

## Chapter 8

# Vegetable Oils in Paint and Coatings

Michael R. Van De Mark and Kathryn Sandefur

University of Missouri-Rolla Coatings Institute, Rolla, MO 65409-1020

## Introduction

Triglycerides and their derivatives have been used as a binder or additive in coatings for possibly as long ago as 30,000 years going back to the days of cave paintings. The early oil-based products would simply be derived from the use of a drying oil selected from any naturally occurring plant or several fish oils and a naturally occurring pigment such as red iron oxide or carbon black. Because no catalyst was added, the curing or oxidation process was slow and yielded a soft coating. Technology over the centuries has improved the use of oils in coatings. In addition to the classic triglycerides, sulfonated oils and many other derivatives are used today, including lecithin, as additives to coatings.

The primary use of oils in coatings is as a drying oil. Drying oils are highly unsaturated oils that will oligomerize or polymerize when exposed to the oxygen in air, usually in the presence of a catalyst. The result is an increase in the molecular weight including cross-linking. Oils have the distinct advantage of being able to penetrate into wood before polymerization (1) and thus are ideal wood primers. Some of the common fatty acids (2) found in drying oils are listed in Table 8.1. Only linoleic, linolenic, pinolenic, dehydrated ricinoleic, and  $\alpha$ -eleostearic acids are truly drying oils. These all have two or more units of unsaturation separated by

**TABLE 8.1**  
Common Fatty Acids Found in Drying Oils

Common name	Formula
Myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$
Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$
Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$
Oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
Linoleic acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
Linolenic acid	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
Pinolenic acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{H}$
Ricinoleic acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
$\alpha$ -Eleostearic acid	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$

no more than one methylene. It should be noted that moving the unsaturation into conjugation, as is the case for  $\alpha$ -eleostearic acid, increases the reactivity.

Typical sources for drying oils include linseed, soybean, tung, sunflower, and dehydrated castor, as well as many fish oils. Their cost, coupled with the distribution of the various drying acids in the triglyceride, often governs their use. Trace contaminants in the oils can also influence their acceptability in a given market. For example, the presence of various phenolic contaminants can increase the color of the resin as it oxidizes in air. Formulations requiring a white or clear appearance may not allow their use.

### **True Oil Coatings**

True drying oil coatings are those based upon an unsaturated oil as the only binder. Typically linseed or tung oil is used in these applications. Only oils with a high drying index are used (3). The drying index is equal to the sum of the percentage of linoleic acid plus two times the linolenic acid content of the oil. If this value is  $>70$ , it is considered to be a drying oil. Many use the iodine number which is the number of grams of iodine required per 100 g of oil as an indication of oxidative drying ability (4). Table 8.2 gives the iodine number, drying index, and a partial composition for some typical oils. It should be noted that genetic engineering has resulted in plants that are capable of producing oils with compositions substantially different from those shown. In the coming years, the available oils may be significantly different with very high unsaturation. Soybean oil currently can have the acid distribution shown in [Table 8.3](#) or as much as 85% oleic acid with genetic engineering.

Oil coatings are used to finish wood carvings, as wood deck stains and finishes, cedar shingle coatings, and other applications for which penetration is desired and a slow cure rate is not a significant problem. The deck finish market has grown from ~\$30 million in 1980 to >\$400 million in 2000. The formulation and mechanism of cure are discussed in the following section. Oils are classified as drying if the iodine number is  $>130$ , semi-drying if between 115 and 130, and nondrying if  $<115$ .

**TABLE 8.2**

Iodine Number, Drying Index, and Partial Composition for Some Typical Oils<sup>a</sup>

Oils	Iodine number	Drying Index	% Saturated
Drying oils			
Soybean	130	66	14
Linseed	185	123	10
Sunflower	139	66	8
Tung	165	$>172$	5
Semidrying oils			
Corn	124	54	17
Nondrying oils			
Coconut	8	2	92

<sup>a</sup>Note: Although oleic acid is unsaturated, it is not a drying acid.

## ***Curing Mechanism and Catalysts***

The curing mechanism for oil-based products, including alkyds, follows an air oxidation mechanism (5). Oxygen diffuses into the film and reacts with the diallylic hydrogens to produce a hydroperoxide (Fig. 8.1). The hydroperoxide is formed at a relative rate of 1:120:330 for the trioleate:trilinoleate:trilinolenate (3). The curing mechanism then involves the decomposition of the hydroperoxide by a redox catalyst. The most popular catalysts for the decomposition of the hydroperoxides are cobalt and manganese naphthenate salts. These add color to the coating and thus are kept at a low concentration. Other additives are used to improve the drying characteristics. These include calcium and zirconia salts as driers and 9,10-phenanthroline, a complexing agent that accelerates cure. To retard the curing process, a cobalt complexing agent, called an antiskinning agent, ties up the cobalt in the can but evaporates and thus activates the cobalt after application. The skinning of oil-based products in the can has been a problem since they were first used.

## ***Alkyds***

Alkyds comprise a large class of coatings. It includes the three normal alkyd classes, which are based upon the amount of unsaturated oils used in the manufacture of the alkyd resin: (i) Long Oil Alkyds are used typically for architectural paints. They contain >60% oil, are soluble in mineral spirits, and are slow drying and soft. (ii) Medium Oil Alkyds are used typically for architectural paints and as a co-resin in some original equipment manufacturers (OEM) coatings. Their oil content is between 40 and 60%; they are soluble in mineral spirits and aromatic solvents and are slow to dry but faster than long oil alkyds and slightly harder. (iii) Short Oil Alkyds are used typically for OEM and other rapid dry applications. They contain <40% oil, are soluble in aromatics but not mineral spirits, and are fast drying to touch and significantly harder than medium and long oil alkyds.

*Oils.* The oils used to make alkyds vary based upon the cure speed desired, cost, odor, and many other factors. Table 8.3 shows several of the oils used in the manufacture of alkyds. The unsaturation number is used again to aid the resin formulator in choosing better drying oils. In general, the higher the unsaturation number, the better the oil is for drying. The desire is to have many di- or trienes in the oil, containing two and three double bonds, respectively. Excellent drying oils for alkyds include soybean oil, linseed oil, tung oil, and dehydrated castor oil. These oils are cooked with various polyols to produce a polyester resin called an alkyd. Figure 8.2 illustrates the formation of a typical alkyd.

All alkyds, including modified alkyds, cure through air oxidation and require chemical driers, accelerators, and antiskinning agents as did the oils. Because the molecular weight of alkyds is larger and cross-linking is more probable, skinning or livering becomes a significantly larger problem than in simple oil coatings.

**TABLE 8.3 (left)**

Typical Composition of Vegetable Oils

Vegetable oil	Iodine number <sup>a</sup>	Average fatty acid concentration (% of total fatty acid)					
		Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic
Carbon atoms (n)		8	10	12	14	16	18
Double bonds (n)		0	0	0	0	0	0
Castor	85					1.0	2.0
Coconut	8	8.0	7.0	48.0	18.0	9.0	2.0
Corn	124					13.0	4.0
Cottonseed	107				1.0	22.0	2.0
Crambe	94					3.0	2.0
Linseed	185					6.0	4.0
Menhaden <sup>b</sup>	170				7.0	16.0	1.0
Mustard	120					2.0	
Oiticica <sup>c</sup>	150					7.0	6.0
Olive 80						8.0	2.0
Palm kernel	20	3.0	6.0	50.0	15.0	8.0	1.0
Peanut	90					7.0	6.0
Rapeseed	101					2.0	2.0
Rice Bran	102					17.0	1.0
Safflower oil	141					6.0	2.0
Sardine, Pilchard	190				5.0	14.0	3.0
Sesame	110					9.0	4.0
Soybean	130					8.0	6.0
Sunflower	139					6.0	2.0
Tallow	40				3.0	31.0	22.0
Tung (Regular) <sup>d</sup>	165					4.0	1.0
Tung (African) <sup>e</sup>	160					4.0	1.0
Walnut (English)	150				1.0	9.0	1.0

<sup>a</sup>Indicates the degree of unsaturation.<sup>b</sup>Also contains 17.0% palmitoleic fatty acids 16 C-1 double bonds.<sup>c</sup>Contains 82% licanic acid.<sup>d</sup>Contains 82% oleostearic acid.<sup>e</sup>Contains 71% oleostearic acid.

Alkyds, in general, do not function well over galvanized steel or on concrete. The alkalinity of the substrate coupled with traces of water causes the oils to hydrolyze to produce long-chained carboxylic acids. The calcium or zinc salts of these “fatty acids” are basically a mold-release agent. Because this mold release agent is formed under the paint film, it can cause the paint to easily peel off in large sections. This phenomenon can be observed when alkyds are used to paint galvanized duct work on the roof of many buildings. If moisture can be avoided, alkyds may work on these substrates.

Soybean oil is often used as the base oil but will often yellow. Various types of linseed oil are also very popular because are very readily cured. Several other

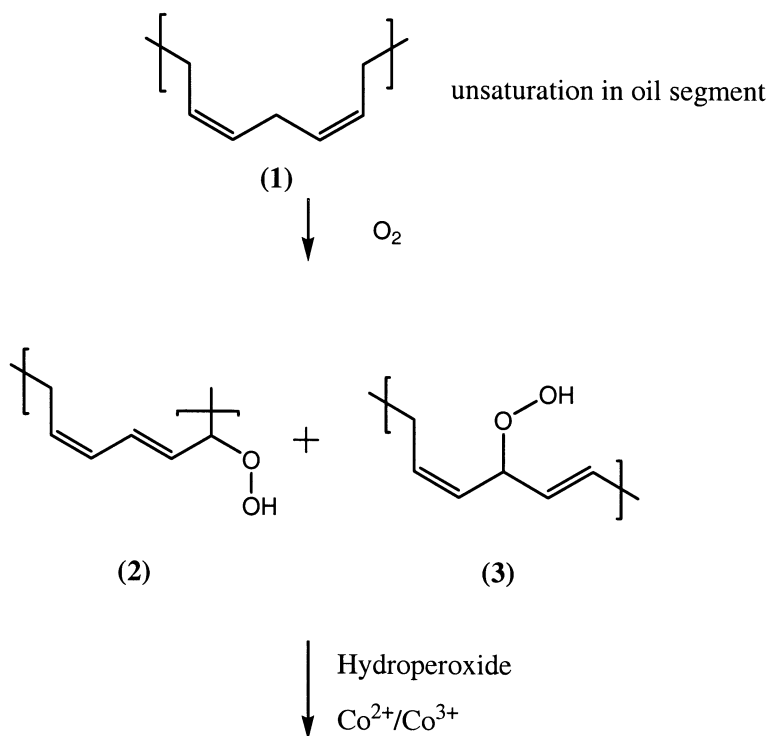
**TABLE 8.3 (right)**  
(Continued)

Average fatty acid concentration (% of total fatty acid)							
Oleic	Linoleic	Linolenic	Palmitic- Oleic	Ricinoleic	Erucic	Unsaturated fatty acids	Saturated fatty acids
18	18	18	16	18	22	20–22	20–24
1	2	3	1	1	1	3+	
2.0	5.0			90.0			
6.0	2.0						
29.0	54.0						
21.0	54.0						
18.0	10.0	5.0			56.0	3.0	2.0
20.0	17.0	53.0					
27.0			17.0			32.0	
24.0	20.0	6.0			43.0		5.0
5.0							
82.0	8.0						
16.0	1.0						
60.0	22.0						5.0
16.0	16.0	8.0			45.0	6.0	4.0
47.0	35.0						
13.0	79.0						
10.0	15.0		12.0			41.0	
46.0	41.0						
28.0	50.0	8.0					
26.0	66.0						
42.0	2.0						
5.0	8.0						
9.0	15.0						
16.0	60.0	13.0					

highly unsaturated oils such as sunflower oil are gaining popularity as the supply grows. Sunflower oil is a very good drying oil and produces less color.

*General Issues of Alkyds.* Air dry curing may require several weeks to reach full performance. In the laboratory, curing can be accelerated by aging at 50°C for 7 d. This is a well-accepted test criterion to evaluate corrosion, flexibility, hardness, and many other variables.

To cure, the oxygen in the air must penetrate through the coating all the way to the substrate. The coating thickness should be limited to <3 mil/coat. Recoating should be done only when sufficient time has been allotted to allow the antiskinning agent to escape and the oxygen to react with the alkyd. The common belief is that solvent evaporation and oxygen permeation are the only issues; however, the loss of the antiskinning agent may be more important to the overall performance. Unless sufficient time has been allowed, the cohesive strength, adhesion and pro-



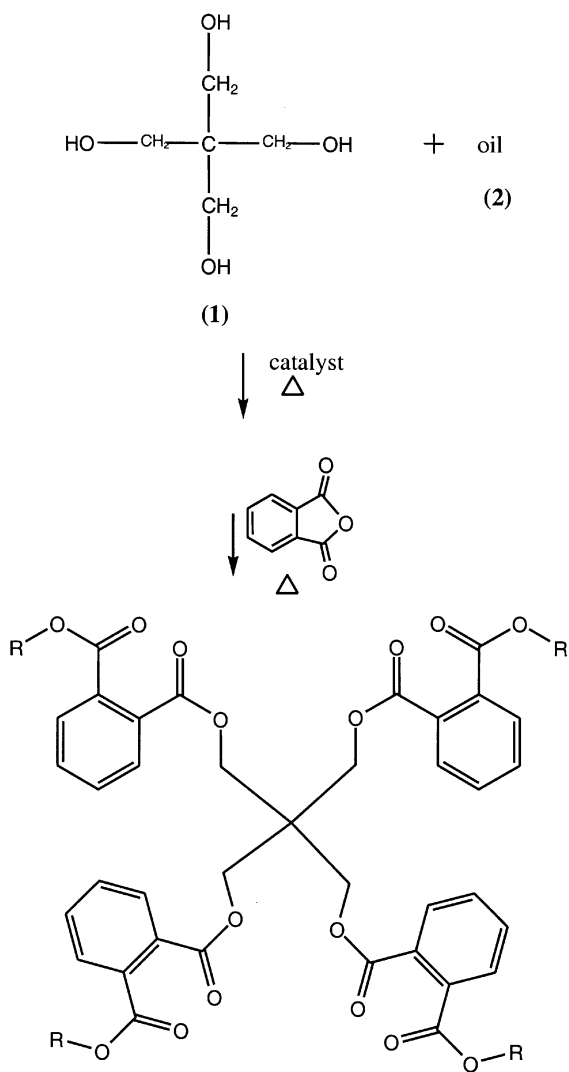
**Fig. 8.1.** Radical-induced polymerization.

tection may all be poor. Our tests indicated a direct proportional drop in adhesive and cohesive performance of an alkyd with film thickness.

All alkyd waste, overspray, spray booth filters, rags, and applicators containing alkyd or its washes are prone to spontaneous combustion under certain circumstances. All of these materials should be stored properly to prevent storage fires. Filters should be changed regularly and disposed of properly and safely. All of these waste materials are capable of starting a fire. Most alkyds are solvent-borne and require significant volatile organic chemicals (VOC). Aromatic solvents are to be avoided in air quality control areas that are not in compliance. Utilization of oxygenated solvents in conjunction with mineral spirits can substitute for the aromatics but do raise the cost slightly.

### ***Modified Alkyds***

Modified alkyds utilize the general alkyd backbone or chemistry and typically modify it with a more costly component that improves the performance of the resin. Many of the aspects of alkyds are very desirable. These properties include penetration into wood and air oxidative cross-linking. However, alkyds are not



(3) Here R is a random mix of oil, another polyol, oligomer, or H

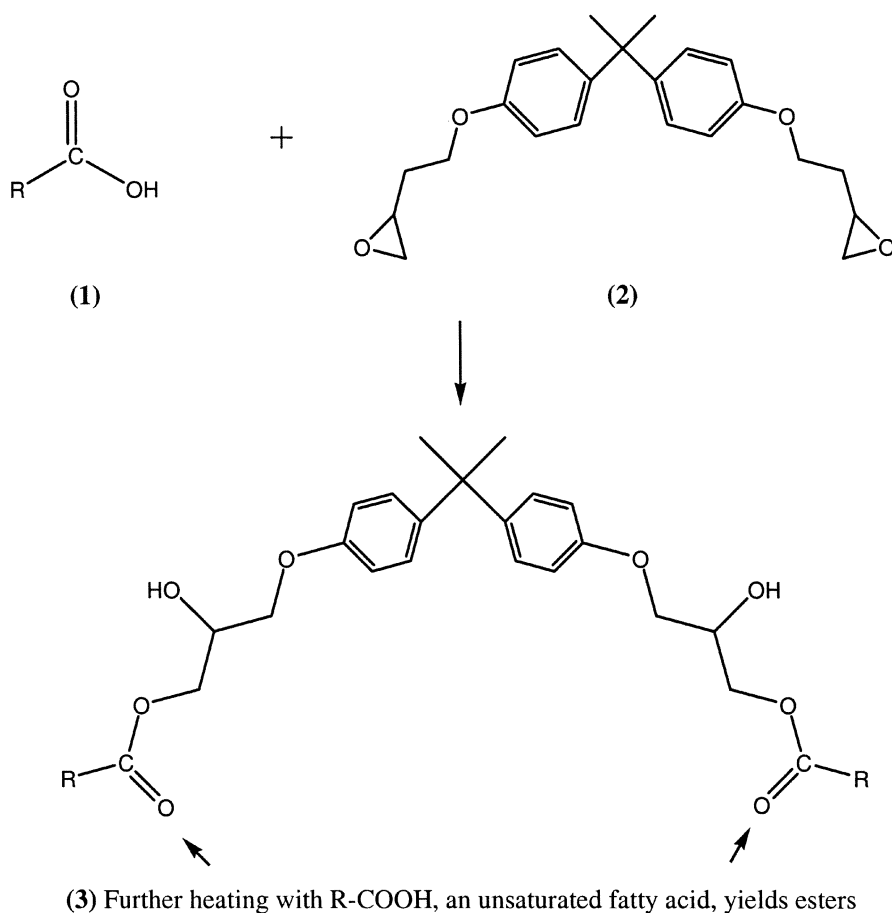
**Fig. 8.2.** The formation of a typical alkyd.

very abrasion resistant, solvent resistant, or hard. Chemistries that enhance these properties have been well received including urethane, epoxy, silicone, and many other technologies (6).

*Epoxy.* Typically 5–45% of the resin is based upon epoxy chemistry. This imparts better solvent resistance and the alkyd is often used as a primer. Ultraviolet (UV)

stability is poor. Both bisphenol A and other phenolic-based epoxy chemistries have been used. These coatings are not as solvent resistant as the typical two-component epoxy primers but offer better performance than a simple alkyd. The most common modification of this type is based upon the fatty acid reacting with the epoxy group to form an ester (Fig. 8.3). As for most alkyds, the final curing is oxidative.

*Acrylic.* From 15 to 50% modification is typical and can produce a quicker hard film. These are useful for OEM applications but require significant VOC. In this chemistry, the normal low-molecular-weight alkyd is prepared and cooled to  $\sim 120\text{--}140^\circ\text{C}$  and the monomers added with a radical initiator, usually benzoyl per-



**Fig. 8.3.** The formation of an ester from the reaction of the fatty acid with the epoxy group.

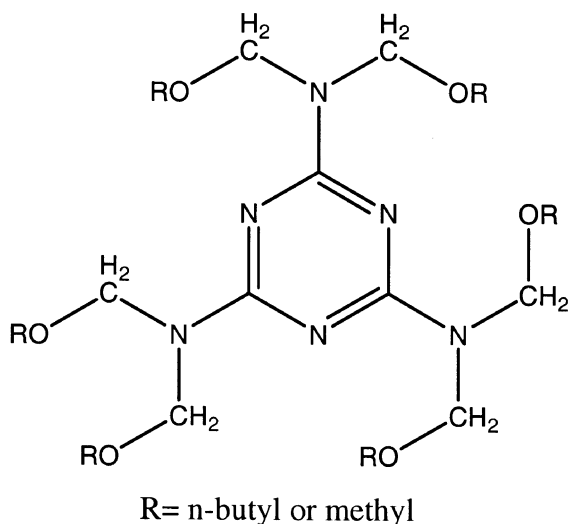


oxide. The monomer polymerizes and is grafted onto the alkyd. This chemistry works equally well for styrene and vinyl toluene (VT). Although this modification improves the properties of the alkyd, it increases the molecular weight and thus the viscosity also increases. Therefore, the VOC for these coatings is generally high.

*Styrene.* Typically a graft of styrene of 10 to 50% onto the alkyd is used. The properties it improves are gloss, cost, and hardness with rapid drying. The disadvantages include poor UV stability with rapid yellowing, significantly higher VOC required for application, and decreased adhesion to many substrates. Both styrene- and VT-modified alkyds will photooxidize. If three or more styrene units are in a row in a polymer chain, it will appear as a yellowing with exterior exposure.

*Vinyl Toluene.* Commonly called VT-modified alkyds, these have properties and problems very similar to those of the styrene-modified alkyds.

*Melamine.* The use of melamine derivatives allows alkyds and modified alkyds to be cured thermally. These are baking systems. The melamine derivative acts as a cross-linking agent to produce a cross-linked film when baked. These are typically baked at 120°C for 30 min, with shorter times for elevated temperatures. The structure of a typical melamine used in mineral spirits-based alkyds is shown in Figure 8.4. Toluene sulfonic acid or the amine salt of a sulfonic acid is usually used as a catalyst at a concentration of 0.5% based upon resin solids. These resins are soluble in aromatics, ketones, esters and, when hot, alcohols such as *n*-butyl alcohol. Use of *n*-butyl alcohol as 10% of the solvent helps to keep the surface open longer to allow solvent to escape during baking, thus preventing solvent popping.



**Fig. 8.4.** Melamine derivatives for alkyd formulations.

*Urethane Modified Alkyds.* This system is a one-can coating based upon the use of an alkyd polymer that was modified with 15–30% urethane chemistry (Fig. 8.5). These systems have better solvent resistance, abrasion resistance, and overall properties than typical alkyds. They are usually 3.5–4.5 lb/gal VOC and dry relatively quickly to handle rates of 30 min to 24 h, depending upon the oil content. The higher the oil content, the longer the drying time. These alkyds have been applied to OEM, maintenance, and architectural coatings. Their performance is very good and their cost is relatively low (3).

As with all urethane systems, these come in aliphatic or aromatic urethanes. Usually toluene diisocyanate, an aromatic isocyanate, or hexamethylene diisocyanate, an aliphatic isocyanate, are reacted with a monoglyceride made by reacting a di-, tri- or tetraol with the oil. The resultant urethane oils are then used as clear or pigmented coats for wood. The aliphatic systems are excellent for exterior use or where UV exposure is possible. The aromatic-based urethane systems usually have better abrasion resistance but will yellow and degrade if exposed to UV, even through a normal window. The higher the urethane content, the better the coating will generally perform, but the more VOC will generally be required and the higher the cost. A novel approach to the synthesis of urethane oils utilized a chemoenzymatic synthesis. The use of enzymes produces better control of stereochemistry and thus can impart unique properties. This methodology may have future potential (7).

*Silicone.* Silicone coatings are based mainly on dimethyl or diphenyl siloxane with significant cross-linking (Fig. 8.6). These coatings are very expensive because the resin can cost >\$14/lb. The advantage of silicone coatings is a high degree of thermal stability, typically stable to 250°C for >100,000 h. The coating is also relatively stain resistant and nonstick. The dimethyl siloxanes are very flexible even at very low temperatures, whereas the diphenyl siloxanes are hard. Due to their high cost, siloxanes are often used to modify the properties of other resins such as acrylics or alkyds where they can be used cost effectively.

### ***New Oils and Their Use***

Several new oils have been studied for their potential use in coatings. Today the oil market is not local but global. Soybean oil is produced around the world and its production in Brazil or elsewhere will affect its price and use in all parts of the world. Oils formerly produced only in a remote area but found to be of value can be converted into a new agricultural product.

Lesquerella oil (LO) and the dehydrated lesquerella oil (DLO) were studied for use in alkyd-type coatings. Their performance was found to be comparable to that of castor oil and dehydrated castor oil, respectively. The lesquerella oil resins were generally found to perform better in drying time, flexibility, and corrosion resistance (8).

Another interesting oil derived from *Euphorbia lagascae* and *Vernonia galamensis* is 9c,12,13 epoxy-octadecenoic acid (vernolic acid) (9). This epoxy acid and its

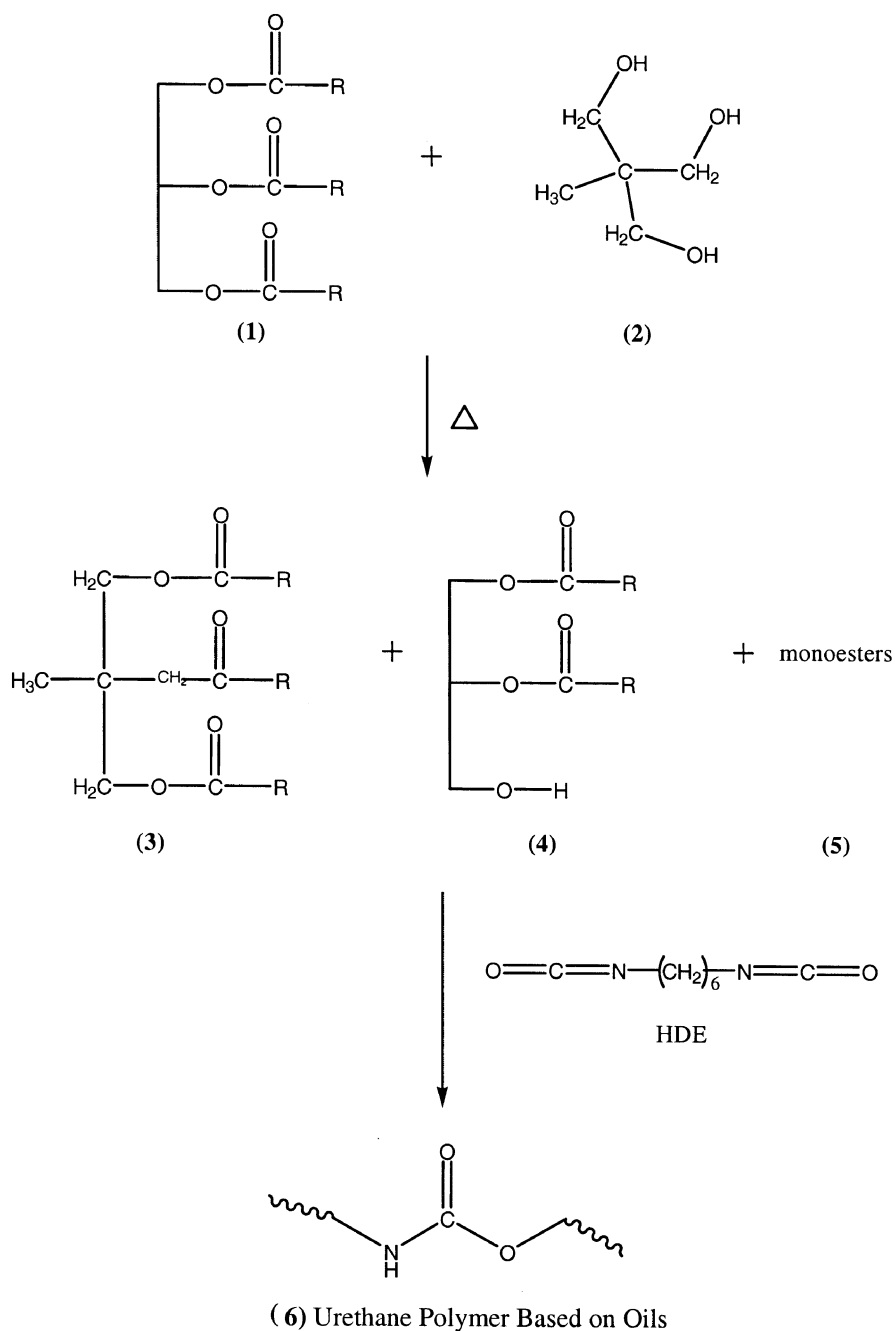
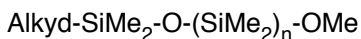


Fig. 8.5. Urethane modified alkyd.



Typically,  $n = 5\text{--}10$

Fig. 8.6. Siloxane.

esters can function as a reactive diluent in many solvent and water-borne coatings. Its use in UV cure systems will be discussed later (10,11). This epoxy system can be polymerized through the action of any carboxylic or mineral acid. Thus, in a conventional baking system, these epoxy groups could be used to cross-link an acid-rich resin.

A rapid cure oil derived from *Calendula officinalis*, “Marigold,” was found to comprise >63% of the  $C_{18}$  triene *8*t*,10*t*,12*c**-octadecatrienoic acid, calendic acid. This acid is analogous to the well-known drying oil, tung oil (11). Conventional drying oils can be modified through a conjugation of the double bonds. Various catalysts have been employed to put the double bonds into conjugation, including bases and metal catalysts. Here the new diene or triene is much more reactive and curing is more rapid.

The future of oils will continue through the use of genetic engineering. The development of new soybean varieties as well as other oil-producing plants that can produce highly specific fats will continue to increase. Today soybeans, which are high in oleic acid, are available, and work is underway to produce high triene content soybean oil. Having plants custom-make our chemicals will increase the performance of these natural products. The high cost and lack of availability of tung oil makes the high triene soybean oil an attractive technological breakthrough. The scientific and social acceptance of this technology as well as the full evaluation as to the safety of the use and production of such products through genetic engineering must first be accomplished. Once proven safe, these new plant-based chemical producers will reduce our need for petroleum-based products in coatings.

### Water-Borne Coatings

Water-borne coatings can fit into any of the following types: water-soluble, emulsions, dispersions, latex, and water-reducible resins. Water-soluble resins are the least important and are rare because most resins derived from oils are insoluble in water. The true emulsions are based upon the emulsification of the oil or alkyd through either the action of a surfactant or a resin that has a surfactant-like character; these are oil-in-water emulsions. In this system, the resin must be a liquid emulsified in water. A few systems utilize water dispersed in an oil or alkyd. This latter system is termed a water-in-oil emulsion. If the resin is a solid and is dispersed in water, it is termed a dispersion. The last class is the latex. Here the resin is usually vinyl acetate, styrene, acrylates, or methacrylates radically copolymerized in a micelle to form particles 0.1  $\mu\text{m}$  in diameter. Water-reducible resins are similar to the dispersions in that they are particles; however the particle size is generally <8  $\mu\text{m}$  in diameter.

In recent years, researchers have been developing an oil-modified latex technology (12–14). The goal is to reduce the need for a coalescent aid by incorporation of the oil into the latex resin. After application, the oil portion of the resin,

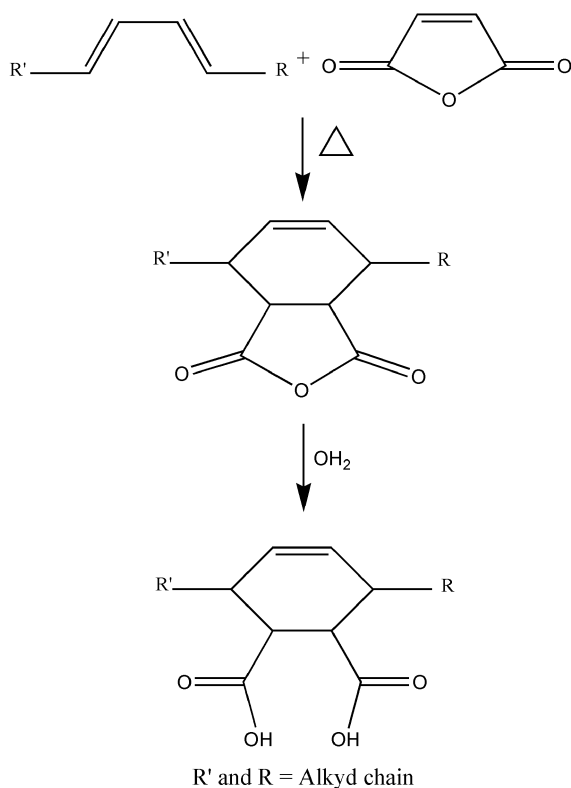
which lowered the glass transition temperature of the resin to allow coalescence into a film, cross-links the resin to produce a hard, durable finish. Acrylated oils are an excellent co-monomer to use in the synthesis of the latex.

Alkyd emulsions are readily prepared and can be employed for OEM coatings as well as for architectural applications. These resins have been utilized as an additive resin for years to improve the performance of latex paint on chalking surfaces. Because the resin is a liquid, it can penetrate the chalk and improve adhesion. Typical use levels are between 0.1 and 1 lb/gal. To emulsify the resin, typically an acid-rich resin neutralized with an amine is sheared into the paint. The submicron size droplets are stabilized by the thickeners (15–17). The use of ultrasonic technology has also been utilized in the preparation of mini-emulsions (18).

Water-reducible technology relies upon the presence of water-loving groups, usually the salt of carboxylic acids, on the polymer chain to act as an internal emulsifying agent. The polymer is dissolved in a high-boiling, water-loving solvent such as ethylene glycol monobutyl ether. An amine such as ammonia or triethyl amine is added to form the salt of the acid groups. Then water is added very slowly. The result is the formation of very small particles of polymer, typically from 5 to 100 nm. If formulated correctly, the polymer solution is clear and the solution is thermodynamically stable due to Brownian motion keeping the particles suspended. The polymer is not water soluble but is actually dispersed, and many of the particles are single polymer chains. To obtain the requisite acid functionality on the chain, maleated alkyds are often used. In [Figure 8.7](#), maleic anhydride is reacted thermally with a conjugated oil component in the alkyd through a Diels Alder reaction.

Water-reducible resin systems have been available for over 50 years but did not gain popularity until the mid-1980s when environmental regulations caused the industry to move more to water-borne coatings. The formulation and manufacture of these coatings are much more difficult and less forgiving than those of either latex or alkyd coatings. The amount of added base, the molecular weight of the resin, the acid value of the resin, and the rate and amount of water added all play an important role in their properties. As water is added to the resin, the viscosity drops with the first small amount of water, then it rises to a very high level. When the solvent composition becomes more like water, the resin's polymer/polymer interactions overcome the polymer/solvent interaction and the resin collapses into a sphere with the carboxylate ions on the exterior. A spherical geometry is typically observed because this places the ions at the furthest points from each other. After application, the water evaporates and the solvent redissolves the particles and coalesces into a film. The use of water-borne driers promotes air oxidation and the subsequent decomposition of the hydroperoxide to cross-link the resin (19,20).

Water-reducible coatings can be used for many OEM and maintenance applications. For direct application of the coatings to metal, flash rusting is a frequently encountered problem. Flash rust inhibitors must be used when water-borne coatings are applied directly to metal, and nitrites are commonly employed.

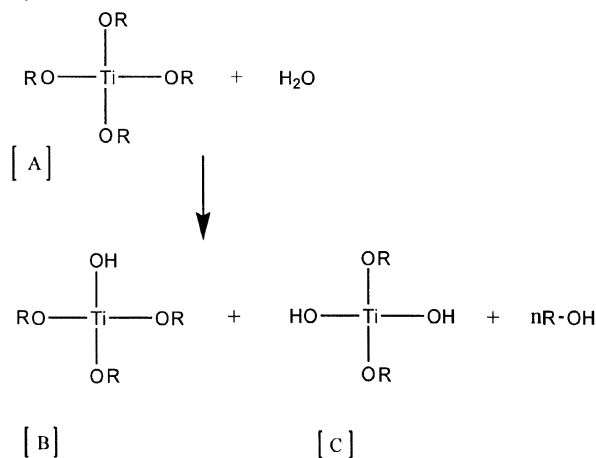


**Fig. 8.7.** Diels Alder Reaction.

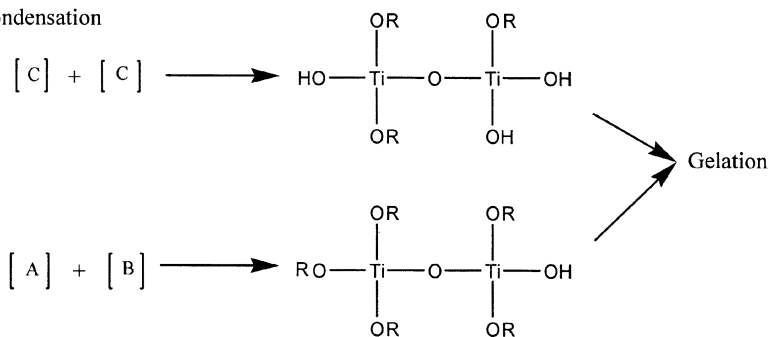
### ***Inorganic/Oil Hybrid Coating***

A new approach to producing coatings with better adhesion, corrosion resistance, and hardness is to combine inorganic and oil technologies into a hybrid system. Several different approaches have been used to produce high-quality durable films. Tuman and Soucek (21) investigated the use of a sol-gel precursor based upon titanium(di-isopropoxide) bis (acetyl-acetonate) and titanium (IV) isopropoxide in conjunction with either linseed or sunflower oil with a zirconium drier. In this system, the titanium sol-gel formed a cluster when moisture entered the film. To improve performance, the coating was baked at 210°C after ambient drying. The sol-gel inclusion at the 5–50% level produced coatings that were stable at 284°C to as high as 306°C with only 5% weight loss by thermogravimetric analysis. In the scheme depicted in [Figure 8.8](#), the –OR, which originally was the isopropoxide, is presumably now the polymerized oil. Thus the resin and inorganic segments are linked together after the baking process, adding strength and cross-linking density. A similar approach was used with zirconium *n*-propoxide, which performed analogously (22). Both the zirconate alone and titanium (IV) isopropoxide sol-gel alone improved performance. However, the results indicated a synergistic effect of a 5% titanium (IV) isopropoxide:5% zirconium *n*-

### Hydrolysis



### Condensation



**Fig. 8.8.** Sol-gel.

propoxide sol-gel in linseed oil, which showed better hardness, up to 6H, and better adhesion to metal substrates. The fracture toughness was also found to improve through the use of titanium and zirconium sol-gels (23–26).

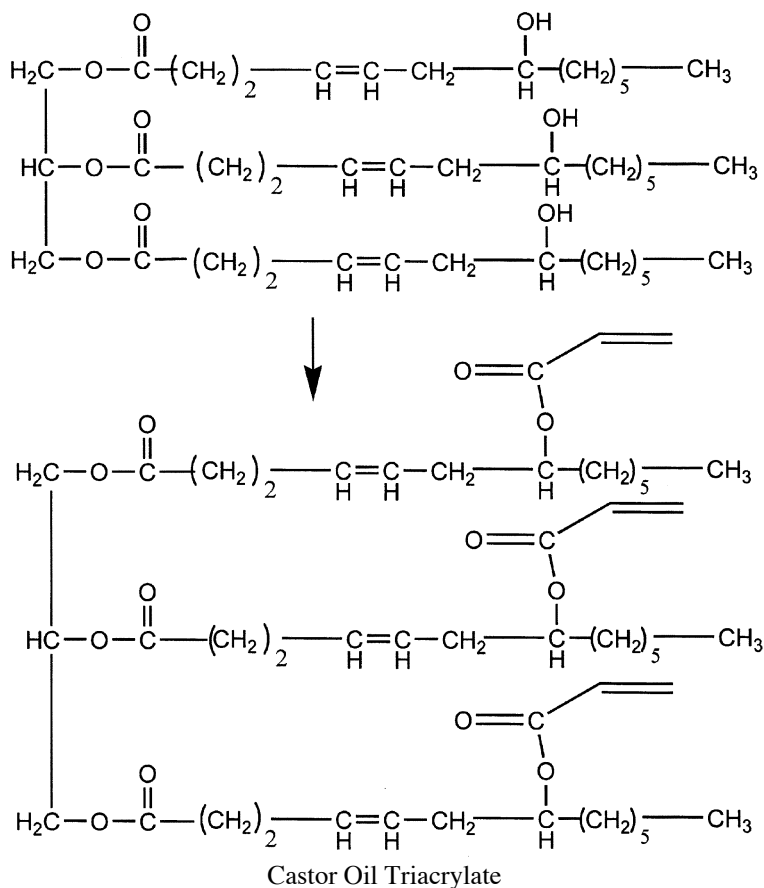
High-solid alkyds have also been improved by the addition of aluminum complexes. The addition of typically 1% of an aluminum complex enhances the hardness and general performance of alkyds. However, accelerated weathering or exterior exposure results in crack formation due to embrittlement from oxidative degradation (27,28).

### **UV and Radiation Cure Technology**

One of the fastest growing areas of coatings is that of radiation cure. This area is divided into three areas; radical UV cure systems, ionic cure systems, and e-beam. Of the three, the radical cure systems are the most popular in part due to their cost

and their cure speed. Radical cure processes require only seconds to reach full cure, whereas ionic cure systems can require 20 min. The e-beam and a few other high-energy cure systems have small markets, but the ionic and radical systems are the largest markets. The use of oils in this market is growing as new, more compatible and reactive monomers are created from low-cost oil feedstocks.

Castor acrylated monomers as well as various acrylate adducts of epoxidized oils such as lesquerella oil are a few of the monomers used in the radical curing systems. In general, acrylates cure readily through UV radical polymerization, whereas styrenic, methacrylates, and vinyl ethers react too readily with oxygen in the air to be as useful. These latter monomers require a blanket of inert gas over the coating during curing to reduce the oxygen radical scavenging. The scheme in Figure 8.9 illustrates the typical reaction of an acrylate. Castor oil is simply esteri-



The Acrylate group is free radically polymerizable

**Fig. 8.9.** Typical reaction of an acrylate.



fied as the triacrylate. When cured, all of the acrylates are incorporated into the backbones of various chains creating a highly cross-linked film. The oil side chains act as internal plasticizers to keep the coating flexible. It is important to note that over time, these coatings will gain hardness due to the oxidative cure of the residual unsaturation (29). Many oil-based products are not compatible with the very polar acrylate monomers, and urethane derivatives are also frequently used in the radical cure systems to improve adhesion and impart toughness. In these cases, the amount of oil-based monomer must be kept low to avoid phase separation during polymerization.

Cationic cure systems have seen significant interest in recent years even though they are only ~8% of the UV cure market. The cost of highly epoxidized soybean, linseed, and other oils is relatively low compared with the typical aliphatic epoxy monomers used in cationic cure systems. The epoxidized oils are significantly more polar and thus more compatible with the other components of the cationic cure system. Unlike the radical cure systems, these have generally less shrinkage, can cure more deeply on pigmented systems, and are much slower to cure.

Vernonia oil and epoxidized soybean oil were studied by Thames and Yu (30). They found excellent adhesion, impact, UV stability, gloss retention, and corrosion resistance with the oils. However, the pencil hardness and tensile strength of the coating decreased with increasing oil content. Gu *et al.* (31) found that as the percentage of epoxidized soybean oil increases in a cationic UV cure system with a cycloaliphatic epoxy, the adhesion and solvent resistance increase. The hardness, however, generally decreases unless a postbake is performed after UV exposure. The postbake is often employed to cause a subsequent increase in the rate of cationic reaction, including acid-catalyzed reactions. Usually the cross-link density and subsequent hardness increase due to baking. Epoxidized palm oil was also used and may prove useful for coatings in the immobilization of herbicides (32).

One study utilized oil-modified polyols derived from Chinese melon oil (*Momordica charantia*) and tung oil. These oils are highly unsaturated and excellent drying oils. The system was formulated with the oil-modified polyol, cycloaliphatic epoxides, and a cationic initiator. These systems had excellent gloss and adhesion with improved impact resistance and flexibility (33). Zou and Soucek (34) successfully modified linseed oil by reaction with 1,3-butadiene and subsequent epoxidation. This new monomer can also be used for cationic UV cure systems and should be cost effective. In another study, Soucek *et al.* (35) utilized tetraethoxysilane oligomers in conjunction with epoxidized norbornene-derivitized linseed oil to form an organic/inorganic hybrid cationic UV cure coating. The performance enhancement was attributed to the nanoscale phase separation of the inorganic and larger organic phases. The inorganic phase was discontinuous, whereas the organic formed a continuous phase around the islands of inorganic polymer. The use of inorganic ceramic-type building blocks can enhance both the abrasion resistance and the adhesion of the coating to metals.

## Oil-Based Additives in Coatings

The environmental movement of the past 25 years has driven a deep interest in natural products and their potential use in coatings. The general goal of VOC elimination has been the primary driver. Oils have a high potential of reducing VOC because they are a liquid at room temperature and polymerize, or at least oligomerize, with air oxidation. Therefore, with time, they become a solid. Today, several of the additives, especially in water-borne coatings, are being replaced with unsaturated oils and their derivatives. The goal is to replace additives that may degrade the performance of the coating or are VOC with an additive that adds to the performance but not the VOC.

The major VOC in a latex paint is the coalescent aid; typically an ester or ether such as 2-butoxyethanol is used. Van De Mark and Jirautumnukul (36,37) utilized simple monoesters of unsaturated oils with ethylene, diethylene, triethylene, propylene, and dipropylene glycols and other simple alcohols such as the methyl and ethyl ester of unsaturated fatty acids as potential coalescent aids. Vegetable oils as potential coalescent aids are not compatible with latex paint; they are too nonpolar and phase separate from the resin. Oils such as soybean oil were transesterified with a glycol. The simple monoesters were highly compatible for most commercial latex resins, particularly ethylene glycol and propylene glycol monoesters. Virtually a 1:1 replacement amount of the new coalescent aid was effective for many conventional coalescent aids. The new oil-based esters were nonvolatile. As they age, the properties of the latex paint improved very much like the conventional aids as they evaporated over several days or weeks. The amount of resin needed decreased slightly and the efficacy of the associative thickener improved; thus less is required. This additive is now a commercial product.

Unsaturated oils are being used as surfactants as the fatty acid or are derivatized. These additives are targeting the air oxidative cure mechanism of alkyds to make the additive lose its mobility and become a binder in the coating. Thus the additive does its job, and then becomes part of the binder (38–40).

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