latex [24]. The two graft copolymers were based on a poly(methyl methacrylate-methacrylic acid) backbone with methoxy-capped PEO side chains ($M_w = 750$). Two commercially available graft copolymers, namely Hypermer CG-6 and Atlox 4913 (both supplied by UNIQEMA, Wilton, U.K.), were used. The two copolymers are structurally the same, except that Hypermer CG-6 contains a higher proportion of methacrylic acid in the backbone. The adsorption isotherms of the graft copolymers were of the high-affinity type (showing no desorption under practical conditions). The adsorption plateau value was higher for Atlox 4913 when compared to CG-6 (~1.5 mg/m^2 for Atlox 4913 and ~1.2 mg/m^2 for CG-6). The higher adsorption with Atlox 4913 is due to the higher surface density of PEO chains. Increase of temperature caused an increase in adsorption due to the reduction of solvency for the PEO chains.

The stability of the dispersions was investigated using rheological measurements. The storage modulus (which could be measured using oscillatory measurements) was followed as a function of temperature in the presence and absence of Na_2SO_4. In the absence of salt, no flocculation was observed up to 65°C (the maximum temperature at which measurements were made). However, addition of Na_2SO_4 caused a reduction in the critical flocculation temperature (CFT). With Atlox 4913, the CFT is ~40° in 0.1 mol/dm^3 and ~30°C in 0.2 and 0.3 mol/dm^3 Na_2SO_4. CG-6 gave higher CFT values when compared with Atlox 4913. This shows the importance of the molecular architecture of the polymeric surfactant on the stability of the dispersion.

Another graft copolymer that could be used for stabilization of suspensions is that based on a polyfructose backbone on which several alkyl groups have been grafted (INUTEC SP1), mentioned earlier for stabilization of emulsions. This polymeric surfactant was used to investigate the stability of polystyrene (PS) and PMMA suspensions in the presence of electrolytes [NaCl, $CaCl_2$, and $Al_2(SO_4)_3$] [25]. The polystyrene latex was prepared by emulsion polymerization without surfactant, and it was fairly monodisperse, with a diameter of 210 nm. The PMMA latex was prepared by emulsion polymerization using sodium dodecyl sulfate as emulsifier. The latex had an average diameter of 61.8 nm, and it was fairly monodisperse. The critical coagulation concentration (CCC) was determined by gradually increasing the electrolyte concentration and observing floc formation using optical microscopy. Alternatively, the CCC was determined using turbidity measurements. The turbidity of the latex was determined as a function of the wavelength of light (400–600 nm). Log-log plots of turbidity (or percentage transmission) versus wave length gave straight lines, from which the slope of the line n was calculated. By plotting n versus electrolyte concentration, the CCC could be accurately determined (n remains constant up to the CCC, after which it shows a rapid decrease). The CCC values for 5% PS latex containing 0.25% INUTEC SP1 surfactant are: >5.7 mol/dm^3 for NaCl, >4.37 mol/dm^3 for $CaCl_2$, and >0.5 mol/dm^3 for $Al_2(SO_4)_3$. For 2.5% PMMA latex containing 0.5% INUTEC SP1 surfactant, the CCC for CaI_2 was >2.29 mol/dm^3. This clearly shows the considerable stabilization effect of the INUTEC SP1 surfactant. A low surfactant concentration is sufficient for stabilization, and a very high CCC value is obtained when compared with the latex without adsorbed polymer. This high stability in the presence of high electrolyte concentration is due to the polyfructose stabilizing chains, which remain highly hydrated at such high electrolyte concentrations. This was explained in detail in the section on emulsions.

14.8 POLYMERIC SURFACTANTS IN MULTIPLE EMULSIONS

The main criteria for the preparation of stable multiple emulsions are summarized as follows [26]. First, one needs two optimum emulsifiers, one with low and one with high HLB numbers. Emulsifier 1 (with low HLB number), which is used to prepare the primary w/o emulsion (for the case of w/o/w multiple emulsion), should prevent any flocculation or coalescence of the emulsion droplets. This emulsifier should ideally produce a viscoelastic film at the w/o interface that ensures the stability of the emulsions and prevents any transport of components from the internal droplets to the outer continuous medium during storage. Recent work in our laboratory [27] showed that Aralcel P135 satisfies these criteria. It produces a viscoelastic film, and the w/o emulsions prepared using this polymeric surfactant are stable over a long period of time and at various temperatures. The secondary emulsifier, with the high HLB number, should also produce an effective barrier to prevent flocculation and coalescence of the resulting multiple emulsion drops. Again, a polymeric surfactant, such as Synperonic PF 127 (an ABA block of PEO-PPO-PEO produced by ICI) or INUTEC SP1 is ideal in this case.

The second criterion for stabilization of the multiple emulsion on storage is to have an optimum osmotic balance between the internal (water droplets) and the external continuous medium. This can be achieved by the use of electrolytes or nonelectrolytes. Usually, one keeps the osmotic pressure in the external continuous medium slightly lower than that of the internal water droplets.

The multiple emulsion is prepared by a two-stage process. The primary emulsion is prepared by adding the aqueous phase to an oil solution of the polymeric emulsifier 1 with low HLB number, for example, Aralcel P135, using a high-speed stirrer. Using this polymeric emulsifier, primary water droplets that are smaller than 1 μm in diameter can be produced. The size of the droplets in the primary emulsion can be determined using photon correlation spectroscopy. This primary emulsion is then emulsified into aqueous solution of the high HLB polymeric surfactant (INUTEC SP1) using a low-speed stirrer (paddle stirrer) to produce multiple emulsion drops of the order of 10–100 μm in diameter.

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15 Application of Surfactants in Environmental Remediation

Uri Zoller

CONTENTS

15.1 INTRODUCTION: THE PROBLEM

Contamination of soils, aquifers, and groundwater by organic nonaqueous phase liquid (NAPL) pollutants, that is, fossil fuels, chlorinated hydrocarbons, and other organic chemicals (e.g., polycyclic aromatic hydrocarbons, methyl tertiary butyl ether), constitutes a major environmental issue of concern worldwide [1–4]. The penetration of NAPLs into soil and groundwater is, in most cases, a result of accidents, improper codes of fuel handling and disposal, as well as the leakage of storage tanks and fuel conveying systems. The migration of NAPLs in the soil occurs via various mechanisms such as advection, dispersion/dissolution (in the aqueous medium within the porous soil matrix), and diffusion, resulting, ultimately, in accumulation of entrapped NAPLs as residual saturation in both the unsaturated and saturated zones of aquifers.

Subsurface soils, aquifers, and groundwater are quite different from other environmental heterogeneous solid and aqueous systems. Typical characteristics are long residence times, low (relative to that of surface soil and water) temperature, low degrees of desorption, dispersion, mixing, and dilution processes, decreasing aerobic conditions, and therefore, decreased microbial populations, and fewer—albeit occasionally more complex—operative biochemical organic transformations. The ultimate result is a slow environmental response. Consequently, soils, aquifers, and groundwater are susceptible to long-term contamination by hydrophobic organic substances, particularly those having a high degree of hydrophobe branching or aromatic backbone, which constitute the main cause for their being biodegradation-resistant, and consequently, environmentally persistent organic pollutants (POPs). Fossil fuels, chlorinated hydrocarbons, and low hydrophilic–lipophilic balance (HLB) branched-chain surfactants are environmentally the most abundant examples of such pollutants.

The increasing production and use of fossil fuels have substantially increased the probability of soil and water resource contamination by them, particularly groundwater and aquifers. Indeed, aquifers and groundwater contamination by fuels and other NAPL compounds (e.g., chlorinated hydrocarbons) associated with industrial, commercial, and military activities already constitute an environmental issue of major concern worldwide [1,5]. In fact, nearly one quarter of the organic chemicals listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) are organic NAPLs, which like the petroleum-originated products are immiscible with water. Once they penetrate into the subsurface, they may be trapped as residual saturation in the unsaturated or saturated zones.

Since aquifer water is widely used as a main source of potable water in many countries worldwide, the NAPL POPs significantly affect its quality. Petroleum-based fuel hydrocarbons, for example, kerosene, constitute a high contamination potential to soil and groundwater, due to their low viscosity and high persistence.

Because of the low solubility of most NAPLs in water and the very low limits that are considered safe for human consumption, a relatively small volume of NAPL can contaminate millions of cubic metrics of groundwater [6,7]. Significantly, the taste and odor of petroleum hydrocarbons in water can be detected in concentrations of as low as 50 μg/L. Therefore, a full reclamation of fuel-contaminated aquifers is a precondition for their being used as a source of potable water.

Once the NAPLs (light and dense: LNAPLs and DNAPLs, respectively) penetrate into the subsurface, their migration in the soil may occur via various mechanisms, ultimately resulting in either accumulated bulk, or trapped NAPL in the aquifer's unsaturated zones, as well as above or below its saturated zones. The conceptualization of this penetration/migration process is illustrated in Figures 15.1 and 15.2 concerning LNAPLs and DNAPLs, respectively [8].

Contamination by LNAPLs is common, occurring near airfields, petroleum manufacturing plants, storage facilities, and fueling stations. The number of such sites is estimated to be (in the United States only) in the hundreds of thousands [9]. In many cases, the LNAPL spill was large enough to exceed the absorptive capacity of the soil, so that downward migration of the NAPL has led to formation of a *lens* on top of the water. Consequently, as the water table rises and falls throughout the year, the floating LNAPL lens becomes distributed in droplets both above and below the water table. High interfacial tensions trap the NAPL (e.g., kerosene, gasoline, crude oil) drops inside the pores of the substrate, preventing the LNAPL from being removed by pumping. Additionally, small amounts of the oil are constantly dissolving into the water and being carried away by the groundwater flow in the aquifer, causing the formation of a down-gradient dissolved contaminant plume, which may extend miles from the source location [10].

Contamination by DNAPLs is usually more difficult to deal with. When sufficient quantities of DNAPL are released into the environment, the spill typically penetrates the water table and migrates downward until it forms a lens at the bottom of the aquifer. During the downward

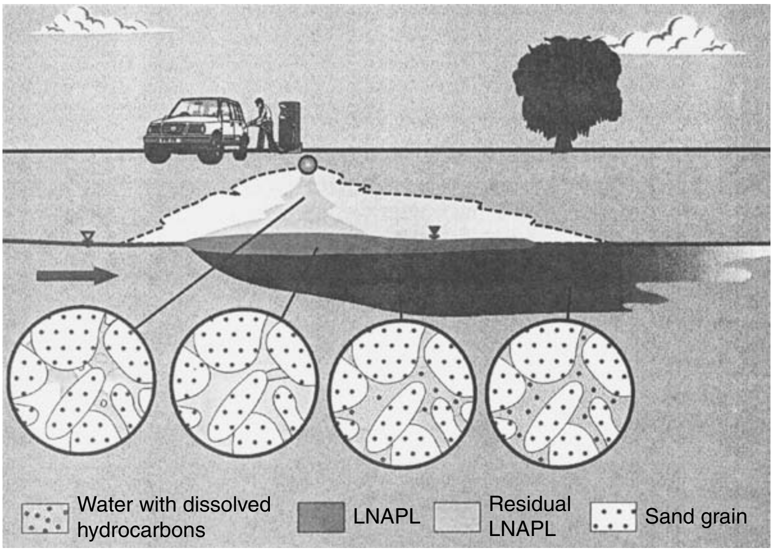

FIGURE 15.1 Conceptual LNAPL migration.

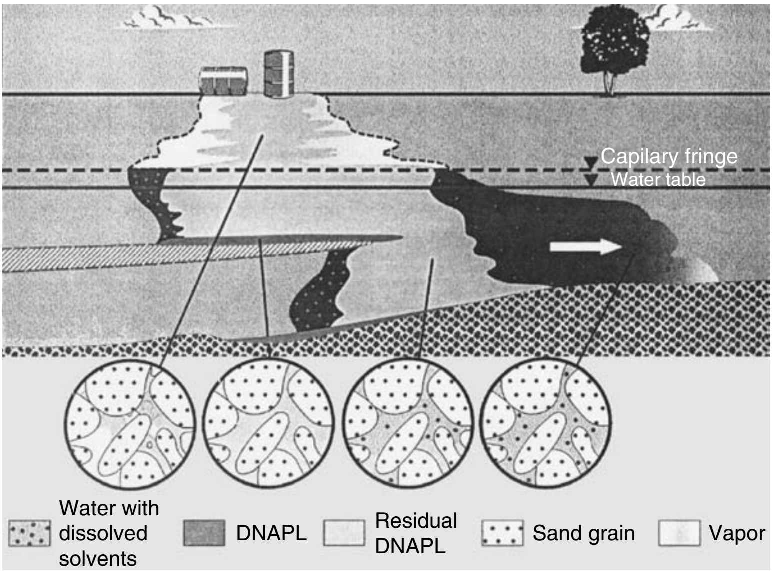

FIGURE 15.2 Conceptual DNAPL migration.

migration, interfacial forces trap droplets of the DNAPL within the pores of the substrate, and groundwater flow will spread the affected groundwater down gradient.

The fate of fuel hydrocarbons in the subsurface environment is affected by (1) the character of soil (grain size, porosity, permeability, surface area, organic matter content, cation exchange capacity, etc.) and (2) the chemical structure, composition, and physicochemical properties of the various components of the NAPL fuel (e.g., water solubility, soil adsorption, vapor pressure, and so on). Their fate in the subsurface can be volatilization, adsorption onto the soil or rock, dissolution in either the pore water or the water film surrounding the soil particles, trapping in the pores of fractures of the rock; floating on, trapping under, or dissolution in the groundwater, and undergoing biochemical transformations or biodegradation. The latter processes, in turn, are critically dependent, not only on the particular physicochemical characteristics of the NAPL-contaminated site, but also on the bioavailability of the NAPL organic substrates and the presence of sufficient inorganic nutrients (e.g., N and P) required for the biodegradation to take place, as well as the specific microorganisms present in the soil environment [11].

The residual (biodegradation-resistant) hydrophobic fuel hydrocarbons entrapped in the soil/porous matrix possess a particular bioremediation challenge due to their becoming virtually immobile, being neither absorbable nor water dispersible, and consequently they are not available as substrates to microorganisms-based biodegradation. As such, the NAPL pollutants constitute POPs in the environment, and their impact on groundwater resources follows accordingly [4].

The real issue, however, is not whether or not the cleanup/remediation mission is technologically possible, or what is the best available technology to carry out the job in each NAPL-contaminated site, given its specific local constraints; rather, it is whether or not, or to what extent, the planned remediation is economically feasible and in line with the newly evolving concept of sustainable remediation [12].

The EPA has long ago concluded that the environmental *pump-and-treat* remediation technology that has been used for removing NAPL hydrocarbon contaminants from aquifers is not working [2]. Indeed, field demonstrations of soil flushing have illustrated potential problems [13], and aquifers contaminated with DNAPLs were shown to be extremely difficult to remediate with the standard *pump-and-treat* methods.

The major problem in remediation of NAPL-contaminated aquifers is not the pumping out of either the high- or low-density NAPLs that are trapped in the aquifer—immiscible with the water phase—below, above, or within the saturated zone. Rather, the major difficulty is the removal of the entrapped residual saturation, which is strongly held by the capillary forces of the soil/porous matrix, causing the former to become virtually immobile. Currently, entrapped NAPLs in aquifers seem to be one of the biggest existing remediation problems [11]. These petroleum products have low water solubilities so that once they penetrate into the subsurface, they may be trapped as residual saturation. Sooner or later, such NAPL-contaminated aquifers would need to undergo remediation if the safe use of their water is to be continued. The emerging need for NAPL-contaminated aquifer remediation has driven the search, development, and application of new remediation technologies, accompanied by critical consideration of the cost/benefit and effectiveness of each.

Thus, although *pump-and-treat* technologies allow, in principle, the effective remediation of NAPL-contaminated aquifers, particularly as far as NAPL lenses are concerned, they appear to be infeasible economically in large-scale remediation operations, and not effective in the removal of entrapped NAPL residual saturation [5,8,11,13]. The latter is strongly held by the capillary forces of the soil/porous matrix, causing the former to become virtually immobile. Its desorption-mobilization from the soil matrix into the aqueous phase requires, therefore, a special attention on designing an effective remediation process.

The above has led to the identification of five areas of research needed that, eventually, advanced the usage of surfactants in soil and more so aquifer remediation: (1) solubilization of hydrophobic organic compounds, (2) mobilization of hydrophobic organic compounds, (3) modification of colloidal stability, (4) immobilization of hydrophobic organic compounds, and (5) alteration of the matrix formation permeability.

The basic premise behind these remedial categories was the alteration of the subsurface physicochemical system. This indicates the realization that comprehensive remediation of subsurface contamination will require more than physical alterations (excavation, extraction, etc.) to meet increasingly stringent regulatory cleanup standards in a timely and economical matter [14].

15.2 SURFACTANT-ENHANCED REMEDIATION

The use of surfactants for remediation of contaminated soils and aquifers has been widely examined. Techniques for remediation are conveniently denoted as *in situ* and *ex situ*, where the former refers to treatment of soil or aquifers in place (in the subsurface) and the latter indicates excavation of soil for treatment above ground and *pump and treat* in the case of aquifers. The literature is quite extensive on surfactant-enhanced subsurface remediation [15] and has relied on the basics of surfactant-based remediation chemistry-physicochemistry-hydrology [16–27]. It was further demonstrated that the recovery and reuse of the surfactant (if applicable), is critical for maintaining the economic feasibility of this remediation technology applied [28].

Although surfactant-enhanced remediation technologies have significant potential for aiding in the remediation of both LNAPL and DNAPL contaminated sites, it is in the area of DNAPL remediation where the largest gains may be achieved [29]. Surfactants have the ability to solubilize NAPL into the aqueous phase and to reduce interfacial tensions between contaminants and substrates, thus enhancing mobility. The development of these technologies may be aided by the preferable usage of biodegradable surfactants, thus avoiding site contamination by the surfactant added.

The general mechanisms by which surfactants can enhance the removal of residual and free-phase NAPL from the saturated and unsaturated zones of aquifers are mobilization, solubilization (Figure 15.3), and dispersion.

The latter two are straightforward processes, operating whenever a surface active agent (surfactant) is added to an aqueous system. Also, they are the easiest to apply from an engineering standpoint. Mobilization refers to those special cases when the interfacial tension between the entrapped residual phase and the flowing aqueous phase is reduced by several orders of magnitude. As the

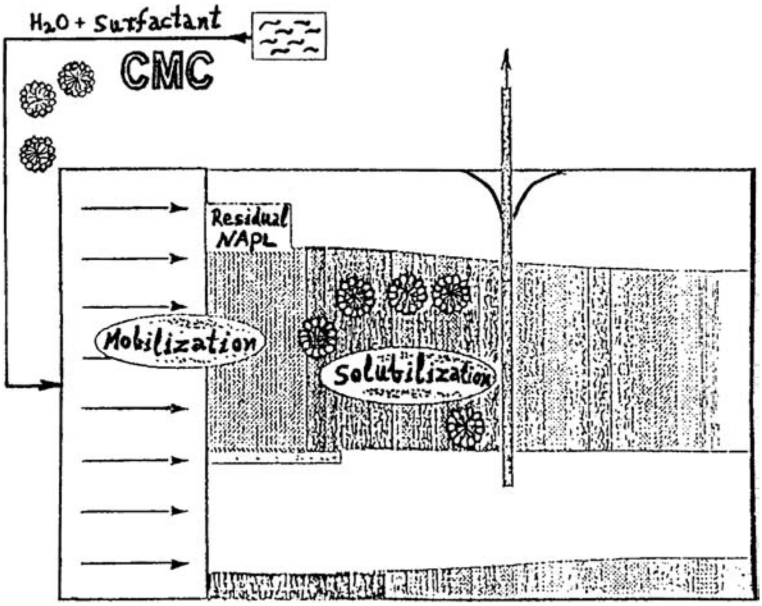

FIGURE 15.3 NAPL mobilization/solubilization by surfactant(s).

interfacial tension decreases by the adsorption of the surfactant added at the hydrocarbon/water interface, the capillary number (dimensionless) decreases and, consequently, the mobilization of the NAPL hydrocarbon becomes easier. The design of an appropriate surfactant system for such reduction in the interfacial tension will require the matching of the HLB of the surfactant (or surfactants mixture) with the particular properties of the residual NAPL fuel.

15.3 FACTORS AFFECTING SURFACTANT'S PERFORMANCE IN AQUIFER REMEDIATION

The following factors are of particular importance for the surfactant-enhanced remediation of fuel-contaminated soils and groundwater: (1) the effect of the soil character on the partitioning of the entrapped NAPL between the stationary soil particles and the mobile water phase; (2) the aqueous solubility of the NAPL contaminant in the absence and presence (of different types and in various concentrations) of (commercially) available, biodegradable surfactants; (3) the biodegradation rate of both the NAPL hydrocarbons and the added surfactants in the subsurface; and (4) the efficiency of surfactant-enhanced extraction of residual NAPL adsorbed on the soil matrix. Thus, the effectiveness of a surfactant in enhancing the removal of a contaminant from the subsurface can be expected to be a function not only of the surfactant's structure or type, but also of its interaction with the contaminants as well as with the aquifer media at the conditions in the aquifer. The particular behavior of the surfactant used can be anticipated as potentially capable of reducing the surfactant's ability to remove the contaminant: precipitation, liquid crystal formation, formation of a coacervate phase, partitioning into trapped residual phases, or adsorption onto the aquifer's solid surfaces. All of the above should be taken into account in the design of any surfactant system for any remediation project. Further, the interaction of contaminants with the surfactant solution formed in the aquifer should be anticipated to be highly dependent on temperature, electrolyte concentration, and the concentration of the contaminant(s) [30].

Further, the fate of the NAPL hydrocarbons in the subsurface environment is affected by (1) the character of the soil (grain site, porosity, permeability, surface area, organic matter content, cation exchange capacity, etc.); (2) the composition, and physical and chemical properties of the NAPL fuel (e.g., its water solubility, soil adsorptivity, vapor pressure, and so on) [31]; and (3) the characterization (qualitatively and quantitatively) of the particular subsurface site in terms of available organic substrates and inorganic nutrients (e.g., N and P) required for the biodegradation to take place, and the specific microorganisms present [32]. The migration of the NAPL materials may be caused by advection, dispersion, or diffusion. Ultimately, their fate in the subsurface can be volatilization, adsorption to the soil or rock matrices, dissolution in either the pore water or the water film surrounding the soil particles, trapping in the pores or fractures of rock; floating on, trapping under, or dissolution in the groundwater, and simultaneously, undergoing biochemical transformations or biodegradation. In view of the heterogeneous composition of the soil matrix and the complex nature of the pore network, the description of transport processes of NAPL in terms of mass transfer, adsorption, and diffusion models is inherently difficult [33].

Typically, NAPL contaminants have low water solubilities (see Table 15.1), and their mass transfer rates in weathered soils are small. These, together with the slow dissolution/elution rates of residual and pooled NAPLs into the aqueous soil solution and the accompanying diffusion and adsorption processes in the micropores, are responsible for the persistence of the hydrophobic NAPL hydrocarbons in aquifer soils [33–35]. The ultimate *in situ* mineralization of residual entrapped NAPL via biodegradation is clearly the most desirable as far as the remediation of the NAPL-contaminated aquifers is concerned. This requires (1) accessibility of the NAPL substrates to microorganisms capable of degrading the former within the two-phase (solid soil/aqueous solution) subsurface system and (2) mitigation of the toxicity to the microorganisms present by several components of the NAPL contaminant itself [36]. Surfactants have the ability to increase the desorption, aqueous solubility [37], and mobility in soils [38,39] of poorly soluble hydrophobic compounds, and thus the potential to improve the accessibility to microorganisms of these substrates, resulting ultimately in enhanced biodegradation [40,41]. Therefore, the use of surfactant-based technologies in subsurface remediation appears to be very promising [42].

TABLE 15.1
Water Solubilities and CMCs of Selected NAPLs and Surfactants

Compound	Mol. Wt.	C-Atoms	Water Solubility (mg/L)
Benzene	78	6	1790.0
Toluene	92	7	579.0
m-Xylene	106	8	215.0
Naphthalene	128	10	30.6
Phenanthrene	178	14	1.2
n-Hexane	86	6	9.0
Surfactant	**Mol. Wt.**	**C-Atoms**	**CMC**
LABS[a]	295	12	0.40
DDBS[a]	348	18	0.40
Triton X-100[b]	646	34	0.11
Igepal CO 660[b]	660	35	0.06
Zoharteric D[c]	502	44	0.16

[a] Anionics.

[b] Nonionics.

[c] Amphoterics.

Source: Zoller, U., in *Soil and Aquifer Pollution*, Springer-Verlag, Berlin, 1998, 322–334.

Finally, remediation by solubilization is a robust process, relatively independent of the type of surfactant used, and has little impact on the movement of liquid contaminants. The critical micelle concentration (CMC) of the surfactant, however, does determine the quantity of the surfactant used (see Table 15.1 for CMCs of surfactants used in aquifer remediation).

Although it provides a decided enhancement over traditional pump and treat technologies, it provides less of an enhancement than does mobilization. On the other hand, in remediation by mobilization within these technologies, the time to remediate the site is independent of the amount of contamination; that is, only a few pore volumes will be pumped through the site, whereas no more surfactant is used than in the solubilization method. Overall, there is a much higher enhancement of the solubility of the NAPL in the aqueous phase. On the other hand, remediation of DNAPLs by mobilization may cause the organic phase to move vertically within the aquifer, leading to formation of a pool at the bottom, and the microemulsions formed may require the addition of a cosolvent.

Given all of the above, clearly, the natural attenuation—that is, the unassisted (by human intervention) biodegradation of NAPL contaminants by living microorganisms under the natural conditions prevailing in the unsaturated and saturated zones of aquifers—is very attractive and, in some cases, is perhaps the best possible process leading; ultimately, to complete mineralization.

The enormous natural capacity of microorganisms to degrade NAPL organic compounds is the basis for bioremediation. However, since microorganisms cannot adequately decompose every NAPL component, particularly under natural subsurface conditions, bioremediation has limitations that must be recognized when considering its use [2,43].

15.4 SURFACTANT-ENHANCED BIOREMEDIATION

Bioremediation is the intentional use of the biodegradation processes to eliminate environmental pollutants (e.g., NAPL fuels), from sites into which they have been intentionally, or inadvertently, released. Bioremediation technologies use the physiological potential of microorganisms to remove/eliminate the contaminants—mainly organic compounds—at field sites [44].

The optimization of NAPL-contaminated aquifers' bioremediation is clearly needed, since many of the NAPL constituents either inhibit microorganisms due to their potential toxicity, or completely prevent their growth, which in turn lengthens the acclimatization period prior to biodegradation [36]. Furthermore, the effectiveness of the biodegradation is contingent on the availability of sufficient inorganic nutrients (e.g., nitrogen and phosphorus) and dissolved oxygen in the saturated and unsaturated zones of the aquifer. The effectiveness of the bioremediation is thus dependent on all the above limiting factors. Significantly, due to its being too tightly bound to the soil particles, the entrapped residual NAPL is not bioavailable to begin with and may be biodegradation-resistant or nonbiodegradable for other reasons (e.g., presence of toxic compounds, inappropriate pH, or unavailability of nutrients). As a result, biodegradation does not take place. Application of biodegradation-enhancing technologies of NAPL-contaminated aquifer remediation is then required. Consequently, the economical feasibility of on-site application of such technologies, under actual field conditions, has become a major issue with respect to the ultimately selected method of choice.

The subsurface biodegradation of NAPL contaminants is critically dependent on their being available to the microorganism populations present in their close proximity. A major problem, in this respect, is the slow dissolution/dispersion rates of the residual entrapped NAPL into the aqueous soil solution [34] following (or concomitantly with) its rather slow desorption from the soil (or rock) matrix.

Two major approaches have been taken by researchers with respect to the development of enhanced bioremediation-based technologies. One is based on extending the range of the biodegradation process *per se*, that is, expanding the range of microorganisms used for attaining better pollutant degradation kinetics and attacking a wider range of NAPL contaminants, and doing so under extreme subsurface environmental conditions. The other takes advantage of the fact that the solubility of hydrocarbons in water can be increased by several orders of magnitude by the addition of surfactants acting as emulsifiers, dispersants, and desorbing agents [15,34]. Thus, the latter approach is focusing on NAPLs' desorption from the soil matrix [42] and their dissolution [45] into the aqueous phase of the aquifer. This should substantially increase the NAPLs' accessibility and, therefore, bioavailability—as nutritional substrates—to the microorganisms present and, thus, to facilitate effective biodegradation. Accordingly, the screening of surfactants having the highest potential for enhancing the bioremediation via desorption-dissolution-mobilization of NAPL *per se,* or (in addition) enhancing its biodegradation, is also followed by efforts to optimize these surfactant-enhanced processes under real field conditions [15,46]. The bioremedial technologies, which evolve as a result of the above research efforts, appear to have the potential for becoming cost-effective (and, therefore, economically feasible) processes, leading to the objective so long aimed for: sustainable remediation of NAPL-contaminated aquifers.

Based on the state of the available data, accumulated experience, and economical/feasibility considerations, it appears that when it works, and in spite of existing shortcomings previously discussed, the site-specific, *in situ* bioremediation of the residual entrapped NAPL in NAPL-contaminated aquifers by a biodegradable nutrient-surfactant mix is the approach of choice [2,47].

In accord with the above, a conceptual approach has been recently proposed for the bioremediation of NAPL-contaminated aquifers, using biodegradable surfactant-surfactant/nutrient mix (SSNM) (Figure 15.4) [8].

Based on this conceptualization, a recently published paper [47] reported that for two NAPL *representatives*—toluene and kerosene—the highest values of the mobility enhancement factor *f*

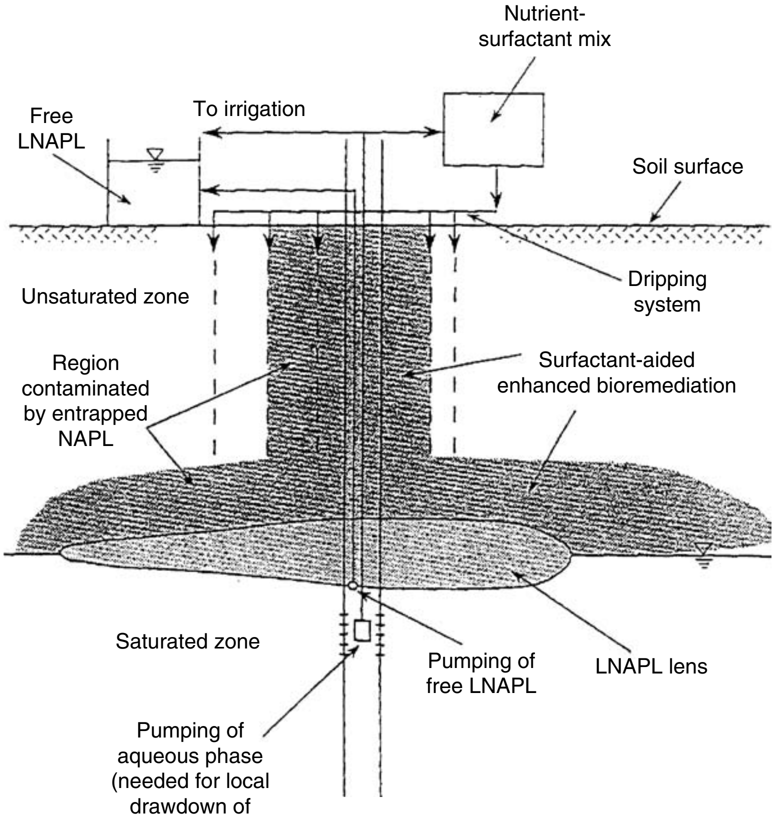

FIGURE 15.4 Schematics of the research conceptual approach. (From Zoller, U. and Rubin, H., *J. Environ. Sci. Health A*, 36(8), 1451–1471, 2001.)

were obtained for systems containing the SSNM amphoteric cocoamphodiacetate and the anionic linear alkylbenzene sulfonate (LABS), combined with the nutrient-surfactant X (containing N and P within its molecular structure). The combination of LABS (0.15 g/L) + cocoamphodiacetate (0.10–0.15 g/L) + X (0.05 g/L) provides the highest mobilization/elution of toluene and kerosene from sandy soil: $f = 2.0$ and 3.6, respectively [47]. Significantly, kerosene (a LNAPL "representative") was shown to be 68% biodegrade in 21 days, independent of the SSNM present.

Based on the above and related experimental results, it was recommended that (1) the major effect of the SSNM added is the enhancement of the mobilization and desorption from the soil matrix and solubilization/dispersion of the released entrapped NAPL in the aqueous soil solution and (2) the bioremediation process is positively related to time duration, and a specific-site-tailored, preoptimized SSNM should be used for ensuring the sustainable bioremediation of both vadose and saturated zones in NAPL-contaminated aquifers [8].

15.5 FIELD DEMONSTRATION OF SURFACTANT-ENHANCED SUBSURFACE REMEDIATION

Several field demonstration studies were conducted in the United States, mainly in the 1990s. These demonstrations have shown that surfactant-enhanced subsurface remediation (SER) is relatively rapid and economical, and can be competitive with conventional *pump and treat* remediation, if—in *ex situ* bioremediation—surfactant losses can be minimized, contaminated elution maximized, and surfactant-contaminant separation and the former's reuse implemented [46].

Soil washing in *ex situ* (above ground) processing is a proven remediation technology that is also robust and versatile. Previous field demonstrations have shown that this technology can achieve high levels of contaminant removal at relatively low costs. As the technology matures, the cost of treatment may be expected to decrease.

The use of micellar-enhanced ultrafiltration (MEUF) of solutions to concentrate pollutants already bound to, or solubilized by, surfactants is an important option that can make a wide variety of SER projects economically feasible. In contaminated groundwater, at sites in which the pollutant is primarily dissolved, the water can be economically treated by MEUF processes, concentrating and removing contaminants, recovering surfactants, and preventing the leakage of surfactants into receiving waters.

A related area requiring additional study is the surfactants-enhanced biodegradation of both NAPLs and surfactants in aquifers, so that we can assess the long-term impact of SER projects on humans and the environment. Still, there is an insufficient data base, pertaining to biodegradation and the relationships between adsorption and biodegradation at subsurface and aquifers. Understanding biodegradation phenomena may well be the key to determining the acceptability of planned uses of surfactant-enhanced remediation technology [46,48].

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16 Application of Bleaching Detergent Formulations

Gerd Reinhardt and Georg Borchers

CONTENTS

16.1 INTRODUCTION

Since the publication of the first volume of this *Handbook of Detergents* in 1999 [1], substantial progress has been made in the development of new raw materials and in the design of detergent formulations. About 10 years ago, the bleach chapters focused mainly on the properties of bleach activators [2] and hypochlorite bleach [3]. Since then, considerable R&D effort has been invested in the development of new systems to satisfy the upcoming ecological challenges of the new millennium. Reactive preformed peracids or bleach catalysts for cold wash formulations are just the first step in providing creative solutions for energy saving and water conservation. The success of new bleach systems is not only based on the properties of the chemicals themselves, but also relies on new delivery forms such as granules with time-controlled release of the active ingredient or new packaging devices such as dual-chamber bottles and multicompartment devices.

This chapter will cover low-temperature bleach activators, catalysts utilizing peroxide or atmospheric oxygen for the oxidation reaction, and oxygen transfer agents that act as performance boosters for common bleach systems. Optimum conditions of use to maximize performance and avoid negative secondary reactions are described. Special attention is given to the various finishing processes, application forms, and delivery concepts that enable sensitive bleach components to be incorporated in household products, improve stain removal performance, and deliver an attractive appearance for consumers.

16.2 BLEACH SYSTEMS: FUNDAMENTALS

16.2.1 STAINS AND BLEACH SYSTEMS

Bleach systems are used in domestic laundry and cleaning applications, whitening raw cotton, pulp and paper production, and wastewater treatment. Their main task is to remove colored stains from fabrics, hard surfaces, or aqueous solutions. This is achieved by chemical degradation of the chromophoric units present in colored soils. In the course of the reaction, conjugated electron systems are interrupted so that the color disappears. Large molecules are broken down and polar groups are introduced, so that the stain becomes more hydrophilic and easier to dissolve or disperse.

Most stains consist of colored substances of natural origin belonging to the polyphenol, carotenoid, or chlorophyll class. Artificial food colorants, cosmetic ingredients, and decorative dyes complete the stain portfolio. Very often stains are complex mixtures of spilled food preparations or beverages. Combined with oils, fats, or other organic material, such as proteins, starch, or waxes, the properties of stains are quite different from those of isolated dyes. Only a small proportion of all stains is fixed on surfaces by physical adhesion. On fibers, in particular, strong interactions often result in covalent bond formation. This process is more important on cotton than on synthetic fabrics.

Many bleaching agents are also highly active against microorganisms such as bacteria and viruses, and can be used for sanitization or disinfection purposes to ensure high standards of hygiene. This biocidal action not only kills germs sticking to fabrics, but also prevents the formation of persistent biofilms in the washing machine.

Bleach products can be classified into two groups: chlorine and oxygen based systems. Historically, chemical bleaching started in the middle of the eighteenth century with the development of Eau de Javelle. As sodium hypochlorite (NaOCl) still is the most widespread bleach system, the term *bleach* is regarded worldwide as a synonym for chlorine bleach.

An aqueous solution of NaOCl is a strong bleaching agent and powerful disinfectant. It guarantees cleanliness and germ removal even at cool temperatures. Low-cost availability makes it affordable in most regions of the world. On the other hand, hypochlorite bleach must be handled with care, as it is aggressive to colors and fabrics, and may cause yellowing of fabric, color fading, and severe fiber damage when used repeatedly.

Bleaching with NaOCl is the subject of much debate, since chlorinated byproducts are formed, which are harmful to the environment. In many applications, NaOCl has therefore been replaced with more environmentally compatible oxygen-based bleach systems. They, too, have good bleaching properties; however, as they are milder, they need more time or higher temperatures to work effectively. Oxygen bleaches are gentler to colors and fibers, odorless, and of low toxicity.

16.2.2 HYDROGEN PEROXIDE AND PERSALTS

Hydrogen peroxide (H_2O_2) is not only the most common bleaching agent, but also the starting material for almost all other oxygen-based bleach systems. Its consumption is currently in the range of 2.2 million tons [4]. Hydrogen peroxide has a theoretical active oxygen content (Oa, active oxygen = oxygen in peroxide form) of 47%, and is difficult to handle in the pure state. In industrial applications 35, 50, and 75% active material is used, whereas in domestic applications its concentration is normally below 10%, preferably between 3 and 6%.

H_2O_2 is a very weak acid and only slightly dissociated (pKa = 11.6). It is relatively stable in undissociated form, and therefore mostly used in weakly acidic formulations. New stabilizer packages, however, make it possible to formulate weak alkaline hydrogen peroxide at concentrations up to 6% [5]. UV light and metal traces promote its decomposition; therefore, stabilization by chelating agents is required. The enzyme catalase, which is present in many stains, splits hydrogen peroxide immediately into oxygen and water.

Inorganic salts are widely used as solid H_2O_2 carriers in powdered formulations (Table 16.1). In laundry and cleaning applications, percarbonate and perborates are preferred. Perborates are real peroxides containing a B-O-O-B bond and commercially available in two forms, perborate

TABLE 16.1
Properties of Persalts

	Sodium Perborate Tetrahydrate	Sodium Perborate Monohydrate	Sodium Carbonate Peroxyhydrate	Potassium Mono Persulfate
Formula	$NaBO_3*4H_2O$	$NaBO_3*H_2O$	$Na_2CO_3*1.5H_2O_2$	$2KHSO_5*$ $KHSO_4*K_2SO_4$
Active oxygen (%)	>10	>15	>13	4.7
pH	10.0–10.4	10.0–10.4	10.5–10.7	2.0–2.3
Bulk density (g/L)	700–900	500–600	900–1200	1100
Solubility (water) (g/L)	23	15	140–150	250
Dissolution rate (20°C) (min)	6–8	<1	<2	Readily

tetrahydrate (PB*4) and perborate monohydrate (PB*1). In some regions, ecotoxicological question marks over boron and perborates have led to their replacement by sodium percarbonate (SPC), the peroxyhydrate of soda ash, which is manufactured by either the classic crystallization route or a new spray granulation process. Modern SPC granules are spherical particles with high bulk density and an active oxygen content of ~15%. In coated form they are highly stable, and can be pneumatically conveyed and stored in silos [6].

SPC is an attractive detergent ingredient [7], as it delivers not only bleach but also alkalinity, and the carbonate ion assists in removing water hardness. At low temperatures, it has higher solubility than perborate, and delivers more environmentally friendly breakdown products.

The peroxide of sulfuric acid, monoperoxysulfuric acid, is difficult to handle, but its triple salt potassium monopersulfate (KMPS = $2KHSO_5{*}KHSO_4{*}K_2SO_4$) is storage-stable. Its fast dissolution rate in cold water supports its powerful oxidizing and disinfection properties. Intrinsic acidic properties, however, make KMPS (pH = 2.3) less suitable for use in alkaline formulations.

16.2.3 Organic Peracids

Major application advantages of preformed peroxy acids are their immediate availability in the bleach process and their stability in the presence of the enzyme catalase. Derived from aliphatic or aromatic carboxylic acids, the lower members of this class are liquid at room temperature, whereas higher homologues are stabilized in crystalline form by dimer formation. Aliphatic monoperoxycarboxylic acids provide optimum bleaching at chain lengths of C6–C9, whereas α, ω-diperoxycarboxylic acids perform best at chain lengths of C10–C14 [8].

Peroxycarboxylic acids with an Oa content >7% are thermodynamically unstable, and tend to explode under thermal or mechanical stress. For safe handling in consumer products, either diluted application forms or phlegmatized powders and granules have to be used. As an alternative, the peroxy acid can be generated *in situ* from bleach activators.

Hydrophilic peracids with less than four carbon atoms are effective bleaches, oxidizers, and disinfectants. The most important is peroxyacetic acid, which is often used in equilibrium mixture with acetic acid and hydrogen peroxide as a 5, 10, or 15% active solution. Its characteristic odor and safety aspects, however, prevent its widespread use in homecare applications.

In the 1980s, a number of solid preformed peracids were tested for use in domestic laundry applications. Magnesium monoperoxyphthalate-hexahydrate (Mg-MPP) [9] (Figure 16.1) contains 5.5% active oxygen and is safe to handle. Moderate bleach performance and the potential risk of dye damage, however, have reduced its use to niche applications for cleaning and disinfection. Another preformed peracid, 1,12-diperoxydodecanoic acid (DPDDA) [10], had very favorable bleaching properties. Stability issues in detergent formulations, handling problems, and economic aspects, however, prevented a successful commercialization of this product.

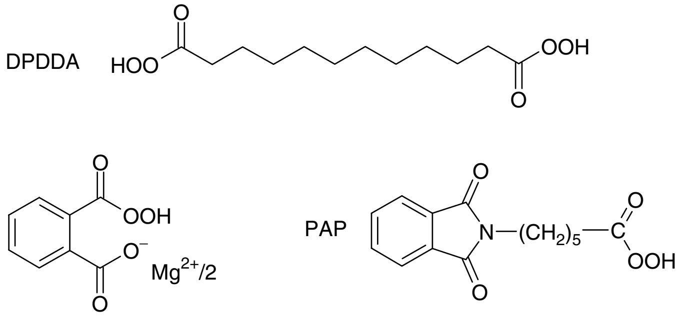


FIGURE 16.1 Preformed peracids.

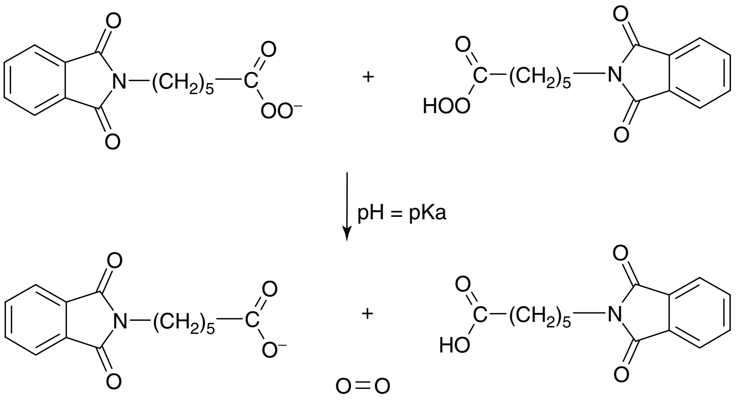


FIGURE 16.2 Side reaction of PAP: decomposition and singlet oxygen formation.

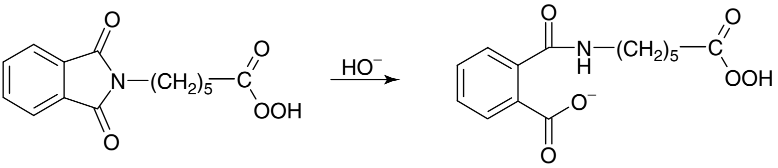


FIGURE 16.3 Side reaction of PAP: hydrolysis of phthalimido group.

The incorporation of a polar functional group into an alkyl peroxycarboxylic acid increases melting point and thermal stability. Amido and imido linkages, in particular, improve the intrinsic properties of the molecule. Optimum thermal stability, bleach performance, and accessibility are found in phthalimido peroxycaproic acid (phthaloyl amidoperoxy caproic acid, PAP) [11], which is now used in several domestic and industrial applications.

White odorless PAP powder with active matter >95% has an Oa content of 5.8%, melts at 90°C, and decomposes smoothly at about 100°C, as evidenced by oxygen release. Even in the pure state, the compound is not explosive. PAP is commercially available as a powder or aqueous slurry, or in granular form.

As a hydrotropic peracid, PAP is only sparingly water-soluble (0.2 g/L at 20°C, pH 4.5), and allows stable aqueous dispersions or slurries to be prepared in the acidic pH range [12]. Its solubility improves with increasing pH and temperature; at pH 10 and 20°C, 80% of PAP dissolves within 5 min. The aromatic ring boosts its affinity to oily soils, resulting in improved removal of both hydrophilic and hydrophobic stains. The peracid shows optimum performance at 20–50°C in the pH range 7–10.

Like all peracids [13], PAP tends to decompose at its pKa, forming the acid and significant amounts of singlet oxygen (Figure 16.2). In strong acidic or alkaline conditions, hydrolysis may occur with formation of hydrogen peroxide. Additionally, under alkaline conditions, the phthalimido ring system may open irreversibly (Figure 16.3). At pH 9.2 and 40°C, the half-life of the ring system is about 20 min. Carrying a negative charge, the ring-opened peracid is less bleach active than the intact molecule.

16.2.4 PERACID PRECURSORS (ACTIVATORS)

In contrast to sensitive preformed peracids, bleach activators are safe to handle and, in granulated form, reasonably storage-stable in alkaline detergent powders or tablets. Bleach activators are organic compounds having at least one reactive acyl group R-CO (peracid precursor group), which

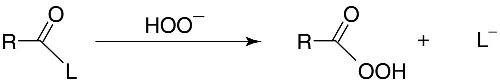


FIGURE 16.4 Perhydrolysis of reactive esters or imides.

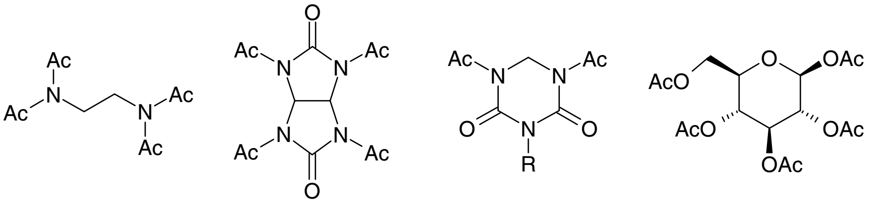


FIGURE 16.5 Hydrophilic bleach activators. TAGU = tetraacetyl glycolurils; DADHT = diacetyl dioxohexahydrotriazine; PAG = pentaacetyl glucose.

is connected to a leaving group L. In the reaction with a perhydroxyl anion, an organic peroxycarboxylic acid is formed *in situ* (Figure 16.4).

Activator molecules can be designed for their application by modifying either the peracid precursor or the leaving group. The former defines the bleach and sanitizing properties of the peracid and determines its reactivity and selectivity, hydrophilic/hydrophobic balance, and oxidation potential. The leaving group influences the solubility, perhydrolysis rate, and storage stability of an activator. For fast perhydrolysis reactions, a pKa of 6–13 of the acid form of the leaving group is often preferred.

16.2.4.1 Hydrophilic Activators

With a total consumption of ~90 kt in 2005, tetraacetyl ethylene diamine (TAED) [14] (Figure 16.5) is the most widely used bleach activator. The product fulfills the basic principles of green chemistry [15], as it has maximum atom efficiency; both starting materials (ethylene diamine and acetic acid anhydride) are fully incorporated in the molecule. Its low toxicity profile and ready biodegradability reinforce the sustainability claim. The activator is weight-efficient, as one molecule generates two molecules of peracetic acid. Under European washing conditions at 30–60°C, it has an excellent cost–performance ratio. The kinetic stability of peracetic acid at lower temperatures, however, limits its use to warm wash applications.

Under optimized conditions, TAED shows a performance comparable to the corresponding peroxyacetic acid (Figure 16.6). There is a negligible performance deficit at temperatures below 40°C, based on delayed dissolution and perhydrolysis. Above 60°C, however, activator systems benefit from the excess of persalt, which contributes significantly to stain removal.

All other peracetic acid-generating activators demonstrate performance profiles similar to TAED. Tetraacetyl glycoluril [16] also has two active groups. It was used for several years in Europe, but disappeared from the market because of biodegradation issues with the leaving group. Similar negative aspects prevent the market success of diacetyl dioxohexahydrotriazine [17] and the even more weight-effective triacetyl dioxohexahydrotriazine (TADHT) [18]. Pentaacetyl glucose [19] and other sugar-based activators were seen on the market some years ago. This class of activators may regain popularity as the activators are based on renewable resources.

16.2.4.2 Hydrophobic Activators

A major break-through in activator technology came with the development of nonanoyloxy benzenesulfonic acid sodium salt (NOBS) [20], which was incorporated in a North American detergent

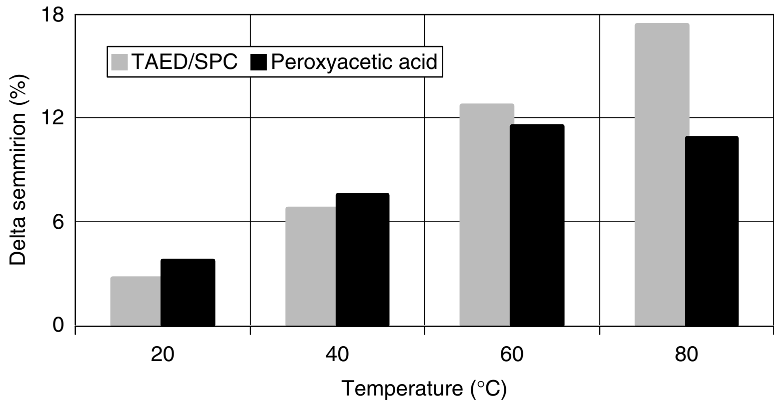


FIGURE 16.6 Bleach performance of TAED/SPC versus peroxyacetic acid at various temperatures.

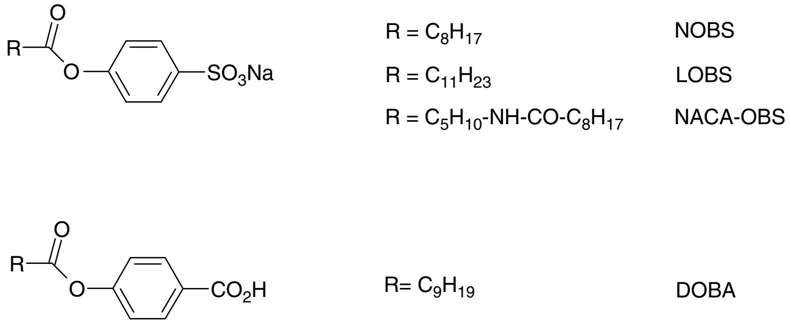


FIGURE 16.7 Hydrophobic bleach activators.

in 1989. Based on the polar sulfonate group, NOBS (Figure 16.7) is about 100 times more soluble than TAED at 20°C. This significantly improves performance at low washing temperatures or in short washing cycles, which are common in many parts of the world. The phenolate leaving group supports a fast perhydrolysis reaction resulting in the liberation of peroxynonanoic acid, which is not only effective on hydrophilic stains but also has a pronounced affinity for oily food stains and dingy soils such as sebum residues in collars. LOBS (lauroyloxy benzenesulfonic acid sodium salt), the higher homologue of NOBS, is even more hydrophobic and less water-soluble. It forms peroxylauric acid, which is able to remove highly lipophilic stains that are otherwise hard to attack. Another long-chain bleach activator, nonanoyl amido caproylacid oxybenzenesulfonate (NACA-OBS) with an amido function in the acyl group, was test-marketed in Europe at the end of the 1990s [21], but has not yet been commercialized.

A second group of hydrophobic activators is based on hydroxybenzoic acid as the leaving group. The carboxylic acid group of decanoyloxybenzoic acid (DOBA) [22] determines the solubility of the molecule. At neutral or slightly acidic pH, the activator is practically insoluble in water, and allows storage-stable aqueous dispersions and slurries to be prepared, which are useful for many applications. Under alkaline washing conditions, DOBA dissolves quickly and generates peroxydecanoic acid.

16.2.4.3 Highly Reactive Activators

Decreasing water temperatures, shorter washing cycles, and economic factors are driving the development of more reactive bleach activators. Earlier attempts focused on peroxybenzoic acid-generating systems (Figure 16.8), such as benzoyloxy benzenesulfonate sodium (BOBS) [23] or benzoyl caprolactam (BCL) [24]. Electron-withdrawing groups in para-position on the aromatic ring increase the rate of perhydrolysis and stain removal performance of the peracid.

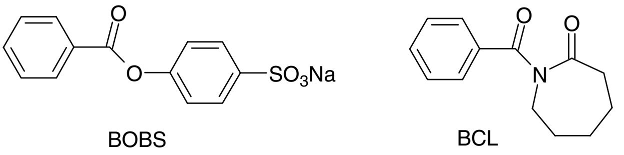


FIGURE 16.8 Reactive bleach activators.

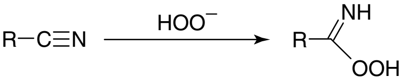


FIGURE 16.9 Formation of peroxyimidic acid.

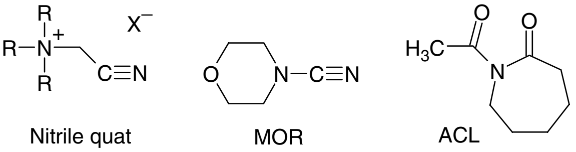


FIGURE 16.10 Nitrile quats and liquid bleach activators.

The addition of a perhydroxyl anion to a nitrile group generates a peroxyimidic acid (Figure 16.9). This highly reactive and extremely unstable compound does not allow isolation, but is safe to handle when prepared *in situ*. In chemical reactions, peroxyimidic acids differ significantly in reactivity and selectivity from aromatic or aliphatic peroxycarboxylic acids.

Nitrile-based activators [25] are highly weight-efficient, since no leaving group is liberated as a byproduct in the peracid-generating step. Whereas in principle all nitriles show activator properties, only aminonitriles are of practical interest (Figure 16.10). Cyanamide derivatives are preferred for industrial applications, whereas nitrile quats are the first choice in domestic use.

Cyanomorpholine (4-morpholinocarbonitrile, MOR) [26] is a low-viscous colorless liquid, which is easy to dose in industrial applications. It is fully water-miscible, and allows the preparation of aqueous solutions that are storage stable at neutral pH. The bleach active species formed in reaction with hydrogen peroxide matches the performance of chlorine bleach in certain applications.

Nitrile quats are white powders, characterized by high melting points and excellent water solubility. Their positively charged ammonium group allows favorable interactions with the negatively charged surface of a fabric and assists fast stain removal. Aliphatic short- and long-chain nitrile quats [27,28], as well as polymeric derivatives [29], are described in patent literature; a cyclic morpholine-based system [30] is commercially available. Nitrile quats are low-temperature bleach activators with optimum performance between 20 and 40°C in the pH range 9–11.

16.2.4.4 Liquid Activators

Liquid activators are preferred in industrial applications, because they are easy to dose via pumps and dissolve more quickly in the bleaching bath than solid activators. Besides MOR, acetyl caprolactam (ACL) [31] (Figure 16.10) can also be used for this purpose.

16.2.5 BLEACH CATALYSTS

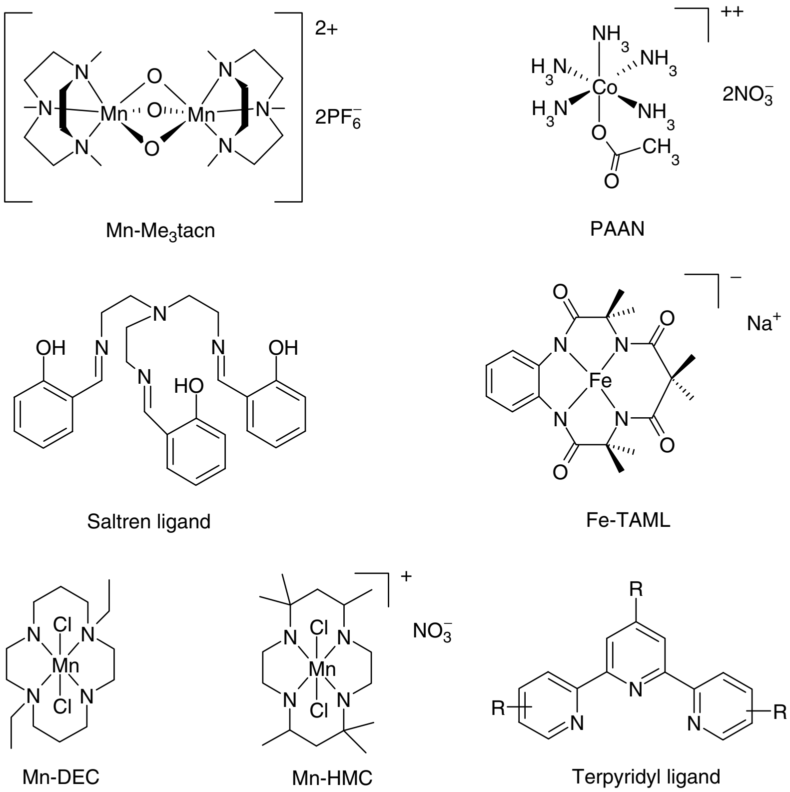
Common bleach activators are not very weight- and volume-effective, as they work stoichiometrically with peroxide. This drawback is overcome by using bleach catalysts, normally transition metal complexes with nitrogen- or oxygen-containing ligands.

The type of transition metal and spatial arrangement of the ligand determine the reactivity and stability of the catalyst. For toxicological and ecological reasons, iron and manganese are the first choices as central atoms, and rigid three-dimensional ligands are preferred for complex stability [32]. Stability in an alkaline matrix is a prerequisite, as decomposition or hydrolysis may generate free metal ions, their oxides, or hydroxides, which are not only deposited on the fabric as black spots but may also destroy H_2O_2 and induce radical chemistry.

In the early stages of catalyst development, metal salts of chelating agents such as picolinic acid or ethylenediamine tetraacetic acid were investigated. In the 1980s, research was focused on various types of amine and sugar complexes. Some years later, bioinorganic model compounds (enzyme mimics) were recognized as suitable bleach catalysts.

A milestone in terms of performance was reached with iron and manganese trimethyltriazacyclononane complexes, which are highly effective when used in the range of 0.5–10 ppm at 20–40°C [33]. The market launch of Mn-Me_3tacn (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane)-containing powder detergents, however, turned into a disaster when it was recognized that the catalyst caused severe fiber damage on specific dyeings.

Mn-Me_3tacn (Figure 16.11) is still used in automatic dishwashing products, where color and fiber damage is of lesser importance. Another metal complex used in machine dishwashing detergents is pentaamine acetate cobalt (III) nitrate (PAAN) [34]. This highly water-soluble, relatively inexpensive catalyst is effective at very low concentration.



Mn-Me_3tacn PAAN

Saltren ligand Fe-TAML

Mn-DEC Mn-HMC Terpyridyl ligand

FIGURE 16.11 Bleach catalysts and ligands.

Recently, a granulated manganese (III)-saltren complex [35] has been incorporated in bleach boosters and a powder detergent in Europe. Activated by peroxide, the catalyst has a bleaching optimum around pH 11, and is most effective between 30 and 60°C. It bleaches on fabric but also fugitive dyes in solution and prevents graying of white fabrics. It is gentle to fabrics and fibers and compatible with a number of enzymes [36].

Several interesting bleach catalysts are described in recent patent literature and are currently under evaluation. Fe-TAML (tetraamido macrocyclic ligand), for example, was selected from a large number of similar tetraamido complexes, and has excellent dye transfer inhibition properties, as it selectively destroys many dyes dissolved in the wash liquor [37]. The catalyst is being tested in several applications, such as effluent bleaching, the pulp and paper industry, desulfurization of diesel, and decontamination [38].

The original Mn-Me_3tacn complex contains PF6 – as a counter ion, which simplifies purification and handling and improves storage stability, but reduces the solubility of the catalyst. Recent developments in using Mn-Me_3tacn derivatives for raw cotton bleaching, the pulp and paper industry, and industrial cleaning are based on more soluble counter ions such as chloride, sulfate, or acetate. Such catalysts are more cost-effective to produce, and allow stable weak acidic solutions to be prepared [39].

Instead of using a preformed catalyst, the metal complex can very often be formed *in situ* by adding the ligand and an appropriate amount of manganese salt to the cleaning solution [40]. Even if no metal traces are added separately, Me_3tacn salts are able to improve stain removal performance [41]. It is presumed that in this case the ligand binds to the metal ions present in many stains and specifically works in that way [42].

A new class of bleach catalysts is based on the 2, 2′: 6′, 2″ terpyridine (terpy) ligands [43]. Whereas nonsubstituted Mn(II)-terpy complexes show only poor activity, the incorporation of electron-donating substituents in the 4-position significantly improves performance in solution and surface bleaching [44].

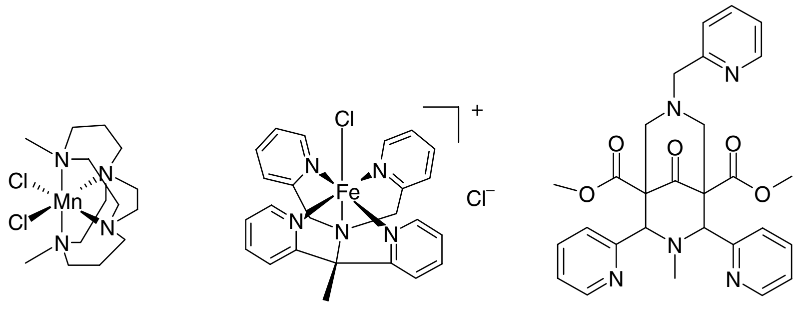
Polyoxometalates are well-defined inorganic metal-oxygen cluster anions, whose oxidizing power is influenced by the properties of the different metal atoms. Their straightforward synthesis enables them to be tailor-made for bleach reactions [45].

A further group of bleach catalysts is based on medium-sized azacyclic ligands, especially on cyclen or cyclam derivatives. Alkyl groups on the nitrogen atoms often have a positive impact on performance. The catalysts are relatively stable under alkaline conditions, and reach a performance optimum at 25–40°C and pH 10. Especially preferred compounds are the cyclam derivatives Mn-DEC (diethyl-cyclam) [46] and Mn-HMC (hexamethyl-cyclam) [47].

16.2.6 AERIAL BLEACH SYSTEMS

A number of iron and manganese bleach catalysts (Figure 16.12) are patented for stain bleaching in the presence and absence of a peroxide source [48]. In the latter reaction, atmospheric oxygen is used in the oxidation step. The ethylene-bridged cyclam complex Mn-(Me_2EBC)Cl_2 with Me_2EBC = 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2] hexadecane is one of several compounds described for this purpose [49]. The cage-like ligand enhances the stability of the catalyst; the two chloride ligands are rapidly exchanged in the aqueous washing liquor by aqua ligands that allow redox chemistry to take place to form reactive species. Iron complexes containing pentadentate-*N*-donor ligands, such as MeN_4Py, form another group of aerial bleach catalysts [50]. Recently, metal complexes containing bispidon-derived ligands [51] have been claimed for the same purpose [52].

The bleach performance profile of aerial bleach catalysts is quite different from that of peroxide bleaching. Whereas a wide range of oxidizable stains is attacked by the activated catalyst in the presence of perhydroxyl ions, in combination with atmospheric oxygen, only oily food stains, such as tomato oil, mango or annatto-derived stains [53], are targeted. It is assumed that under aerial bleach conditions the catalyst induces the formation of hydroperoxides in the food stain. In a second



Mn-(Me$_2$EBC)Cl$_2$ Fe-MeN$_4$Py Bispidon ligand

FIGURE 16.12 Aerial bleach catalysts and ligands.

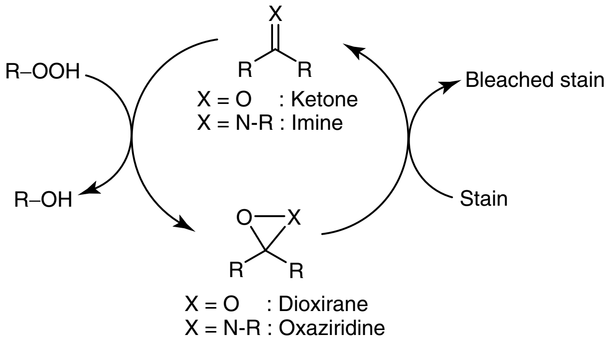


FIGURE 16.13 Oxygen transfer reaction.

step, these peroxides of unsaturated oils and fats react with the chromophoric systems of carotenes, in a process similar to naturally occurring autoxidation reactions.

Photobleaches are another class of aerial bleach systems, since they also use oxygen from the air, but in a quite different way. In the presence of water and sunlight the water-soluble Zn or Al phthalocyanine derivatives transform triplet oxygen into highly reactive singlet oxygen [54]. Such photobleaches are mainly used under line-drying conditions in Latin America, North Africa, and India.

16.2.7 OXYGEN TRANSFER AGENTS

Oxygen transfer agents (OTA) are low-temperature bleaching agents with catalytic functions (Figure 16.13). The metal-free systems, often formed *in situ* in the bleaching bath, belong to the dioxirane and oxaziridine classes, well-known oxidizers in organic chemistry. These highly strained three-membered heterocyclic compounds transfer the oxygen atom to a substrate and form back the precursors, either a ketone or an imine compound (Figure 16.14). In many applications, OTAs are able to match the performance of hypochlorite bleach. Prepared *in situ*, they are safe to handle, odorless, and allow stain removal at very low temperature.

The reaction of potassium monopersulfate with certain ketones at a weakly alkaline pH results in the formation of dioxiranes [55]. By modeling the ketone, bleaching optima in a neutral or alkaline medium can be tailored to match the desired application pH. Best results are achieved with solid cyclohexanone derivatives [56], sugar-based ketones (SK) [57] (bleaching optimum at pH 10), or with substituted aminoacetones such as DMAA (bleaching optimum at pH 8–9).

Oxaziridines are versatile epoxidizing agents in synthetic chemistry [58]. They are prepared by oxidation of imines or imminium compounds with peroxy acids or KMPS in the alkaline pH

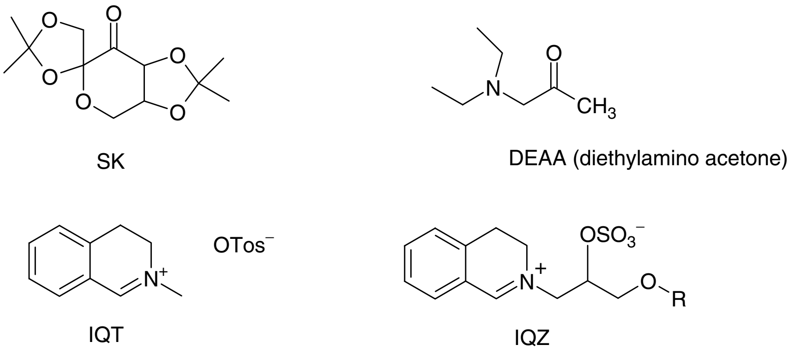


FIGURE 16.14 Examples of oxygen transfer agents.

range. Dihydroisoquinoline derivatives, such as cationic salts (N-methyl-3,4-dihydroisoquinolinium-tosylate—IQT) [59] or betaines (dihydroisoquinolinium-zwitterion—IQZ) [60] that form highly reactive electrophilic oxidants at pH 8–10, are of special interest for bleach reactions. The systems are claimed as performance enhancers for activated bleach systems based on TAED or NOBS, and allow better low-temperature performance at reduced levels of activator concentration.

16.2.8 OPTIMIZING THE BLEACHING PROCESSES

16.2.8.1 Factors Influencing the Reaction

Optimizing a bleach reaction is a very difficult task, as an incredible number of factors control the process [61]. Besides the two reaction partners, the bleach active species and the stain, the reaction matrix, and especially the reaction conditions have a major impact on the result. Before oxidation can take place, both reaction partners have to come into close contact. In this respect, bleaching in solution is easier than fabric bleaching, as under alkaline washing conditions, cellulosic fibers are negatively charged, and electrostatic repulsion has to be overcome. Cationic charges such as ammonium groups in bleaching agents lead to favorable interactions, whereas negatively charged substituents often result in a poor performance. The delivery of bleach to the fabric is the rate-determining step in many of these reactions. Increasing the ionic strength in the washing liquor or high temperatures assists in overcoming the repulsion of negatively charged surfaces. If this is not possible, prolonged reaction times (soaking) always have a positive impact.

The hydrophilic/hydrophobic characters of the bleach system and the stain play an important role in the interaction of both components. Whereas hydrophilic peracids (e.g., peroxyacetic acid) are optimum for bleaching polar polyphenolic stains, such as tea and red wine, they are normally less effective on water-insoluble stains like spaghetti sauce or grass. Long alkyl chain–or aromatic-ring–containing compounds are preferred, as they are attracted more easily and are able to penetrate hydrophobic stains.

16.2.8.2 Bleaching Mechanism

When dissolved in water, perborate and percarbonate generate hydrogen peroxide. Although peroxoborates [62] and peroxocarbonates [63] are analytically detectable in such solutions, under normal usage conditions both persalts deliver comparable bleaching results.

Bleaching reactions with hydrogen peroxide or persalts follow a second order law (first order with respect to both the substrate and hydrogen peroxide concentration). Although the mechanism of peroxide bleaching has been a subject of some debate in the past [64], now it is generally accepted that the nucleophilic perhydroxyl anion is the powerful bleach active species. For effective stain removal, pH values >10.5 and temperatures higher than 70°C are required. For use at lower temperatures, prolonged reaction times (soaking) or addition of an activator are recommended.

Bleaching with activator-persalt mixtures is a multistep process. Both reaction partners are provided in solid form and have to dissolve quickly and completely, as otherwise valuable raw materials are lost. Chelating agents are added to suppress decomposition of hydrogen peroxide by metal traces, and additional precautions have to been taken to avoid decomposition of H_2O_2 by the enzyme catalase. A high pH, usually between 10 and 11, is essential to generate enough perhydroxyl anions to accelerate the perhydrolysis step and generate the bleach active peroxycarboxylic acid. This reaction follows second order kinetics overall and first order with respect to each reactant. In general, persalt to activator ratios of >2:1 (on a molar basis) are used for complete perhydrolysis. Ester-based activators tend to react with peroxy acid, which has already formed to produce less bleach active diacylperoxides. To suppress this side reaction, persalt-to-activator ratios of at least 3 to 1, preferably 5 to 1, are recommended when using this type of activator [65].

Following the formation of the peroxy acid, the pH of the washing liquor should ideally drop to 8.5–9.5 to fully utilize its bleaching power. Controlling the pH is one of the essential factors for optimum bleach reaction. In peracid bleaching, the active species is usually the undissociated peroxy acid. The reaction is electrophilic in nature, and first order with respect to its concentration.

Model reactions in homogeneous solution indicate that the bleach reaction itself is a multistep process [66]. The reaction is first order with respect to both the active oxidant and the stain, and depends on the ionization state of the reactants; one has to be dissociated, and the other one should be in undissociated form. A transition complex is formed, in which one hydrogen atom is involved, and finally the oxygen is transferred to the substrate to complete the reaction. The reaction is governed by the pH of the solution, and maximum bleach rates are achieved at a pH that is the mean of pKa (stain) and pKa (peroxy acid) [67].

$$\text{pH (bleach max.)} = (\text{pKa (stain)} + \text{pKa (peroxy acid)})/2$$

The pKa of peracids depends on the type of acid and its electronic factors. Starting with pKa 7.1 (peroxyformic acid) up to pKa 11.6 (hydrogen peroxide), commonly known bleaching agents cover a range of 4 units (Figure 16.15) [68], which gives some flexibility to formulators to choose the right oxygen bleach systems for the required application pH.

Unfortunately, natural stains are complex mixtures of colored compounds with unknown protonation constants. Even knowing the pKa of the peroxy acid, the optimum reaction pH has to be determined experimentally. Using the TAED/persalt system, maximum stain removal on tea is achieved at pH 8.3, whereas red wine has an optimum around pH 9. Higher alkalinity favors the removal of curry, grass, and oily food stains (Figure 16.16). Each bleach system also has an optimum pH for the removal of a given stain. Tea, for example, is best removed at pH 10–11 by using a catalyst, whereas a preformed peracid bleaches this stain best at pH 7–8 (Figure 16.17).

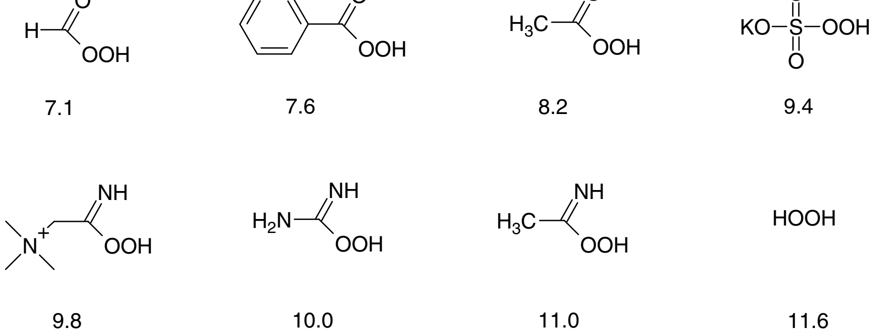


FIGURE 16.15 pKa values of peracids. Data for peroxyimidic acids (from Eilers, B., Mechanistische Untersuchungen zur nucleophilen Aktivierung von Wasserstoffperoxid mit Hilfe der Sigulettsauerstoff-Phosphoreszenz, Thesis, University Frankfurt am Main, 2002.)

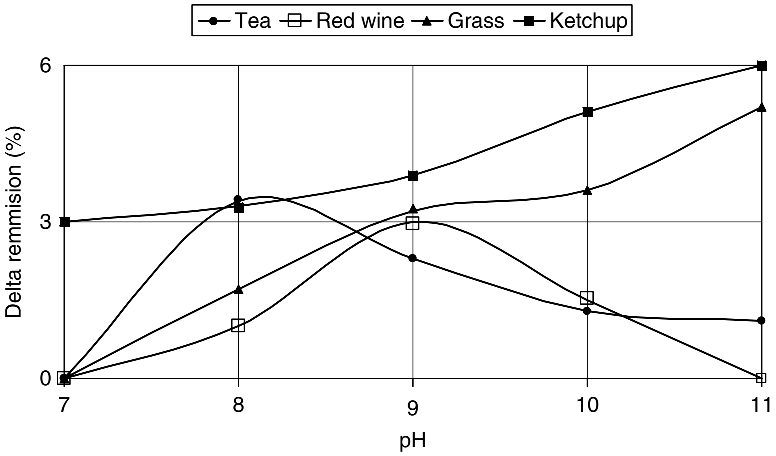


FIGURE 16.16 The pH effect on bleach performance of TAED/PB*4.

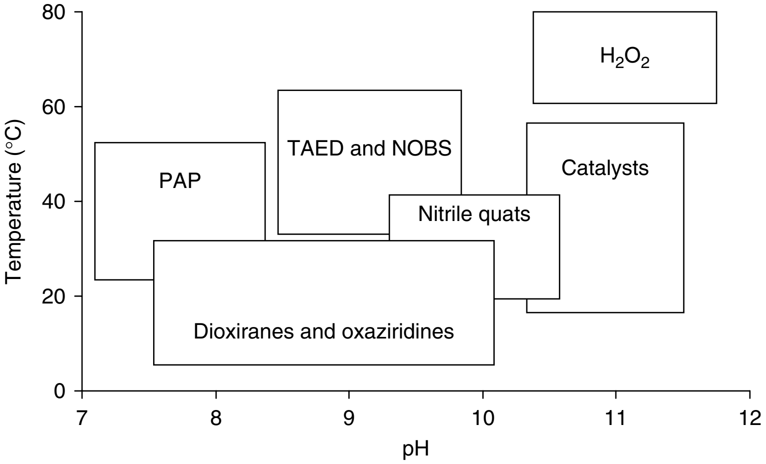


FIGURE 16.17 Optimum conditions for various systems to bleach tea stains.

Current literature hardly describes any mechanistic details of catalytic bleaching in washing liquors [69]. Studies using homogeneous dye solutions give some insight into the complex process [70]. The mechanistic pathway depends on the catalyst type and substrate. Oxygen transfer or hydrogen abstraction are possible; in some cases electron transfer may also take place. Unlike bleach activators and peroxy acids, the activation barrier for peroxide bleaching is relatively low and permits excellent bleaching results at low temperatures.

16.2.9 COLOR AND FABRIC CARE

In chemical terms, there is virtually no difference between a natural dye as a color-imparting component of a stain and a synthetic dye used to give a garment a colorful appearance. It is therefore always a challenge to remove stubborn stains from a colored fabric without affecting the synthetic dyes.

There are a number of chemical reactions taking place in the washing process that might damage colored fabrics. Besides hydrolysis of the dye-fiber bond, the most important reaction is the oxidative destruction of the chromophoric system, which results in visible damage after only a few washing cycles. Sulfur dyes are extremely sensitive, as are direct dyes to some extent, but the most differences are seen with reactive dyes, the group that has the highest market importance. In this context, trichromatic mixtures, that is, combinations of red, blue, and yellow dyes used to produce a desired shade, are particularly critical. Damage to one dye will immediately result in a color shift. Vat dyes and dyeings on polyester, polyamides, and polyacrylonitriles are largely stable in the presence of bleach systems.

Owing to the importance of color care under bleach conditions, two test protocols have been developed to assess color-damaging properties of bleach systems. The first one (ISO 105-C09) [71] is a diagnostic single wash test carried out at 60°C using a high bleach concentration. The test works well with peroxy acids, but fails to predict reliable results for bleach catalysts. Better differentiation is possible using the color damage profile test (CDP test) [72], a repeated washing test at 40°C under real-life conditions. In both tests, normally a representative collection of 40 commercially important dyeings on different textiles is used (AISE Dye Set).

Persalts and H_2O_2 are generally color-safe, and only a very limited number of dyes are damaged in the CPD test. All other bleach systems are more reactive, and each bleach system shows a characteristic fingerprint profile [73] on the AISE Dye Set. In general, aromatic and aliphatic peroxycarboxylic acids show very similar damage profiles. Imidoperoxy acids generated from nitrile quats react with different dyes (Figure 16.18) according to the various bleach active species [74]. In catalytic bleaching, the effect depends on the catalyst type. Whereas Mn-Me_3tacn causes significant damage on a number of dyes, other catalysts and especially most aerial bleach systems can be classified as color-safe (Figure 16.19).

Whereas the reactivity of a bleach system can be controlled by its concentration, selectivity is an intrinsic property. To suppress dye damage, a number of patents claim the use of agents able to interfere with the reactive bleach intermediates such as radicals or singlet oxygen [75]. In most cases, however, their effect is only minimal or dye-specific [76,77].

Sometimes dye damage is a first step to fabric damage, as a reactive intermediate in this process may be able to interact with polymeric cotton molecules, resulting in a weakening of the fiber. On a molecular level, the cellulose units are oxidized to form carbonyl compounds, and carbon–carbon bonds are broken. Under the stress conditions of the washing process, the fiber then will tear and the garment is irreversibly damaged.

Two methods are used for determining the fabric-damaging properties of bleach systems: tensile strength loss, on a macroscopic level, and the decrease in the degree of polymerization, on a microscopic level. Recently it was shown that there is only poor correlation between the results of both test methods. To obtain reliable data, measurement of tensile strength loss after 20 or 50 wash cycles is recommended [78].

Occasionally, manmade fibers are also sensitive to oxidative stress. Certain types of polymers, such as elastanes, are known to react with oxygen species or may be activated to add oxygen (autoxidation). As a long-term consequence, the fibers will lose their form-giving properties, and underwear or swimwear may lose its shape.

16.3 APPLICATION FORMS AND FINISHING PROCESSES

The broad field of use for bleaching agents covers industrial process applications, such as paper manufacture, industrial and institutional cleaning (factories, hotels, hospitals), and the household sector, with applications in laundry, dishwashing, and hard surface cleaning. In industrial applications, bleach systems are typically used as liquids, which are stored separately in tanks or cans. The dosage systems are designed for easy, simple handling of liquids. In household applications, convenient, simple use of the cleaning agents is also a primary requirement but, in comparison, many more challenges need to be tackled, especially when bleach systems are introduced into the formulations. As the patent literature shows, many attempts have been made, and many proposals

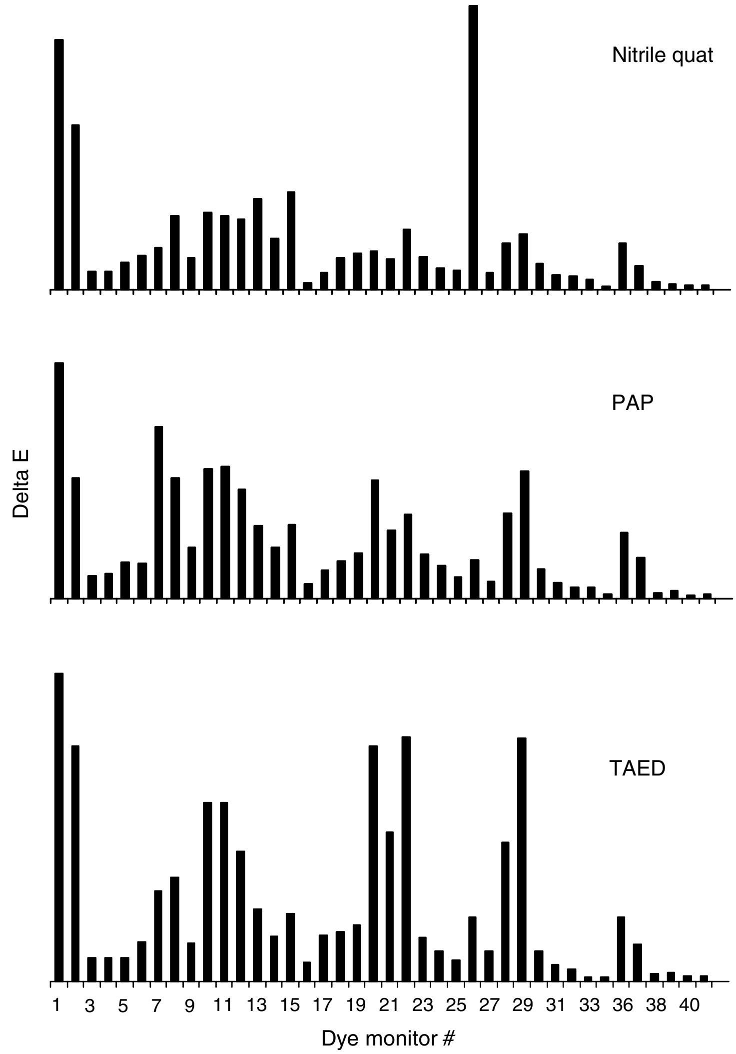


FIGURE 16.18 Fingerprints of bleach systems: Characteristic color damage profiles of TAED/PB*4, PAP, and nitrile quat/PB*4 on AISE Dye Set. (Test method taken from Luijkx, G.C., Hild, R., Krijnen, E.S. et al., *Tenside Surfactant Detergents*, 41, 156–162, 2004.)

described for incorporating bleaching agents into these consumer products. This chapter therefore focuses on the finishing of bleach systems for household applications.

16.3.1 REQUIREMENTS

With regard to the composition of common household cleaning formulations, a complex system of different ingredients has been developed over time. The surfactant or builder systems form the main part of such formulations, but a wide variety of other components is also included, such as enzymes, textile care additives, fragrances, and last but not least, the bleach system. To meet the customers' needs, each component of the cleaning formulation has to fulfill certain requirements [79]. Two main criteria require special attention:

1. A key point is the performance of the bleach system, which includes sufficient chemical and physical stability over the complete handling process through to final application in

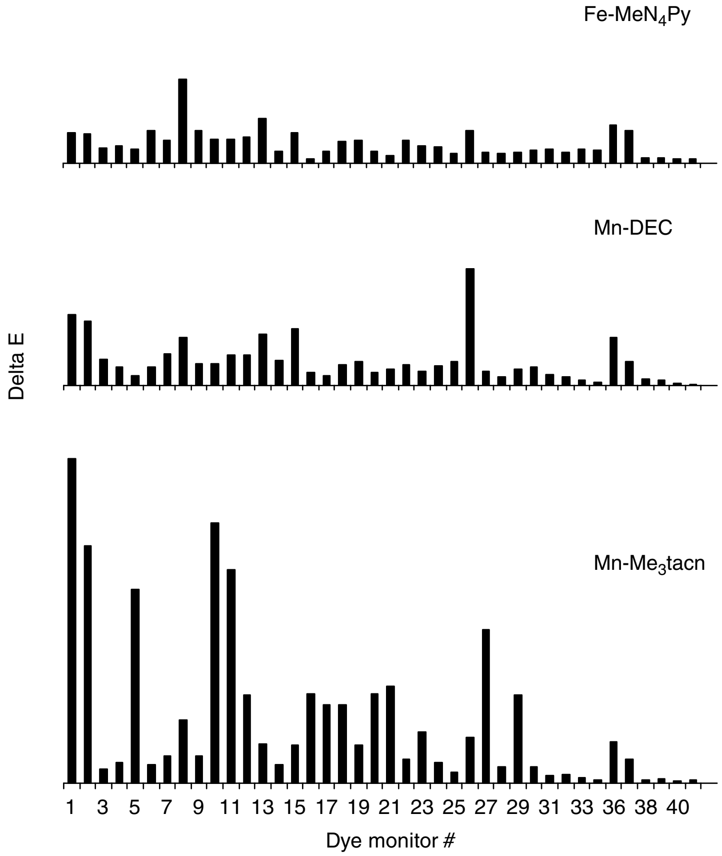


FIGURE 16.19 Fingerprints of bleach systems: Characteristic color damage profiles of Mn-Me$_3$tacn/SPC, Mn-DEC/SPC and Fe-MeN$_4$Py/air on AISE Dye Set. (Test method taken from Luijkx, G.C., Hild, R., Krijnen, E.S. et al., *Tenside Surfactant Detergents*, 41, 156–162, 2004.)

the household. In addition, it might be necessary to adjust the release or dissolution profile in a defined way to ensure an optimum performance profile (see examples for NACA-OBS in Ref. 80, SPC in Ref. 81, and mono-persulfate triple salt in Ref. 82).

2. The bleach system has to be color- and fabric-safe, which is especially important in laundry applications (see Section 16.2.9). To avoid color damages, as for example spotting (see Figure 16.20), the ingredients have to be applied in an appropriate physical form (see example for nitrile quat in Ref. 83).

If bleach and bleach activators are to be incorporated in solid formulations, additional aspects need to be taken into account [84].

- If the solid components of the detergent powders are mixed together, product separation during transport and handling must be avoided. This means that requirements need to be specified for particle size distribution (see examples for SPC and TAED in Ref. 85), bulk density, and in some cases, particle shape (see example for NOBS in Ref. 86).
- Considering handling and production of the materials, criteria such as good flowability, low caking tendency, and easy handling properties are of importance. The active ingredients should therefore preferably not show any negative properties such as a high hygroscopicity (see example for nitrile quat in Ref. 87) or low melting point, which interfere with a stable physical form.

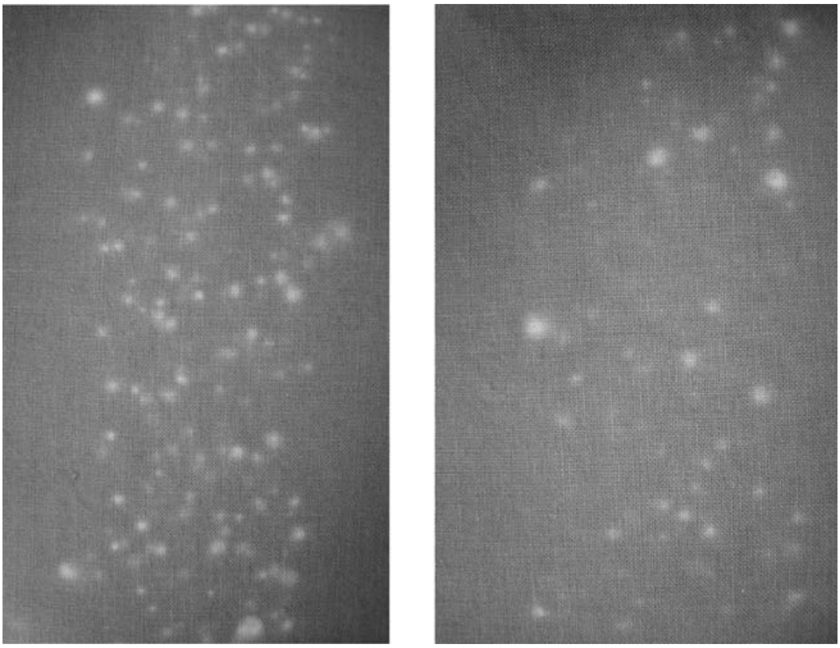


FIGURE 16.20 Dye damage caused by bleach systems: spotting on test fabrics.

- In the field of household cleaners, particularly, certain esthetic requirements also have to be fulfilled in terms of particle shape and surface, color (see example for NOBS in Ref. 88), and odor (see example on odor suppression of nitrile quats in Ref. 89).
- For safety reasons, it might be necessary to provide a special product form, mainly to minimize particle attrition and dust generation (see example for SPC in Ref. 90), but also to prevent allergic reactions (see example for KMPS in Ref. 91). In some cases, the physical properties of the bleach component itself require special attention, for example, to reduce the risk of self-decomposition (see Section 16.3.5).

These different requirements need to be balanced and optimized but, in many cases, there are conflicting performance criteria, for example, an effective coating layer to achieve chemical and physical stability may prevent rapid dissolution.

16.3.2 Additives

To achieve an optimum product profile for the bleach ingredients, in most cases, one or more suitable additives are necessary to adjust the product properties.

- Typically, these additives are used as binders, coating agents, or carrier materials for liquids. But they might also be necessary to achieve sufficient chemical stability (see example for aerial bleach catalyst in Ref. 92), improve the dissolution profile, or simply for esthetic reasons (see example for PAP in Ref. 93).
- Sometimes other active ingredients may serve as additives as well and may generate additional benefits. For example, a combination of different bleach activators makes it possible to cover the full temperature range (see example for TAED + nitrile quat in Ref. 94) or spectrum of stains (see example for TAED-DOBA in Ref. 95) in the wash.
- Difficulties may arise with respect to the compatibility of the additive with the active component as well as with other detergent formulation ingredients. For example, the storage stability of the bleach active can be improved by choosing additives that are less prone to

causing a hydrolysis reaction (see example for TAED in Ref. 96). With newly developed structures and substances, in particular, potential incompatibilities are difficult to predict and require experimentally confirmed data.

16.3.3 PROCESSING

There is a wide variety of different processes, unit operations, and combinations of several process steps available to transform the active ingredient into the desired physical appearance. The potential results of processes to adjust the appearance of the bleach ingredients are illustrated in Figure 16.21, which shows different forms of bleach active particles. Besides the simple morphology of a fine powder, it is possible to produce slightly spherical, irregular, angular, or sharp-edged granules, as well as cylindrical or almost ideally spherical particles and in some cases also colored or coated granules.

A general overview of possible process options, starting from different states of aggregation, is presented and discussed in Ref. 97.

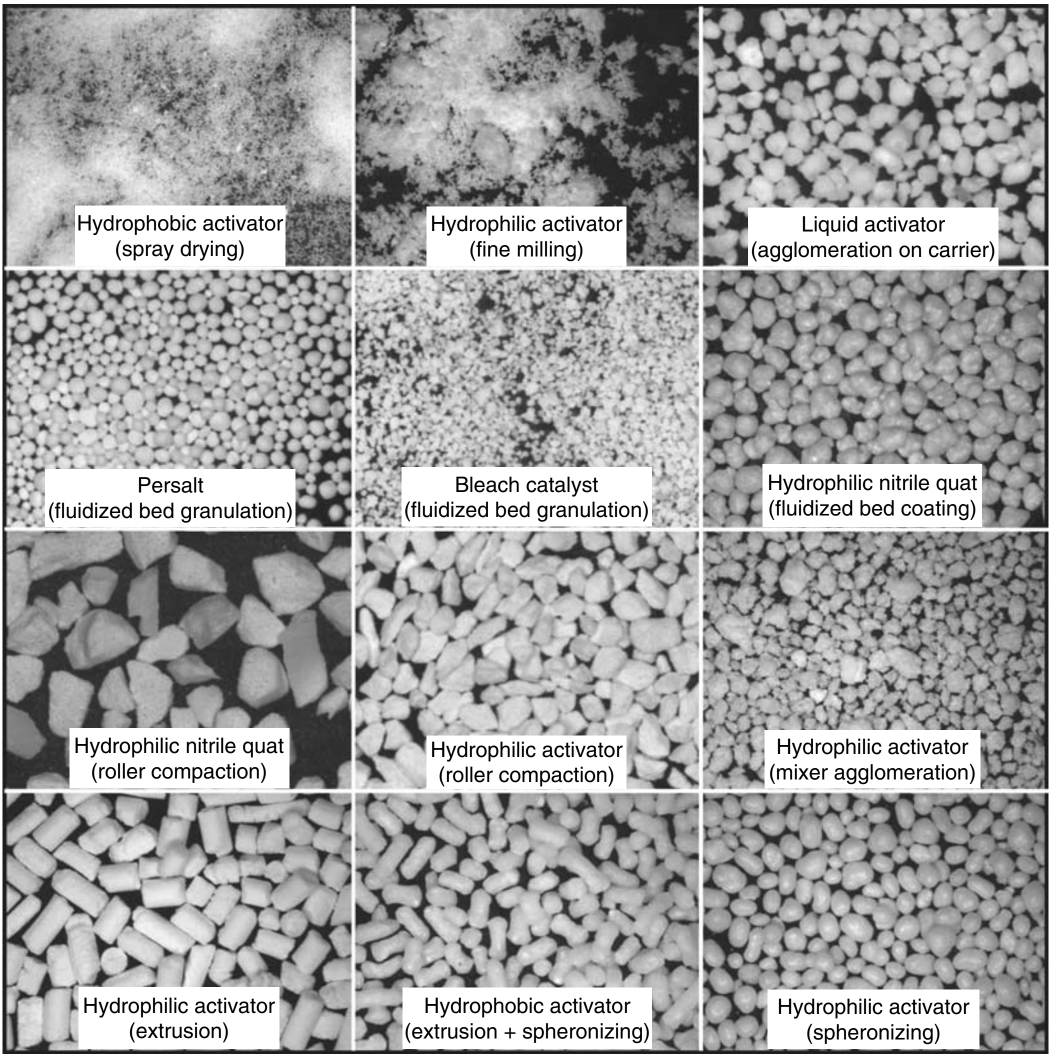


FIGURE 16.21 Appearance of solid bleach active substances.

16.3.3.1 Active Component as a Solution or Suspension

16.3.3.1.1 Spray Drying

Spray drying is a very common and well-known process for transforming a liquid active ingredient into a solid particle. Typically, the active matter is sprayed from a solution or slurry at the top of a spray dryer. For liquid atomization, several systems are available, such as nozzles (one-phase, two-phase, etc.) or atomizer wheels in different designs. The droplets are dried in a hot gas stream with co- or counter-current flow through the dryer. The dried particles are finally separated from the drying gas by means of cyclones, filters, or combinations of different units. Besides spraying conditions, the temperature profile in the spray dryer is important for the drying step and final product quality (moisture, morphology). More details may be found in Ref. 98, and an example of a spray drying process for TAED is given in Ref. 99 and for DOBA in Ref. 100. Spray drying typically generates a fine powder with a particle size of slightly <200 µm. Depending on product properties or technical features [101], larger particle sizes may also be possible.

As reported in literature, many bleach actives are chemically unstable in an alkaline detergent formulation if they are incorporated as a fine powder (see example for TAED in Ref. 102 or nitrile quats in Ref. 103). A further granulation step is therefore usually necessary to transform the fine powder obtained from spray drying into a stable granule.

16.3.3.1.2 Fluidized Bed Granulation

As an alternative to spray drying followed by further processing of the fine powder particles, the fluidized bed granulation process may be considered. This allows simultaneous drying and granulation of the liquid. A fluidized bed of the active component or further additives is generated by a heated gas stream, and one or more liquid components are sprayed onto the bed (see example for bleach catalyst with bispidon ligands in Ref. 104). Depending on the process conditions, larger particles are generated by agglomeration of wet particles or layer-by-layer growth. A more detailed description of the size enlargement principles as well as the different aspects of the granulation process can be found in Ref. 105. Examples describing fluidized bed granulation processes for SPC are given in Refs 106 and 107.

The fluidized bed process offers wide flexibility to adjust the particle properties according to the requirements. So it is possible to generate only slightly agglomerated granules with excellent dissolution properties, but also very spherical particles with an even particle surface and low risk of attrition and dust generation (examples are shown in Figure 16.21).

16.3.3.2 Active Component as a Powder

With the bleach active ingredient available as a solid, for example, from spray drying or from filtration/contact drying of a wet cake, different options may be considered for granulation [97]. Solid or liquid additives, serving as binders or stabilizing agents, are usually added prior to or during the granulation step.

16.3.3.2.1 Mixer Agglomeration

Mixer agglomeration is a standard procedure to achieve granulation of solid ingredients. Equipment suppliers offer a broad range of different types, tools, and modes of operation (e.g., batch or continuous mixers). The different mixer types are commonly classified by the Froude number Fr, which describes the energy input to the system. The Fr number ranges from $Fr < 1$ for gentle systems, such as rotary drum mixers, to $Fr > 1$ for ribbon or ploughshare mixers, and $Fr >> 1$ for high-speed mixers with high shear and very intensive mixing. More details may be found in Refs 108 and 109.

In the detergent industry, ploughshare and high-shear mixers are widely used, operated both as single devices and combination with several mixing/agglomeration steps and mixer types (see example for TAED in Ref. 110 or Ref. 111).

To achieve particle size enlargement, mixer agglomeration is carried out with granulation liquids, which might be pure liquids, solutions, suspensions (commonly all water-based systems), or melts. Since the raw granules still appear wet and sticky after the granulator, the material normally has to be posttreated in a dryer to remove excess water or a cooler to solidify the melt. Fluidized bed dryers are preferably used for this purpose. The process is completed with granule classification to obtain the target particle size fraction and recycling of fines and coarse material, including milling of oversize material. A typical process for the granulation of TAED using different solid binders and water as the granulation liquid is described in Ref. 112.

16.3.3.2.2 Compaction

Another widely used granulation principle is roller compaction, where pressure forces compact the fine primary particles together to achieve particle bonding and size enlargement. Typically, the process is operated under dry conditions, using only solid active ingredients and additives, but under certain conditions small amounts of liquids are also added. An example of the compaction of TAED with an inorganic binder is given in Ref. 113.

Roller compactors are available in different designs and can be equipped with a variety of differently profiled rollers to produce compacted material, pellets, or briquettes. Usually, the compacted product then has to be milled to the desired particle size. To minimize dust and fines, which have to be recycled back to the compaction process, selection of suitable milling equipment is important. Gentle systems, such as roller mills or sieve mills, are preferred. As Figure 16.21 shows, compacted granules appear as more irregular, sharp-edged particles.

16.3.3.2.3 Extrusion

If extrusion is used, the base powder, consisting of the bleach active ingredient and optionally other additives, has to be mixed with a plasticizer. The easiest approach is to use water as the plasticizer, which is subsequently removed by drying (see example for DOBA in Ref. 114). In many cases, plasticizers are used that soften and melt at higher temperatures (see example for nitrile quats in Ref. 115), but remain in the final particle. The plasticized product mixture is extruded through a perforated die to form cylindrically shaped strands. Typically, the diameter of the extrudates ranges from 0.7 to 2.0 mm.

To carry out the extrusion process, different types of equipment are available, for example, extruders with a single or twin screw, basket and dome extruders, or pellet presses with flat or ring dies. Besides the different equipment designs, the pressure applied during extrusion may also be an important factor to consider. Obviously, the extrusion pressure may have impact on the resulting particle properties, for example, the dissolution profile (see example described for NACA-OBS in Ref. 116). Other examples discussing the use of extrusion technology are given in Refs 117 and 118 for NOBS or similar bleach activators. The use of pellet presses for the granulation of TAED is described in Refs 119 and 120.

16.3.3.2.4 Posttreatment of Extrudates

After the extrusion process, a posttreatment step is usually necessary to size and shape the strands to the preferred particle length and shape. These types of granule are normally specified by the aspect ratio (also called L/D ratio; L = length, D = diameter) or a shape factor Ψ [121]. A typical range for the L/D ratio of detergent ingredients is L/D = 1–3; the shape factor characterizes approximation to an ideal spherical particle ($\Psi = 1$). Depending on the definition, the shape factor of a nonideal sphere is $\Psi < 1$ or $\Psi > 1$.

To obtain the required particle length or L/D ratio, the extruded strands need to be sized down. For this purpose, cutting devices operating in front of the drill holes are available, which use fixed blades, rotating knifes, or cutter wires. Different cutting technologies are described for hydrophobic bleach activators such as NOBS, LOBS, and DOBA in Ref. 122, and a device for nitrile quats is given in Ref. 123. As a result of the cutting process, the sized cylindrical particles are obtained with sharp edges that are vulnerable to breakage and dust generation. As an option, the sized granules may be treated in a so-called spheronizer or marumarizer to round off the sharp edges to form cylinders or beads with a smooth surface (see examples in Figure 16.21). Other examples describing a spheronizing process for NOBS are given in Ref. 124, and for TAED in Ref. 125.

16.3.3.3 Active Component in Melt Form

In some cases, it may be possible to isolate the active ingredients as a melt, so providing options to carry out the finishing process directly from the melt, if necessary in combination with other substances. Important parameters for the selection of a suitable process are the properties of the melt, including melt viscosity and solidification behavior.

To achieve solidification of the melt, the product has to be exposed to a cooling medium, which can be present as a cooling fluid or a cooling surface. Cooling fluids (mostly cooling gas) are utilized in spray and prill towers or drop-cooling columns. In this regard, melt flow properties are of primary importance, since the various spray systems are limited to a certain maximum viscosity. If a cooling surface is used for solidification, the melt is applied as layers, strips, or droplets onto the surface. The available equipment includes cooling belts, disks, or drums, delivering pastilles or flakes.

As an alternative to these specific melt granulation systems, previously mentioned methods such as fluidized-bed granulation or mixer granulation with suitable additives or other detergent ingredients can be used to shape particles (see examples for nitrile quat in Ref. 126 and for TAED in Ref. 127).

16.3.3.4 Coating and Microencapsulation

Coating and microencapsulation of particles or granules play a very important role in finishing bleach active ingredients. Key reasons for coating or microencapsulation are chemical stabilization of the core material and minimization of chemical interactions between the bleach active and other formulation ingredients (see example for SPC in Ref. 128). Another important function of coating is to obtain a defined dissolution or active release profile. As an example illustrating the achievement of both goals, the coating of persalts to optimize the activity of enzymes may be considered. Owing to the delayed release of the coated persalt, the enzymes may be active prior to the bleaching step, with reduced activity loss from degradation (see examples for PB*1 and SPC in Ref. 129). Another approach to precise adjustment of the dissolution profile is reported in Ref. 130, where SPC is prepared with a double coating, consisting of an inner and an outer coating layer.

Other reasons for coating or microencapsulation may include protection of the core from moisture (see example for nitrile quats in Ref. 131) or improvement of mechanical stability to prevent dust generation, which may be particularly important for critical substances such as sensitizers (see example for bleach activators in Ref. 132). Whereas coatings are typically applied to particles and granules of larger dimensions (e.g., >100 μm), microencapsulation is commonly used for small particle sizes (e.g., <100 μm). For both technologies, but especially in the case of microencapsulation, an efficient release mechanism for the enclosed bleach active is essential. The mechanisms normally used include change in temperature, pH, or concentration, or simply mechanical impact during the application. An example of the temperature-controlled release of PAP is mentioned in Ref. 133. The product properties of both the core and coating substance (e.g., compatibility, surface wettability), as well as the function of the coating, need to be considered in selecting the appropriate coating or encapsulating agent.

16.3.3.4.1 Coating

A technology frequently employed to apply a coating layer onto primary particles is a fluidized-bed process but, in principle, it would also be feasible to use some types of mechanical mixer (see example of TAED coated with fatty acid in Ref. 134). With both methods, even distribution of the coating layer on the particle surface is of primary importance. To achieve this requires both a suitable distribution system for the coating agent and uniform movement of the base particles along the liquid distribution system. To fulfill these criteria, specially designed mechanical systems and fluidized-bed technologies have been developed (an overview of fluidized-bed technologies is given in Ref. 105).

Typically, coating agents may be applied as solutions, suspensions, or melts, which then require postdrying or postcooling to solidify the coating layer. In this respect, the fluidized-bed process offers the advantage of being able to spray on the coating liquid and solidify the coating layer simultaneously, which provides greater flexibility during processing; better coating quality may also be expected. Examples of coating PAP in a fluidized-bed process are given in Refs 135 and 136.

16.3.3.4.2 Microencapsulation

In microencapsulation technology, different particle structures as well as different processes are possible [137,138]. The particle may have a mononuclear structure, consisting of a core and a shell, or polynuclear structure, where many cores are encapsulated in one shell. Finally, the particles may have a matrix structure, where the core material is homogeneously distributed in a shell material. A possible disadvantage of such a delivery system is that parts of the core substance may not be completely covered by the shell material (especially with high payloads).

The available technologies include typical chemical processes, such as polymerization or polycondensation, and physical processes. A further distinction is made between physicochemical processes, including coacervation and supercritical CO_2-assisted microencapsulation, and physicomechanical technologies, such as spray drying or multiple-nozzle spraying.

In relation to detergent ingredients, different microencapsulation technologies are often used for fragrances and flavors. Coacervation and spray drying are mentioned in various patent applications (see example of coacervation in Ref. 139 and spray drying in Ref. 140). In the case of bleach active substances, microencapsulation of TAED using a polycondensation process is described in Ref. 141, and a coacervation process for the encapsulation of PAP is mentioned in Ref. 142. In both cases, the use in liquid applications is intended.

16.3.3.5 Specific Approaches

As described, a wide range of techniques is available to develop a suitable physical form for the bleach active ingredient. Nevertheless, a substantial number of substances have properties that demand a specific solution. As these solutions are very product-specific, only general principles can be discussed.

The substance in question may exhibit very difficult physical properties, which require special attention to develop a product with acceptable characteristics (e.g., flow properties, physically stable solid). Problems that frequently have to be addressed include:

State of aggregation	Liquid under ambient conditions
High hygroscopicity	High moisture sensitivity to the point of complete liquefaction
Low melting point	High risk of caking at moderately elevated temperatures
Solubility	Poor dissolution and reduced performance during application

If a liquid (bleach) active substance has to be transformed into an appropriate solid form, a suitable solid carrier material is necessary onto which the liquid may be absorbed at high concentrations without lumping or caking. The carrier substances preferably used should have a large specific surface area and be compatible with the cleaning formulation. Materials such as silicas, zeolites, inorganic salts, or cellulose-based materials are typically used as the carrier. The preferred technologies are mixer and fluidized-bed processes. For example, the absorption of H_2O_2 solution onto silicas is described in Ref. 143.

In the case of substances with high hygroscopicity or low melting point, stabilizing additives also need to be used to help control the critical physical properties. Quite obviously, high dilution of the active substance with a stable additive could counter the effect of these disadvantageous properties, but the required dilution levels might not be feasible. Specific product formulations therefore have to be found that make it possible to obtain a sufficiently high active concentration and acceptable properties at the same time. As a possible option, combinations with other detergent ingredients could be considered, for example, as a cogranule with different bleach activators. Examples describing the development of a stable granule form for a hygroscopic nitrile quat activator are given in Refs 94 and 144.

To improve solubility, an appropriate particle formulation with fast-dissolving additives might be tried first (see example for NOBS in Ref. 145). Alternatively or additionally, disintegrants may be used. This is described in Ref. 146 for a peroxycarboxylic acid combined with swellable polymers such as carboxymethylcellulose. On the other hand, the primary particle size of the active material prior to granulation could be considered, since smaller particles typically show a shorter dissolution time, and if residues are inevitable, are likely to be less visible. If necessary, combinations of both measures (suitable additives and small particle size) may be employed. Several examples are described for the granulation of a manganese catalyst in Ref. 147.

16.3.3.6 Implementation

Once a suitable formulation and physical form of the bleach active substance have been achieved, the products may be introduced into the specific household cleaning agents. These products are usually available in the form of powder, granules, tablets, or liquids.

For use in powders and granules, the tailored bleach active particles are normally added to the base powder in a postdose step, taking into account the previously mentioned chemical and physical interactions with the other ingredients.

With regard to tablets, certain requirements have to be met in terms of physical properties (e.g., particle size, flowability, stickiness) to ensure a trouble-free manufacturing process. On the other hand, multiphase tablets offer the benefit of separating critical components from each other by portioning them into different phases. For example, in Ref. 148, the separation of SPC and TAED into two different tablet phases to increase the storage stability of both components is described. In Ref. 149, the introduction of a third phase is mentioned, which acts as an inert barrier between the two outer phases containing SPC and TAED, respectively. The barrier phase may help to prevent migration effects, and if designed as an effervescent system, improves the dissolution rate of the tablet.

The use of bleach in liquid systems and the related difficulties will be described in more detail in Section 16.4.3. If the incorporation of solid bleach active ingredients is considered, storage stability, prevention of uncontrolled particle sedimentation, and liquid rheology all need to be addressed. Various approaches are described to achieve sufficient storage stability of the bleach components. These mainly involve particle coating and encapsulation (see example for SPC with a double-coating in Ref. 150). To provide stable suspensions containing solid bleach components, a defined particle size of the active and a specific formulation are important. For example, the bleach active has to be milled to a defined maximum particle size prior to incorporation in the liquid formulation. Additives to prevent particle sedimentation may include polymers or thickeners (see example for TAED in Ref. 151). Alternatively, the use of solvents instead of aqueous systems is also reported (see example for PAP in Ref. 152).

16.3.4 PRODUCT CHARACTERIZATION

Once the appropriate treatment process has been selected to transform the bleach active into a suitable physical form, a manufacturing process has to be developed. Alternatively, sourcing from a supplier can be considered. In both cases, the product properties of sample material must be examined, and the fit to the defined requirements needs to be assessed. To characterize the product and powder properties of the finished (solid) bleach components, a wide variety of test methods is

TABLE 16.2
Product Characterization—Examples

Property	Test Method
Particle size distribution	Sieve analysis, laser diffraction
Particle shape, morphology	Microscope, image processing
Bulk density	ISO apparatus, jolting meter, measuring cylinder
Flow and handling properties	Shear testers, angle of repose
Caking (storage, transport)	Shear testers, specific cake test
Caking (mechanical impact)	Kneader, mixer, specific stress test
Physical stability	Hygroscopicity test, hot-bench, specific storage tests
Attrition, dust generation	Shear tester, dust-meter, specific attrition test
Solubility	Dissolution test under specific conditions
Chemical stability	Titration, performance test or specific test after storage
Moisture	Karl Fischer titration, infrared dryer, oven

available. Table 16.2 gives an overview of typical product properties to be analyzed and examples of possible test methods.

The most common tests involve analytical data such as particle size, particle size distribution, and particle shape. The standard method for more granular materials and coarser powders is sieve analysis [153], whereas for fine materials laser diffraction is well established [154]. If the particle shape and particle shape distribution are of special interest, optical systems are preferred, in which a multitude of single particles are detected by a camera and pictures of the particles may be analyzed [155].

Important criteria for easy, problem-free processing and handling are the flow properties and caking behavior of the bleach active materials. For assessment and characterization of bulk solids, a variety of test methods have been developed in the past (overview and comparison in Ref. 156). To select the appropriate procedure, it is necessary to consider how the results will be interpreted. If the focus is on comparative measurements of samples against a standard material, qualitative methods could be advantageous. These can be set up and carried out very easily [157]. With regard to the layout and design of equipment pieces in a production unit, such as silos, bins, and hoppers, test methods and procedures that can deliver quantitative data are preferable. A comprehensive summary of the methodology and related topics is given in Ref. 158, and a standard method to determine the flow properties of bulk solids is described in Ref. 159.

For other powder properties, such as bulk density, particle attrition, or dustiness, some standardized methods [160] exist that may serve as a guide to establishing a test method but may not be applicable in every case. For example, the dustiness of a material is a matter of definition, depending on the initial particle size of the tested product. If the determination of dustiness is combined with testing the attrition stability of the particles, the stress mechanism also has to be considered. Consequently, the methods for determining dustiness and particle attrition are mostly very specific to the product and the stress mechanism that is to be simulated [161]. In many other cases (e.g., solubility, moisture, and temperature sensitivity), no general standardized tests are available, and different approaches are used to describe the powder properties (see examples in Refs 110 and 162).

16.3.5 SAFETY ASPECTS

In producing, handling, and processing bleach active substances, safety issues obviously also need to be addressed. Usually, the typical questions concerning physicochemical properties (e.g., thermal stability, dust explosiveness, or minimum ignition energy) have to be considered. In addition, the peroxy bleaching agents such as persalts (e.g., sodium perborate or sodium percarbonate) or peracids (e.g., PAP) pose an additional hazard owing to their chemical structure (O-O linkage). As a result, hazard assessment of these peroxy substances requires special attention [163]. Besides decomposition, measurements such as differential scanning calorimetry, differential thermal analysis, and determination of the Oa content, thermal activity monitor, oxygen balance limits, and self-accelerating decomposition temperature are important. On the basis of these data, recommendations, and measures for safe handling, processing and storage may be specified, for example, the appropriate storage volumes for the peroxy substances or definition of suitable formulation additives. For example, phlegmatizers may be added to the particles to control thermal stability or exothermic reactions. Some substances for use in handling PAP are described in Refs 164 or 165. Since it is also known that contact with other materials, such as impurities, water, metal traces, or simply other organic substances may trigger a decomposition reaction of the peroxy bleaches, many efforts have been made to stabilize these materials. The use of suitable stabilizing agents and application of protective coating layers have gained particular importance. Examples of the stabilization of sodium percarbonate are given in Refs 166 and 167.

16.4 BLEACHES IN HOUSEHOLD APPLICATIONS

The composition [2], properties [168,169], and environmental behavior [170] of bleach-containing powder and liquid detergent formulations have already been reviewed in detail in other parts of this series. In this chapter, we will therefore concentrate mainly on the optimum use of bleaching systems in heavy-duty powder detergents (HDPDs) and heavy-duty liquids (HDLs); formulation and application examples are given in the tables.

16.4.1 BLEACH-CONTAINING DETERGENTS: MARKET OVERVIEW

Along with surfactants and builders, the bleach system significantly contributes to the cleaning performance of a detergent. Its main tasks are

- Oxidative destruction of persistent stains, which are not removable by dissolution or solubilization
- Decolorization of dissolved dye particles to prevent dye transfer and to inhibit graying of white fabrics
- Scavenging of washwater chlorine to prevent color fading
- Improvement in the overall whiteness of garments after multicycle washes
- Removal of malodorous components to give the laundry a clean, fresh smell
- Disinfection of the laundry, removal of allergens [171], and improvement of hygiene
- Prevention of biofilm formation [172] and mold spore proliferation in the washing machine

Hygiene aspects, in particular, are becoming increasingly important in view of the global trend toward lower wash temperatures, shorter wash times, and reduced water consumption. Under such conditions, resistant bacteria, viruses, and fungi are able to survive the laundry process [173]. The occurrence of new diseases such as SARS or bird flu will increase the risk of transferring infections. Bleach-containing detergents help ensure a high standard of hygiene.

In detergent formulations, stain removal is not a function of the bleach alone; surfactant cocktails, enzyme mixes, and polymeric performance boosters also substantially assist this process. The bleach effect is generally additive in nature to detergent soil removal, but synergisms among the systems may create extra benefit. Therefore, the design of bleach-containing detergents follows two strategies:

1. By fully exploiting all synergies, the bleach system can become an essential component of the formulation, which contributes not only by bleaching but also by interacting with other ingredients to improve their overall cleaning performance. As a result, the formulation

becomes more cost- and volume-effective. However, the downside of this strategy is that in reformulation work one bleach system cannot simply be replaced by another one without reducing the performance of the detergent.

2. More frequently, the bleach system is used as an add-on component of the formulation, whose effect is additive in nature to the washing action of the other ingredients.

Although over the past 30 years a large number of quite different bleach systems have been described in the literature, and some have been extensively test-marketed, only a few products have gained commercial attention. With an estimated annual consumption of ~75 kt, TAED is the most widely used bleach activator for laundry applications. In combination with perborate or percarbonate, it is the major component of nearly all European HDPDs. Within the past decade, new markets for TAED have opened up in Eastern Europe, North Africa, the Middle East, and parts of South America.

Under cold wash conditions, hydrophobic bleaching activators are preferably used, as their peracids are more reactive and show a certain affinity for dirt, resulting in reasonable bleaching even in diluted detergent solutions. In addition, the surface-active activator supports the surfactant system in removing particularly persistent dirt, such as dingy stains from collars, sleeves, and socks. Currently the activator NOBS dominates the North American market, whereas in Japan and parts of Asia the related systems LOBS and DOBA are in use. The global consumption of hydrophobic activators amounts to approximately one third of the quantity of TAED.

Today, the use of bleach catalysts and preformed peracids is still of minor importance. Although under cold wash conditions catalysts are more effective than activators, this technology has hardly been used so far. The detergent industry is still extremely cautious to avoid a disaster such as occurred with Mn-Me_3tacn more than 10 years ago. It was only in 2006–2007 that a manganese-based catalyst was used again in Europe, initially in stain remover salts and shortly afterwards in a heavy-duty powder detergent. Here it is combined with specially developed enzymes in an ecofriendly, low-temperature detergent. Parallel with this development, an increased use of photobleaches (sulphonated Zn or Al phthalocyanines) is currently being observed in sunbelt regions all over the world. Even in several European detergents, photobleaches are incorporated, but more as blueing agents than for their original purpose.

The use of volume-effective preformed peracids should be facilitated by the current trend toward more compact formulations. Stability problems in alkaline compositions and economic reasons, however, still prevent more widespread use. The only peracid of commercial importance is PAP. In mid-2007, a color detergent powder containing PAP was introduced in Switzerland, claiming the color-safe properties of the peracid. The future of PAP is currently seen in liquid applications, especially when dual-chamber bottles are used. A PAP-containing HDL was intensively test-marketed some years ago in North America, and a similar concept has been used successfully in a Swiss liquid detergent since 2006.

16.4.2 BLEACHES IN POWDER DETERGENTS AND TABLETS

16.4.2.1 Optimized Conditions

The use of oxygen bleaches in powder detergents has a long history in Europe. As early as 1907, a mixture of perborate, silicate, and soap was sold as the first HDPD. Used at boiling temperature, it saved time and effort, and rapidly became a tremendous market success. As a consequence of the oil crisis in the 1970s, bleach activator technology was introduced, which allowed wash temperatures to be reduced from 90 to 60°C without performance shortfalls. Now more than 80% of all European HDPDs contain TAED. Properties of HDPDs and tablets are given in Table 16.3.

Historically, European washing powders contain high amounts of persalts. Even after the introduction of activator technology, formulations with more than 20% perborate were state of the art. From the stoichiometric point of view (for complete perhydrolysis of one molecule of TAED, two

TABLE 16.3
Properties of European Powder Detergents and Tablets

	Regular Powders	Concentrated Powders	Detergent Tablets
Dosage (g/wash)	95–110	65–80	65–80
Bulk density (g/L)	600–950	800–1100	1000–1300
SPC content (%)	8–12	12–15	12–18
TAED content (%)	1–3	4–8	3–5
Ratio persalt: TAED	4–8:1	2–3:1	3–4:1

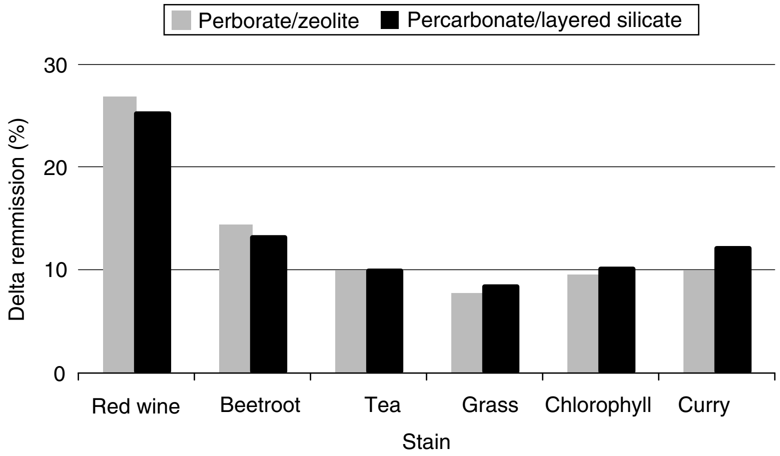


FIGURE 16.22 Bleach performance of TAED/PB*4 on various stains at 40°C; effect of detergent composition.

molecules of hydrogen peroxide are required), weight-by-weight ratios of 1 to 1 should be sufficient to gain full performance. In practice, to take care of any losses of persalt during storage or by contact with catalase, a ratio of TAED to persalt of 1:2 to 1:3 is recommended. This ratio is currently only achieved in concentrated powder detergents. Depending on the detergent type, a TAED content of up to 8% is incorporated in brand products. Higher concentrations do not make economic sense, as they will not significantly improve the bleaching result.

In North American detergents, much lower levels (1–5%) of perborate or percarbonate are used, mainly for scavenging chlorine residues in the washwater to prevent long-term dye damage. In activated powder formulations, 1–4% NOBS is combined with 3–8% percarbonate.

Changing detergent ingredients may have an impact on the performance of a bleach system, as the following case study shows. Under cold wash conditions, zeolite-based builder systems frequently cause consumer complaints, as white particulate residues stick on the fabric. For this reason, in some formulations, zeolite has been replaced by a water-soluble builder system, comprising a mixture of soda ash, layered silicates, and polymers. A parallel replacement of perborate by percarbonate shifts the pH of the formulation by about one unit into the alkaline range. As a result, the bleach performance of the reformulated detergent differs significantly from that of the old one, although the TAED concentration remains unchanged (Figure 16.22).

pH control is a key factor in optimizing the bleaching performance of a detergent. At the beginning of the wash process, the alkalinity of percarbonate favors the rapid release of the bleach-active peracid. On completion of perhydrolysis, the pH should ideally drop by one unit to support the bleach chemistry. In practice, this pH shift is induced by the release of an organic acid such as citric acid or polycarboxylic acid from a coated particle into the washing liquor [174]. The reaction is triggered either by temperature, so that the coating material, usually a wax, melts during the heating phase, or by time-delayed dissolution of a fatty acid via a neutralization step.

A wide variety of technical options is used to improve the storage stability of bleach systems under alkaline conditions and to avoid negative interactions with sensitive ingredients such as enzymes, optical brighteners, or fragrances (see Section 16.3). Controlled release of these compounds, first the enzymes, followed by bleach, and last the perfume, guarantees complete soil and stain removal and adds whiteness as well as a fresh scent to the cleaned garment.

16.4.2.2 Synergistic Effects

Positive interactions of bleach with other detergent ingredients provide an opportunity for value creation via synergies (examples are given in Table 16.4):

- To improve performance on a broader range of stains
- To allow the detergent to be used over the full temperature range and
- To increase the system's biocidal activity

TABLE 16.4
Synergism of Bleach Systems

Patent and Year	Inventors and Company	Synergistic Mixture	Benefits Claimed
EP 0 257 700 (1988)	P. S. Sims et al., Unilever NV	TAED, NOBS	Improved performance on multistained fabrics
U.S. 5405412 (1995)	A. D. Willey et al., Procter & Gamble	*N*-acyl caprolactam, NOBS	Effective bleach system under mixed soil conditions
WO 96/17920 (1996)	A. Wilde et al., Henkel	TAED, Nonanoyl succinic imide	Improved performance at low temperature
WO 97/35950 (1997)	T. Wehlage et al., BASF	TAED, secondary amine	Improved removal of chlorophyll stains
GB 2 323 371 (1998)	R. B. Hall et al., Procter & Gamble	PAP, cationic surfactants	Improved removal of greasy stains
WO 99/25796 (1999)	E. L. M. Lempers et al., Unilever PLC	TAED, polyhydroxy fatty acid amide	Stain removal enhancer
U.S. 5998350 (1999)	M. E. Burns et al., Procter & Gamble	BCL, NOBS, lipases	Improved cleaning performance
EP 0 699 232 (1999)	A. D. Willey et al., Procter & Gamble	TAED, BCL	Rubber safe bleach
WO 00/15750 (2000)	K. H. Baker et al., Procter & Gamble	Hydrophobic bleaching agents, TAED	Reduction of gram-positive and gram-negative bacteria
EP 0 968 266 (2000)	A. T. Brooker et al., Procter & Gamble	NACA-OBS, cationic surfactants	Improved performance on greasy stains
EP 1 122 300 (2001)	N. Ogura et al., Kao Corp.	Nitrile quat, NOBS	Improved bleach and dye transfer inhibition
WO 02/083829 (2002)	E. Haque et al., Warwick Int.	TAED, Sulfophenyl carbonates	Improved performance at low temperature
WO 2006/027178 (2006)	G. Reinhardt et al., Clariant	TAED, TADHT (triacetyl dioxo hexahydrotriazine), DOBA	Improved performance at low temperature
WO 2006/027179 (2006)	G. Reinhardt et al., Clariant	PAP, TAED, TADHT	Improved performance at low temperature

Mixtures of TAED and DOBA, for example, improve performance on multistained fabrics [100]. Whereas their effect is additive in nature on red wine and grass, significant benefits are seen on tea, curry, and other stains. Performance increases of about 30% are achievable. In addition, the combination of TAED with DOBA also reduces the bacteria count. The bacteriostatic action of the peracetic acid is supplemented by the action of the hydrophobic peroxydecanoic acid, making it possible to destroy numerous gram-negative and gram-positive bacteria.

To improve the cold-water performance of a European HDPD, the addition of a nitrile quat is most beneficial. Whereas the peroxyimidic acid formed is active at 20–40°C, the peroxyacetic acid covers the high temperature range of 50–90°C. The detergent can therefore be claimed as suitable for use at all temperatures ranging from 20 to 90°C. In such mixtures, synergistic benefits arise mainly between 40 and 60°C.

Synergistic effects are also frequently observed in combinations of hydrophobic bleaches with cationic surfactants such as hydroxyethyl quats. It is assumed that deposits of lime soap on stained fabrics prevent the interaction of bleach with oily and greasy stains. The cationic surfactant seems able to reduce the lime soap layer and diminish the interfacial tension between the fabric and the wash solution, thereby facilitating interaction between the bleach and stain. In addition, the negatively charged peracid may form a neutral complex, which might penetrate into the stain more easily. Similar advantageous interactions are found between TAED and secondary amines, or between PAP and ammonium compounds.

16.4.2.3 Performance Boosters

Since common bleach activators lack reactivity below 40°C, several attempts have been made to boost their performance by adding on catalytically acting molecules. In the 1980s, the use of sodium bromide [175] was recommended, which then forms hypobromite in the wash process—an effective but not environmentally friendly compromise.

At the beginning of the 1990s, certain sulfonimines were recognized as potential performance boosters for TAED. In reaction with peroxyacetic acid, highly reactive oxaziridines are formed, which act as oxygen transfer agents, being active at 10–20°C. Whereas most linear sulfonimines decompose during the reaction, cyclic derivatives such as 3,4-dihydroisoquinolinium quats, especially *N*-methyl-3,4-dihydroisoquinolinium-tosylate (IQT), are reasonably stable and act catalytically in the process [176]. A mixture of 1% TAED and 0.01% IQT outperforms 5% TAED at 20°C.

Under certain conditions, positively charged quaternary imine salts may cause unacceptable levels of dye damage. Overall negatively charged or zwitterionic derivatives (IQZ) were found to provide improved safety profiles [177]. Used in relatively small amounts (0.01–0.05%) in combination with NOBS or TAED (1–5%), they have enhanced enzyme compatibility and provide effective bleach performance at an application pH of 8–10 and water temperatures below 20°C [178].

16.4.3 BLEACHES IN LIQUID DETERGENTS

16.4.3.1 Concepts

The market share of HDLs is rapidly growing all over the world. Most consumers prefer these products because of their advantages over powder products:

- They are easy to measure and dose without generating dust.
- They dissolve rapidly and uniformly at low temperature, without leaving solid residues on the fabric.
- The liquid can be used for prespotting heavily soiled laundry.

In general, HDLs contain similar ingredients to their powder counterparts, but they usually lack a bleach system. To compensate for this, HDLs *with bleach alternative* often contain higher amounts of complexing agents for improved tea stain removal or optical brighteners to provide whiteness for consumers.

The incorporation of an activated bleach system into an HDL is still one of the biggest challenges in formulation technology, as the three basic components of a bleach system (hydrogen peroxide, activator or catalyst, and alkalinity) will normally decompose as soon as they come into contact with each other.

The literature describes several technologies to overcome this problem (examples are given in Table 16.5):

- Weak acidic or neutral formulations containing peracids and a pH jump system
- Spatial separation of the sensitive components by using a multicompartment device for storage
- Anhydrous HDL formulations in which water is replaced by an organic solvent to suppress negative interactions
- Use of aerial bleach systems, which do not require the presence of a peroxide source

16.4.3.1.1 Low-pH Formulations

Preformed peracids are relatively stable in liquid formulations at a slightly acidic pH. For improved storage stability, peracids of low water solubility such as PAP are preferred. Structured liquids or thickener systems increase the viscosity of the formulation and prevent the sedimentation of the peracid. Mixtures of linear alkylbenzene sulfonates or secondary alkanesulfonates with fatty acids are typical examples. Alternatively, two nonionic surfactants, for example, C14/15 fatty alcohol ethoxylate with 8 EO in combination with a C11 alcohol ethoxylate (3 EO) can be used for this purpose. By altering the concentration and weight ratio, viscosity can be varied over a wide range. Three to eight percent of milled PAP powder are easily incorporated [179]. Chelating agents are added to inactivate metal traces that might induce decomposition of the peracid. Such formulations have long-term physical and chemical storage stability in the pH range 3.5–6.0. However, as long as their pH is below neutral, such formulations are not very efficient in soil removal.

By incorporating a pH jump system, it is possible to shift the pH of the formulation during application into the alkaline range. Well-known examples are polyol-borate complexes, which in concentrated form have a pH between 4 and 6. When diluted in the wash liquor, the complex dissociates, liberating the borate ion, and thus resulting in a pH shift into the alkaline range. Current systems consist of sugars and boron compounds such as borax or boric acid [180]. Mixtures of amines and zinc salts show similar properties [181]. Simplified alternatives are prepared by coating alkalinity sources with a material that dissolves only in the diluted wash liquor or at higher washing temperature.

16.4.3.1.2 Multicompartment Devices

Packaging technology has made considerable progress over the past 10 years, allowing inexpensive production of multicompartment devices that facilitate spatial separation of sensitive bleach components from other detergent ingredients during storage. A number of packaging concepts for multicompartment systems, with in some cases amazingly simple but often highly complex dispensing devices, have been described in the patent literature (examples see Table 16.5).

In 2002, a TAED-containing liquid detergent in a dual-compartment bottle [182] was introduced in the Dutch market. It contained a clear blue phase with ~6% hydrogen peroxide, whereas in the white phase a surfactant mixture and ~4% TAED powder were incorporated. The phases had a pH of 8.5 and 7.0, respectively, resulting in a final pH of ~8.2. Both phases had similar viscosities to ensure uniform dispensing. Before starting the washing process, the two phases were mixed in equal amounts in the dispensing container provided, and subsequently added to the wash water. In this way, the advantages of liquid detergents could be combined with the benefits of active oxygen bleaching.

TABLE 16.5
Applications of Bleach Systems in Liquid Detergents

Patent and Year	Inventors and Company	Bleach System	Benefits Claimed
EP 0 217 545 (1985)	R. J. Green et al., Unilever NV	TAED, anhydrous perborate	Anhydrous HDL with improved storage stability
DE 3829087 (1989)	G. Broze et al., Colgate-Palmolive	TAED, perborate	Anhydrous HDL with improved storage stability
EP 0 564 250 (1993)	J. L. Coope et al., Unilever PLC	Amido or imido organic peroxyacid	Structured liquid with acid or neutral pH, containing a pH jump system
WO 99/00481 (1999)	A. Meyer et al., Procter & Gamble	Bleach activators, persalts	Nonaqueous liquid detergent comprising organic acid to reduce solubility of bleach system
WO 99/00482 (1999)	J. P. Boutique et al., Procter & Gamble	Bleach activators, persalts	Nonaqueous liquid detergent with water content <1%
WO 99/64556 (1999)	D. Perry, Procter & Gamble	NACA-OBS, perborate	Nonaqueous liquid detergent comprising gasified particles
WO 01/000765 (2001)	F. De Buzzaccarini et al., Procter & Gamble	PAP, H_2O_2, catalase, dual-compartment bottle	Effervescent systems to improve solubility of PAP
WO 01/16281 (2001)	K. F. M. Depoot et al., Procter & Gamble	PAP, dual-chamber bottle	Improved stability of the suspension by use of polyesters
WO 02/099026 (2002)	N. T. Becker et al., Genencor	PAP, H_2O_2, catalase	Enhanced dissolution of solid material by effervescent system
WO 2004/053038 (2004)	R. Weber, Henkel	PAP	Liquid detergent for delicate fabric containing low-temperature bleach system
WO 2004/053042 (2004)	H. D. Speckmann et al., Henkel	PAP, enzymes, multichamber bottle	Liquid detergent for delicate fabric containing low-temperature bleach system
WO 2005/035707 (2005)	S. Scialla et al., Procter & Gamble	PAP, enzymes, dual-chamber bottle	Improved performance by separating bleach and enzyme during storage
EP 1 717 302 (2006)	K. Kleeli et al., Mifa	PAP, dual-compartment bottle	Sulfosuccinate as bleach stabilizer
EP 1 717 303 (2006)	K. Kleeli et al., Mifa	PAP, dual-compartment bottle	Improved low-temperature performance

Also in 2002, a bleach-containing HDL in a dual-chamber bottle [183] was test-marketed in North America [184]. One chamber contained a suspension of PAP in combination with hydrogen peroxide, and the surfactant systems and a certain amount of the enzyme catalase were stored in the second chamber. By mixing the two liquids, the enzyme destroyed hydrogen peroxide, the resulting effervescent system improved the dissolution of PAP, and the foam that was generated signaled some kind of performance to consumers. A similar concept of an HDL with bleach was introduced in Switzerland in 2006. The formulation contains a PAP suspension as the active ingredient. However, the formulation concept and design of the dual-chamber bottle [185] are simplified.

16.4.3.1.3 Anhydrous Formulations

Anhydrous HDL formulations are characterized by high concentrations of active ingredients, which allow lower quantities to be dosed. To formulate these product forms, solid detergent components are suspended in mixtures of liquid surfactants and non-aqueous solvents. Application examples are given in Table 16.5. Particularly suitable surfactants are fatty alcohol ethoxylates or propoxylates, and preferred solvents are ethylene glycols, higher diols, glycol ethers, or low-molecular weight polyethylene glycols. Solid ingredients, such as specially dried LAS powder, alkalinity sources, and builders, are incorporated by grinding them all together in a ball mill. Traces of water are removed by drying over molecular sieves, if necessary. In the last stage, the bleach system is added.

16.4.3.1.4 Aerial Bleach Systems

Several years ago it was recognized that certain Mn- or Fe-based catalysts are able to use oxygen from air in certain bleach reactions. The catalysts described work very well at low temperatures on colored oily food stains. The incorporation of such bleach systems in a liquid detergent is facilitated by the fact that no hydrogen peroxide is required for activation; the catalyst can be stored together with other detergent ingredients in one bottle. Formulation and application details are given in Table 16.6. As the mechanism of the bleach process [186] is related to the natural autoxidation/cooxidation process, the bleach reaction is still ongoing when the stained fabric is removed from the washing liquor. Tumble drying or ironing will accelerate and complete chromophore destruction. Full bleach effects are only seen on the completely dry garment.

16.4.4 OXYGEN-BASED BLEACH BOOSTERS

16.4.4.1 Stain Remover Salts

In many parts of Europe, oxygen-based stain remover salts (in German: “Fleckensalze”) have been used for decades. In recent years, as a result of lower washing temperatures and concern about chlorine bleach, their market penetration has also increased significantly in other parts of the world, especially in North America [187]. These products mostly benefit from the advantages of oxygen bleach: color-safe, nonyellowing, and environment-friendly. As multifunctional additives, they are used in many indoor and outdoor applications for destaining, deodorizing, whitening, and sanitization.

All dry oxygen bleaches contain inorganic peroxygen compounds, mostly percarbonate. The product class is subdivided into three categories,

1. Ultra concentrates with an SPC content of more than 80%
2. Concentrates with 50–80% of persalt
3. Multiaction powders with <50% persalt, but with special ingredients, such as optical brighteners, photobleaches, enzymes, or dye transfer inhibitors

Whereas in North America most powders are nonactivated, European formulations frequently contain TAED as a bleach activator, 2–3% in regular brands, 8–12% in premium brand products.

To achieve full bleach performance, nonactivated formulations often contain sodium carbonate or layered silicates to increase the application pH, as the perhydroxyl anion is the bleach active species. Formulations containing bleach catalysts also work best at high pH. In contrast, TAED-based products often contain a certain amount of acidification agent, such as citric acid or sodium bicarbonate for optimum performance of peroxyacetic acid.

The safety aspects of preparation and storage have to be kept in mind when formulating dry bleaches with a high concentration of SPC. Because it is a strong oxidizer, its direct contact with organic material should be avoided to reduce the risk of self-heating and thermal decomposition under stress conditions. Activated formulations with a high level of SPC and more than 5% TAED therefore require a certain amount of inert material such as sodium bicarbonate, sesquicarbonate, or dihydrogen orthophosphate for stabilization [188].

TABLE 16.6
Applications of Aerial Bleach Systems

Patent and Year	Inventors and Company	Bleach System	Benefits Claimed
WO 01/16271 (2001)	R. Hage et al., Hindustan Lever	[Fe(MeN$_4$Py)Cl]Cl, aerial bleach catalysts	Postwash bleach effect
WO 02/24852 (2002)	D. V. Avila, Hindustan Lever	Aerial bleach catalyst, posttreatment with PAP	Removal of hydrophobic and hydrophilic stains
WO 02/068577 (2002)	N. Gupta et al., Hindustan Lever	Aerial bleach catalyst, anhydrous HDL	Unit dose system
WO 02/072746 (2002)	R. Hage et al., Hindustan Lever	[Fe(MeN$_4$Py)Cl]Cl, unsaturated surfactant, antioxidants	Improved bleach performance
U.S. 6653270 (2003)	R. LaBeque, Procter & Gamble	Mn-(Me$_2$EBC)Cl$_2$, antioxidants, reducing agent	Improved stability and performance
U.S. 6667288 (2003)	M. E. Burns et al., Procter & Gamble	Mn-(Me$_2$EBC)Cl$_2$	Improved stability and performance
WO 2004/039933 (2004)	T. Wieprecht et al., Ciba	Terpyridyl complexes	Improved bleach performance
WO 2004/111171 (2004)	Van Asten et al., Hindustan Lever	Aerial bleach catalyst, perfume, antioxidants	Improved stability of the liquid composition
WO 2004/111173 (2004)	M. Ouwendijk-Vijenhoek et al., Hindustan Lever	Bispidon complexes, Mn-(Me$_2$EBC)Cl$_2$, pH jump system	Improved storage stability at pH 6–7, improved performance at pH 7.5–9
WO 2004/111174 (2004)	Van Asten et al., Hindustan Lever	Aerial bleach catalyst, terpene perfume, antioxidants	Improved stability of the liquid composition
WO 2005/059075 (2005)	M. Ouwendijk-Vijenhoek et al., Hindustan Lever	Bispidon complexes	Improved storage stability by storing in containers containing UV absorbers
WO 2006/053614 (2006)	A. T. Hight et al., Hindustan Lever	Bispidon complexes or Mn-(Me$_2$EBC)Cl$_2$	Improved storage stability by using encapsulated bleach particles
EP 1 616 936 (2006)	O. C. P. Beers et al., Unilever	Aerial bleach catalyst, pH <7, nonionic surfactant, fatty acid	Favorable storage properties, moderate foaming characteristic

16.4.4.2 Liquid Bleaches

In recent years, in addition to dry powder bleaches, liquid hydrogen peroxide-based formulations have gained significant market shares. Liquid oxygen bleaches contain 3–7% hydrogen peroxide as the active ingredient, and are used as prespotters in combination with powder or liquid detergents. Formulated with small amounts of surfactant and chelating agent as a stabilizer, they have an acidic pH to guarantee storage stability. In the washing process, hydrogen peroxide is activated by the alkalinity of the detergent [189]. The addition of water-soluble polymers, such as soil-release polymers, enhances the removal of skin oils and prevents the buildup of yellow residues on the fabric [190].

A variety of liquid bleach additives are now being offered in dual-chamber bottles to separate the bleach active component from alkalinity or sensitive enzymes. Several patents also describe the use of the peracid PAP in such formulations, but to date no such product is commercially available.

16.4.4.3 Special Devices

Fresh food and drink stains are easier to bleach than old ones. Several devices have therefore been described in the literature, which allow instant stain removal from fabric independently of the washing process. Such portable devices take the form of pen-like applicators, and contain a bleach liquid comprising hydrogen peroxide, chelating agents, radical scavengers, cleaning solvent, and small amounts of surfactant [191]. A similar concept is that of stamp-like bleach applicators to apply a bleach solution in a rocking motion [192].

For pretreatment of stains, bleach activators in stick form are claimed [193], consisting of a water-soluble surfactant binder and TAED powders. The activator is applied directly on the stain before the wash process and activated by a persalt-containing detergent. A similar concept based on single-dosed laundry boosters was used some time ago in Europe. It comprised a nonsoluble sheet of nonwoven material, which contained a high amount of bleach activator but no peroxide source [194]. To work, the sheet had to be added to persalt-containing detergents.

16.4.5 BLEACHES IN AUTOMATIC DISHWASHING DETERGENTS

16.4.5.1 Market Development

Although their market share differs from country to country, household penetration rates of dishwashers continue to grow year by year [195]. The appliance simplifies the consumer's life, as dishwashing by hand is not only time-consuming, but also requires mechanical action in hot water. Various product forms of automatic dishwashing detergents (ADD) can be found on the market. Whereas in Europe dishwashing tablets and powder products predominate, North American consumers prefer liquid or gel-like products. The main challenges in this home care segment are cleanliness and shine on dishes and kitchenware without damaging surface and decor.

Multiphase dishwashing tablets allow spatial separation of the sensitive compounds to avoid negative interaction during storage and loss of performance during application. Temperature- or pH-controlled release of the active ingredients guarantee their optimum performance in the washing liquor. Whereas the first "2-in-1" tablets contained only detergent and rinsing aid, new "7-in-1" products also claim salt function, stainless steel shine, long-term glass protection, improved cleaning boosters, and low-temperature activator properties.

The two main components of all ADDs are a detergent and a rinse aid. In the main wash step at 55–65°C, alkalinity, builders, enzymes, and small amounts of low-foaming surfactants dissolve or disperse food residues, and prevent water hardness from forming calcium carbonate on hard surfaces. Stubborn stains such as tea or beverage stains are removed by the bleaching system, supported by complexing agents. In the rinse step, low-foaming surfactants and hydrotropes ensure surface wetting and prevent the formation of visible spots. Finally, the dishes are dried at ~60°C.

Ongoing trends of lowering the washing temperature to 45°C and reducing water quantity to 4 L/wash are an upcoming challenge for dishwashing agents and especially the bleach system.

Until the end of the 1980s, almost all dishwashing detergents were highly alkaline formulations, based on meta silicate, phosphate, and chlorine bleach (trichloroisocyanurate). Later they were replaced by low-alkaline P-free or P-reduced formulations comprising disilicates and perborate, with a pH of 9–11. Replacement of chlorine bleach and pH reduction allowed the use of enzymes, especially amylases and proteases, but caused serious problems with tea stain removal.

16.4.5.2 Improved Stain Removal

Tea stains are dry films of tea scum adhering strongly onto the surface of porcelain cups. They are complex mixtures of organic material from the oxidation of soluble tea components interspersed with calcium carbonate crystals [196]. Other metal ions, either from tap water or from tea leaves, are also present, and may form complexes with polyphenolic tea components. Strong complexing agents such as phosphates or phosphonates are capable of extracting the earth alkali metal ions to loosen the polymeric framework and support the action of the bleach systems.

Typical European ADDs contain 1–5% TAED in combination with 3–12% percarbonate. However, even high TAED concentrations are not able to match the bleaching power of chlorine-generating bleach systems in this application. Here, the use of bleach catalysts offers advantages over activator systems. Mn-Me_3tacn, in particular, removes tea stains completely, even in P-free formulations; the cobalt catalyst PAAN also shows good properties. In both cases, the positive charges of the catalyst seem to promote reaction with peroxide anions and support interaction with the stains on ceramic surfaces. In addition, both catalysts show improved compatibility with enzymes, allowing better removal of starch and proteinous residues. Comparable bleach results are obtained by using nitrile quats or cationic esters, which also exhibit good tea stain removal and reduced interactions with amylases. Details are given in Table 16.7.

The use of preformed peracids may cause storage problems in the highly alkaline matrix of a compressed ADD tablet. To incorporate PAP in a premium brand dishwashing detergent, a different technology has been developed. The detergent, PAP, and rinsing aid are separated in single-dosed, water-soluble, three-compartment containers, which allow controlled release of the single components to ensure optimum bleach results [197].

Besides residual tea stains, discolored plastic dishes often lead to consumer complaints. If, during food preparation or the cleaning process, plastic surfaces come into contact with hydrophobic stains such as ketchup, curry, or paprika, their coloring components are able to migrate into the plastic surface, leaving stubborn red or yellow spots that are extremely difficult to remove. Currently, only separately added boosters based on diacylperoxide chemistry are able to remove this type of stain effectively.

16.4.5.3 Silver Tarnishing

The phenomenon of silver tarnishing increased in automatic dishwashers with the introduction of low-alkaline formulations containing oxygen bleaches. As a consequence, the oxidation potentials were shifted to favor the formation of black silver oxide during the cleaning process. To suppress this reaction, the concentration of the bleach system has to be optimized, and antitarnishing agents such as benzotriazoles have to be added [198].

16.5 OUTLOOK

Future requirements on bleach systems will focus even more on environmental aspects and the conservation of resources. This will have a positive impact on wash-cycle time and temperature, as well as water amount and detergent dosages. To match the new requirements, conventional bleaching

TABLE 16.7
Application of Bleach Systems in ADD Formulations

Patent and Year	Inventors and Company	Bleach System	Benefits Claimed
EP 0 530 870 (1993)	R. W. van Dijk et al., Unilever PLC	Mn-Me$_3$tacn	Improved bleaching and starch removal properties
U.S. 5480576 (1996)	R. G. Gary et al., Lever Brothers	Bleach system and 1,3-*N*-azole compounds	Reduced silver tarnishing
WO 97/36986 (1997)	H. Blum et al., Henkel	Oligoammine activator complex	Improved tea stain removal
U.S. 5763378 (1998)	J. D. Painter et al., Procter & Gamble	Diacylperoxide-containing particle	Superior stain removal from plastic
U.S. 6214782 (2001)	C. Chiou et al., Unilever HPC	Cationic nitriles	Reduced silver tarnishing
U.S. 6277802 (2001)	C. Chiou et al., Unilever HPC	Cationic nitriles with enzymes	Enhanced tea stain and starch removal
EP 0 807 160 (2001)	A. S. Goldstein et al., Procter & Gamble	Co-based bleach catalyst, e.g. $[Co(NH_3)_5Cl]Cl_2$	Superior tea stain removal performance
EP 0874 895 (2002)	D. J. Haeggberg et al., Procter & Gamble	Phosphate built ADD composition comprising PAAN	Superior tea stain removal performance
WO 02/12427 (2002)	R. Wiedemann et al., Reckitt Benckiser	Cationic nitrile cogranule	Improved tea stain removal
WO 2004/048507 (2004)	L. Geret et al., Reckitt Benckiser	Sulfophenyl alkyl carbonate	Removal of colored stains from plastic
WO 2004/081161 (2004)	D. Fregonese et al., Reckitt Benckiser	Encapsulated PAP in granular form	Excellent bleach activity
WO 2006/096676 (2006)	A. D. M. Brooker et al., Procter & Gamble	Host–guest complex of diacyl peroxide	Improved storage stability
WO 2006/120405 (2006)	D. Fregonese et al., Reckitt Benckiser	PAP (special particle size)	Improved tea stain removal
EP 1 741 774 (2007)	H. Euser et al., Unilever PLC	Mn-Me$_3$tacn, granulated nonionic surfactant	No discoloration during storage

technologies have to be complemented or replaced with new systems. The first step in this direction was already made with the development of low-temperature activators, preformed peracids, and suitable catalysts. In the long term, the replacement of conventional activators with catalytic bleach could save an amount of ~100,000 tons per year of bleach activators. If atmospheric oxygen could be made accessible as a peroxide source, the utilization of persalts could also be abandoned to a large extend. For this, however, it is necessary to extend the range of activity of the known aerial bleach systems from only oily food stains to the full spectrum of soils.

Besides the chemicals, new technologies will improve packaging devices and intelligent delivery systems to further increase the storage stability and allow a defined and controlled release of actives during the individual applications.

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17 Role of Surfactants in Paints, Inks, and Polishes

Rakesh Kumar Khandal, Geetha Seshadri, Gunjan Suri, and Dhriti Khandal

CONTENTS

17.1 INTRODUCTION

Surfactants are unique substances made up of two entities or moieties of completely different nature in the same molecule. Because of the fact that the two opposing moieties of the same molecule enable the surfactants to reorient themselves at the interface of completely different surfaces, the surfactants remain active at the interfaces involving substances of different phases as well as of similar phases. Analyzed at the macrolevel, all systems (natural or human-made) can easily be categorized into two major groups, based on their polarity, as polar (water-soluble or water loving) and nonpolar (oil-soluble or oil loving or water-hating).

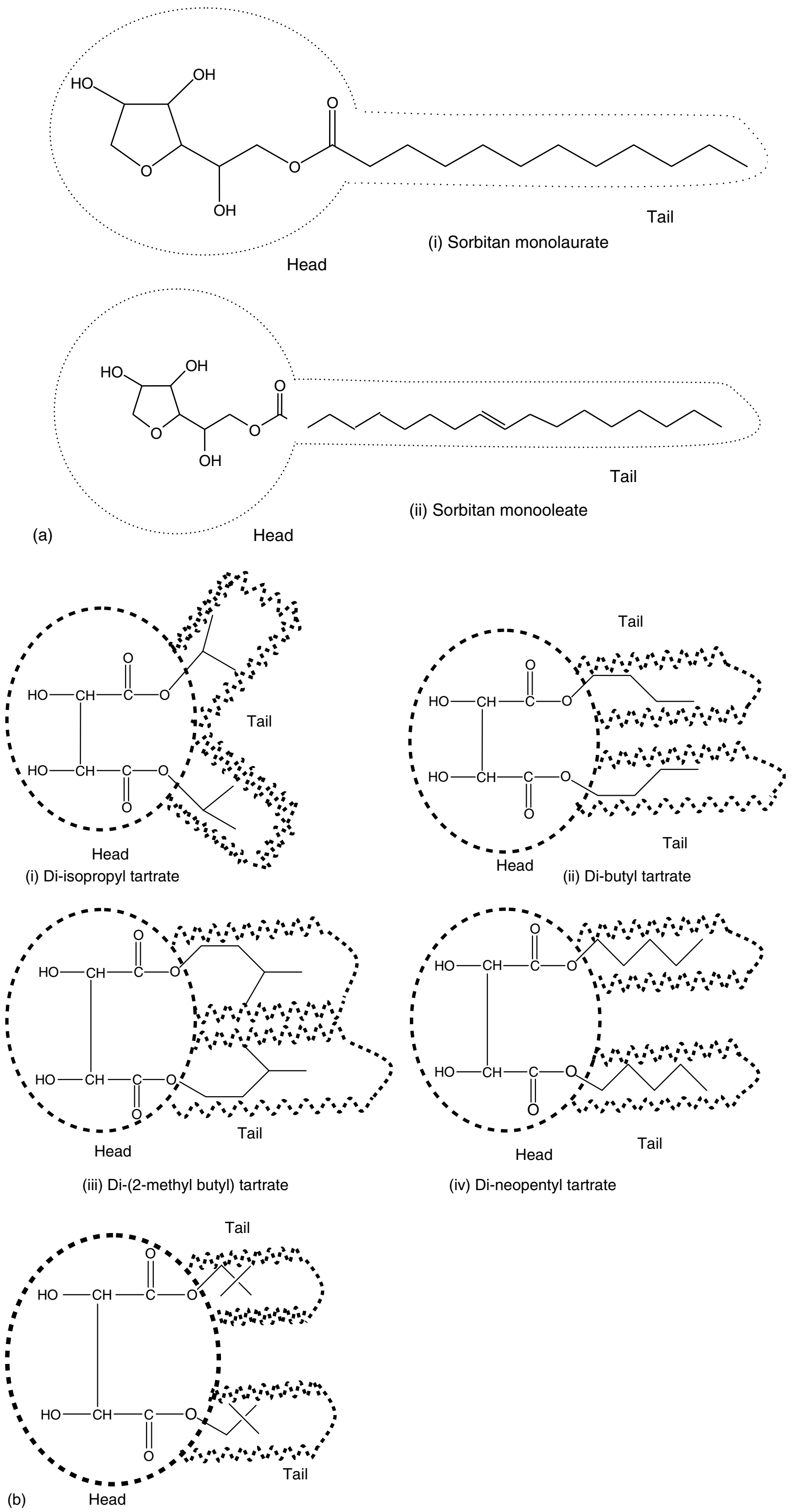
Because of the presence of a polar and a nonpolar moiety in the same molecule of a surfactant, the two opposite systems (polar and nonpolar) can be homogenized due to the presence of a surfactant. Depending on the difference in the degree of polarization of the surfaces concerned, surfactants have to be selected accordingly. The role played by the surfactants in making the opposite surfaces exist as a uniform single phase can never be overemphasized. However, it must be noted here that most of such systems are only kinetically stable, having a limited stable shelf life. The aim has always been to design surfactants that can provide thermodynamically stable systems. Further, surfactants are used not only for stabilization of the multiphase systems but often also for the destabilization of the existing (natural or human-made) stable systems.

Surfactants play a key role in numerous industrial systems and products. One such category of products for which surfactants are most essential include products such as paints, inks, and polishes. The role of surfactants in the three industrially important products, that is, paints, inks, and polishes, are better understood when the three products are defined from the point of view of the objectives for which these products are used. This will also explain why all of these three products are discussed together as one category.

The composition of paints, inks, and polishes is the next important aspect to be considered while assessing the role as well as the selection of suitable surfactants. Once the components of the three products are finalized, suitable surfactants are selected to formulate the homogenized products. Depending on the nature of the constituents, processes involved in transforming them into stable products, and performance criteria of these products, suitable surfactants have to be selected. For selection of surfactants for making paints, inks, and polishes, it is important to have a look at the structure of some of the commonly used surfactants and for various industrial applications (Figures 17.1 through 17.5). As presented in Figures 17.1 through 17.5, all the surfactants have common feature of two groups: polar (called head) and nonpolar (called tail).

The most common and widely accepted classification of surfactants is based on the nature of the hydrophilic (head) group of the surfactants. They can belong to either of the following classes:

1. Nonionics
    a. Esters
    b. Ester ethoxylates
    c. Alkyl-EO
    d. Fatty acid ethoxylates
2. Anionic
    a. Alkyl sulfates
    b. Alkyl aryl sulfonates
    c. Naphthalene sulfonates
    d. Alkyl phenol ethoxylates sulfates
    e. Fatty alcohol ethoxylates sulfates
3. Cationic
4. Amphoteric



(i) Sorbitan monolaurate

(ii) Sorbitan monooleate

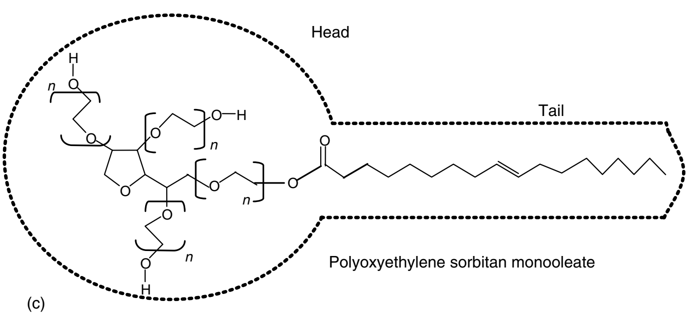
(i) Di-isopropyl tartrate

(ii) Di-butyl tartrate

(iii) Di-(2-methyl butyl) tartrate

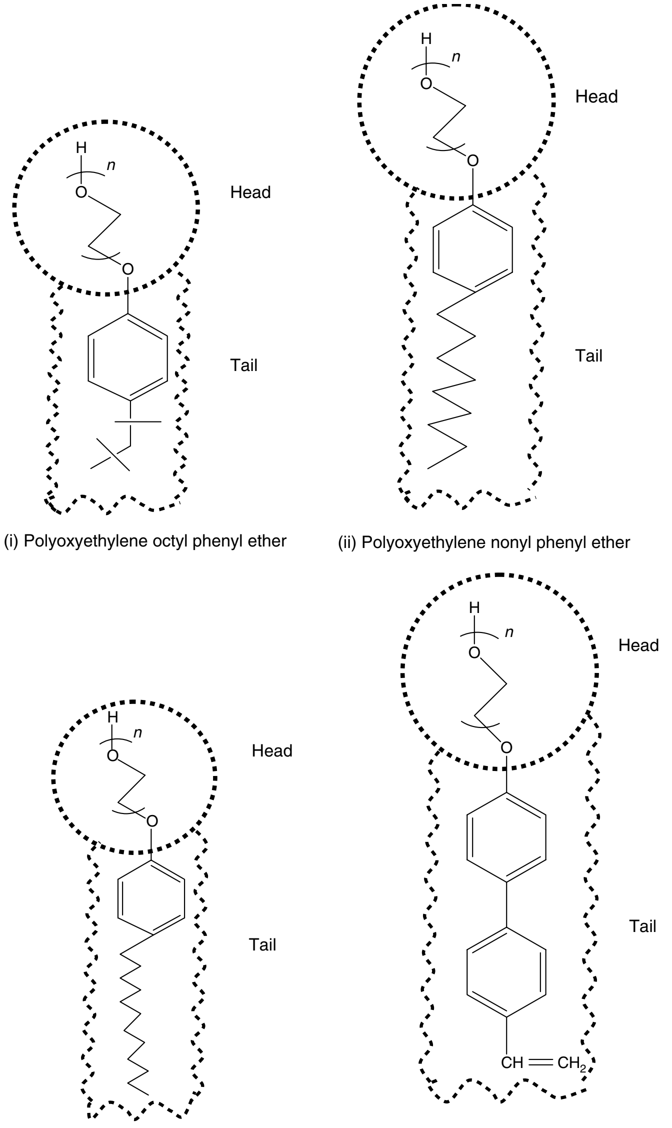
(iv) Di-neopentyl tartrate

FIGURE 17.1 (*Continued*)



Polyoxyethylene sorbitan monooleate

(c)



(i) Polyoxyethylene octyl phenyl ether

(ii) Polyoxyethylene nonyl phenyl ether

(iii) Polyoxyethylene dodecyl phenyl ether

(iv) Polyoxyethylene styrenated phenyl ether

(d)

FIGURE 17.1 (*Continued*)

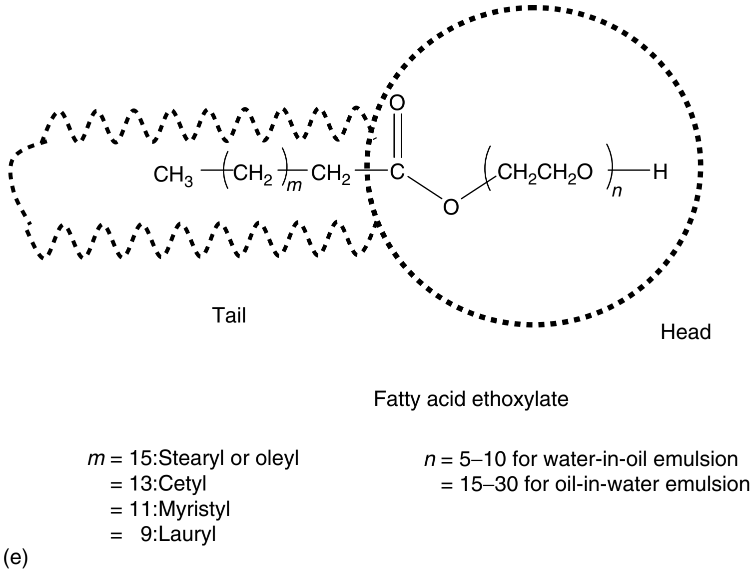


FIGURE 17.1 (a) Fatty acid esters (i and ii) of polyol, such as sorbitol, are the class of nonionic surfactants known for their excellent behavior as water-in-oil emulsifiers. They are used for emulsifying the resins in emulsion polymerization for paints, inks, and polishes. (b) Tartrates are the special (biosurfactants) category called gemini surfactants. Tartrate esters are characterized by their low surface tension and high wetting characteristics. They are used for a variety of water-borne coatings such as inks. The two hydrophobic chains with branching, along with the two hydroxyl groups on the hydrophile, make them excellent emulsifiers for oil in water emulsions in inks. (c) The ethoxylated fatty esters of sorbitan are nonionic surfactants used as oil-in-water emulsifiers for emulsion polymerization of binders for paints, inks, and polishes. The fatty acid group can vary (e.g., lauryl, palmitoyl, stearyl, and oleyl), and there can be mono-, di-, and triesters. Similarly, the number of molecules of ethylene oxide can be varied to vary the hydrophilic-lipophilic balance (HLB) of the surfactant. (d) The alkyl phenol ethoxylates or polyoxyethylene alkyl phenyl ether belong to a class of nonionic surfactants. Polyethylene oxide linkages are stable to acids, alkalis, and oxidizing agents. The length of the alkyl group can be varied to give a range of products with varying solubility achieved through the addition of a varying number of ethylene oxide molecules. Alkyl phenol ethoxylates are the most versatile surfactants used as dispersants and emulsifiers in paints, inks, and polishes (i–iv). (e) Fatty acid ethoxylates are a class of nonionic surfactants used as emulsifiers for oil-in-water as well as water-in-oil emulsions. The hydrophobe may vary from C_{12} to C_{18} chain length with and without any unsaturation, whereas the number of moles of ethylene oxide can vary from 5 to 10 for the water-in-oil and from 15 to 30 for the oil-in-water emulsions in paints, inks, and polishes.

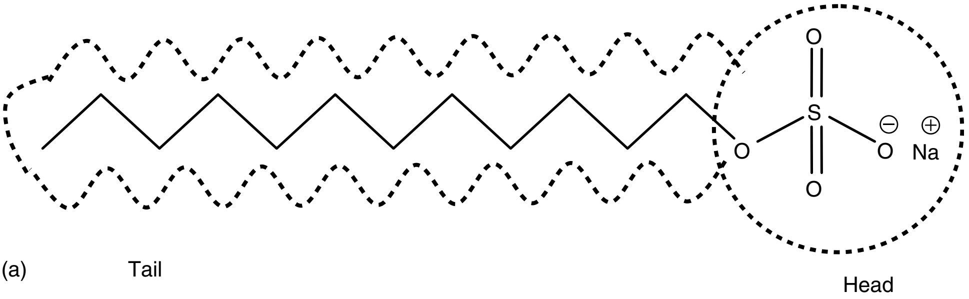


FIGURE 17.2 (*Continued*)

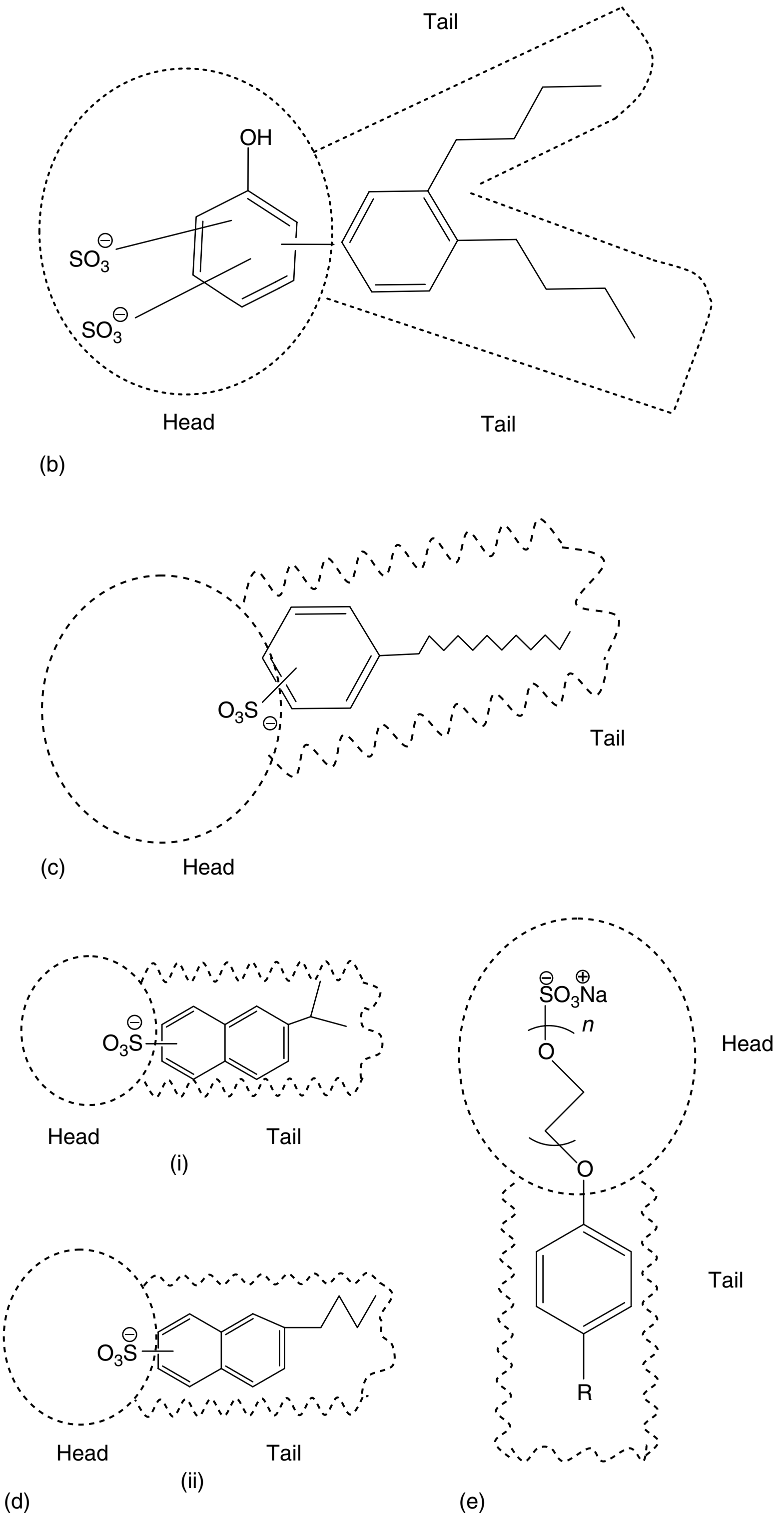


FIGURE 17.2 (*Continued*)

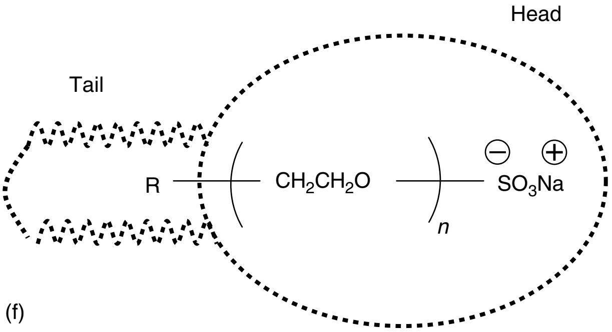
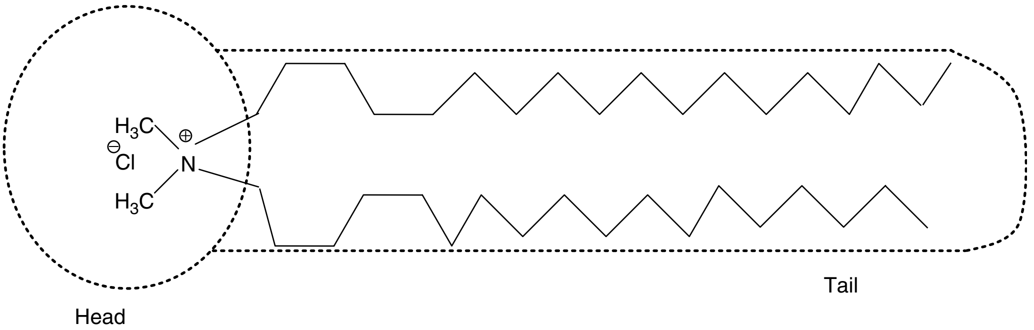
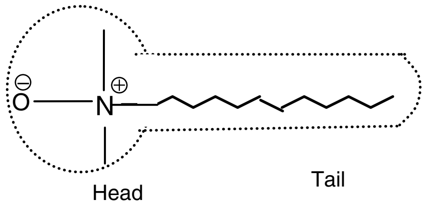


FIGURE 17.2 (a) Sodium lauryl sulfate is an anionic surfactant belonging to a class of alkyl sulfates. It is a water-soluble surfactant used as an emulsifier and dispersant in paints, inks, and polishes. It is considered a green surfactant, derived from a renewable resource (coconut oil), with complete biodegradability. However, it generates high foam, for which care must be taken. (b) Dibutyl phenyl phenol disulfonate belongs to a class of anionic surfactants. They are known as excellent dispersants for pigments used for paints, inks, and polishes. (c) Dodecyl benzene sulfonate belongs to a class of alkyl benzene sulfonates of anionic surfactants. Owing to being a long chain alkyl group, this class of surfactants has a wide variety of applications. Owing to low cost of production, dodecyl benzene sulfonate is the most commonly used synthetic surfactant. (d) Naphthalene sulfonates (i) isopropyl naphthalene sulfonate and (ii) butyl naphthalene sulfonate are a class of anionic surfactants. They are used as wetting agents for powders, and also as wetting agents in paint formulations. The large alkyl diaryl hydrophobic group plays an important role in the wetting of pigments in water at the time of preparation of dispersions of pigments. They are usually used in combination with nonionic surfactants. (e) Alkyl phenol ethoxylate sulfates are the special category of anionic surfactants having a nonionic hydrophile in the form of an ethylene oxide chain attached with the anionic (sulfate) group. The hydrophobe is an alkyl phenol chain. There can be a range of such surfactants, depending on the number of ethylene oxide molecules attached to the alkyl phenol. They are used as emulsifiers for emulsion polymerization of binders and as dispersants for pigments. $n = 5–40$; R = nonyl, dodecyl, octyl, styrene, and the like. (f) Fatty alcohol ethoxylate sulfates are the special class of anionic surfactants used as dispersants and emulsifiers for components of paints, inks, and polishes. The hydrophile group here consists of the polyoxyethylene chain attached to a sulfate group. Thus, the long ethoxylate chain and an anionic group makes them very useful surfactants for paints, inks, and polishes, beside their capacity to stabilize the dispersions by electroviscous effect. R = C_{12}–C_{18} chain; $n = 5–40$.

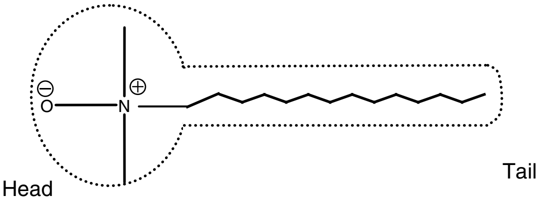


Disteryl dimonium chloride

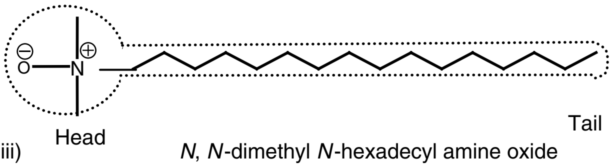
FIGURE 17.3 Disteryl dimonium chloride is a cationic surfactant with two hydrophobic chains (tails) of a steryl group and a quaternary ammonium group (head). The two long chains of a hydrophobic group provide it with excellent adsorption capacity on the surfaces. It is used as the dispersant for pigments mainly in furniture polishes. It also acts as an emulsifier for oil-in-water emulsions.



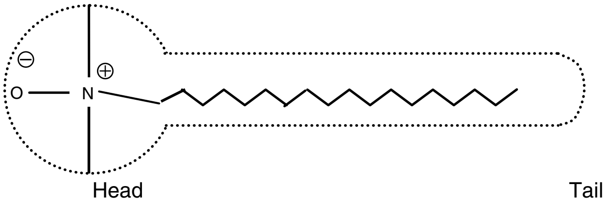
(i) *N*, *N*-dimethyl *N*-dodecyl amine oxide



(ii) *N*, *N*-dimethyl *N*-tetradecyl amine oxide

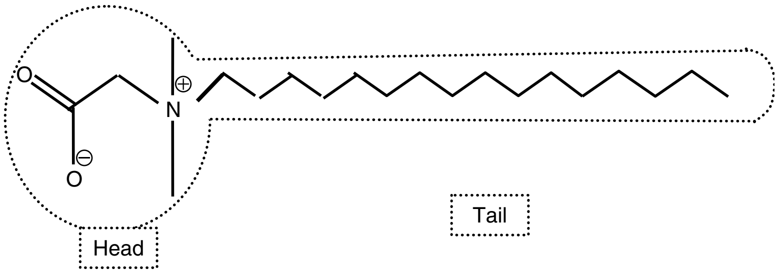


(iii) *N*, *N*-dimethyl *N*-hexadecyl amine oxide



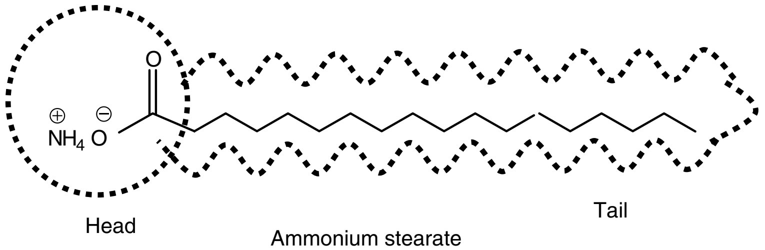
(iv) *N*, *N*-dimethyl *N*-octadecyl amine oxide

(a)

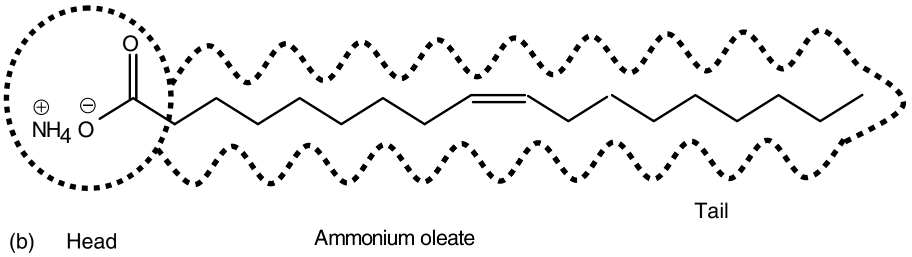


(b)

FIGURE 17.4 (a) (i–iv) Amine oxides, which are protonated in the presence of an acid to form a cationic surfactant, are known for their excellent wetting properties, and are used in coating industries such as inks. The varying hydrophobic chains provide the maneuverability of wetting properties as per the systems involved. (b) Structure of cetyl betaine with a cetyl chain as its hydrophobe (tail) and betaine group as hydrophile (head). This is used for pigment dispersions for paints, inks, and polishes. The unique feature of betaines is their antimicrobial characteristics.



(a) Ammonium stearate



(b) Ammonium oleate

FIGURE 17.5 Ammonium esters of fatty acids (a) stearic and (b) oleic are the surfactants of the category of soaps. The hydrophobic chain of the alkyl group (stearyl and oleyl) helps in good adsorption on the surfaces. These types of surfactants are more suitable for polishes.

Designing of surfactants as per requirements is possible once all aspects necessary for making paints, inks, and polishes are understood. This is covered in this chapter with the following outlines:

1. Defining paints, inks, and polishes
2. Composition and manufacturing processes for making paints, inks, and polishes
3. Defining surfactants
4. Types of surfactants
5. Role of surfactant as dispersants, emulsifiers, and solubilizers
6. Surfactant selection criteria for paints, inks, and polishes
7. Path forward to meet future challenges

17.2 DEFINING PAINTS, INKS, AND POLISHES

Paints are used for coating surfaces of various types, such as buildings, metals, wood, and plastics, for the purpose of protecting them from weathering, as well as for enhancing their life. Inks are meant to write or print on surfaces, mainly paper, for the purpose of conveying some message or for depicting some expression. Inks are also used for other types of surfaces coated with paints.

Like paints and inks, polishes are also used for coating various types of surfaces, mainly to protect them from the weathering elements. In all three cases, the application of the product results in the formation of a coating layer on the surface. The components of the three products are so chosen that after their application, they form a long-lasting attachment to the surface on which they are applied. Since all three products leave a coat on the surfaces, they are always discussed together. Further, basic principles used for designing the formulations of paints, inks, and polishes being similar, it is logical that they are discussed together.

Before going into detail about the role of surfactants in making as well as working with paints, inks, and polishes, it would be worthwhile to briefly discuss the compositions of paints, inks, and polishes. This will help in understanding the role played by surfactants, at each stage, from making to applying the product, including the stages of handling, transportation, and storage of the product. Incidentally, surfactants play a key role in the whole life cycle of these products. Let us then discuss all three of them separately.

17.2.1 CLASSIFICATION OF PAINTS

Paints can be classified on the basis of their application (Table 17.1) as follows:

1. Oil-based paints
2. Water-based paints

17.2.1.1 Oil-based Paints

Most oil-based paints contain polymer binders dissolved in organic solvents. These polymer molecules float about separately in the liquid solvent. For the preparation of water-insoluble paints, appropriate solvents are required. Enough solvent is added to make the paint spreadable and solvents usually exceed 25% of the paint's weight. When the paint is applied to a surface, the solvent molecules evaporate into the air, and the polymer molecules are left behind as a thin plastic layer. Most acrylic paints are of this type.

An example is the dissolution of a polymer in a solvent, where its molecules must be attracted fairly strongly to those of the solvent. It is quite possible to select the polymer molecules of the binder such that they dissolve completely in the solvent. However, it is not so easy to get the pigment particles in the paints to dissolve in the solvent. Pigments remain solid and tend to settle to the bottom of the paint container as the paint sits on the shelf. This is why oil-based paints should be stirred before use.

When the oil-based paint is applied, for it to spread out on the surface rather than beading up into droplets, the paint must wet the surface. Wetting occurs when the molecules in a liquid are attracted strongly enough to bind to the surface molecules instead of one another. Not all liquids wet any particular surface. For example, water beads up on wax because water molecules are not attracted strongly to wax molecules. Oil-based paints tend to wet most surfaces, although these surfaces should be clean and dry. Oil-based paints will not wet the damp surfaces, just as water-based paints will not wet oily surfaces. Sometimes primer coats are used to help the final paint wet and bond to the surface being painted.

After applying the paint, the solvent begins to evaporate from its surface. At first the solvent molecules travel easily through the open gaps between polymer molecules, and the entire layer of paint dries together. Even the relatively large pigment particles drift freely in the fluid. As the solvent evaporates, the polymer molecules move closer together, and the viscosity of the paint increases. First, the pigment particles stop moving, then the polymer molecules, and finally the solvent itself becomes immobile. At that point, the paint feels dry to the touch. This drying sequence creates a thin layer of clear polymer on the surface of the paint. As it evaporates, the solvent tends to carry

TABLE 17.1
Application and Types of Paints

No.	Applications	Paint Types
1	Buildings	Water-based and oil-based paints
2	Metals	Oil-based paints
3	Wood	Oil-based paints
4	Containers	Oil-based paints
5	Canvas	Water-based and oil-based paints
6	Textiles	Oil-based paints

polymer molecules past the larger pigment molecules to the surface of the paint. Even after the pigment molecules have become immobilized, the solvent and polymer still diffuse past them and create a micron-thick layer of clear polymer at the surface. This smooth, clear surface layer is what gives many oil-based paints their glossy appearance; most oil-based enamel paints achieve their high gloss on application.

Most oil-based paints never dry completely without baking. Although the solvent molecules diffuse rapidly to the surface and evaporate early, they have more trouble leaving the surface as the paint becomes more viscous. Eventually, the polymer tangle becomes so dense that even the tiny solvent molecules cannot work their way through it. What appears to be a dry paint actually contains a substantial amount of trapped solvent. The trapped solvent molecules that escape occasionally give the paint its long-lasting odor, which is not considered good for customer acceptance.

Further, because of their rigid, impermeable nature, oil-based exterior house paints tend to bubble and crack. Water migrates through wood and gets under the layer of paint. This water is unable to escape through the paint, and can create blisters when the paint is heated by sunlight. Changes in temperature and moisture content also cause the wood to expand and contract. Rigid oil-based paints are also known to experience different relative expansions and contractions, making the paint coatings crack. Here it may be noted that the oil-paints are also known for their durability. Hardness and rigidity of oil paints make them easy to clean. Dirt on the surface of these paints can be easily removed by vacuum cleaner or by washing with water.

Many oil-based house paints exhibit drying oil behavior too. As the solvent evaporates and oxygen enters the paint, cross-linking occurs between the polymer chains. Most alkyd paints are of this type. The cross-linking process creates many tiny fragment molecules that evaporate as the paint dries. These drying oil-like paints use drying agents to speed up the cross-linking. Surfactants play a key role at all stages of application on the surface, including the wetting, solvent diffusion, formation of coat, and drying of paint.

17.2.1.2 Water-based Paints

Water-based paints are also known as latex paints, because the binder used is the latex emulsion. Latex paints are not uniform liquids. Unlike oil-based paints, latex paints contain polymer molecules not dissolved in a solvent, but dispersed or emulsified in water. The polymer molecules are actually insoluble in water, and to emulsify or disperse them in water, surfactants are incorporated.

It may seem that such polymer particles could never get together to form a uniform coating, but they actually do. Once the paint is applied to a surface, the water evaporates, and the polymer particles move closer together. They are pulled together by water and their polymer chains begin to mingle together (Figure 17.6). By the time the water is gone, the molecules are tightly interwoven. They trap the pigment particles and create a layer that is often more durable than that of an oil-based paint, as the water-based paints do not suffer from the drawbacks of oil paints.

To keep the polymer particles suspended as an emulsion, where one phase of material is dispersed as tiny particles in another continuous phase of material, the pigment particles are coated with special chemicals called surfactants. Surfactants are molecules such as soaps and detergents that naturally migrate to the interface between pigment surface and water, and stabilize the dispersions. Surfactant molecules allow water to cling to the oil-like polymer particles. Each particle thus maintains at least a thin layer of water molecules around it, so that the polymer particles do not agglomerate together while the paint is in the can.

As water evaporates from the drying latex paint after application on the surface, the remaining water pulls the polymer particles toward one another. The surfactant molecules cling to the polymer particles with van der Waals forces. Because latex particles are large, they do not diffuse to the surface of the paint as the water evaporates. As a result, latex paint does not form a clear, pigment- free layer at its surface. The presence of pigment particles all the way to its surface makes latex paint rough on the scale of a wavelength of light. That is why latex paints are not as glossy as oil-based

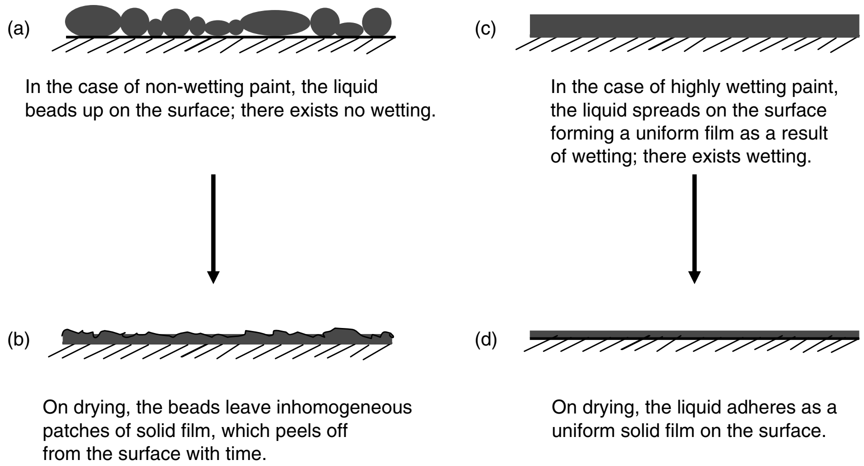


FIGURE 17.6 Wetting of the surface by the paint is highly essential for the uniform coating of the paint on the surface. In the case of a paint, which does not wet or spreads on the surface, on drying, patches are left sticking on the surface, which peel off with time as shown in (a) and (b). On the contrary, a paint, which wets the surface well, leaves a cohesive long-lasting film on the surface as shown in (c) and (d).

paints. Because the principal liquid in latex paints is water, latex paints contain less volatile organic chemicals than oil-based paints. However, most latex paints contain some organic solvent to soften the polymer particles so that they can coalesce easily.

17.2.2 CLASSIFICATION OF INKS

Ink is a liquid or semiliquid material used for writing, printing, or drawing. It is a colloidal system of fine pigment particles dispersed in a solvent. Various types of inks are available as per their application requirements. They are classified based on their form and their application.

17.2.2.1 On the Basis of Their Form

1. *Solid ink*. electrographic toners and hot-melt ink
2. *Liquid ink*. flexographic, rotogravure and jet inks
3. *Paste ink*. letter press and lithographic inks

17.2.2.2 On the Basis of Their Application

1. Standard printing inks
   a. Web offset (heat-set and nonheat-set)
   b. Process ink for color printing and others
   c. Sheet-fed
   d. Soybean based
2. Specialty inks
   a. Metallic
   b. Security
   c. Fluorescent
   d. Phosphorescent and others

All these classes of inks can basically be categorized as follows:

1. Pigmented inks
2. Dye-based inks

17.2.2.2.1 Pigmented Inks

Pigmented inks contain agents that ensure adhesion of the pigment to the surface and prevent it from being removed by mechanical abrasion. These materials are typically referred to as resins (in solvent-based inks) or binding agents (in water-based inks).

Pigmented inks are advantageous while printing on paper, because the pigment stays on the surface of the paper rather than getting diffused into the paper. This is desirable because more ink on the surface means that less ink needs to be used to create the same intensity of color. The size of the pigment particles is very important for the ability to diffuse in the solution. Qualities such as hue, saturation, brightness, or lightness are inherent in the ink, and they vary depending on the source and type of the pigment.

Pigments are all hydrophobic solids that are to be dispersed in water or the mixture of water and a suitable solvent. The dispersion is possible only due to the presence of surfactants. The stabilization of the dispersion of pigments also depends on surfactants.

17.2.2.2.2 Dye-Based Inks

Dye-based inks are generally much stronger than pigment-based inks, and can produce much more color of a given density per unit mass. However, because dyes are dissolved in the liquid phase, they have a tendency to soak into paper, thus making the ink less efficient and also potentially allowing the ink to bleed at the edges of an image, producing poor-quality printing. To circumvent this problem, dye-based inks are made with solvents that dry rapidly or are used with quick-drying methods of printing, such as blowing hot air on the fresh print. Other methods include harder paper sizing and more specialized paper coatings. The latter is particularly suited to ink used in nonindustrial settings (which must conform to tighter toxicity and emission controls), such as inkjet printer inks. Another technique involves coating the paper with a charged coating. If the dye has the opposite charge, it is attracted to and retained by this coating, whereas the solvent soaks into the paper. Cellulose, the material that paper is made of, is naturally charged, and so a compound that complexes with both the dye and the paper's surface will aid retention at the surface. Such a compound in common use in ink-jet printing inks is polyvinyl pyrrolidone.

An additional advantage of dye-based ink systems is that the dye molecules interact chemically with other ink ingredients. This means that they can benefit more than pigmented ink from optical brighteners and color-enhancing agents designed to increase the intensity and appearance of dyes. Because dyes get their color from the interaction of electrons in their molecules, the way in which the electrons can move is determined by the charge and extent of electron delocalization in the other ink ingredients. The color emerges as a function of the light energy that falls on the dye. Thus, if an optical brightener or color enhancer absorbs light energy and emits it through or with the dye, the appearance changes as the spectrum of light reemitted to the observer changes. A disadvantage of dye-based inks is that they can be more susceptible to fading, especially when exposed to ultraviolet radiation as in sunlight.

Surfactants play an important role in the success of dye-based ink as well as of pigment-based ink.

17.2.3 CLASSIFICATION OF POLISHES

Polishes are products that when applied on surfaces leave a fine coating, making the surfaces hydrophobic. The coating of polishes is quite fine, though the surfaces behave differently from their inherent nature. Polishes are made as solids, semisolids, and liquids, and in most cases they leave a transparent, fine layer of coating on the surfaces. The major constituents of polishes are

1. Layer-forming resin or hydrophobic substance
2. Vehicle for the coating component: water or oil
3. Additives

Most of the polishes are emulsions and are rubbed on the surfaces to ensure that the coating is glossy and the vehicle liquid is evaporated from the surface completely. They are basically categorized as

1. Oil-based polishes
2. Water-based polishes

Various types of solid, semisolid, and liquid polishes are available in the market. The major polishes are discussed here.

17.2.3.1 Floor Polish

Water is by far the most common component in a floor polish formulation, amounting to ~80% of the total weight of a floor polish, as it is manufactured. Water is the continuous medium that allows all the active components to form a stable mixture until the wet polish is applied to a floor and the complex process of drying occurs (Figures 17.7 and 17.8). The drying process is the evaporation

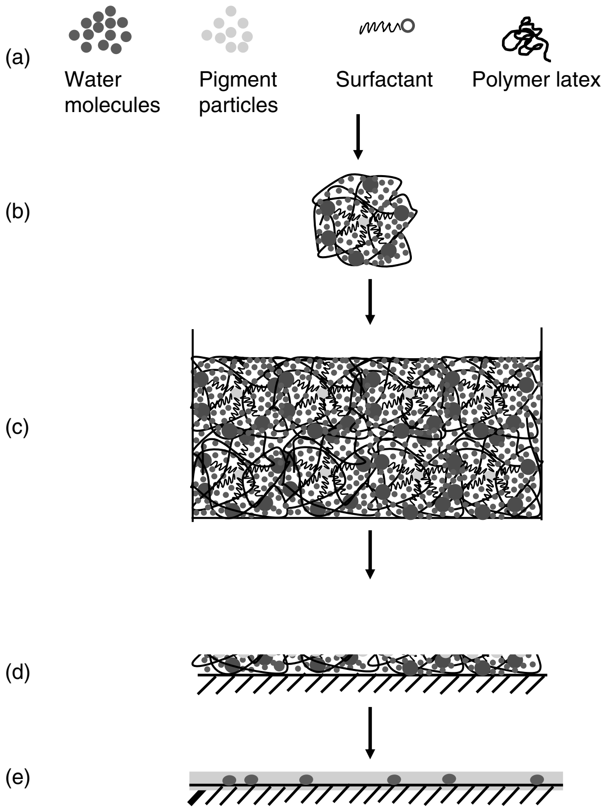


FIGURE 17.7 Action of water-based paints when applied on a surface can be described based on the various constituents and composition of the paint: (a) The constituents of a water-based paint consisting of pigments, surfactant, water, and polymer latex, (b) Formation of a paint molecule consisting of pigment, surfactant, water, and polymer latex. Here, the pigment particle disperses in water as a result of the surfactant that adsorbs onto the pigment with its nonpolar part while reorienting its polar part in water. The dispersed pigment is further stabilized through structuring by the polymer latex, which is also dispersed in water, (c) Constitution of a water-based paint, (d) Application of the layer of water-based paint on the surface, (e) As the water evaporates, the polymer particles mingle closely to form a tight network. The pigment particles are entrapped within the network of latex sticking to the surface to form a layer. A few water molecules also remain entrapped even though the paint gives a dry feel from outside.

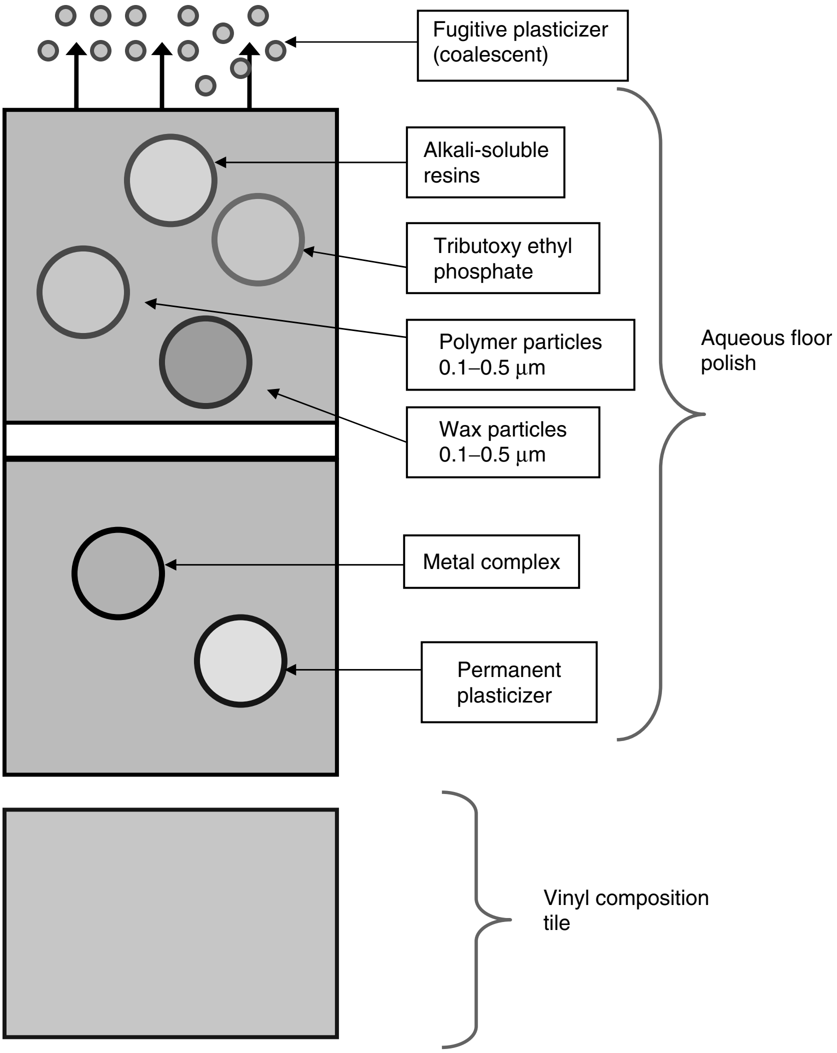


FIGURE 17.8 Steps involved in the application of a floor polish to a vinyl tile.

of water and other volatile components, and the formation of a film. The water-based polishes are manufactured as per a process that involves the use of surfactants to homogenize the different and usually completely opposite phases and surfaces.

17.2.3.2 Furniture Polish

Furniture polishes are pastes, creams, or lotions used to clean, protect, and shine wooden furniture. These products were originally made from natural waxes, which were hard to apply and tended to leave a heavy buildup over time. Formulations for furniture polishes combine natural waxes and oils with petroleum-based ingredients and synthetic polymers. These modern formulations can clean the film residue and lay down new polish in a single step, so periodic stripping of old polish layers is not necessary.

Natural plant wax such as carnauba wax and blends of carnauba with ouricui, candelilla, esparto, sugar cane, cotton fiber, flax, palm, hemp, and raffia waxes have been used to impart a fine shine.

Paraffin waxes (which can be varied in melting point and hardness) and inexpensive solvents (like kerosene and naphtha) have also been used, as raw materials in the formulation of polishes.

Self-polishing wax emulsions have been prepared by using carnauba wax in a soap and water base. This formulation requires less buffing, but causes streaking, and the soap tends to make it more easily removable on contact with water. In the past few decades, synthetic polymer emulsions have been introduced that offer significant improvements over wax systems. The most widely used polymers are based on silicone oils, which provide lubricity and good gloss. Aerosol sprays are the most popular delivery system for these products, because they offer easy application over a large surface area. In addition to ease of application, today's products offer excellent gloss, durability, and water resistance. Surfactants play a key role in making the oil-in-water emulsions work for the furniture polishes.

17.3 COMPOSITION AND MANUFACTURING PROCESS OF PAINTS, INKS, AND POLISHES

17.3.1 COMPOSITION AND MANUFACTURING PROCESS OF PAINTS

17.3.1.1 Composition of Paints

There are four primary components of paint:

1. Pigment, also known as coloring materials
2. Binder, also known as nonvolatile vehicle or resin
3. Vehicle, also known as volatile vehicle or solvent
4. Additive, also known as specialty adjuvant

Paints and coatings are normally formulated as liquid compositions, which can be easily applied on the surfaces by brush or spray; formulations in the form of paste or powders need to be brought into liquid form at the time of application. Once applied, manually or mechanically, paints dry to form well-adhering film surfaces. The composition of the paint determines whether a high gloss or a dull surface is formed to last for a long time.

Paint is basically a semifinished product, as the final product is the painted article itself. From the point of view of the user, a good paint, therefore, is the one that serves the purpose after it is applied on the surface.

Pigments are finely divided, insoluble powders (mostly metallic or organometallic) that give paint its color, opacity, and other optical properties. These powder particles are normally suspended in the paint when it is fluid, and become trapped in the polymer molecule as the paint dries. There are some coatings that do not contain pigments, such as clear varnishes. There are also paints in which the pigments do more than simply provide color, such as in magnetic recording media. For desired effects and performance of paint, it is essential that the pigments remain finely dispersed in the paint formulation. Any settling of pigment particles during the shelf life of paint would adversely affect the behavior of the paint when applied.

Additives help these three components, that is, pigment, vehicle, and binder work together to form a uniform coating. Some additives aid in the drying process by initiating the formation of polymer molecules out of much smaller molecules. Others help keep the binder or pigment particles from clumping together before the paint is used or help prevent freezing. In still others, the viscosity of the paint makes it easy to be applied.

The basic components of paint are

1. *Film-forming substances*. These are macromolecular or low-molecular mass compounds that react to form a film on curing. Cellulose nitrate, vinyl chloride copolymers, polyurethane, and epoxy resins are examples of film-forming compounds.
2. *Resins*. Resins are used to increase the solid content of paints, and improve the gloss and adhesion to the surface. Commonly used resins include alkyd resins, epoxy resins, and rosin.

3. *Plasticizers*. Plasticizers are organic liquids of oily consistency and low volatility. Esters of polyamides such as dioctyl phthalate are the most commonly used plasticizers for aiding the film formation of the resin.
4. *Volatile substances*. Volatile substances are chemicals that keep the paints fluid enough to be applied easily, and that subsequently evaporate during drying. In some cases, these volatile substances actually dissolve the binders and other chemicals so that the paint is nearly a uniform liquid. Modern paints actually contain tiny solid binder particles that are suspended in the volatile substances. These particles become a continuous coating as the volatile substances evaporate.
5. *Additives*. Additives are auxiliary products, which are used in very small concentrations but are essential for improving the technological properties of films. They are classified according to their use as follows:
   - *Driers* catalyze the decomposition of peroxides and hydroperoxides formed by the action of atmospheric oxygen on binders like alkyd resins. Generally, they are vegetable oils with a high degree of unsaturation and a large alkyl chain length.
   - *Anti-skinning agents* are antioxidants that counteract the tendency of drier-containing paints to form an insoluble surface skin on contact with atmospheric oxygen.
   - *Curing agents* catalyze the cross-linking of binder systems.
   - *Leveling agents* promote the formation of a smooth, uniform coating.
   - *Flattening (matting agents)* provide flat layers or films with satin gloss.

17.3.1.2 Manufacturing Process of Paints

The manufacturing of paints involves four basic operations (Figures 17.9a and 17.9b):

1. Mixing
2. Grinding
3. Thinning
4. Refining

17.3.1.2.1 Mixing

In mixing, major constituents of the formulation of paint, for example, pigments, solvents, surfactants, and thickeners, are mixed thoroughly in a mixer. Here, surfactants cover all the surfaces to form the pigment paste.

17.3.1.2.2 Grinding

The paste from the mixer is transferred to the grinding equipment, in which further dispersion of the pigment is effected; deagglomeration of the pigments is achieved as a result of fairly high shear rate. This is followed by the dispersion of the fine particles of the pigment due to the surfactants added for this purpose. At this stage, a homogeneous formulation consisting of fine dispersion with uniform adsorption of binders is obtained.

17.3.1.2.3 Thinning

The pigment paste is allowed to pass from the grinding mill to a tank, where more thinner, dryers, and other additives are added. At this stage, all finer performance-related parameters including the shade are adjusted with stains.

17.3.1.2.4 Refining

The removal of extraneous matter, such as skins, is done in this stage. This is readily achieved by sieving. At this stage, the product is ready to be packed for the market.

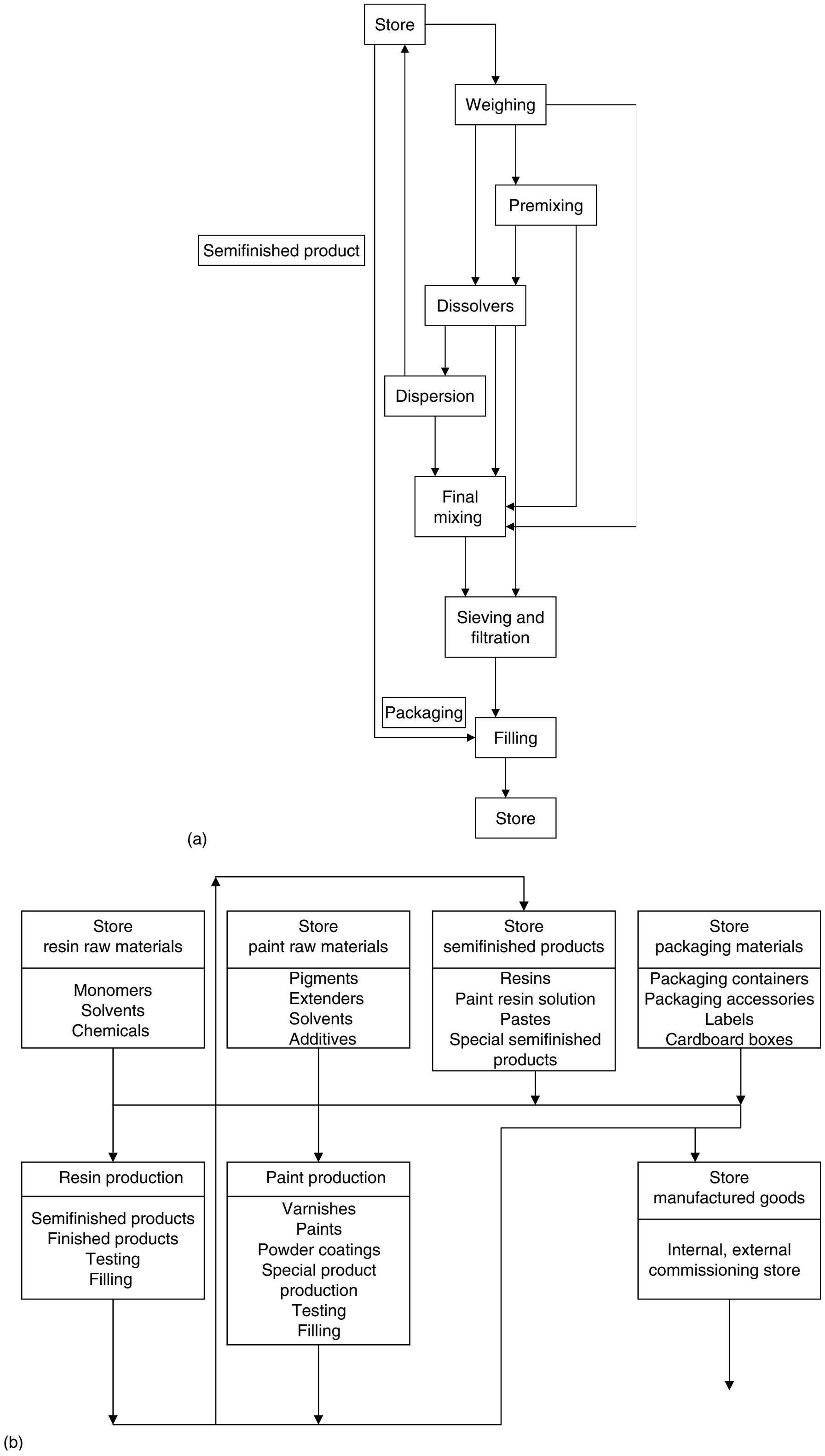


FIGURE 17.9 (a) Steps involved in the manufacture of paint. (b) Steps of paint production.

17.3.2 COMPOSITION AND MANUFACTURING PROCESS OF INKS

17.3.2.1 Composition of Inks

Like paints, inks are also categorized as

1. Oil- or solvent-based inks
2. Water-based inks

For both these categories of inks, the formulations can either be pigment-based or dye-based, depending on the base material used for providing the color to the product. Some of the important ink formulations are listed in Tables 17.2 through 17.5.

As evident from the formulations, inks are composed of

1. Pigment or dye
2. Solvent or water
3. Surfactants
4. Auxiliaries

17.3.2.2 Manufacturing Process of Inks

To manufacture inks, one has to have the ingredients (mainly polymeric) ready in separate vessels; they are mixed together to obtain the desired formulation as per the flow diagram (Figure 17.10).

TABLE 17.2
Water-Based Ink-Jet Ink Composition

Component	Function	Concentration (%)
Deionized water	Aqueous carrier medium	60–90
Water-soluble solvent	Humectant, viscosity control	5–30
Dye or pigment	Provides color	1–10
Surfactant	Wetting, penetrating	0.1–10
Biocide	Prevents biological growth	0.05–1
Buffer	Controls the pH of ink	0.1–0.5
Other additives	Chelating agent, defoamer, solubilizer, etc.	>1

TABLE 17.3
Phase-Change Ink Composition

Component	Function	Concentration (%)
Solid wax mixture	Ink vehicle	40–70
Viscosity modifier	Lowers viscosity	5–20
Tackifier	Imparts adhesion	1–15
Plasticizer	Provides flexibility	1–15
Dye or pigment	Provides color	1–10
Antioxidant	Provides heat stability	0.05–2

TABLE 17.4
Newspaper Black Ink Formulation

Component	Web Offset (%)	Letterpress (%)
Carbon black	17–20	12–14
Resin	3–18	0–4
Oils	50–65	70–85
Additives	1–6	0

TABLE 17.5
Newspaper Color Ink Formulation

Component	Web Offset (%)	Letterpress (%)
Carbon black	10–15	7–19
Resin	10–25	5–10
Oils	30–40	75–85
Pigment extenders	10–20	0–10
Additives	1–5	0

17.3.3 COMPOSITION AND MANUFACTURING PROCESS OF POLISHES

17.3.3.1 Composition of Polishes

The primary ingredients used to prepare polishes are polishing agents, solvents, surfactants, and auxiliary materials as discussed below:

1. *Polishing agents.* Waxes, polymers, and oils are used to improve the condition of the furniture surface, and are commonly known as polishing agents. The waxes employed can be of vegetable, animal, or mineral origin. Common examples of vegetable waxes are carnauba and candelilla. Sugar cane wax, cotton wax, and many others are also used. The primary animal wax is beeswax, which is useful and has unique physical and chemical properties. Shellac is another popular insect wax, which comes from the lac insect. Spermaceti wax, from the sperm whale, was popular at one time but has been replaced by synthetic waxes. Lanolin fractions from sheep are also used as animal waxes. Mineral waxes can be categorized as ozokerite, paraffin waxes, microcrystalline waxes, oxidized microcrystalline waxes, Fischer–Tropsch waxes, and montan waxes. In addition to these naturally derived waxes, synthetic resins are also commonly used in polishes. These include polymers, some of which were originally developed for use in the paint and coating industry. These are materials like methyl acrylate, ethyl acrylate, butyl acrylate, vinyl acetate, styrene, vinyl chloride, and acrylonitrile. Oils derived from vegetable, petroleum, or silicone sources are added to the formulations to enhance the shine.
2. *Solvents.* Solvents are used to help dissolve or soften some of the water-insoluble materials used in polishes. Common solvents include mineral spirits, turpentine, and naphtha. In addition to solvency, factors to be considered during solvent selection include flammability and toxicology.

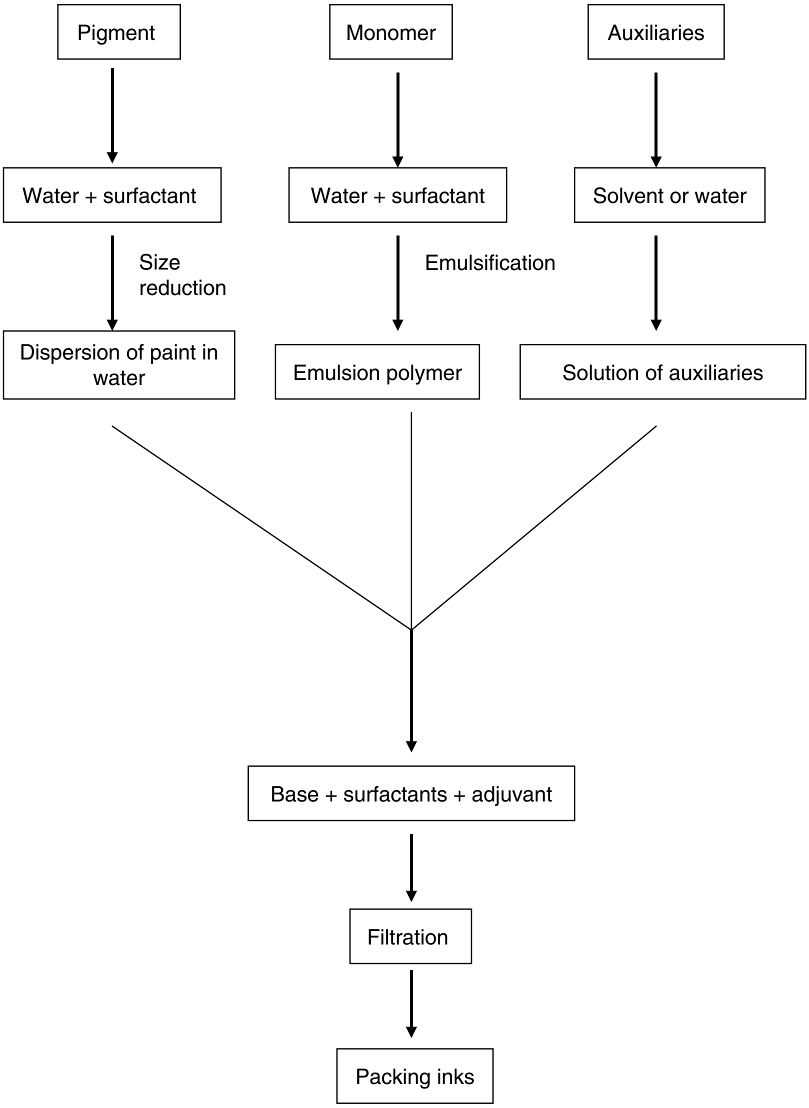


FIGURE 17.10 Steps involved in the manufacture of inks. Inks are composed of pigments, monomers, and auxiliaries.

3. *Emulsifiers/surfactants*. Proper blending of oil with water-soluble elements requires the addition of surfactants (short for surface active agents), which have the ability to bridge water and oil to create a stable cream, paste, or lotion called an emulsion. If the oil phase is emulsified in water the emulsion is called an oil-in-water emulsion, and if it is water emulsified in oil, the emulsion is called a water-in-oil emulsion. For each type of emulsion, the surfactants are of different characteristics. The emulsifiers used for the oil-in-water emulsions are water soluble with a high degree of hydrophilicity, and water-in-oil emulsions need oil-soluble emulsifiers of a highly hydrophobic nature. Surfactants are also used for the dispersion of hydrophobic solids in water. For dispersions, various types of surfactants—nonionic, ionic, and zwitter ionic—are designed to meet the requirements of formulations for paints, inks, and polishes.

4. *Propellants.* Propellants are liquified gases that are used to dispense aerosol products as a spray. The most common propellants are short-chain hydrocarbons, such as propane or butane, both of which are highly flammable.
5. *Other ingredients.* In addition to the ingredients listed above, polishes may contain abrasives, colorants, fragrance, and preservatives. Still other ingredients are added to limit the chance of corrosion of the metal can. These are often nitrogen-containing materials that raise the pH of the solution.

These ingredients can be formulated into pastes, creams, liquids, and aerosol (including nonaerosol pump sprays).

17.3.3.2 Manufacturing Process of Polishes

Polishes are basically of two types:

1. Oil- or solvent-based polishes
2. Water-based polishes

To manufacture oil-based polishes, the process is quite simple, as all the components are mixed and homogenized by the continuous medium, which acts as a solvent. Here, the surfactants are also part of the solution. To manufacture water-based polishes, there are two methods: (1) emulsion polymerization and (2) emulsification.

1. *Emulsion polymerization.* The monomer is taken along with water and polymerized using surfactants in the presence of catalyst and initiator. The increase in the polymer chain is accompanied by the absorption of surfactant (emulsifier) on the growing particles. Surfactants also help in stabilizing the emulsion form. The polymer, which is the predominant active component, accounts for 60–80% of the material in the dry film. Therefore, its effect on the performance of the polish is very important. The polymer in the wet polish consists of spherical emulsion particles ranging in size from 0.1 to 0.5 μm. The emulsion particles are stabilized with anionic and nonionic surfactants. Inside the particles, the polymer molecules are composed of acrylate, methacrylate, and styrene monomers that have been polymerized to a molecular weight that in some cases exceeds 1,000,000. The particles may also contain some low-molecular weight material, known as oligomers.
2. *Emulsification.* Instead of starting with monomers, one can start with long-chain hydrocarbons and emulsify them in water as an oil-in-water emulsion.

The polyethylene or wax emulsion particles are another important component of a floor polish. A wide variety of synthetic and natural waxes have been used in floor polish; however, the most popular types are oxidized polyethylenes and polyethylene copolymers. These generally have a molecular weight of 1000–5000 and varying degrees of crystallinity. Owing to their physical properties, the important characteristics of buffability and scuff resistance are imparted to a floor polish.

17.4 DEFINING SURFACTANTS

Substances acting on the surfaces are called *surfactants* or surface-active agents. For a material to be active at the surface, it is essential that the material exhibit liking for the surface rather than the bulk. For example, let us take the case of water in a vessel; water surface is in equilibrium with the air above the surface. A substance added to water would become active at the surface (water–air interface) only if that substance does not like the bulk (water). Any hydrophobic substance added to water would not like the bulk phase of water, and as a result would separate out from water to either float on the surface or sink to the bottom of water depending on the density of the hydrophobic material. But will this type of material be active at the surface? The answer to this is clearly no, because the surface is actually an interface of water–air, and for the material to be active at the interface, there must also be a hydrophilic moiety in the hydrophobic material added. Mere separation from bulk does not mean being active at the interface (Figures 17.11a through 17.11c).

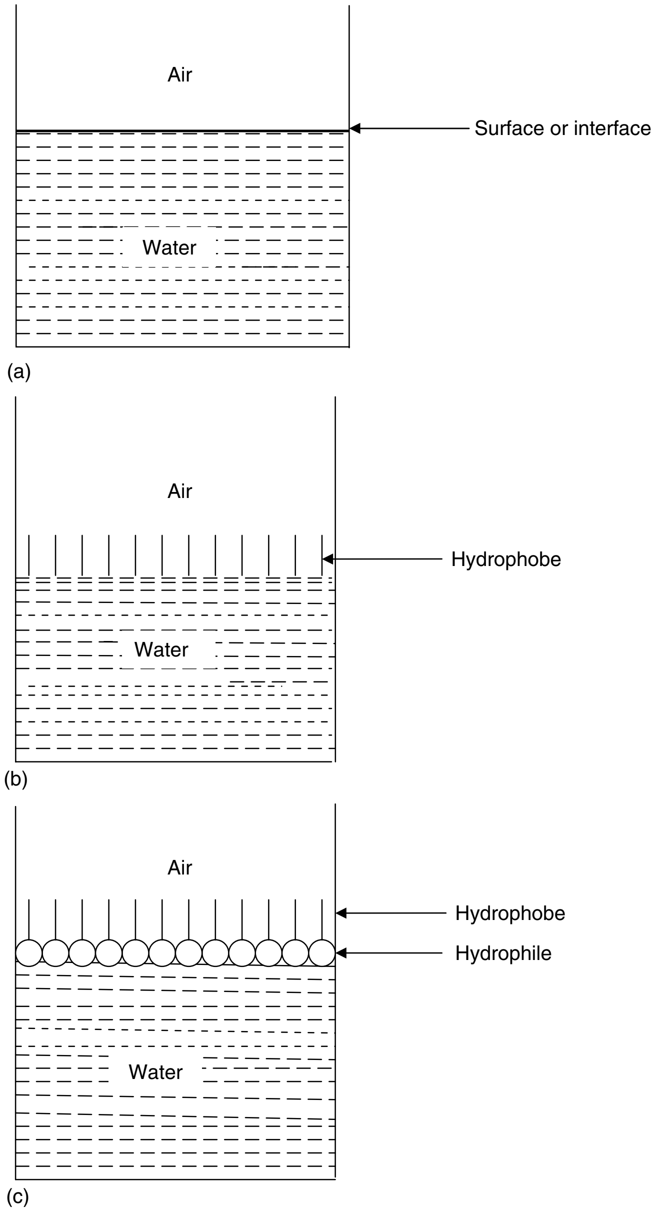


FIGURE 17.11 Behavior of various substances when added in water. (a) Equilibrium between water and air interface, (b) hydrophobic material separating out and floating on the surface, and (c) surfactant adsorbing at the interface in a manner that the hydrophilic group directs toward water, whereas the hydrophobic group stays in the air.

This example can easily be extended to other surfaces or interfaces. Thus, the surfactants are active at the interface only because the former is composed of a hydrophobic and hydrophilic moiety in the same molecule of surfactant.

Here, it may be noted that all organic substances consisting of a hydrophobic alkyl chain and hydrophilic functional group, such as hydroxyl, amine, and carboxylate, cannot qualify to be a surfactant. For a substance to be termed as a surfactant, it is essential that there must be a balance between the hydrophobic and hydrophilic groups. This is also called the hydrophilic–lipophilic balance (HLB) of the surfactant molecule. In other words, neither the excessively large hydrophobe and insignificant hydrophile, nor the large hydrophile and very small hydrophobe, can act as a surfactant. Based on a given hydrophobe, one can add the desired hydrophile and vice versa to obtain the surfactants.

To understand the role of surfactants in different systems, it is important to know what basic effects are exhibited by the surfactants. For this, let us again take the simple case of water surface in equilibrium with air; the liquid phase (polar; water) is in equilibrium with the gas phase (nonpolar; air) in the presence of a surfactant. The surfactant molecule has a head (polar or hydrophilic group) attached to a tail (nonpolar or hydrophobic group); the tail would not like water, whereas the head would not like air, and vice versa. As a result, the surfactant molecules would neither go into the bulk of water nor into the bulk of air; in fact they would remain at the interface negotiating with both phases (Figure 17.12). For staying at the interface, the surfactant molecules reorient themselves in such a way that the head part bends toward the water, whereas the tail part extends toward the air. This way, surfactant molecules form a bridge between the water–air interface, and this results in a decrease in surface tension.

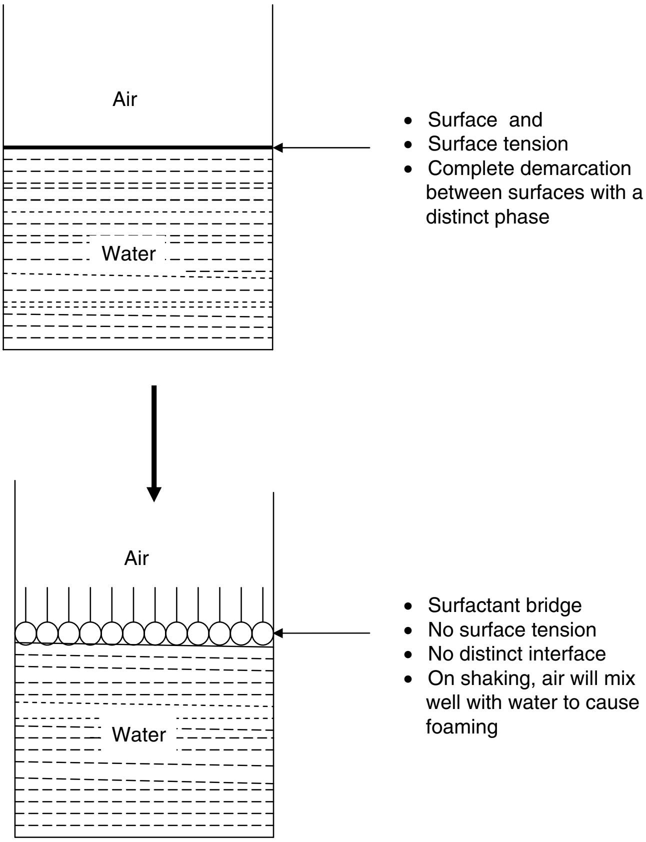


FIGURE 17.12 Bridging of the surfactant molecule between water–air interface lowers the surface tension.

17.5 TYPES OF SURFACTANTS

As said before, surfactants have hydrophobic and hydrophilic moieties in the same molecule. Depending on the nature, type, shape, and size of the hydrophobic and hydrophilic parts, a range of surfactants with varying HLBs can be designed. Keeping the hydrophobic chain (tail) the same, one can attach various types of hydrophilic groups; each one resulting in a different type of surfactant. Further keeping the hydrophobic chain and hydrophilic group the same, and varying the size of the hydrophilic group, one would obtain a range of surfactants from a given type of surfactants.

Further, based on the charge on the hydrophilic groups, surfactants can be categorized into four basic groups:

1. Nonionic, no charge on the hydrophile
2. Anionic, negative charge on the hydrophile
3. Cationic, positive charge on the hydrophile
4. Zwitterionic, positive and negative charges present in the same molecule

It may be noted here that the behavior of surfactants in the multiphase and multisurface systems is mainly determined by the balance between the hydrophobic forces and hydrophilic forces of the surfactants (Figures 17.13a through 17.13f).

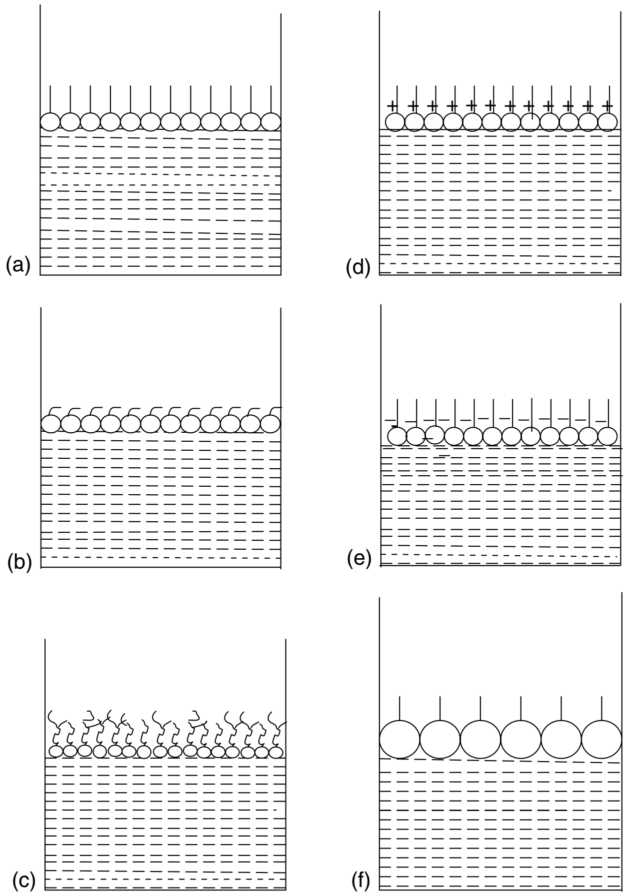


FIGURE 17.13 Different types of surfactants bring the same effect of reducing surface tension to a different extent depending on the various structural attributes of surfactants. (a) Hydrophobe extending upward, (b) hydrophobe lying flat, (c) hydrophobe with long dangling tails with asymmetric chains, (d) hydrophile with positive charge, (e) hydrophile with negative charge, and (f) a large hydrophile.

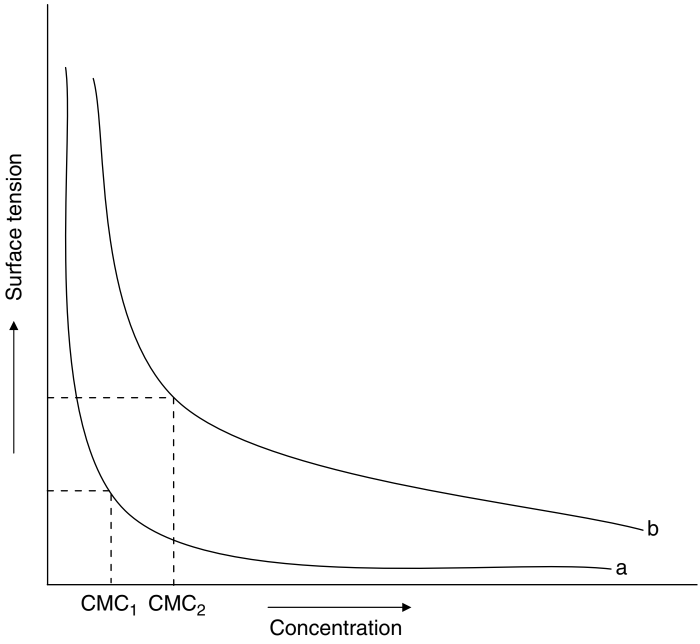


FIGURE 17.14 Effect of surfactant concentration on the surface tension. The minimum surface tension achieved is different for different surfactants depending on their structural attributes. The minimum surface tension achieved is in the order of a<b. The concentration of minimum surface tension is called CMC.

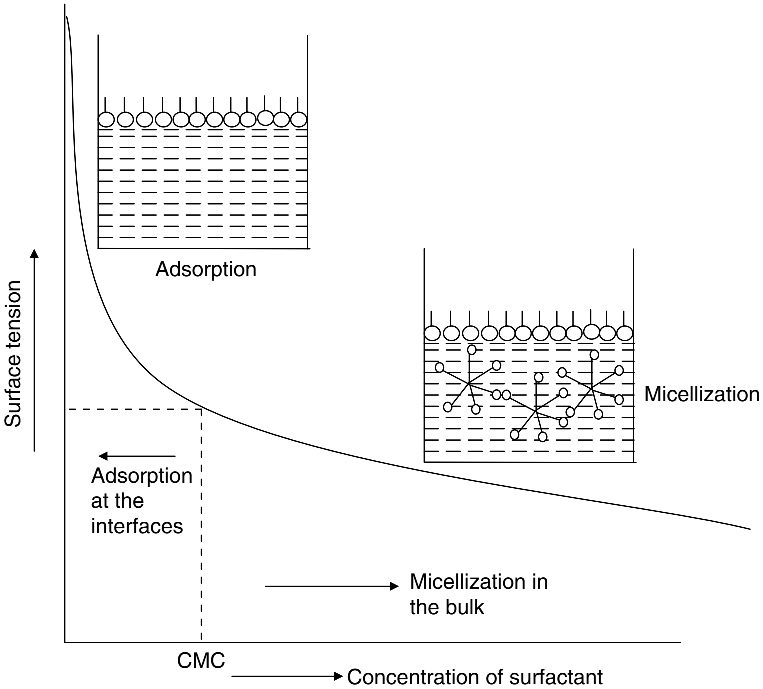


FIGURE 17.15 Effect of concentration on the surface tension of a surfactant in a water system. Surfactants beyond CMC result in micellization and before CMC adsorb at the interface.

Surfactants with varying structural attributes provide different effects relevant to the extent to which the intensity of surface tension reduction would vary. The plot of effect of concentration on surface tension would differ, as can be seen in Figure 17.14.

As seen in the figure, beyond the minimum surface tension achieved, further addition of surfactants in the system would not result in any change in surface tension. The excess surfactant added beyond the concentration of minimum surface tension (known as critical micelle concentration or CMC) would go into the bulk-forming micelles, as indicated in the figure. It can be seen that the adsorption of the surfactant at the interface occurs only up to the point of minimum surface tension and beyond this, the adsorption stops and micellization begins.

Surfactants beyond CMC result in micellization, and before CMC they adsorb at the interface.

Thus, the complete range of applications of surfactants can be explained and exploited based on the understanding and maneuvering of two basic phenomena: adsorption at the interface and micellization in the bulk (Figure 17.15). Adsorption enables the two different surfaces to coexist as a homogeneous system, and micellization helps in solubilization of the hydrophobe into the hydrophilic phase and vice versa.

17.6 ROLE OF SURFACTANTS AS DISPERSANTS, EMULSIFIERS, AND SOLUBILIZERS

The role of surfactants in paints, inks, and polishes can be better understood if the designed effect is clearly envisaged: both in the making of paints, inks, and polishes, and in their application.

Surfactants play a big role in resolving most of the issues that go against oil-based paints by enhancing the following:

1. Wetting of surfaces by oil-based paints by causing the spreading of the paint, and thereby ensuring no beading of the paint drops on the surface
2. Drying of the paints by modifying the interfacial tension, and ensuring that the painted surface remains unaffected by the adverse effects of water
3. The positive aspects of the rigid behavior of oil-based paints, again by adsorbing at the interfaces

Unlike the oil-based paints, where all the constituents except pigments are in the solution, the water-based paints consist of constituents that are either dispersed or emulsified. Thus, the role of surfactants in the case of water-based paints starts right from the making of the paints and continues until their application, including their storage. The following roles are played by surfactants:

1. Emulsification of the resin monomers to develop polymers of desired molecular weight distribution
2. Dispersion of various solid particles including pigments in water
3. Emulsification and solubilization of organic additives in water
4. Stabilizing the formulation of paints by creating the electroviscous effect, thereby generating the barrier for the tendencies of separation of different phases from each other

17.6.1 ROLE OF SURFACTANTS IN THE MAKING OF PAINTS, INKS, AND POLISHES

The making of paints, inks, and polishes involves the following basic effects:

1. Dispersion of the pigment material (mainly in water)
2. Stabilization of the formulated product without any separation during storage
3. Emulsification of the resins (in water)
4. Solubilization of the solvents (in water)

Let us discuss them individually to appreciate the role of surfactants in making paints, inks, and polishes.

17.6.1.1 Dispersion of Pigment Material (Mainly in Water)

Pigment particles are basically inorganic materials with hydrophobic surfaces. When brought in contact with water, the pigments do not mix with water unless a surfactant is added to the system. As shown in the Figure 17.16, the first step is the wetting of the powdered material surface in water, with adsorption of surfactants at the interface of solid and water.

17.6.1.2 Stabilization of the Formulated Product without Any Separation during Storage

This is followed by the breaking of the bigger particles into smaller ones. This increases the number of particles, and obviously increases interfacial area. Surfactant molecules staying at the interfaces of all the small particles in contact with water would ensure the dispersion of the tiny particles in water. The next stage of stabilization is critical for the product to survive on the shelf, whereas the first two stages are essential for making the product.

The stabilization of the dispersed systems is achieved through the creation of a barrier, which prevents the particles from colliding and agglomerating. This basically means that the dispersed particles always repel each other rather than attracting each other.

With an understanding of the potential energy curve, one can maneuver the stabilization of the dispersed pigments.

The Van der Waals attraction and electrostatic or steric repulsion operates as the distance between the particle decreases, resulting in different zones of stability.

At long distances, there is a possibility of reversible coagulation of systems; at medium distance, the repulsive forces act more strongly than the attraction forces, forming a zone of stable dispersion; and at very short distances, there exists the zone of irreversible unstable dispersion.

It may be noted that the aim of the formulation development scientist is to have a product with the dispersed phase stabilized by creating a large barrier as a result of repulsion among the particles. The energy barrier, which prevents the coagulation or flocculation of dispersed particles, can be created by the use of surfactants of desired characteristics. Whereas nonionic surfactants generate steric repulsions, anionic surfactants create electrostatic repulsion between the particles. This can be understood from Figure 17.17a.

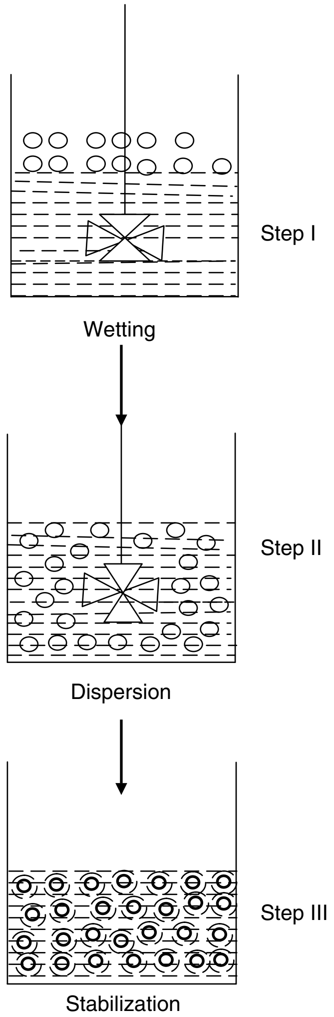


FIGURE 17.16 Pigments are dispersed via wetting, and hence they are stabilized in the system with the help of surfactants.

As evident from Figure 17.17b, the systems stabilized with anionic surfactants have a higher energy barrier than the ones stabilized with nonionic surfactants.

1. *Caking and claying in paints.* Here, it would be worthwhile to explain the phenomenon commonly known as caking and claying in paints. This occurs mainly due to the fact that the paint systems stabilized with the anionic surfactants, having a high-energy barrier, undergo settling of particles with time. As the energy barrier in such systems is very high, once the particles cross the barrier, they fall in the well of an irreversibly unstable

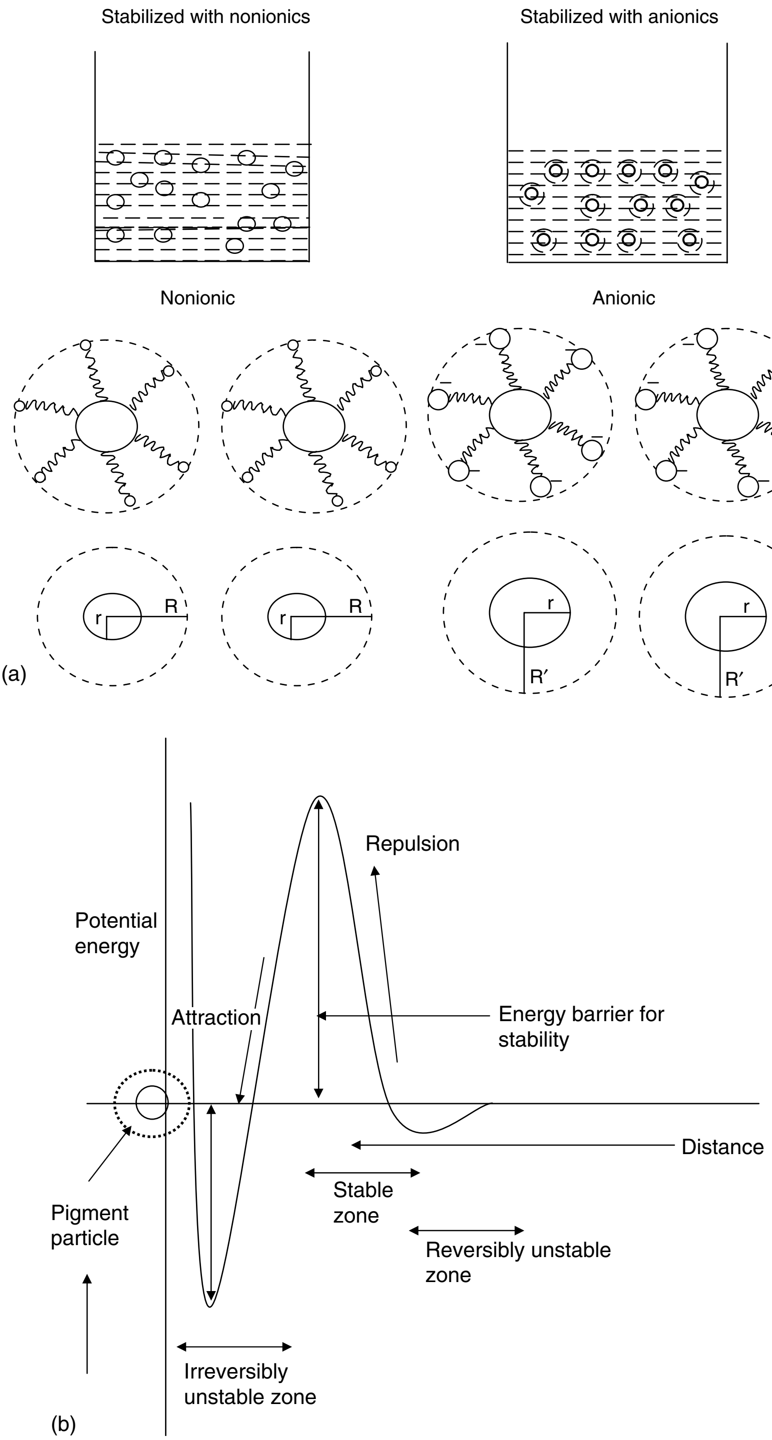


FIGURE 17.17 (a) Figure depicting stabilization role of surfactant. Long dangling tails of nonionic surfactants adsorbed on the dispersed particles create a steric barrier with the effective radius (R) of the particles much larger than the real radius (r) of particles (steric repulsion). For anionic surfactants, the negative charge on the adsorbed surfactants generates a layer with the charge distributed around the particle. The effective radius (R′) is much higher than the real radius (r), and also higher than the effective radius (R) with nonionics (electrostatic repulsion). (b) Potential energy curve of a pigment particle dispersed in water.

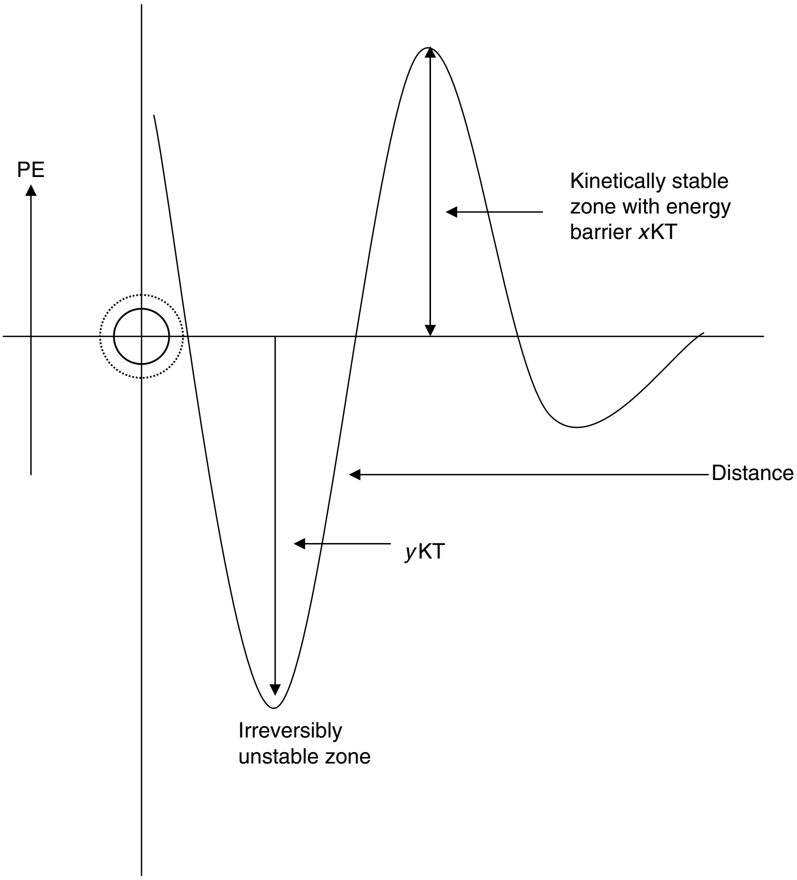


FIGURE 17.18 Pigment particles stabilized with anionic surfactants adsorbed on their surfaces. The kinetic stability is ensured by the barrier of energy *x*KT. If the particles cross over the barrier, they fall into the unstable zone from where, to redisperse them, one would need $(x + y)$KT of energy. PE = potential energy.

zone, which means that, to redisperse the particles, one would need very high energy, as explained in the Figure 17.18.

2. *Ideal pigment dispersion.* Therefore, while developing formulations, one will have to address the implications of a high-energy barrier; an optimization is necessary. The ideal pigment dispersion for paints, inks, and polishes has an extraordinarily high barrier, but allows the effortless redispersion of the particles. Surfactant–polymer interactions are important in stabilizing the pigment formulations. These surfactant–polymer interactions result in an unstable system that can be easily stabilized with a little shaking. They are also referred to as *depletion flocculation*, and in the energy curve (Figure 17.18), they fall in the zone of reversibly stabilized state.
3. *Interparticle interactions; modification by surfactants.* So far, the aspect of adsorption of surfactants on solid pigment surfaces to effect their dispersion has been discussed. Let us now look at the interparticle interactions that are modified as a result of surfactants adsorbed on the surface of the dispersed particles. Depending on the nature of the surfactants adsorbed, the interactions can be either of short range or hard type and long range or soft type. As per the interactions, the stability of the dispersions can be designed.
    a. *Short-range interactions.* Short range means that the presence of one particle on the other would be felt at a very short distance. This happens when the effective radius, as

a result of the surfactant adsorbed on the surface, would be not much different from the real radius of the dispersed particles. This means that in a given volume, more particles can be adjusted. Pigment dispersions of high solid content with minimum dispersing medium can be developed by taking advantage of short-range interactions. Generally, nonionic surfactants of the following types are used to develop pigment dispersions with high solid or short-range interactions. Such systems are stabilized by the use of

  i. Ethoxylated alkyl phenols
  ii. Ethoxylated alcohol
  iii. Fatty esters of polyols

b. *Long-range interactions*. Long-range interactions are those in which the presence of one particle by the other is felt at long distances. In such systems, the effective radius of the dispersed particles is much larger than the real radius. As a result, one can fill a limited amount of solid pigments in the medium. Such systems are stabilized by the use of anionic surfactants such as

  i. Sulfonated alkyl aryls
  ii. Sulfonated alcohol
  iii. Phosphated esters
  iv. High-molecular weight copolymer of ethylene oxide and propylene oxide
  v. Multifunctional anionics such as tartrates

The concept of modification of interparticle interactions amongst the dispersed particles can be understood from the depictions in Figure 17.19.

Here, it may be noted that the interparticle interactions in the pigment dispersions are manifested by the increase in the viscous behavior of the dispersions. Based on the studies on the viscous

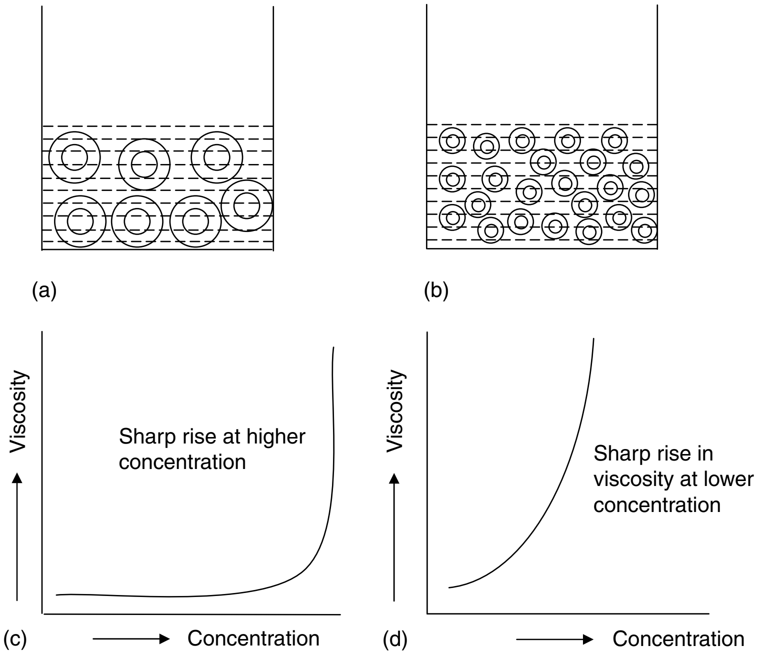


FIGURE 17.19 The nature of interparticle interactions. (a) Long range and (b) short range. The solutions behave differently when checked for their viscosity. The viscosity rises (c) only at a higher concentration in the case of short-range interactions, whereas viscosity shows a steep rise (d) at a very low concentration of solids.

behavior of dispersed systems, the desired type of surfactants can be selected, and the formulations can be designed accordingly.

In the case of inks, where one needs to maximize the pigment content on the surface, the pigments stabilized with short-range interactions would be preferred. Likewise, in the case of paints, to generate the viscous effect in the formulation mainly to counter the settling of the dispersed particles, one would use long-range interactions.

17.6.1.3 Emulsification of Resins and Similar Materials (in Water)

One of the important components in paints, inks, and polishes are the hydrophobic substances used to make the coated surface resistant to water. Since hydrophobes cannot be directly incorporated in the products, hydrophobic (oily) substances have to be emulsified in water as oil-in-water emulsions using suitable surfactants. For oil-in-water emulsions, surfactants must have a smaller hydrophobic group and larger hydrophilic group. For example, the ethoxylated alkyl phenols with higher ethylene oxide content or the anionic surfactants with medium size alkyl chain length would be effective surfactants for this purpose. In inks and polishes, one of the major components is based on wax and fatty esters in the form of emulsion in water. The emulsions are generally prepared with ~50% by weight of the waxy material, and then added to the formulations. Surfactants used for the stabilization of oil-in-water emulsions also play the role of homogenizing the emulsion.

17.6.1.3.1 Emulsion Polymers

In paints, inks, and polishes, the component used for binding the pigments to the surfaces to be coated is based on different types of polymeric substances. The monomers are polymerized either by the process of emulsification or dispersion in water. The monomers are immiscible in water, and to prepare the emulsion polymers, a portion of the monomer is to be emulsified using high HLB surfactants. The rest of the monomer is then added to the monomer emulsion, kept at the desired temperature and in the presence of the initiator and catalyst. On addition of the monomer, the polymerization takes place exothermally, and thus polymerization is achieved under controlled temperature achieved through heat removal from the system. In the same way, polymerization can also be carried out by dispersion of monomer in water. The only difference in the two techniques of polymerization pertains to the molecular size and molecular weight distribution of the polymer obtained; emulsion polymerization leads to larger polymer size than the one obtained from suspension or dispersion polymerization. According to the molecular size desired, one adopts the appropriate polymerization techniques for the given purpose.

17.6.1.4 Solubilization of the Hydrophobes

Some of the auxiliary components of hydrophobic nature need to be solubilized in water in certain specialized formulations of paints, inks, and polishes. The solubilization of hydrophobes in water would require the use of surfactants as well as cosurfactants, and for this a mixture of nonionic and anionic surfactants is often used.

Surfactants play the following major roles:

1. Dispersion of pigments
2. Emulsification of waxy solids and liquids
3. Emulsion polymerization of resin binders
4. Suspension polymerization of resin binders
5. Solubilization of hydrophobes

With surfactants in water, the decrease in surface tension at a lower concentration is accompanied by the adsorption of surfactants at an interface up to the point of CMC. Beyond this CMC, the surfactants form the micelles or the aggregates of surfactants. Whereas adsorption helps in making suspensions, dispersions, and emulsions, micellization helps in solubilization.

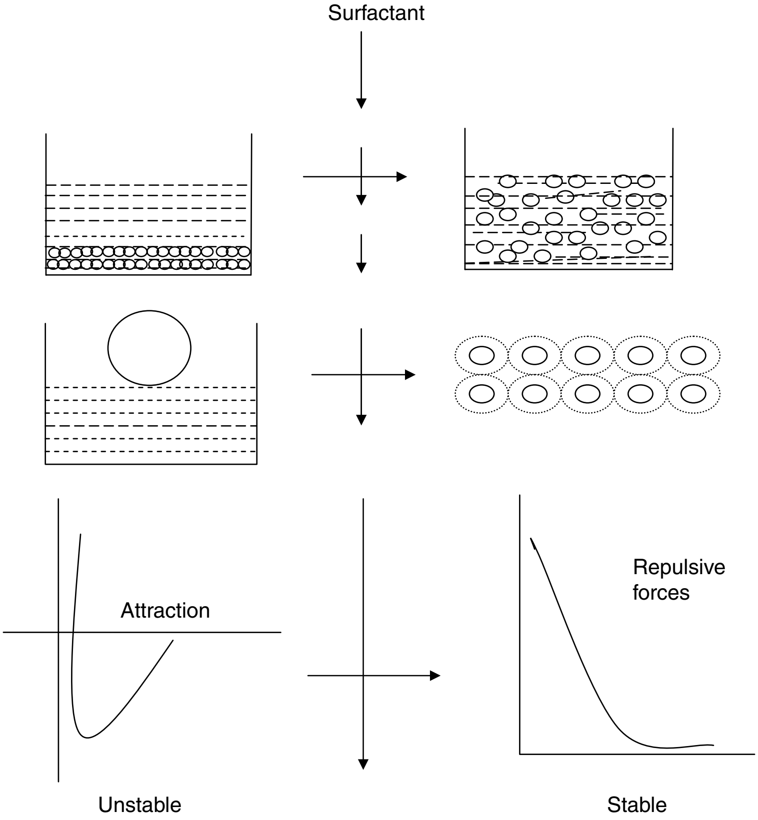


FIGURE 17.20 The surfactants adsorbed on the small particles create interparticle repulsion, effecting the homogenization of one phase into another.

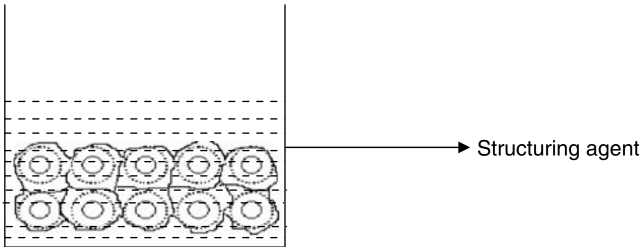


FIGURE 17.21 Structuring (by polymers) of paints, inks, and polishes for long-term stability. Surfactant–polymer interactions result in the antisettling network to retain stability of dispersion or emulsion.

For enhancing the stability of paints, inks, and polishes, sometimes (polymeric) structuring agents are also used. The surfactant–polymer interactions help in stabilizing the formulation, as described in Figures 17.20 and 17.21.

17.6.2 Role of Surfactants in Application of Paints, Inks, and Polishes

The application of paints, inks, and polishes on various surfaces require the following:

1. Wetting and spreading on the surface
2. Adhesion of coating to the surface

3. Drying of the applied product on the surface
4. Weather resistance of coating on the surface

For all the above, the adsorption of surfactants on the surfaces is the key. Depending on the requirements of the application, the desired type and quality of surfactants are used.

17.7 CRITERIA FOR SELECTION OF SURFACTANTS FOR PAINTS, INKS, AND POLISHES

Surfactants are used for the following major applications:

1. Wetting
2. Dispersion
3. Emulsification
4. Solubilization
5. Electroviscous effect for stabilization of dispersions and emulsion

For evaluating the surfactants for the abovementioned applications, one approach is to select the suitable surfactants based on the hit and trial methodology. By this way, each candidate surfactant would have to be evaluated by actually making the given formulation and checking the formulation for various criteria. This is a sure short method of selection of a surfactant for a given formulation. However, this is not a scientific approach.

The scientific way of selecting the surfactant is based on the characterization of surfactants for the following properties:

1. Solubility with temperature
2. Adsorption at interface
3. Contact angle and wetting behavior
4. Interfacial tension
5. CMC
6. Solubilization
7. Rheology of surfactant solubilization in water

Solubility of surfactants in different solvents and in water, and effect of temperature and electrolytes on the solubility of the surfactants in different solvents, determine the usability of the former for a given formulation. For example, a surfactant with great affinity for water would mean that the surfactant would form oil-in-water emulsion.

Similarly, the surfactant insoluble in water would go well for the water-in-oil emulsions. The nonionics generally separate out from water at higher temperatures, mainly due to the dehydration of the water-soluble surfactants. At the temperature at which the dehydration of surfactant occurs, the solution turns turbid, and the temperature is considered as the cloud point of the surfactant. The cloud point is lowered in the presence of electrolytes. Based on the effect of temperature and electrolytes on the cloud point of nonionic surfactants, one can select the suitable surfactant; contrary to this, the solubility of anionic surfactant increases with increase in temperature. The temperature at which solubility shows a sharp rise is called the *Kraft point* of anionic surfactants.

The anionics are more vulnerable to electrolytes than the nonionics. Hence, for determining which anionic would work better for a given formulation, studies of the effect of electrolytes on solubility at elevated temperatures would be quite useful.

Adsorption studies of surfactants for the given solid surfaces would help in ascertaining the capability of the surfactants for causing the desired modification of the given surface. The one that gives the maximum adsorption would obviously be considered a better dispersant for a solid surface. Further, the nature of the adsorption isotherm would also help in determining the right concentration of the surfactant to be used for the formulation.

Contact angle measurements indicate the capability of a surfactant to spread a desired formulation on a given surface. For example, for developing printing ink for a plastic surface, the surfactant should result in a very low contact angle with the surface. In a way, contact angle measurements also explain the wetting of the surface, besides the spreadability of paints, inks, and polishes on the surface to be coated.

Interfacial tension measurement, both static and dynamic, provide clues about the usefulness of the surfactant as an emulsifier for a given system of oil and water. Not only is the sharp decrease in interfacial tension desirable, but it is also important to produce the minimum tension possible from a given surfactant. In fact the results of interfacial tension measurements can provide information about the effectiveness and efficiency of surfactants for a given system. A sharp decrease in interfacial tension with the increase in concentration of surfactant indicates that the surfactant is effective, whereas one that causes minimum interfacial tension although not with a sharp rate would be considered efficient. Depending on the requirements, one can use the effective or the efficient surfactant for a given formulation of paints, inks, and polishes. Interfacial data of surfactants can be used as the main criteria for quality by the users of surfactants.

Studies of CMC of surfactants also provide a useful tool for selection of surfactants. The low CMC surfactants mean that such surfactants saturate the surface at very low concentrations, and thus they start aggregating in the bulk. The CMC is basically affected by the size and shape of the hydrophobic chain (tail part) and the charge on the hydrophilic group (head part) of the surfactant. Low-CMC surfactants generally consist of branched hydrophobes of large size, and they are considered suitable surfactants for solubilization of hydrophobes in water.

Solubilization of different solvents (oils) in water by a given surfactant is determined by checking the maximum amount of solvent dissolved in a given volume of water per gram of surfactant. This is also called the water number. A higher water number means a higher capability of the surfactant to solubilize the oil in water. Similarly, a lower water number means poor solubilization power of surfactant for oil in water. A correlation between solubilization and CMC is a key indicator regarding selection of surfactants.

Rheology of surfactant solution in water provides a tool to gauge the behavior of surfactants regarding the stabilization of a formulation. If rheological studies are conducted for surfactant polymer mixture dissolved in water, one gets an idea also about the role of surfactant–polymer interactions useful for effecting stabilization of the formulation. Rheology data are also essential for determining the short-range and long-range interactions of a formulation, and thus it is possible to develop the formulation as per the requirements.

For developing the desired formulation of paints, inks, and polishes, generally a combination of nonionic and ionic surfactants is used to address the synergistic effect of combined surfactants. The characterization of the surfactants as per the abovementioned characteristic is essential for developing suitable formulations.

17.8 PATH FORWARD TO MEET FUTURE CHALLENGES

From the discussions presented in this chapter, the following basic conclusions can be drawn:

- The need for new materials are ever changing and each time a new type of material with improved performance is desired for the same application.
- The advent of new materials directly means that new types of surfaces are created.

- Dealing with surfaces especially when multi-components are involved can be quite challenging and often the modification of surfaces becomes imminent.
- Use of surfactants has been known where several types and categories of surfactants are being developed for different requirements. The development of surfactants leads to the creation of several types of products with a high degree of commercial potential.
- Surfactants not only play the key role in the making and stabilization of a multi-component formulation but they also are responsible for some of the desired performance-related characteristics of the formulated product. The list of products for which surfactants are being used today is in fact, endless.
- One of the most important categories of products used for surface modification includes products like paints, inks, and polishes. Eventhough they form a small fraction of the composition of paints, inks, and polishes, surfactants are the most essential component of these products.
- As said earlier, the criteria of selection of surfactants would change with changes taking place due to developments of new surfaces, new application methods and new regulations. This is precisely true when we look at the developments taking place in the fields of paints, inks, and polishes.
- Paints, inks, and polishes are all surface modifiers on the one hand and they leave a long-lasting impression on the surfaces on the other hand. The path forward in the development of paints, inks, and polishes is thus determined by the purpose for which these three products are used.

Taking the above conclusions into consideration, following key steps would form the path forward as far as the role of surfactants for paints, inks, and polishes is considered:

1. *Development of a new range of surfactants*
   The most important research and development effort would involve the development of surfactants with the following features:
   a. Biodegradable and preferably based on renewable resources
   b. Environment-friendly
   c. Nontoxic
   d. High performance with low cost
2. *Development of new formulations of paints, inks, and polishes*
   The next step where research and development efforts would be directed towards developing newer type of formulations of paints, inks, and polishes with following features:
   a. Solvent-free and preferably water based
   b. Biodegradable and nontoxic
   c. Improved performance

The path forward to meet challenges, thus, would involve a concerted research and development effort on various aspects of inputs, formulation, and applications of paints, inks, and polishes.

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18 Applications of Surfactants in Pharmaceutical Dosage Forms

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CONTENTS

18.1 INTRODUCTION

To impose a desired effect on the human body, a therapeutically potent substance (drug molecule) must be present in suitable concentration at its target organ. More than 40% of the new pharmacologically potent molecules exhibit poor biopharmaceutical properties, which prevents them from reaching the target organ in a sufficient quantity at the appropriate rate [1]. Those molecules must be formulated (pharmaceutically prepared in their final dosage form) prior to administration as a medicine. The main goals of such formulations are [2]

1. To improve the bioavailability of the drug (to increase the fraction of an administered dose of unchanged drug that reaches the systemic blood circulation)

2. To alter the release rate of the drug
3. To target the drug to a specific organ

Much effort is therefore invested in research and development by the pharmaceutical industry in finding the optimal dosage forms for the potent molecules. Surfactants (or amphiphilic molecules) play one of the most important roles in creating the suitable vehicle for drug administration. Amphiphilic molecules consist of at least two parts, hydrophobic tail and hydrophilic head groups. Owing to this structure, interactions of the drug with amphiphilic molecules in pharmaceutical dosage form can significantly alter the solubility, permeability, and dissolution properties of a drug. Thus, surfactants are mostly added to dosage forms as inactive excipients, which improve the bioavailability of the drug. Such improvement can be achieved by [2]

1. Enhancing the aqueous solubility of the drug
2. Prolonging the time that the target tissue is exposed to the drug
3. Improving permeability of the drug through the body's membranes and barriers

Surfactants may also be used for targeting a drug to a specific organ in the body, or for achieving better physical and chemical stability of the dosage form.

Owing to the significant influence of surfactants on the biopharmaceutical properties of the drug compounds, they are of great interest for pharmaceutical, biotech, and drug delivery sectors. Nontoxic amphiphilic molecules, which are already recognized as safe for administration in different drug dosage forms by authorities such as the Food and Drug Administration (FDA) in the United States and the Committee for the Safety of Medicine in the United Kingdom, are especially valuable for those sectors due to a relative ease of regulatory approval. Several examples of such amphiphilic molecules that are approved for incorporation in pharmaceutical dosage forms are summarized in Table 18.1 [3–5]. Many other surfactants (including surface active polymers such as proteins or polysaccharides) can also be utilized as pharmaceutical excipients in limited quantities. The official FDA database of Inactive Ingredients for Approved Drug Products should be referred to for the exact quantity of each amphiphilic molecule approved for incorporation into each pharmaceutical dosage form in the United States [5]. It should be noted that the list is constantly updated, so it is advisable to consult the relevant health authorities for specific uses of the surfactants.

There are many naturally occurring surfactants in our body. Several structures of those endogenous surfactants are shown in Figure 18.1. The cell membrane is composed of two layers of several surfactant molecules. Polar lipids, called phospholipids, are the primary building blocks of this bilayer. Other molecules, such as proteins and cholesterol, are also incorporated within the cell membrane. Cholesterol is a nonionic amphiphilic molecule, and its role is to alter the cell membrane fluidity. Phospholipids are derivatives of glycerol, in which two of the alcohol groups are esterified with fatty acids, and the third with phosphoric acid. The resultant molecules have two hydrophobic tails and a hydrophilic head, the charged phosphate ester. Common head groups are choline, ethanolamine, serine, and inositol [6]. Those are mainly zwitterionic molecules, containing two oppositely charged groups. Lecithin is a common name for the mixture of phospholipids in which the main component is phosphatidylcholine. It is extracted from phospholipid-rich sources such as soybean and egg. Another example of surfactants that are naturally present in the human body is the bile acids. Bile is formed by the liver, and secreted to the gastrointestinal lumen for emulsification of dietary fat and oils and assisting in their absorption. Bile consists of the bile acids, phospholipids, cholesterol, and bilirubin. The bile acids are derivatives of cholesterol, in which hydroxyl and carboxy groups are attached to the steroid nucleus, converting them into powerful natural surfactants [6,7].

The use of the surfactants in pharmaceutical dosage forms is indeed so widespread that a comprehensive and thorough review of each practical and theoretical application is simply beyond the scope of this chapter. We will discuss the utilization of amphiphilic molecules in various pharmaceutical dosage forms, divided according to their route of administration.

TABLE 18.1
Surfactants Approved for Usage in Pharmaceutical Dosage Forms

Surfactant	Class	Structure	Regulatory Status
Cetearyl alcohol	Nonionic	Mixture of stearyl and cetyl alcohols	FDA approved for oral, buccal, ophthalmic, rectal, vaginal, topical, and transdermal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Cetrimide	Cationic	Trimethyltetradecylammonium bromide	Included in nonparenteral medicines licensed in the United Kingdom
Cetyl alcohol	Nonionic	Cetyl alcohol (hexadecan-1-ol)	FDA approved for oral, otic, ophthalmic, rectal, vaginal, and topical preparations. Included in nonparenteral medicines licensed in the United Kingdom
Cetyl pyridinium chloride	Cationic	1-Hexadecylpyridinium chloride	FDA approved for oral, inhalation, iontophoresis, and transdermal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Cholesterol	Nonionic	Cholest-5-en-3β-ol	FDA approved for epidural, intravenous, ophthalmic, vaginal, and topical preparations. Included in nonparenteral medicines licensed in the United Kingdom
Docusate sodium (dioctyl sodium sulfosuccinate)	Anionic	*Bis*(2-ethylhexyl) sodium sulfosuccinate	FDA approved for intramuscular, oral, and topical preparations. Included in nonparenteral medicines licensed in the United Kingdom
Glyceryl monooleate (glyceryl oleate)	Nonionic	9-Octadecenoic acid monoglyceride	FDA approved for oral, transdermal, and topical preparations. Included in nonparenteral medicines licensed in the United Kingdom
Glyceryl monostearate (glyceryl stearate)	Nonionic	Octadecanoic acid monoglyceride	FDA approved for dental, oral, ophthalmic, otic, rectal, sublingual, topical, and vaginal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Glyceryl palmitostearate	Nonionic	Mixture of mono-, di-, and triglycerides of oleic and stearic acids	FDA approved for oral preparations. Included in nonparenteral medicines licensed in Europe.
Lanolin (wool wax)	Nonionic	Mixture of fatty esters, sterols/triterpene alcohol esters, free alcohols, sterols and terpenes	FDA approved for ophthalmic, topical, vaginal, and transdermal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Lecithin (soy bean or egg yolk)	Zwitterionic	Phosphatidylcholine	FDA approved for inhalation, intravenous, intramuscular, oral, otic, rectal, topical, vaginal, and transdermal preparations. Included in parenteral and nonparenteral medicines licensed in the United Kingdom
Oleic acid	Anionic	9-Octadecenoic acid	FDA approved for inhalation, oral, nasal, topical, and transdermal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Poloxamers (124, 181, 188, 237, 331, 338, 407)	Nonionic	Polyoxyethylene-polyoxypropylene block copolymers	FDA approved for oral, intravenous, ophthalmic, subcutaneous, and topical preparations. Included in nonparenteral medicines licensed in the United Kingdom

(*continued*)

TABLE 18.1 (Continued)

Surfactant	Class	Structure	Regulatory Status
Polyoxyethylene alkyl ethers (laureth, cetheth, oleth, steareth)	Nonionic	Polyoxyethylene glycol ethers of *n*-alcohols	FDA approved for topical, vaginal, and rectal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Polyoxyl castor oil (35, 40, 40 hydrogenated, 60, 60 hydrogenated)	Nonionic	Polyoxyethylene castor oil derivates	FDA approved for intravenous, intravesical, intramuscular, subcutaneous, dental, and topical preparations. Included in parenteral medicines licensed in the United Kingdom
Polysorbates (20, 60, 80)	Nonionic	Polyoxyethylene sorbitan fatty acid esters	FDA approved for otic, subcutaneous, intravenous, sublingual, intraarticular, intralesional, intramuscular, intrasynovial, nasal, ophthalmic, oral, topical, soft tissue, intrabursal, intradermal, rectal, and vaginal preparations. Included in parenteral and nonparenteral medicines licensed in the United Kingdom
Poloxyl stearates (glyceryl stearates)	Nonionic	Polyethoxylated derivates of stearic acid	FDA approved for oral, otic, topical, vaginal, and rectal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Sodium lauryl sulfate (sodium dodecyl sulfate)	Anionic	Sulfuric acid monododecyl ester sodium salt	FDA approved for oral, dental, sublingual, inhalation, buccal, topical, and vaginal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Sorbitan esters	Nonionic	Esters of sorbitol and its mono- and dianhydrides with fatty acids	FDA approved for oral, dental, sublingual, inhalation, buccal, topical, and vaginal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Stearic acid	Anionic	Octadecanoic acid	FDA approved for oral, buccal, sublingual, subcutaneous, topical, and vaginal preparations. Included in nonparenteral medicines licensed in the United Kingdom
Sucrose esters	Nonionic	Esters of sucrose and its monoanhydride with fatty acids	FDA approved for oral and topical preparations. Included in nonparenteral medicines licensed in the United Kingdom

In general, the following dosage forms that utilize surface active agents will be discussed: lipid solutions, micellar solutions, emulsions (liquid/semisolid), self-emulsifying systems, microemulsions, suspensions (liquid/semisolid), capsules, and tablets.

18.2 SURFACTANTS IN ORAL DOSAGE FORMS

Although there are many routes of drug administration, the oral route is the most common and usually the most convenient for the patient. Oral drug delivery exploits the physiological role of the gastrointestinal (GI) tract, which is responsible for the absorption of nutrients from ingested food. The GI system provides a large surface area for absorption of the drug molecule and additional mechanisms for accelerated absorption, such as emulsification with bile salts and active transport to the lymphatic system [2,6–9]. However, absorption of the pharmaceutical dosage form administrated via that route is often incomplete and variable. To be absorbed from the GI tract,

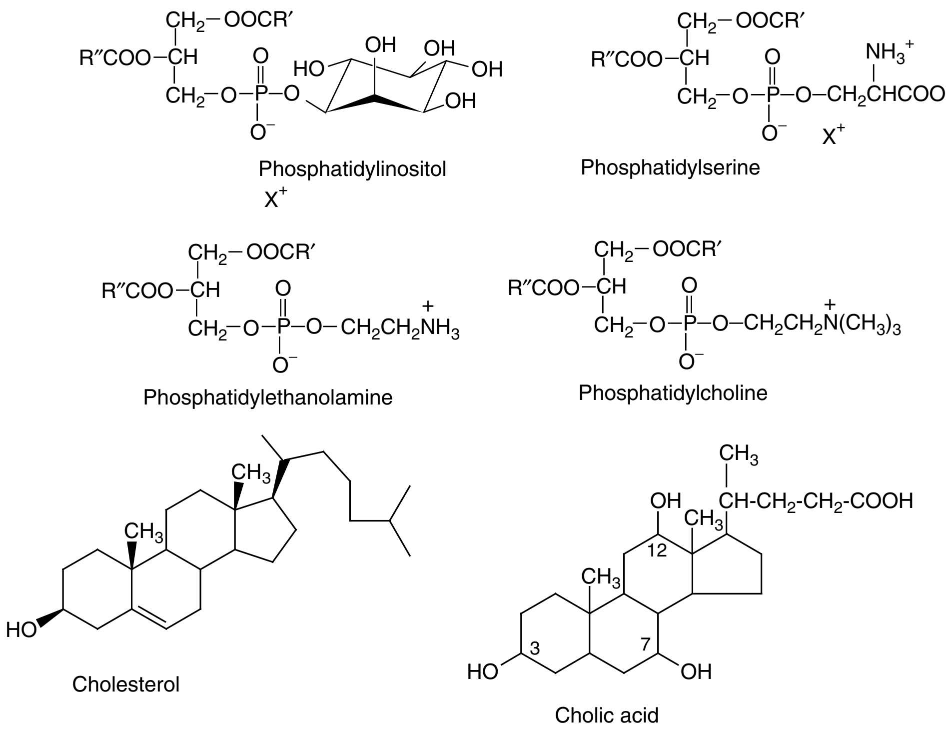

FIGURE 18.1 Examples of several naturally occurring surfactants.

a drug compound must have good dissolution properties in the GI lumen (aqueous environment) and good absorption properties (permeation) through the membranes of the gut wall. Permeation is a function of the solubility of the drug in the aqueous lumen environment and its permeability through the lipid membranes of the gut. The most common mechanism (but not the only one) of penetrating lipid membranes is passive diffusion. This means that, to be absorbed from the GI tract, a drug compound must be hydrophilic enough to be soluble in the lumen, yet lipophilic enough to get across the gastrointestinal membrane [8]. Thus, oral drug absorption can be limited by dissolution rate, permeability through the membranes, and solubility. Another important parameter that affects the efficiency of drug absorption is its stability in different absorptive sites in the GI tract. Those sites differ by their pH, enzymatic activity, blood flow, surface area, exposure time, alternative absorption mechanism (in addition to passive diffusion through membranes), concentration of natural surfactants present (such as bile salts), and influence of coingested food [6–8]. For instance, the liquid contents of the stomach have a very low pH, whereas the small intestine, which is a primary absorption site due to its very extensive surface area, has high enzymatic activity. Furthermore, all the substances absorbed from the small intestine into the blood undergo first-pass metabolism in the liver, processes that can significantly alter the structure of the active substance before it reaches the venous circulation [2,6,8]. Factors that limit the absorption of the drug substance in the GI tract are

1. Aqueous solubility and dispersibility in GI lumen
2. Permeability through the lipid membranes of GI walls
3. Stability against hostile environment in the GI tract and against metabolism by the liver

Interaction with amphiphilic molecules in dosage form can have a significant influence on those factors. For poorly water-soluble and poorly water-dispersible drugs, surfactants can aid in dispersion stabilization. Coating drug particles (dispersion) or droplets of lipid solution (emulsion) containing the drug with surfactants can provide electrostatic, steric, or electrosteric stabilization to the formulation. For poorly permeable substances, surfactants can act as permeability enhancers. Numerous studies conducted *in vitro* and *in vivo* show that surfactant molecules can facilitate permeability of hydrophilic substances through the intestinal wall by several mechanisms [10–18]. As for the drugs that are degradable in the GI tract, coating drug particles with surfactants may protect them from enzymatic degradation and alter their absorption site [2,19,20].

18.2.1 POORLY SOLUBLE AND POORLY DISPERSIBLE DRUGS

Formulation strategies toward poorly soluble and poorly dispersible drugs focus on obtaining as highly dispersed a drug as possible. Such dispersions usually involve stabilization with surface active molecules. Possible dosage forms include lipid-based formulations, nanoparticle preparations, and solid dispersions [7,8,20,21].

Lipid-based formulation is a common name for lipid-containing preparations such as lipid solutions, emulsions, microemulsions, self-emulsifying drug delivery systems (SEDDs), and self-microemulsifying drug delivery systems (SMEDDs). All of those dosage forms utilize endogenous and exogenous surfactants to increase drug solubility. For instance, bile salts excreted to the lumen can enhance the drug solubility *in vivo* up to 100-fold. Surfactants and cosurfactants such as lecithin, monooleins, polysorbates, long chain fatty acids, and sorbitan esters are being successfully used to further increase solubility significantly [7,8,20,22].

Medicated lipid solutions are solutions of the drug in pharmaceutically acceptable digestible lipophilic esters without the addition of surfactants. In the small intestine, they undergo lipolysis and solubilization in mixed micelles of bile salts and phospholipids. One example of this approach is the drug preparation Fortovase®, containing saquinavir, an antiviral drug, dissolved in mono- and diglycerides. The presence of this formulation in the gut acts as a trigger for bile salt/phospholipid release, which results in formation of colloidal particles of the drug and facilitation of the absorption process [7,22].

Oil-in-water medicated emulsions are colloidal aqueous dispersions of a pharmaceutically acceptable oil phase, in which the drug is solvated. Polysorbates, sorbitan esters, glyceryl esters, lecithin, casein, polyoxyl castor oil, and gum arabic are often used to stabilize those preparations [4]. Usually high shear forces are applied toward the formation of the emulsions, to produce macro- or nanosized dispersed oil phase. Absorption is facilitated due to the large surface of the droplets and good permeability of the oil phase through the gut walls. An example of a commercial preparation is Sandimmune® oral solution preconcentrate, which forms an emulsion on dilution with water. This preparation is stabilized by the nonionic surfactant polyoxyl kernel oil [23].

Oil-in-water medicated microemulsions are thermodynamically stable, optically transparent aqueous dispersions of nanometric droplets of the pharmaceutically acceptable oil (having a diameter of 10–100 nm), which are spontaneously formed in the presence of high-surfactant concentrations. Usually, the microemulsions contain cosurfactants in addition to surfactants, which further reduce interfacial surface tension. A wide variety of molecules can function as cosurfactants, including alcohols, alkanoic acids, alkanediols, alkyl amines, and classic nonionic surfactants [19,24]. Oil-in-water medicated nanoemulsions have droplet sizes in the range of 20–200 nm, can be formed with the use of high-energy emulsification methods, and have high kinetic stability; their surfactant concentration is also relatively high [25]. Both micro- and nanoemulsions allow good GI absorption, due to the nanometric droplet size, but have a clinical disadvantage of using significant amounts of surfactants. Another problem is that on dilution with water in the aqueous environment of the GI tract, there is a gradual desorption of the surfactant located at the droplet interface, which can destroy the original droplet structure [19]. Surfactants, which have low critical micelle concentration, are preferably used to minimize the dilution effect.

SEDDs and SMEDDs are used for *in situ* formation of emulsions/microemulsions in the GI tract. Those systems include an oil solution of the drug, surfactants, cosolvents, and other water-soluble excipients. They form either very small droplets in the GI tract (>100 nm SMEDDs) or larger droplets (SEDDs), depending on the concentration of the surfactant. Those systems usually use hydrophilic, nonionic surfactants (polysorbates, polyoxyl castor oil), which in combination with medium chain triglycerides form a self-emulsifying system [22,26]. The resulting system can be incorporated within gelatin capsules (hard or soft). Sandimmune (cyclosporine A) capsules are an example of SEDDs utilizing a nonionic surfactant polyoxyl corn oil for emulsion preconcentrate preparation, whereas Neoral® (cyclosporine A) capsules are an example of SMEDDs, utilizing a nonionic surfactant polyoxyl 40 hydrogenated castor oil [27]. There is a significant improvement in bioavailability of cyclosporine A administered as Neoral compared to Sandimmune [28].

Nanoparticles are also used for the oral delivery of poorly soluble/dispersible drugs. According to the Noyes–Whitney equation [29], there is an inverse dependence between the dissolution rate of solid drug particles in aqueous media and the particles' radii. The absorption of a drug in the GI tract correlates with drug's dissolution rate in the GI lumen. Thus, by reducing particle size to nanoscale, the absorption is significantly facilitated. Furthermore, there are additional paths for GI absorption of nanometric particles, such as direct lymphatic uptake from the intestinal lumen, when the whole nanometric particle undergoes phagocytosis to Peyer's patches—the lymphatic system of the gut [9,30]. Thus, there is a significant increase in plasma concentration of drugs after oral administration in nanosized particles compared to bulk administration. There are several methods proposed for nanoparticle preparation. With most methods, nanoparticles are produced as nanosuspensions, consisting of a drug, surfactants, and a dispersing medium (which later can be evaporated). To be stable to agglomeration, nanoparticles should be stabilized by coating with protective agents, such as surfactants and proteins. The most widely used method for pharmaceutical nanoparticle preparation nowadays is the mechanical reduction of particle size by wet-milling [1,21]. There are four drug products currently on the market that overcome the relative insolubility of drugs by reducing the particle size to 200 nm by wet-milling, and subsequently adding FDA-approved surface active agents into the formulation: Rapamune® tablets (sirolimus, an immunosuppressant drug) containing Poloxamer 188 and glyceryl monooleate, Emend® (aprepitant) capsules containing sodium lauryl sulfate, TriCor® (fenofibrate) tablets containing docusate sodium and sodium lauryl sulfate, and Megace® (megestrol) oral suspension containing polysorbate 80.

In *medicated solid dispersion*, a poorly water-soluble drug is dispersed in a highly water-soluble carrier with the addition of surface active agents. Solid dispersion techniques can yield drug particles embedded in a water-soluble matrix or actually dissolved in it (solid solution). A highly dispersed or dissolved state of the drug and its improved wettability contribute to enhanced solubilization. A solid dispersion of Griseofulvin in polyethylene glycol 400 and 8000-Gris-PEG® tablets is commercially available [21]. Gris-PEG® 250 mg tablets contain sodium lauryl sulfate as an inactive ingredient.

18.2.2 POORLY PERMEABLE DRUGS

Many molecules, despite having excellent aqueous solubility and dispersive properties, are still poorly bioavailable due to problematic permeability through the epithelial cell barrier lining in the GI tract. The tight junctions between the intestinal mucosal cells restrict paracellular permeation, and the hydrophilicity of those molecules reduces their diffusion across the intestinal mucosa (transcellular pathway) [6,8]. Some of the molecules that succeed in penetrating the cell wall are pumped back by the multidrug-resistant protein intestinal efflux transporter (also called P-glycoprotein) [6,14]. Formulation strategies toward poorly permeable drugs include permeability enhancing with amphiphilic molecules having a lipid group that will assist in penetration through lipid-rich cell membranes. Those absorption-enhancing surfactants stabilize the active molecule, lead it to the intestinal lining, and increase residence time at the intestinal wall [20]. Anionic and nonionic surfactants may promote transcellular and paracellular absorption routes [17,31]. The absorption-enhancing effect of surfactant can be attributed to the increased lipophilicity of the formulation and interaction with the tight junctions between the intestinal mucosal cells, but also to the partial damage of the tight junctions and the inhibition of the multidrug resistance protein [10–17]. For instance, it has recently been shown that polyoxyl castor oil is a potent inhibitor of multidrug resistance protein [10]. Other studies show that nonionic surfactants inhibit the multidrug resistance protein in a concentration-dependent manner [8,14,15,17]. It has also been shown that a combination of lysophosphatidylcholine with fatty acids may potentially increase permeability through small domains in biological membranes that are composed of lipids in the gel-phase [13]. Sucrose monoesters have been demonstrated to increase paracellular uptake of ingested substances [12]. It has been also proven that the maximum surface pressure of the surfactant may indicate the ability of this surfactant to permeabilize or actually damage the intestinal wall. Thus, permeability enhancement or acute damage increased as surfactant maximum surface pressure increased beyond 25 dyne/cm [11]. Much research has been focused on chitosan derivatives as paracellular permeation enhancers. Those amphiphilic polysaccharides are able to interact with tight junctions, causing them to open but inflicting minimal damage on the integrity of cell membranes [29]. Another approach to enhancing membrane penetration is entrapping the active molecule in lipid-based formulations, such as water-in-oil emulsions and water-in-oil microemulsions, which are stabilized by one or several surface active agents [31]. Additionally, nanoparticulate formulations, which are also stabilized by the surfactants, promote permeability through targeting absorption via an alternative path. They can be absorbed into the lymphatic system via specialized phagocytic enterocytes lining the intestine [9,20].

18.2.3 Stability of Active Molecules to Hostile Environment of the GI Tract

Preventing exposure of the active molecule to enzymatic activity and harsh pH conditions provides stability of the drug dosage form introduced to the GI tract. One of the ways to promote the stability of the drug is to entrap it into a protective vesicle. Liposomes are phospholipid vesicles containing aqueous compartments between one or more concentric lipid bilayers, which resemble naturally occurring membranes. They can carry both hydrophilic and hydrophobic drugs; hydrophilic drugs are retained within an aqueous compartment and hydrophobic ones become associated with the lipid bilayers [32]. Natural phospholipids used for those structures include phosphatidylcholine (egg and soybean), phosphatidylserine, phosphatidylglycerol, and sphingomyelin. Synthetic phospholipids include dipalmitoylphosphatidylcholine, distearoylphosphatidylcholine, and dimyristoylphosphatidylcholine [2]. Synthetic phospholipids form rigid, impermeable structures, whereas natural ones give permeable and less stable bilayers. Cholesterol may be added to natural bilayers to increase their stability [33]. Entrapping the drug in the liposome may protect it from a hostile environment, such as one that contains degradative enzymes. Drugs can also be controlled-released from liposomal structures [32]. Although the use of phospholipids as vesicular delivery systems is widespread, it should be noted that other surfactants may form vesicles: unsaturated fatty acids form ufasomes; amphipathic peptides and lipids can form similar vesicular structures. Nonionic surfactants, such as alkyl polyoxyethylene ethers, alkyl polyglyceryl ethers, and steroidal ethers form structures called nonionic surfactant vesicles, which can be used as alternatives to liposomes [2]. Another approach to protecting a hydrophilic drug from degradation is entrapping it in water-in-oil or multilayer (water-in-oil-in-water) emulsions or microemulsions. Those systems are usually stabilized by nonionic surfactants such as polysorbates, polyoxyls, or zwitterionic lecithins [34,35].

18.3 SURFACTANTS IN PARENTERAL DOSAGE FORMS

Parenteral (injected) administration of drugs provides a solution to many problems associated with the oral delivery route. A drug injected into the blood circulation is considered to be completely bioavailable; therefore, the quantity of the surfactants and other inactive excipients in intravenous dosage forms are usually strictly limited. The most common alternative routes of parenteral drug administration are intramuscular or subcutaneous injections [2]. Several other injection routes are available to elicit rapid local reaction, such as intrathecal, intraarticular, and intracardiac.

Colloidal systems for parenteral drug administration can be used for controlled drug release or for targeting to specific organs. Thus, aqueous colloidal suspensions of water-immiscible particles can be given intravenously, and oily suspensions can be given intramuscularly. Those dosage forms are stabilized by surfactants approved for parenteral use, such as polysorbates, polyoxyl castor oils, poloxamers, and lecithins (usually in limited amounts), and provide gradual release of the drug over time [3,5,36]. For an injectable colloid, the drug can be micronized and dispersed or dissolved in solidified lipid, or incorporated into biodegradable polymeric microspheres [36]. All those colloidal dispersions are stabilized by appropriate surfactants. For example, Abraxane® is an intravenous suspension of 100-nm solid particles of the antitumor drug Paclitaxel, which are stabilized by the amphiphilic protein albumin at their surface [37]. Submicron emulsions can be used for intravenous delivery of water-insoluble drugs. They provide a reservoir of a drug from which it can be instantly released by partitioning due to short diffusion distances and high surface area, resulting in a fast-acting formulation [21,36]. A commercial example of such emulsions is the intravenous fast-acting anesthetic Diprivan® (profol) stabilized by 1.2% egg lecithin. Another application of intravenous emulsions is fluorocarbon oil-in-water emulsions, acting as an artificial oxygen transport fluid replacing or supplementing the blood. The first fluorocarbon emulsion, Fluosol®, utilized poloxamer Pluronic F-68 as the surfactant [38]. In addition, lipid emulsions are widely used for parenteral nutrition and as a source of essential fatty acids. The classic parenteral lipid emulsion, Intralipid®, is a dispersion of triglyceride droplets (diameter 250–400 nm) in an aqueous phase, stabilized with a phospholipid as an emulsifier [39].

When water-insoluble particles are administered into the blood stream (with intravenous injection, for example), their delivery will depend on their size and surface characteristics. Those particles are recognized by white blood cells and are rapidly removed by phagocytosis; this presents a serious obstacle for colloidal intravenous delivery [2]. It has been shown that coating the colloidal particles with the surfactants not only makes the particles more hydrophilic and hence less likely recognizable by the macrophages due to prevention of absorption of serum recognition factors or opsonins on the particles, but also reduces macrophage–particle adhesion via steric or electrosteric stabilization [40]. It has also been shown that *in vitro* macrophage uptake of polystyrene microspheres was inhibited by coating those microspheres with surfactants, such as poloxamers and poloxamine, and polymers such as xanthan [2]. *In vivo* studies confirmed that different surfactants can alter tissue distribution of microspheres [2]. Surfactant-stabilized colloidal particles can also be targeted by their size. Particles larger than 5 μm will be trapped in pulmonary capillaries, and in small quantities can be used for targeting drugs to the lungs. Particles with a diameter ~100 nm are likely to accumulate at tumors and inflammation sites due to the large pores in the blood vessels near those sites.

Phospholipid liposomes are used in parenteral administration as well. Their circulation time can be prolonged by incorporation of steric surfactants that extend from the liposomal membrane [41]. For instance, polyethylene glycol–conjugated lipids are incorporated in liposomes containing the antitumor drug doxorubicin—Doxil® or Caelyx®—and reduce its interaction with macrophages. Ligands covalently attached to the surfactant molecule enable targeting liposomes to specific areas [42,43]. Liposomal systems can be also delivered subcutaneously to target drug to lymph nodes [44].

Micellar solutions and microemulsions are also used for parenteral delivery of hydrophobic drugs. They are usually stabilized by large amounts of hydrophilic surfactants, such as bile salts and polysorbates. Owing to their small size, micelles are less readily recognized by the immune system, resulting in prolonged circulation [36]. An example of micellar formulation is Taxol®, in which the active antitumor agent paclitaxel is solubilized in micelles of polyoxyl castor oil.

An additional application of surfactants in parenteral preparations is the transport of drug particles via blood–brain barrier, the membrane that protects the brain from toxic substances, assimilating only nutrients. The drug is bound to polymeric nanoparticles having the average diameter of 270 ± 30 nm, and the resulting nanoparticle–drug complex is coated with a surfactant, such as polysorbate 80. After intravenous administration, this complex can easily penetrate the blood–brain barrier [45].

18.4 SURFACTANTS IN OTHER DOSAGE FORMS

18.4.1 Transdermal Delivery of Drugs

Transdermal drug delivery (delivery through the skin into the bloodstream) offers an attractive alternative to oral and parenteral administrations. It avoids gastrointestinal drug metabolism and the first-pass effect, provides sustained release, and yet does not involve breaching the barrier function of the skin associated with parenteral administration. However, the applications of transdermal delivery are limited due to the inability of most drugs to penetrate across the skin at therapeutically effective quantities. Therefore, various approaches have been applied to enhance drug transport through the skin, among them using surfactant-stabilized vehicles that interact with skin cells to incorporate the drug. Surfactant-stabilized drug vehicles used for transdermal delivery include transfersomes, which are extremely deformable liposomes with the ability to squeeze through the pores of the stratum corneum (typically 20–30 nm) [46], and ethosomes, which are soft phospholipid vesicles with a high ethanol content, having better skin penetration properties and much smaller dimensions compared to conventional liposomes [47]. Conventional liposomes, nonionic surfactant vesicles (niosomes), emulsions, microemulsions, and nanoparticulate systems are being studied as potential transdermal delivery vehicles [46,48–50]. Another approach to enhancing penetration is to use the surfactants as penetration enhancers for accelerating the drug's transport through the stratum corneum, the outer skin layer. Amphiphilic molecules acting as permeability enhancers include, among others, phospholipids, polysorbates, sorbitan esters, medium chain triglycerides, oleic acid, bile salts, and other molecules having surfactant type properties. The penetration ability of the drug through the skin layers is enhanced through interaction with the skin cells or through changing the physicochemical parameters of the formulated drug, such as solubility, the skin/dosage form partition coefficient, and the diffusion rates through the skin layers [6,51]. The most powerful surfactants, such as sodium dodecyl sulfate, denature and unfold keratin proteins, leading to a more porous hydrated structure, through which drugs can diffuse more easily [6].

18.4.2 Pulmonary Systemic Drug Delivery

Pulmonary systemic drug delivery takes advantage of the large surface area of the alveoli, the low enzymatic activity in the lungs, and their rich vascular system to deliver different drugs, especially those of high molecular weight (such as peptides and proteins). To successfully deliver through the lungs, there is a need to use absorption enhancers. Surfactants such as bile salts are used as such enhancers [52].

18.4.3 Buccal and Sublingual Systemic Delivery of Drugs

Buccal and sublingual systemic delivery is a useful alternative administration route through oral mucosa. The blood supply from the buccal mucosa does not drain into the hepatic portal vein. Thus, drugs such as nicotine, which is a subject of substantial first-pass effect metabolism when given orally, are being incorporated in chewing gum or sublingual tablets. The use of penetration-enhancing surfactants (such as sodium dodecyl sulfate, bile salts, and oleic acid) may be necessary to achieve adequate absorption of large molecules [6]. Medicated chewing gum preparations may contain solubilizers, such as lecithin, polysorbates, or polyoxyl castor oil [53].

18.4.4 Transnasal Systemic Delivery of Drugs

In transnasal delivery of drugs, surfactants have been used as absorption enhancers to increase the systemic absorption of large or hydrophobic molecules. The mechanism of their action was summarized by Quraishi et al. [54]. The bile salts reduce the viscosity of the mucus, create transient hydrophobic pores in the nasal membrane, remove epithelial cell barriers, and incorporate the drug in bile salt micelles, creating a transmembrane concentration gradient. It was suggested that fatty acid salts create intercellular space by temporarily extracting calcium ions from the nasal mucosa, and nonionic detergents (such as laureth-9) alter membrane structure and permeability.

18.4.5 RECTAL ADMINISTRATION OF DRUGS

Rectal administration with nonionic surfactants also demonstrated an increased absorption. It has been proven *in vivo* that triglycerides, polysorbates, and fatty acids improve rectal absorption of antibiotic agents [55].

18.4.6 TOPICAL ADMINISTRATION

Ophthalmic delivery: For administration of water-insoluble drugs into the eye, colloidal systems are used. Surface active polymers, such as polyvinyl alcohol, poloxamer, and methylcellulose are often added as particle stabilizers and viscosity enhancers. Particle size in such colloidal systems should not exceed 5–10 μm in diameter. Emulsions, liposomes, and micro- and nanoparticles, all stabilized by surfactants, are used in topical ophthalmic drug delivery [56]. For instance, an ophthalmic preparation of cyclosporin A, Restasis®, is an emulsion stabilized by polysorbate 80 and polymer carbomer 1342.

Vaginal formulations may contain the following surface active agents: ceteth-20, cetostearyl alcohol, cetyl alcohol, cetyl palmitate, choleth, polyoxyl castor oil, acacia, cholesterol, diglycol stearate, glyceryl monostearate, glyceryl stearate, hydrogenated palm oil glyceride, hydrous lanolin, laureth, lecithin, diacetyl phosphate, poloxyl stearates, poloxamers, and polysorbates, together with polymers such as hydroxypropyl cellulose, hydroxypropylmethyl cellulose, and carbomers. This information is obtained from the *Compendium of Pharmaceutical Excipients for Vaginal Formulation* [57].

Local nasal delivery may also utilize surfactants such as polysorbates [58].

Local dermal delivery of drugs extensively utilizes surface active agents for formulation stabilizers, solubility, and epidermal permeability enhancers. Drug vehicles comprising surfactants and used for topical dermal delivery include liposomes, nonionic surfactant vesicles (niosomes), emulsions and microemulsions, nanoparticulate systems, transformers, and ethosomes [50,59]. Those formulations can be applied as creams (semisolid emulsions or suspensions containing a low concentration of hydrocarbons or PEGs, which are mostly absorbed or evaporated when applied to the skin), ointments (semisolid viscous emulsions or suspensions containing a high concentration of hydrocarbons or PEGs, which are not easily absorbed/evaporated when applied to the skin), gels (semisolid emulsions or suspensions containing gelling agents), pastes (semisolid suspensions containing a high concentration of solid particles), or lotions (low-viscosity water-based liquid emulsions that evaporate immediately on application to the skin) [60].

18.5 SURFACTANTS AS ACTIVE AGENTS

18.5.1 LUNG SURFACTANT SYSTEM

A lung surfactant is a liquid crystalline or gel structure that primarily consists of phospholipids. It covers the alveolar surface and is constantly renewed. In the absence of the lung surfactant, elastic fibers of the lung and the alveoli cell wall tension would cause the lung to collapse. Generation of surfactant in neonates does not occur until the time of birth, so preterm infants often suffer from respiratory problems. Exosurf®, containing dipalmitoyl phosphatidylcholine (Colfosceril palmitate), is given directly into the lungs of premature babies to replace the natural surfactant. Dipalmitoyl phosphatidylcholine is effective in reducing the surface tension of pulmonary fluids, thereby increasing lung compliance properties to prevent alveolar collapse and improve breathing [61].

18.5.2 Docusate Sodium

Docusate sodium is used as a laxative agent in many commercial preparations. It acts on nerve endings in the gut wall and increases the intestine muscle contraction [62].

18.5.3 Surface Active Agents as Spermicides

Surface active agents are thought to act on the mid-piece and tail of the sperm cells, directly affecting the cell's lipid bilayer, which provides protection to the surface of the cell. By affecting the membranes, they cause the sperm cells to lose motility and to alter their permeability. Nonionic surfactants nonoxynol-9 and octoxynol are approved by the FDA for use as spermicides in humans. In some countries, cationic benzalkonium chloride and anionic docusate sodium are also used for contraception [63].

18.6 SUMMARY

In this chapter, the importance of the amphiphilic molecules as excipients in various dosage forms was discussed. It was shown that surfactants may alter the physicochemical properties of active molecules, enhance penetration through the lipid membranes of the cells, increase the stability of dosage forms, or even act as a therapeutic agent. Several types of pharmaceutically acceptable surfactants were presented, and examples of the commercial formulations containing these surfactants were mentioned. For more detailed information regarding formulations with amphiphilic molecules, refer to Part D of this Handbook. Obviously, while selecting the proper surfactant one should consider its overall effect on the physicochemical properties of the dosage form as well as its therapeutic effect. The selection should be restricted to the surfactants that are currently approved by the regulatory authorities for the specific applications.

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General Chemistry

about the book . . .

This fifth part of the multi-volume *Handbook of Detergents*, deals with the various multi-dimensional aspects and implications of the application of detergent formulations and/or surfactants domestically, institutionally, in industry, agriculture and environmental contamination problems. Thus, **Part E** constitutes a comprehensive treatise of the multi-dimensional issues involved, specifically emphasizing the alignment of scientific knowledge and well-established technological and technical know-how with the relevant contemporary applied practice.

An international effort and industry/academia collaboration, this volume features expert contributions, focusing on the contemporary state-of-the-art concerning the many applications of detergent and surfactant formulations.

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about the editor-in-chief of the *Handbook of Detergents* and the editor of this *Part E: Applications* . . .

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