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Solvent Extraction: Safety, Health, and Environmental Issues

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I. INTRODUCTION

Safety, health, and environmental issues for edible oil extraction facilities vary, depending on the extraction method used. For example, aqueous extraction, supercritical fluid extraction, and mechanical extraction facilities have different requirements than organic solvent extraction facilities. In the United States, edible oil extraction using organic solvents, is a mature industry that has been under increasing regulatory pressure in recent years. In this chapter, regulatory concerns and toxicity of extraction solvents, commercial hexane, and other potential alternative solvents are discussed along with the current methods of edible oil extraction (i.e., mechanical, prepress solvent, and solvent extraction).

Fats, which are solid at ambient temperature, and liquid oils are recovered from diverse biological sources by mechanical separation, solvent extraction, or a combination of the two methods (1, 2). These materials include animal tissues (e.g., beef, chicken, and pork); crops specifically produced for oil or protein (e.g., soy, sunflower, safflower, rape/canola, palm, and olive); byproducts of crops grown for fiber (e.g., cottonseed and flax); crops for food and their coproducts (e.g., corn germ, wheat germ, rice bran, coconut, peanuts, sesame, walnuts, and almonds); nonedible oils and fats (castor, tung, jojoba); and other oil sources (oils and fats from microbial products, algae, and seaweed). There are

many physical and chemical differences among these diverse biological materials. However, the similarities are that oils (edible and industrial) and other useful materials (e.g., vitamins, nutraceuticals, fatty acids, phytosterols) can be extracted from these materials by mechanical pressing, solvent extracting, or a combination of pressing and solvent extraction. The preparation of the various materials to be extracted varies. Some need extensive cleaning, drying (optional), fiber removal (cottonseed), dehulling, flaking, extruding, and so forth, all of which affect the solvent–substrate interaction and therefore the yield, composition, and quality of the oils and other materials obtained.

Historically, the advancement of processing technology for recovering oils and other useful materials has been primarily driven by economics. Each extraction process was optimized through trial and error with the available technology to produce maximal yield of high-quality products at the lowest cost. For thousands of years, stone mills, and for several centuries, simple hydraulic or lever presses were used as batch systems. The continuous mechanical presses only became a reality during the early 1900s. It was not until the 1930s that extraction solvents were used more widely, which greatly enhanced the recovery of oil from oilseeds or other oil-bearing materials. In recent years, safety, health, and environmental regulations for the solvents used for extracting oil from oilseeds have prompted research efforts to find solvents to replace commercial hexane. These solvents, including ethanol, isopropanol, water, supercritical carbon dioxide, and others, are technically feasible as oil extraction solvents but at present are economically unacceptable (1). Recent research to use commercial isohexane in two separate cottonseed oil mills (3, 4) has demonstrated energy savings and throughput increases. In the near term, it appears that commercial isohexane can be used as an alternative to commercial hexane.

II. OIL EXTRACTION PROCESS

Four types of processing systems are used to extract oil from oil-bearing materials: hydraulic press, expeller or screw press, prepress solvent extraction, and direct solvent extraction. Oil-bearing materials have to be prepared for extraction to separate the crude oil from the meal (1, 2) (Fig. 1). Careful control of moisture and temperature during processing must be exercised to maintain the quality of the protein in the meal, to minimize the damage to the oil, and to maximize oil extraction. Crude oils are refined by conditioning with phosphoric acid to promote the removal of phospholipids and treating with sodium hydroxide (alkali refining) (Fig. 2). Refined oil is bleached with activated clay to remove color pigments and residual soap. Bleached oils are then deodorized by steam distillation. When the soybean oil is of good quality and the free fatty acid (FFA) content is low, the oil can be physically refined. Physical refining involves water washing to recover lecithin followed by phosphoric acid pretreat-

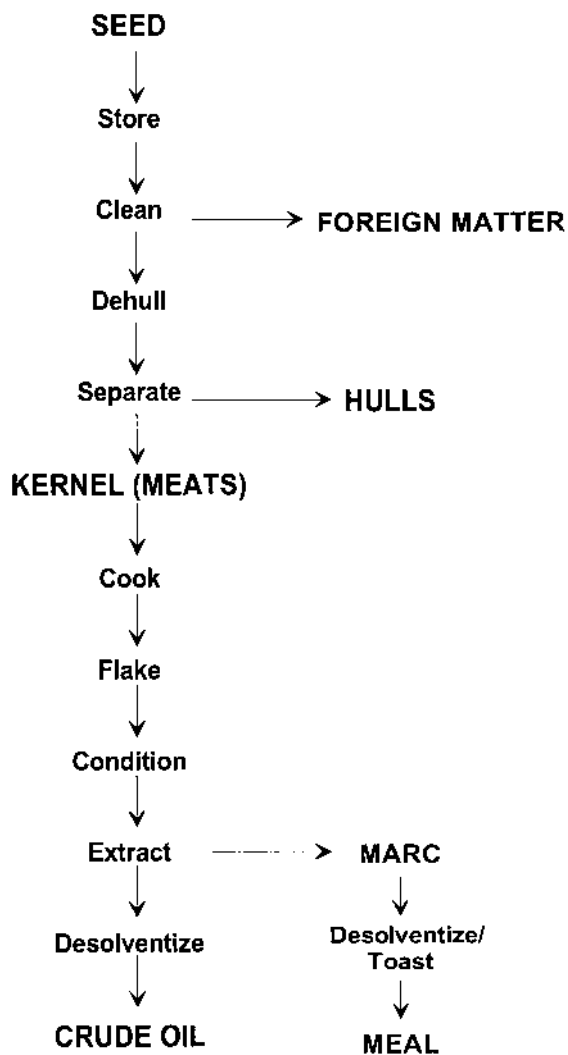


Figure 1 Preparation for extraction to separate the crude oil from the meal in oil-bearing materials.

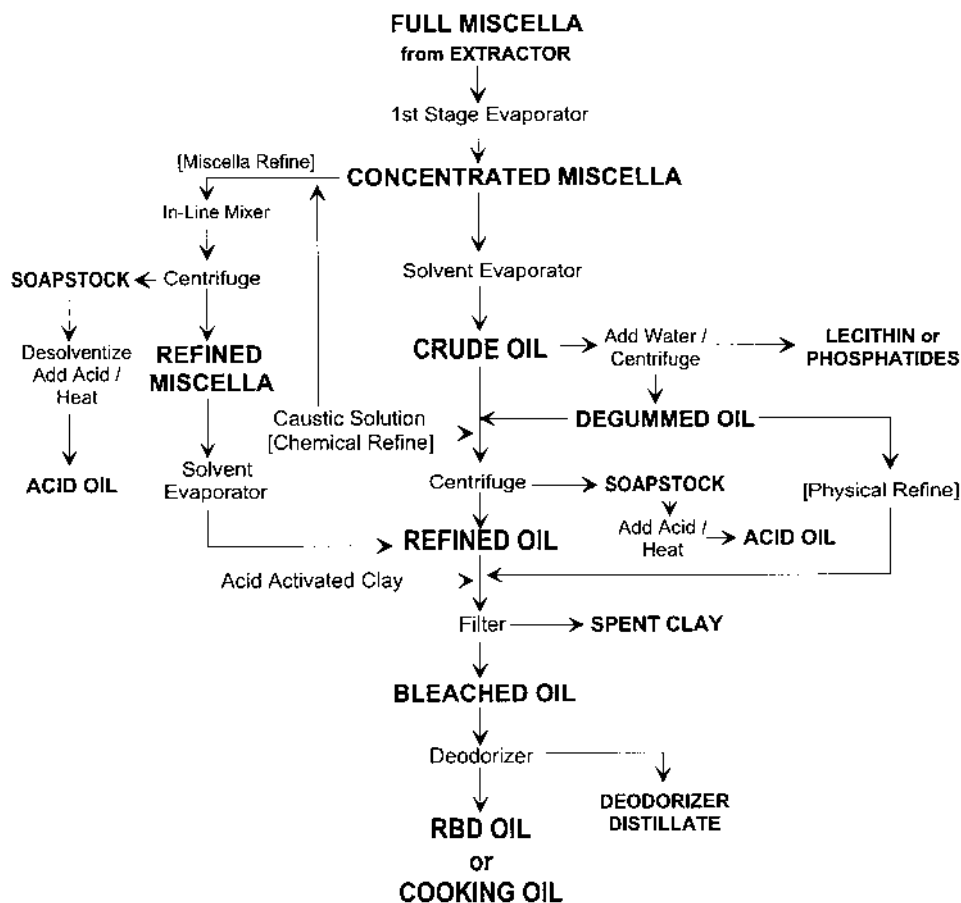


Figure 2 Refining of crude oil.

ment and bleaching to remove the nonhydratable gum. After bleaching, the oil is steam deodorized to remove the FFAs. The refined, bleached, and deodorized oil (RBD oil) is used to produce finished products, e.g., salad and cooking oils, shortenings, and margarine. Some of the finished products also require the oil to be hydrogenated, which changes the consistency and solid content of the oil, and increases stability to oxidation, which extends the shelf life of the finished products. Also, some of the oils (e.g., cottonseed and sunflower) are winterized to remove the higher melting constituents or wax. The solid fraction removed from winterization can be used in confectionery products; the winterized oil is less likely to become cloudy in refrigerated storage.

A. Preparation for Extraction

1. Storage

For optimal extraction and quality of oil, the oil-bearing material should be stored dry and at a relatively low temperature. If the material is wet, it should be processed as soon as possible after harvest. Oils in the presence of water can deteriorate rapidly, forming FFAs and causing greater refining loss.

2. Seed Cleaning

The first step in the commercial processing of oilseeds is “cleaning” to remove foreign materials, such as sticks, stems, leaves, other seeds, sand, and dirt using dry screeners and a combination of screens and aspiration. Permanent electromagnets are also used for the removal of trash iron objects. Final cleaning of the seed usually is done at the extraction plant just prior to processing.

3. Dehulling

The dehulling process may include the removal of excess moisture by drying, cracking the seed, and removing the outer seed coat (hull) of the seed. The hull contains little or no oil, so that its inclusion makes the extraction less efficient and dilutes the protein content of the meal. Also, the hull will reduce the total yield of oil by absorbing and retaining oil in the press cake. An acceptable level of hull removal must be determined, depending on the desired protein level of the final meal. Hulls are removed by aspiration, and un-dehulled seeds are removed from the kernels by screening and returned to the huller. Some meats still adhere to the hulls, which are beaten, then screened again to obtain the meat. In the case of high oil content seed for direct solvent extraction, such as cottonseed, sunflower seed, etc., certain quantity of hull material is added to the kernels to provide the structural strength and matrix needed for the solvent extraction process.

4. Flaking

After dehulling, the meats are reduced in size and “flaked” to increase surface area and to facilitate oil removal. Proper moisture content of the seeds is essential for flaking, and if the moisture level is too low, the seeds are “conditioned,” with water or steam, to raise the moisture to about 11%. In the case of soybean, heat will be applied to soften the meats prior to flaking. For solvent extraction, flakes are commonly not less than 0.203–0.254 mm (0.008–0.010 in), which can be solvent extracted efficiently with less than 1% residual oil. Thinner flakes tend to disintegrate during the solvent extraction process and reduce the miscella percolation rate.

5. Cooking

Prior to extraction, the flakes are heated. The purpose of cooking the flakes is to (a) break down cell walls to allow the oil to escape; (b) reduce oil viscosity; (c) control moisture content; (d) coagulate protein; (e) inactivate enzymes and kill microorganisms; and (f) fix certain phosphatides in the cake, which helps to minimize subsequent refining losses. Flakes are cooked in stack cookers to more than 87.8°C (190°F) in the upper kettle. Flakes with high phosphatide content may benefit from being cooked at slightly lower temperatures to avoid elevating refining losses. The temperature of the flakes is raised to 110–132.2°C (230–270°F) in the lower kettles. The seeds are cooked for up to 120 min. Overcooking lowers the nutritional quality of the meal and can darken both the oil and the meal. Poor-quality seeds with high levels of FFAs cannot be cooked for as long as high-quality seeds because of darkening. Darker oil requires additional refining to achieve a certain bleachable color. For soybeans, this heat treatment is often done prior to flaking.

6. Preparation of Collets with Expanders

Sometimes low-shear extruders, called expanders, are used. This equipment has the capability to process both low and high oil content materials. The meats are fed to an extruder after dehulling, flaking, and cooking and are heated as they are conveyed by a screw press through the extruder barrel. The meats are under considerable shear, pressure, and temperature when they reach the exit of the extruder. The change in pressure as the material leaves the extruder causes it to expand whereupon most of the oil cells are ruptured, releasing the oil, which is rapidly reabsorbed to the porous “collets” or pellets. The expanded collets produced are then cooled and extracted with solvent.

B. Oil Extraction

1. Mechanical Extraction

Olive oil is still routinely obtained from olives by using a low-temperature hydraulic press process, referred to as “cold pressing.” This is done to minimize the heat-related degradation of olive oil. Palm fruit and some cottonseed are extracted with an expeller or screw press, which is a continuous process. To achieve a higher yield of oil, often a higher heat treatment of the cottonseed flakes is carried out prior to expelling. This process can extract up to 90% of the available oil from the cottonseed kernels and leaves about 3–5% residual oil in the pressed cake.

2. Prepress Solvent Extraction

In prepress solvent extraction, the oil-bearing material is first mildly pressed mechanically by means of a continuous screw press operation to reduce the oil

by one-half to two-thirds of its original level, followed by solvent extraction to remove the remaining oil in the prepressed cake. Pressing followed by solvent extraction is more commonly used when high oil content materials (e.g., canola/rapeseed, flaxseed, corn germ, and cottonseed) are processed. This process reduces the amount of oil to be extracted by solvent and, therefore, requires a smaller extractor and less solvent than a direct solvent extraction facility of the same throughput.

3. Direct Solvent Extraction

Direct solvent extraction involves the use of a nonpolar solvent, usually commercial hexane, to dissolve the oil from oilseed flakes or collets without removing proteins and other non-oil-soluble compounds. Solvent extraction yields about 11.5% more oil than does the screw press method, and less oil remains in the meal. The cooked flakes or collets are mixed with solvent in a batch or continuous countercurrent extraction operation. The vapor pressure of hexane limits the practical operating temperature of the extraction and its contents to about 50–55°C. The resulting miscella (or full miscella) (oil-solvent mixture), usually about 18–24% of oil by weight, and the marc (solvent-laden collets or flakes) are heated to evaporate the solvent, which is collected and reused. Occasionally, overheating of the oil-solvent miscella can cause irreversible color changes in the oil.

The oil is freed from the full miscella, by using a series of stills (solvent evaporators), stripping columns, and associated condensers. The hexane-free oil (i.e., crude oil) is filtered and cooled before leaving the solvent extraction plant for storage or further treatment. This is the crude oil normally traded in the commodity market. To minimize the settling problem during storage and shipping, crude soybean oil is often degummed before it is traded.

Due to economic factors and product quality concerns, most of the cottonseed mills in the United States further integrate oil refining as part of the routine operation. The majority of cottonseed mills conduct miscella refining with sodium hydroxide to produce a once refined or prime bleachable summer yellow (PBSY) cottonseed oil. The primary benefit of this additional refining operation is to achieve a more consistent oil quality in terms of its color and reduced refining loss. Several U.S. cottonseed oil mills further process the cottonseed oil to finished RBD cottonseed oil (Fig. 2). In some cases, the oil laden bleaching clay (which is a source of calcium to livestock) is added back to the meal during the deodorization/toasting step. Some operation, besides refining (R), bleaching (B) and deodorization (D), may also do winterization (W) to reduce the amount of the saturated portion of the vegetable oil to produce a finished oil referred to as RBWD or RBDW oil. For these facilities, additional regulatory requirements may be necessary.

The extraction solvent used in the extractor is normally recovered from the

miscella and solvent-laden flakes or collets and reused. The small amount of solvent loss that occurs through vents, crude oil, and desolventized flakes is unavoidable (i.e., fugitive loss). Estimated solvent loss from each of these emission points is given in Fig. 3. Management and control of emission loss during solvent extraction is an important issue for worker safety and protection of our environment.

III. TOXICITY OF EXTRACTION SOLVENTS

Many halogenated and aromatic solvents have been examined in the past and are effective in extracting edible oils (1). However, these solvents have various degrees of toxicity and therefore are not likely to be used as alternates/replacements for commercial hexane for edible oil extraction. Several hydrophilic solvents also have been studied as oil extraction solvents. They are not toxic but their overall performance as an oil extraction solvent is not acceptable. This is why hydrocarbon-based solvents will likely be used for oil extraction for the foreseeable future.

A. Commercial Hexane

Commercial hexane has been used for decades as the solvent to extract oils from biological sources. It is a mixture of six carbon saturated compounds, with *n*-hexane as the predominant component. Pure *n*-hexane causes peripheral nerve damage in rats and humans when inhalation exposures are maintained for several months at 500 ppm in rats or 125 ppm in humans (5, 6). However, commercial hexane, which contains 52% *n*-hexane and a mixture of hexane isomers (see composition below), does not cause peripheral nerve damage in animals.

The composition of commercial hexane tested (7) is as follows:

- 52% *n*-hexane
- 16% methylcyclopentane
- 16% 3-methylpentane
- 13% 2-methylpentane
- 3% cyclohexane

This was shown by extensive animal inhalation studies, which were mandated by the U.S. Environmental Protection Agency (EPA) under Section 4 of the Toxic Substances Control Act (TSCA) (8). The test results, summarized by Galvin (7), showed that this commercial hexane blend was not a neurotoxin. In addition, the following tests also were negative: acute toxicology, subchronic neurotoxicity, mutagenicity (both in vitro and in vivo studies), oncogenicity, and development and reproductive studies (with the above-described commer-

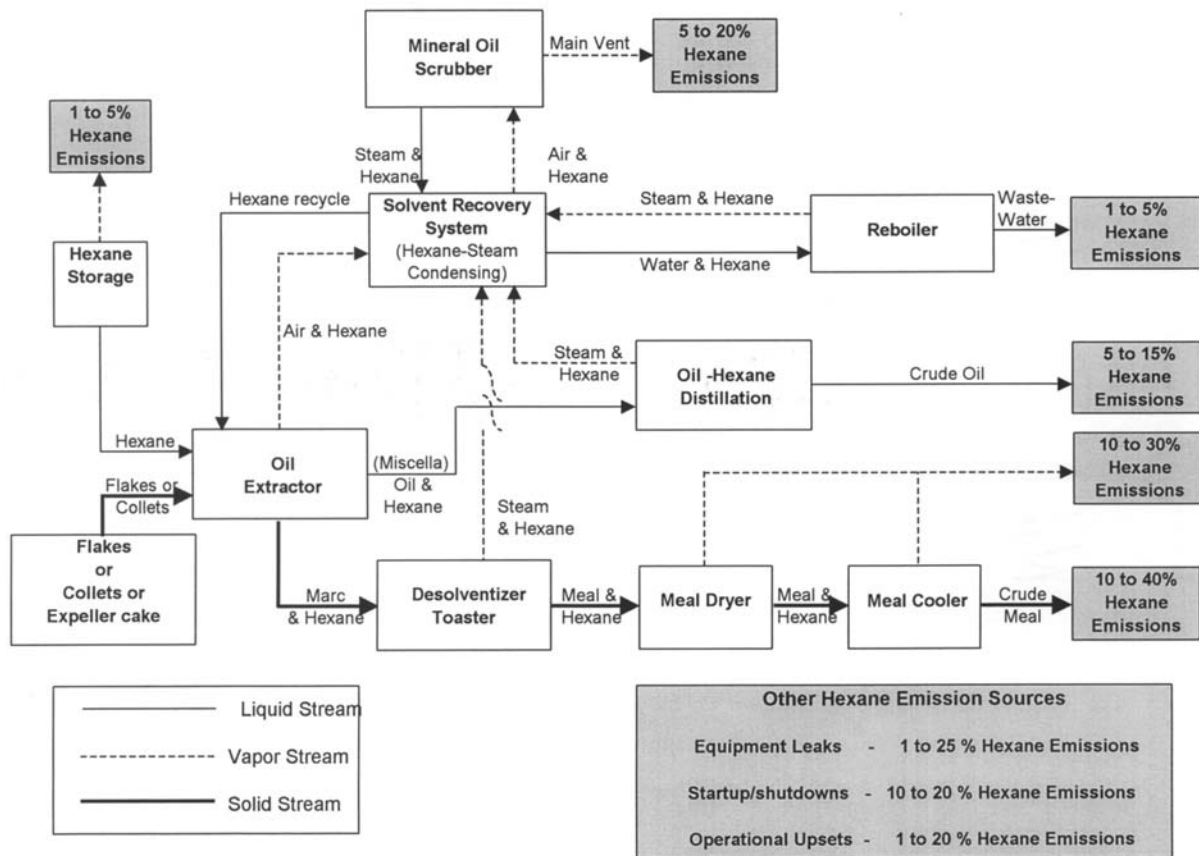


Figure 3 Overview of oilseed extraction operation and identification of hexane emission sources.

cial hexane) at a vapor concentration as high as 9000 ppm for 6 h/d, 5 d/week up to 13 weeks.

B. Commercial Isohexane and Hexane Isomers

An alternative to commercial hexane, which would require minimal retrofit of existing extraction facilities, is commercial isohexane. This solvent, a blend of hexane isomers [2-methylpentane or isohexane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane and *n*-hexane (<1%)], has not been tested as extensively as commercial hexane. However, the individual components have been tested in various toxicological assays. Based on the available information, commercial isohexane is not a neurotoxicant (7).

C. Other Solvents

Many other solvents have been examined by various research teams as potential alternative solvents for commercial hexane for the extraction of edible oils. Some toxicity information of the most common ones is summarized in [Table 1](#).

More discussion on these solvents can be found in the summary by Wakelyn and Adair (9). Most of the solvents mentioned in this section, with the exception of acetone (9a), can undergo photochemical oxidation in the atmosphere in the presence of sunlight and nitrogen oxides (NO_x) to form ozone in a greater rate than ethane (C_2H_6) and, therefore, are classified as volatile organic compounds (VOCs). The main component of the hydrocarbon solvents used for edible oil extraction, *n*-hexane, is a neurotoxin and considered a hazardous air pollutant (HAP) by EPA. Thus, *n*-hexane containing solvents are more stringently regulated than isohexane (see IV. Regulatory Issues).

IV. REGULATORY ISSUES

Many workplace/occupational health and safety, environmental, food safety, and other regulations (see Tables 2 and 3 for summary information on U.S. laws and regulations; a list of terms/abbreviations is given in the Glossary) apply to oilseed processors (10). Most of the environmental and workplace legislation came about in the 1970s in response to increased general public awareness, concern, and desire for a cleaner environment, safer workplace, and safer food supply. This has led to an increasing number of regulations, and it is expected that there will continue to be more and stricter regulation in the future.

How are regulations established? In the United States, first Congress passes a law, e.g., the 1990 amended Clean Air Act, giving the legislative authority to the regulatory agency. Next the federal regulatory agency that has the

Table 1 Some Toxicity Information for Potential Alternate Solvents

Solvent (CAS no.)	LD ₅₀ (g/kg)	Other toxic concerns
Acetone (67-64-1)	5.8 in rats 20 in rabbits	A central nervous system depressant in animals and humans
2-Butanone (methyl ethyl ketone) (78-93-3)	2.74 in rats 13 in rabbits	Eye and skin irritation and cause narcosis
Cyclohexane (110-82-7)	12.7 in rats	Moderate irritation to eyes and mucous membrane
Cyclopentane (287-92-3)		Narcotic
Ethyl acetate (141-78-6)	5.6 in rats 3.0 in cats	Irritation to the eyes, mucous membranes, respiratory tract
Ethyl alcohol (ethanol) (64-17-5)	7.06 in rats	Irritation to the eyes, mucous membranes
Heptane (142-82-5)	2.22 in mice	Central nervous system depressant
Isopropyl acetate (108-27-4)	3.0 in rats	Irritation to the eyes, mucous membranes
Isopropyl alcohol (isopropanol) (67-63-0)	5.05 in rats 12.8 in rabbits	Irritation to the eyes, nose, throat
Methyl alcohol (methanol) (67-56-1)	5.628 in rats 15.8 in rabbits	Headaches and visual impairment
Methylcyclohexane (108-87-2)	—	Similar to that of heptane
Methylene chloride (dichloromethane) (75-09-2)	—	Decreased visual and auditory function; headaches, dizziness, nausea, and memory loss; a B2 probable human carcinogen
<i>n</i> -Propyl acetate (109-60-4)	9.37 in rats	Irritation to the eyes, respiratory system

legislative authority establishes standards/regulations through notice and comment rule making. As long as there is legislative authority, regulations can be established or revised when necessary. A proposed standard is published in the *Federal Register* announcing that the agency is undertaking a rule making (notice) and asking for comments; a hearing can be held also. After comments are received and the comment period closes, the agency prepares and publishes a final standard in the *Federal Register*. The effective dates of various requirements of the new standard are usually phased in under a predetermined timetable (e.g., see the regulation for vegetable oil production under Hazardous Air Pollutants). Each facility is expected to establish programs to ensure proper compliance with the various regulations and that proper corrective actions are taken where necessary. Programs can include written programs, auditing, record keeping, reporting, warning labels, worker training programs, and so forth, according

Table 2 U.S. Environmental Laws and Regulations

Law or regulation	Purpose
Environmental Protection Agency (EPA) (established 1970)	To protect human health and welfare and the environment.
Clean Air Act (CAA) (42 U.S. Code 7401 et seq.)	To protect the public health and welfare. Provides EPA with the authority to set NAAQS, to control emission from new stationary sources, and to control hazardous air pollutants.
Federal Water Pollution Control Act (known as the Clean Water Act) (CWA) (33 U.S. Code 1251 et seq.)	The major law protecting the “chemical, physical and biological integrity of the nation’s waters.” Allows the EPA to establish federal limits on the amounts of specific pollutants that can be released by municipal and industrial facilities.
Toxic Substances Control Act (TSCA) (15 U.S. Code 2601 et seq.)	Provides a system for identifying and evaluating the environmental and health effects of new chemicals and chemicals already in commerce.
Resource Conservation and Recovery Act (RCRA) (42 U.S. Code 6901 et seq.)	A system for handling and disposal of nonhazardous and hazardous waste.
Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) (42 U.S. Code 9601 et seq.)	Known as “Superfund,” gives the EPA power to recover costs for containment, other response actions, and cleanup of hazardous waste disposal sites and other hazardous substance releases.
Emergency Planning and Community Right-to-Know Act (EPCRA; also “SARA Title III”) (42 U.S. Code 1101 et seq.)	(Part of Superfund) Provides authority for communities to devise plans for preventing and responding to chemical spills and release into the environment; requires public notification of the types of hazardous substances handled or release by facilities; requires state and local emergency plans.

to the particular regulations that pertain to that industry. Regulations are enforced by the appropriate federal or state agency.

The regulations discussed here are required in the United States. Many other countries have similar requirements, but if they do not, it would be prudent for oilseed solvent extraction operations to consider meeting these regulations and for these industries to have environmental, health and safety, and quality management programs (11, 12).

Table 3 U.S. Worker Health and Safety Laws and Regulations

Laws:

Occupational Safety and Health Act of 1970 (OSH Act) (PL 91-596 as amended by PL 101 552; 29 U.S. Code 651 et. seq.)

OSHA Health Standards:

Air Contaminants Rule, 29 CFR 1910.1000

Hazard Communication Standard, 29 CFR 1910.1200

Occupational Exposure to Hazardous Chemicals in Laboratories, 29 CFR 1910.1450

Bloodborne Pathogens, 29 CFR 1910.1030

OSHA Safety Standards:

Process Safety Management, 29 CFR 1910.119

Emergency Action Plan, 29 CFR 1910.38(a)(1)

Fire Prevention Plan, 29 CFR 1910.38(b)(1)

Fire Brigades, 29 CFR 1910.156

Permit-Required Confined Space, 29 CFR 1910.146

Lockout-Tagout, 29 CFR 1910.147

Powered Industrial Truck Operator Training, 29 CFR 1910.178

Occupational Noise Exposure, 29 CFR 1910.95 and Hearing Conservation Program, 29 CFR 1910.95(c)

Personal Protection Equipment:

General Requirements, 29 CFR 1910.132

Eye and Face Protection, 29 CFR 1910.133

Respiratory Protection, 29 CFR 1910.134

Head Protection, 29 CFR 1910.135

Foot Protection, 29, CFR 1910.136

A. Environmental Protection

The purpose of the EPA, which administers all regulations affecting the environment and chemicals in commerce, is to protect human health and welfare and the environment. The individual states and state environmental regulatory control boards implement and enforce most of the regulations. The legislation that serves as the basis for the regulations can be divided into:

1. Statutes that are media specific [Clean Air Act (CAA) and Clean Water Act (CWA)];
2. Statutes that manage solid and hazardous waste [Resources Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)]; and,
3. Statutes that directly limit the production rather than the release of

chemical substance [Toxic Substances Control Act (TSCA) and Federal Insecticide, Fungicide and Rodenticide Act (FIFRA)].

The reader is referred to [Table 2](#) for a summary of the information on environmental laws and regulations, [Table 4](#) for an overview of environmental requirements for air and water, [Table 5](#) for a summary of air threshold emissions, and [Table 6](#) for an overview of environmental requirements for waste.

1. Clean Air Act (CAA; 42 U.S. Code 7401 et seq.):

The purpose of the CAA is to protect the public health and welfare. To satisfy the CAA requirements, states and state air control boards are required to implement regulations and develop state implementation plans (SIPs) (13, 14). Criteria pollutants [e.g., ozone (O₃), particulate matter (PM), nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), and lead (Pb)] are regulated with

Table 4 U.S. Environmental Regulations, Air and Water

Chemical name (CAS no)	VOC	HAP	CWA ^a
<i>n</i> -Hexane (110-54-3)	Yes	Yes	Yes
Commercial hexane (none)	Yes		
<i>n</i> -Heptane (148-82-5)	Yes	No	Yes
Cyclohexane (110-82-7)	Yes	No	Yes
Cyclopentane (287-92-3)	Yes	No	Yes
Hexane isomers (none)	Yes	No	Yes
Commercial isohexane (none)	(Same as hexane isomers)	No	Yes
2-Methyl pentane (isohexane) (107-83-5) (a hexane isomer)	Yes	No	Yes
3-Methyl pentane (96-14-0) (a hexane isomer)	Yes	No	Yes
Methyl cyclopentane (96-37-7) (a hexane isomer)	Yes	No	Yes
2,2-Dimethyl butane (neohexane) (75-83-2) (a hexane isomer)	Yes	No	Yes
2,3-dimethyl butane (79-29-8) (a hexane isomer)	Yes	No	Yes
Methyl cyclohexane (108-87-2)	Yes	No	Yes
Isopropyl alcohol (2-propanol) (67-17-5)	Yes	No	Yes
Ethyl alcohol (ethanol) (64-17-5)		No	Yes
Acetone misc. (67-64-1)	No ^b	No	Yes

^aUnder the Clean Water Act there could be storm water and NPDES permit requirements; none of the solvents are listed as priority toxic pollutants in 40 CFR 401.15.

^bAcetone is considered by the U.S. EPA not to be a VOC (60 FR 31643; June 16, 1995).

CAS no., Chemical Abstracts Service Registry number; VOC, volatile organic chemical; HAP, hazardous air pollutant; CWA, Clean Water Act.

Table 5 Summary of Threshold Emission Levels

Regulation	Threshold emission level	Requirement ^a
Major source (40 CFR 70)	100 t criteria pollutant (or less ^b) or 10/25 t HAP (per year)	Title V permit (federal operating permit)
Hazardous Air Pollutants (HAP)	10 t of one HAP/25 t total HAP (per year)	NESHAP/MACT standard
NAAQS: O ₃ (VOC) ^c	10–100 t (depending on degree of severity of nonattainment)	RACT/BACT standard
PM	70 t nonattainment; 100 t attainment	RACM/BACM standard
NSR: PSD ^d	250 t	Preconstruction/building permit, BACT; much paperwork
Nonattainment NSR	100 t/a	Preconstruction permit, LAER, emission offsets
Toxic Release Inventory (TRI)	10,000–25,000 lb/a	Annual reporting (Form R)
112(r) ^e	Hexane/hexane isomers not covered	
PSM ^f	>10,000 lb in one tank (all flammable solvents including hexane/hexane isomers are covered)	Written plan, controls, training, etc.

^aFor NESHAP, MACT, RACM, BACM, RACT, BACT, and LAER, see Glossary.

^bFor example, the threshold can range from 10 to 100 t depending on degree of severity of ozone (O₃) nonattainment.

^cGround level ozone (O₃) is not emitted directly into the air but is formed when sunlight acts on emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOC) like hexane.

^dPSD = prevention of significant deterioration, a requirement of New Source Review (NSR) in attainment areas.

^esection 112(r) of the Clean Air Act (40 CFR 68) is for prevention of chemical accidents.

^fPSM = process safety management (29 CFR 1910.119); OSHA standard to prevent or minimize the consequences of catastrophic releases.

National Ambient Air Quality Standards (NAAQS) and hazardous air pollutants (HAPs), such as *n*-hexane, with National Emissions Standards for Hazardous Air Pollutants (NESHAP).

The 1990 CAA expanded the list of HAPs to 188, including *n*-hexane, and more strictly regulates nonattainment areas for criteria pollutants such as O₃, PM, CO and NO_x.

Table 6 U.S. Environmental Regulations, Solid Waste

Chemical name (CAS no.)	(EPCRA/SARA Title III) ^a			
	(RCRA)	Sec. 304		Sec.313 (TRI)
	RCRA Code ^b	CERCLA (RQ)	Sec.311/312	
<i>n</i> -hexane (110-54-3)		5000 ^c	Yes	Yes
Commercial hexane (none)				Yes ^d
<i>n</i> -heptane (142-82-5)			Yes	No
Cyclohexane (110-87-7)	U056	1000	Yes	Yes
Cyclopentane (287-92-3)			Yes	No
Hexane isomers (none)			Yes	No ^e
Commerical isohexane (none)				No ^e
2-Methyl pentane (isohexane) (107-83-5)			Yes	No ^e
3-Methyl pentane (96-14-0)			Yes	No ^e
Methyl cyclopentane (96-37-7)			Yes	No ^e
2,2-Dimethyl butane (neohexane) (75-83-2)			Yes	No ^e
2,3-Dimethyl butane (79-29-8)			Yes	No ^e
Methyl cyclohexane (108-87-2)			Yes	No
Isopropyl alcohol (2-propanol) (67-63-0)			Yes	No ^f
Ethyl alcohol (64-17-5)			Yes	No
Acetone (67-64-1)	U002	5000	Yes	No

^aFrom Title III Lists of Lists, U.S. EPA, EPA 740-R-95-001 (April 1995); 40 CFR 52-99; (59 FR 4478; January 31, 1994) hexane added to TRI list; (60 FR 31633; June 16, 1995) acetone removed from TRI list.

^b40 CFR 261.33, listed hazardous waste—EPA RCRA Hazardous Waste Number. All the solvents that are on the RCRA list are listed because of Section 3001 of RCRA (part for identification and listing of hazardous waste) except hexane which is on because of CAA Section 112 (HAP).

^cRQ for hexane finalized June 12, 1995 (60 FR 30939)

^dOnly the amount of commercial hexane that is *n*-hexane has to be reported (e.g., if the commercial hexane is 62% *n*-hexane, only 62% of the emissions have to be reported for TRI).

^eThe EPA clarified that the listing for hexane was only for *n*-hexane, other isomers of hexane are not included. (59 FR 61457; Nov. 30, 1994).

^fThe EPA has indicated (62 FR 22318; April 25, 1997) that IPA itself does not meet the criteria for listing on the TRI list. The EPA will remove IPA from the TRI list.

RQ, reportable quantity in pounds.

Hazardous Air Pollutants (HAPs) or Air Toxics (40 CFR 61). If a facility is a major emitter (i.e. a major source or significant area source) of any of the chemicals on the CAA list of HAPs (presently 188), EPA requires sources to meet national emissions standards (13, 15, 16). *n*-Hexane is on the HAP list but isohexane, acetone, and other solvents listed in [Table 4](#) are not.

The air toxic requirements of the CAA for establishing control measures for source categories are technology-based emission standards (not health based) established for major sources (10 t/a of one HAP or 25 t/a of total HAPs per facility) that require the maximal degree of reduction emissions, taking costs, other health and environmental impacts, and energy requirements into account. Standards are set based on known or anticipated effects of pollutants on the public health and the environment, the quantity emitted, and the location of emissions. Compliance with a NESHAP involves the installation of maximum achievable control technology (MACT)—MACT essentially is maximal achievable emission reduction. For new sources, MACT standards must be no less stringent than the emission control achieved in practice by the best-controlled similar source.

On April 12, 2001 (66 FR 19006) EPA published the NESHAP for solvent extraction (40 CFR 63) for vegetable oil production. On April 5, 2002 (66 FR 16317) U.S. EPA amended this NESHAP. The amendments clarify startup, shutdown, and malfunction (SSM) requirements for owners or operators subject to the NESHAP rules applicable to vegetable oil production facilities and also clarifies the applicability of NESHAP General Provisions (40 CFR63). EPA considers solvent extraction for vegetable oil production processes as major sources of the HAP *n*-hexane. [Figure 3](#) shows a general flow diagram of a typical vegetable oil production facility, identifying the most common emission sources of hexane (17). Hexane emissions occur from ten general sources: (a) the main vent; (b) meal dryer vent; (c) meal cooler vent; (d) crude meal; (e) crude oil; (f) equipment leaks; (g) solvent storage tanks; (h) process wastewater collection; (i) facility startup/shutdowns; and (j) operational upsets. Facilities covered are those that produce crude vegetable oil and meal products by removing crude oil from listed oilseeds (corn germ, cottonseed, flax, peanuts, rapeseed, safflower, soybeans, and sunflower) through direct contact with solvent. The rule requires all existing and new solvent extraction processes that are major sources (potential to emit 10 t/a or more of *n*-hexane) to meet these HAP emission standards as a 12-month rolling average based on a 64% *n*-hexane content. HAP emission standards (solvent loss factors) vary for each oilseed ([Table 7](#)) and reflect the application of MACT. Industry will have 3 years to achieve compliance (i.e., Apr 12, 2004). Since the emission loss factor values are 12-month rolling averages, the first compliance report would be due 48 months after the standard is promulgated (i.e., Apr 12, 2005). The requirements cover normal operations and SSM, which was further clarified by EPA (4/5/2002; 67 FR

Table 7 U.S. Oilseed Solvent Loss Factors for Allowable HAP Loss (12-Mo. rolling ave.)

Type of oilseed process	A source that . . .	Oilseed solvent loss factor (gal/t)	
		Existing sources	New sources
Corn germ, wet milling	processes corn germ that has been separated from other corn components using a wet process of centrifuging a slurry steeped in a dilute sulfurous acid solution.	0.4	0.3
Corn germ, dry milling	processes corn germ that has been separated from other corn components using a dry process of mechanical chafing and air sifting.	0.7	0.7
Cottonseed, large	processes 120,000 t or more of a combination of cottonseed and other listed oilseeds during all normal operating periods in a 12-month operating period.	0.5	0.4
Cottonseed, small	processes less than 120,000 t of a combination of cottonseed and other listed oilseeds during all normal operating periods in a 12-month operating period.	0.7	0.4
Flax	processes flax.	0.6	0.6
Peanuts	processes peanuts.	1.2	0.7
Rapeseed	processes rapeseed (e.g., canola).	0.7	0.3
Safflower	processes safflower.	0.7	0.7
Soybean, conventional	uses a conventional style desolventizer to produce crude soybean oil products and soybean animal feed products.	0.2	0.2
Soybean, specialty	uses a special style desolventizer to produce soybean meal products for human and animal consumption.	1.7	1.5
Soybean, small combination plant	processes soybeans in both specialty and conventional desolventizers and the quantity of soybeans processed in specialty desolventizers during normal operating periods is less than 3.3% of total soybeans processed during all normal operating periods in a 12-month operating period. The corresponding solvent loss factor is an overall value and applies to the total quantity of soybeans processed.	0.25	0.25
Sunflower	processes sunflower.	0.4	0.3

16317). A plant processing an oil that is not a listed oil, i.e., not a regulated entity (40 CFR 63.2872; e.g., rice bran oil plant or meadfoam oil processing plant, etc.), and that is a major source, is not covered by the MACT standard but the state is likely to require it to meet a particular level as part of its Title V permit.

There are also variable emission requirements depending on the oilseed for allowable emissions for vegetable oil processing in Europe (Table 8) (18). The EEC directive for Europe is to be fully implemented by all member states by Oct. 30, 2004 for new plants and Oct. 30, 2007 for old plants. However, there are some intermediate targets before full compliance—the target solvent consumption is 1.5 times the final level starting Oct. 30, 2001 for new plants and starting Oct. 30, 2005 for old plants. The EEC counts the total input of solvent into a plant per calendar year or any 12-month period and also requires a solvent management plan, which contains the following and is to be updated yearly: (a) verification of compliance to the EEC regulation through a mass balance; (b) identification of future reduction options; and (c) development of a waste minimization plan.

In the United States a health-based standard would be for a boundary line level of a solvent (e.g., *n*-hexane) based on the inhalation reference concentration (RfC) (19). The current RfC for *n*-hexane is 200 $\mu\text{g}/\text{m}^3$. Recent research suggests that the RfC for *n*-hexane should be at least 10 times higher ($>2000 \mu\text{g}/\text{m}^3$).

Table 8 European Maximal Solvent Loss Factors
(EEC Directive for Vegetable Oil Extraction) (18)

Oilseed	Max VOC usage/t of seed/yr	
	kg/t	gal/t
Olives	2.5	1.0
Castor	3.0	1.2
Rapeseed	1.0	0.4
Sunflower	1.0	0.4
Soybeans	0.8	0.3
Soy flash	1.2	0.5
Other seeds	3.0	1.2
Oil refining and fractionation:		
Fractionation w/o degumming	1.5	0.6
Degumming plant	4.0	1.6

NAAQS (40 CFR 50). The NAAQS are set at levels sufficient to protect public health, including the health of sensitive populations (primary air quality standards) and public welfare (secondary air quality standards; “welfare effects” include protection against decreased visibility, damage to wildlife, crops, vegetation, and buildings, and effects on personal comfort and well-being) from any known or anticipated adverse effect of the pollutant with an adequate (appropriate) margin of safety.

VOCs are essentially considered the same as the criteria pollutant ozone (14–16). Ground level ozone is not emitted directly into the air but is formed when sunlight acts on emissions of NO_x and VOCs. VOCs are very broadly defined by the EPA (40 CFR 51.100): any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, that participates in atmospheric photochemical reactions. This includes any organic compound other than those specifically listed as having been determined to have negligible photochemical reactivity. Reactive VOCs are essentially all those judged to be clearly more reactive than ethane—the most reactive member of the “negligibly reactive” class. C_4 – C_6 paraffins are of relatively low kinetic reactivity but produce NO_2 and potentially ozone (20). *n*-Hexane, hexane isomers, and the other solvents discussed, except acetone, would be considered VOCs (Table 4) that can undergo photochemical oxidation in the atmosphere to form ozone. In the United States, acetone was added to the list of compounds excluded from the definition of VOCs in 1995 because it was determined to have negligible photochemical reactivity (11).

Most U.S. vegetable oil extracting facilities would be major sources of VOCs and would be covered by the requirements for ozone emissions and attainment, unless they used a solvent that was not classified as a VOC. The definition of “major source” changes as the severity of the ozone nonattainment area increases. Plants in marginal and moderate areas are major if they emit 100 t VOC/a; in serious areas, 50 t/a; in severe areas, 25 t/a; and in extreme areas, 10 t/a. All facilities in ozone nonattainment areas could be required to reduce emissions through implementing reasonable available control technology (RACT) or best available control technology (BACT) standards.

Particulate matter (PM) is the solid or liquid matter suspended in the atmosphere. Most vegetable oil production facilities are major sources of PM. Depending on the oilseed processed, PM emissions can be 0.045–0.136 kg of total suspended particulate (TSP) per ton of seed processed. This PM is about 50% PM_{10} (particulate 10 μm and less) and less than 3% $\text{PM}_{2.5}$ (particulate 2.5 μm or less), assuming that PM emissions from oilseed handling operations are similar in particle size distribution to other agricultural operations, such as cotton gins (21). PM controls (Table 5) would also have to be part of a facility’s federal and state permits. Vegetable oil production facilities probably also have to include NO_x , SO_x , and CO emissions in their federal and state permits.

New Source Review. Any new or significantly modified facility would have to comply with the new source review (NSR) requirements. NSR is a preconstruction-permitting program. If new construction or making a major modification will increase emissions by an amount large enough to trigger NSR requirements (Table 5), then the source must obtain a permit before it can begin construction. Permits for sources in attainment areas are prevention of significant deterioration (PSD) permits and those in nonattainment areas are nonattainment NSR permits. For a PSD permit a source must apply BACT and for nonattainment NSR lowest achievable emission rate (LAER) is required.

Odor. There are no specific federal regulations for odor. However, states can regulate odor if they choose to. For example, Colorado requires hog lagoons to be covered because of a state referendum vote. Also, odor can generate complaints that cause states to require more stringent emission controls.

Federal Permits (40 CFR 70). All major sources of regulated solvents are required to have federally enforceable operating permits (FOPs) (13, 14) (also referred to as Title V permits).

State Permits. Most states require state permits for facilities that emit listed air pollutants (13, 14). In some states federal permits and state permits are combined, whereas in other states facilities are required to have both a state and a county (air district) permit and a federal permit. As part of annual emission inventory reporting requirements, many states already require reporting of HAPs and VOCs because of their state implementation plan (SIP).

2. Clean Water Act (CWA; 33 U.S. Code 1251 et seq.)

The CWA is the major law protecting the “chemical, physical and biological integrity of the nation’s waters.” Under it, the EPA establishes water quality criteria used to develop water quality standards, technology-based effluent limitation guidelines, and pretreatment standards and has established a national permit program [National Pollution Discharge Elimination System (NPDES) permits; 40 CFR 122] to regulate the discharge of pollutants. The states have responsibility to develop water quality management programs. Oilseed processing and oil refining are covered by: (a) basic discharge effluent limitations (40 CFR 122); (b) storm water regulations (40 CFR 122 and 123); and (c) oil spill prevention and response plans (40 CFR 112) (14).

Basic Discharge and Stormwater. Vegetable oil extracting facilities and oil refining are covered by basic discharge effluent limitations [direct discharges to receiving waters or indirect discharges to publicly owned treatment works (POTWs)], and stormwater regulations (14). The amount of solvent in effluent discharges and in stormwater (for those covered) needs to be determined and

possibly monitored as part of an NPDES permit and as part of the visual examination or testing of stormwater quality. None of the solvents normally used in oilseed extraction and refining are listed as priority toxic pollutants (40 CFR 401.15).

Oil and Hazardous Substances Spills and Response Plans. Under Oil Pollution Prevention and Response (40 CFR 112) there are requirements for oilseed extraction and oil refining for storage and transportation of vegetable oil. In 2002 EPA amended this rule (67 FR 47042; July 17, 2002). This rule includes requirements for Spill Prevention Control and Countermeasure (SPCC) Plans (i.e., prevention plans) and for Facility Response Plans (FRPs). SPCC plans are required for on site storage and are intended to prevent spills of oil (of any kind; this includes animal fats and vegetable oils) by non-transportation-related on-shore and off-shore facilities into the waters of the United States or adjoining shorelines. The requirements for preparation and implementation of SPCC plans state that if a facility discharges or could reasonably be expected to discharge oil in harmful quantities [a discharge of oil that can cause a sheen (indecent appearance) on the surface of water; 40 CFR 110.3] into navigable waters of the United States or adjoining shoreline, an SPCC plan is required. In the 2002 amended rule facilities with total above-ground storage capacity greater than 5000 L (1320 gal) are covered but underground storage tanks (UST) are exempt if regulated under the federal UST rule (40 CFR 280). Also, under the final rule as published, SPCC Plans must be in compliance by Feb. 17, 2003 and implementation of the amended SPCC Plan must be completed by Aug. 18, 2003. Some of the amendments are controversial and EPA is planning to suspend this deadline at least by one year. Spill reporting is required for any spill ≥ 3788 L (1000 gal) and for any two spills in any consecutive 12-month period of 159 L (42 gal) or greater.

Pursuant to the *Oil Pollution Act of 1990 (OPA-90)*, EPA amended the oil pollution prevention regulations by adding response plan requirements for non-transportation-related on-shore facilities that handle, store, or transport oil. Facilities that could cause substantial harm to the environment are required to prepare and submit response plans to EPA. The “Flowchart of Criteria for Substantial Harm” (14) was published in the *Federal Register* on July 1, 1994 (59 FR 34104); if the facility transfers oil over water to or from vessels and has a total oil storage capacity greater than or equal to 159,000 L (42,000 gal) or the facility has a total storage capacity greater than or equal to 3.8×10^6 L (1 million gal), a response plan is required. EPA further amended this rule (65 FR 40776; June 30, 2000) to provide guidance for handling, storing, or transporting of vegetable oils and animal fats.

Under OPA-90, comprehensive oil spill response plans are also required for transportation of nonpetroleum oils (i.e., vegetable oil) by rail and road in

amounts of 159,000 L (42,000 gal) or more [regulated by Research and Special Programs Administration (RSPA), Department of Transportation (DOT); Final Rule, 61 FR 30533; June 17, 1996] and for marine transportation–related facilities [regulated by the DOT, Coast Guard; Final Rule, 65 FR 40820; June 30, 2000].

3. Resource Conservation and Recovery Act (RCRA; 42 U.S. Code 6901 et seq.)

RCRA gives EPA authority to regulate the handling and disposal of hazardous and nonhazardous waste. *RCRA subtitle C* (40 CFR 261) is a federal “cradle-to-grave” system to manage hazardous waste (including provisions for cleaning up releases and setting statutory and regulatory requirements). *Subtitle D* covers nonhazardous wastes. Materials or items are hazardous wastes if and when they are discarded or intended to be discarded. The act requires generators, transporters, and disposers to maintain written records of waste transfers, and requires EPA to establish standards, procedures, and permit requirements for disposal. The act also requires states to have solid waste management plans, prohibits open dumping, and requires EPA to establish criteria for sanitary landfills. EPA under RCRA also regulates underground storage tanks that store or have stored petroleum or hazardous substances.

Hazardous wastes are either listed wastes (40 CFR 261.30-33) or characteristic wastes (40 CFR 261.21-24). The EPA defines four characteristics for hazardous waste: ignitability (40 CFR 260.21); corrosivity (40 CFR 260.22); reactivity (40 CFR 260.23); and toxicity (40 CFR 260.24). Any waste that exhibits one or more of these characteristics is classified as hazardous under RCRA. The ignitability definition includes a liquid that has a flash point of less than 60°C (140°F); the EPA included ignitability to identify wastes that could cause fires during transport, storage, or disposal (e.g., used solvents). Since all of the solvents in [Table 6](#) have flash points less than 60°C, all could be an RCRA ignitability waste.

Spent bleaching clay is not an RCRA hazardous waste (40 CFR 302). It is usually disposed of by taking it to a regular landfill. Sometimes a spontaneous combustion (oxidation of unsaturated fatty acids in the retained oil causing self-heating leading to combustion) may occur when it is taken to the landfill. The potential for spontaneous combustion in spent bleaching earth depends on the type and amount of oil retained and rises with increasing unsaturation of the fatty acids in the retained oil. U.S. DOT classifies materials liable to spontaneous combustion as Class 4.2 hazardous materials [49 CFR 173.124(b) and Appendix E3]. Spent bleaching clay can be finely ground and put in small quantities into the animal meal in operations that do oil extraction. Zschau (22) describes other ways to utilize spent bleaching clay, including environmentally friendly ways.

4. Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, “Superfund”; 42 U.S. Code 9601 et seq.)

CERCLA “Superfund” gives EPA the authority to force those responsible for hazardous waste sites or other releases of hazardous substances, pollutants, and contaminants to conduct cleanup or other effective response actions.

Section 103 of CERCLA requires the person in charge of a facility to immediately report any release of a hazardous substance in an amount equal to or greater than its reportable quantities (RQ) to the National Response Center (NRC) (see also discussion below on EPCRA Section 304). *n*-Hexane, acetone, and other chemicals in Table 6 as well as NO_x (RQ = 4.5 kg/24 h [10 lb/24 h]), hydrogen sulfide, and ammonia (both 45 kg/24 h [100 lb/24 h]) are CERCLA hazardous substances and have a CERCLA RQ for releases. However, CERCLA and EPCRA do not require notification to the NRC, the State Emergency Response Commissions (SERCs), and the Local Emergency Planning Committees (LEPCs) of “federally permitted releases” of hazardous air releases/emissions as defined in CERCLA Section 101(10)(H): any emission into the air subject to a permit or control regulation under Section 111, Section 112, Title I Part C, Title I Part D, or state implementation plans in accordance with Section 110 of the CAA. In 2002 EPA published final guidance clarifying the CERCLA Section 101(10)(H) federally permitted release definition for “Certain Air Emissions” (67 FR 18899; April 17, 2002) and for “Clean Air Act ‘Grandfathered’ Sources” (67 FR 19750; April 23, 2002). Essentially if the CAA requirements are being met, even without a permit, it is a federally permitted release exempt from reporting.

5. Emergency Planning and Community Right-to-Know Act (EPCRA; 42 U.S. Code 11001 et seq.)

Enacted as Title III of the 1986 Superfund Amendments and Reauthorization Act (“SARA”), the Act mandates EPA to monitor and protect communities regarding release of chemicals into the environment. It requires states to establish emergency planning districts with local committees to devise plans for preventing and responding to chemical spills and releases.

Section 304 (40 CFR 355.40). Section 304 of EPCRA requires the owner or operator of a facility to immediately notify the State SERCs and LEPCs of any accidental releases (that are not “federal permitted”), in quantities equal to or greater than their RQ, of an EPCRA designated extremely hazardous substance (EHS) or a CERCLA hazardous substance (40 CFR 302, Table 302.4) and provide written follow-up notice as soon as practicable thereafter (also see discussion on CERCLA Section 103). *n*-Hexane, cyclohexane, acetone, and

some of the other solvents discussed are CERCLA hazardous substances and have CERCLA RQ for air releases (Table 5).

Section 311, 312 (40 CFR 370.20-.21). Businesses must make MSDSs, for chemicals that are required to have an MSDS, available to state and local officials. Since all of the solvents discussed require MSDSs under the OSHA HCS, all are covered by these requirements.

Section 313 (40 CFR 372), Toxic Release Inventory (TRI). Businesses are required to file annual reports with federal and state authorities of releases to air, water, and land above a certain threshold for chemicals on the TRI/Section 313 list (40 CFR 372.65) by July 1 each year for the previous year's releases (23). TRI requirements are triggered if a facility is involved in manufacturing with 10 or more full-time employees, manufactures, processes, or otherwise uses one or more listed substance(s) in a quantity above the statutory reporting threshold of 11 t/a (25,000 lb/yr) (manufactured or processed) or 4.5 t/a (10,000 lb/yr) (otherwise used). Beginning with the 1991 reporting year, such facilities also must report pollution prevention and recycling data for such chemicals pursuant to Section 6607 of the Pollution Prevention Act (42 U.S. Code 13106).

n-Hexane was added to the TRI list in 1994 with reporting for 1995 emissions (11, 23). The other solvents discussed are not on the TRI list. The EPA can add new chemicals to or delete chemicals from the TRI list as is deemed necessary and any person may petition the EPA to add chemicals or delete chemicals from the list. Acetone (11) in 1995 (60 FR 31643; June 16, 1995) and phosphoric acid in 2000 (65 FR 39552; June 27, 2000) were deleted and no longer require reporting under TRI.

6. Toxic Substances Control Act (TSCA; 15 U.S. Code 2600 et seq.)

If a chemical's manufacture, processing, distribution, use, or disposal would create unreasonable risks, the EPA, under the TSCA (40 CFR section 700, et seq.), can regulate it, ban it, or require additional testing.

Section 4(a). Under Section 4(a) of TSCA, the EPA can require testing (referred to as a "Section 4 test rule") of a chemical substance or mixture to develop data relevant for assessing the risks to health and the environment.

Section 5(a)(1). Section 5(a)(1) of TSCA (40 CFR 720) mandates the EPA to monitor and control the use of toxic substances by requiring the Agency to review the health and environmental effects of new chemicals (referred to as "Premanufacturing Notice" or "PMN") and chemicals already in commerce. The EPA also has Significant New Use Rules (SNURs) under Section 5(a)(2) of

TSCA (40 CFR 721), which provides a way for EPA to restrict use of a chemical substance already in commerce that is proposed for new uses. *n*-Hexane, hexane isomers, acetone, and the other solvents discussed are already commercially available, so a PMN would not apply. However, some solvents other than *n*-hexane could be subject to an SNUR (40 CFR 721, subpart A), since they are not presently being used as extraction solvents in large quantities.

Section 8. Reporting and Retention of Information: Section 8(d) of TSCA (Health and Safety Data Reporting; 40 CFR 716) requires that lists of health and safety studies conducted or initiated with respect to a substance or mixture be submitted to the EPA. Section 8(e) of TSCA (no 40 CFR Ref.) requires that all new toxicological data of the effects of a chemical not previously mentioned must be reported immediately, if the data reasonably support the conclusion that such substance or mixture presents a substantial risk of injury to health or the environment. Testing (Section 4 test rule) was required for several of the solvents earlier [e.g., commercial hexane for which new toxicological information was reported to the EPA since 1992 (24)], and any new toxicological information will have to be reported to the EPA under Section 8(e) and 8(d).

Inventory Update Rule (IUR) (40 CFR 710). The IUR was established in 1986 to require manufacturers and importers of chemicals listed on the master TSCA inventory to report current data every four years on the production volume of chemicals imported or produced. Food and feed products produced from natural agricultural product, such as oilseeds, are not required to be reported, but all oil and meal products obtained by solvent extraction that is sold for other than food or feed use (e.g., oils as chemical raw materials and meal as fertilizer) are. This list from 1990 was used to determine the high production volume (HPV) chemicals (greater than 453 t/a [1 million lb/yr]) that are part of the HPV testing program. Vegetable oils are listed as a category 1 that does not require toxicity testing at this time.

B. Workplace/Occupational Safety and Health

In the United States, workplace regulations (Table 3) are promulgated and enforced by the Occupational Safety and Health Administration (OSHA), which is part of the U.S. Department of Labor. The purpose of OSHA is to ensure that the employers maintain a safe and healthful workplace. OSHA general industry standards (29 CFR 1910) apply to oilseed extraction and oil refining, and several of these workplace standards that particularly apply to oilseed extraction facilities are discussed. Many other health and safety standards (e.g., blood-borne pathogens, noise, operation of fork-lift trucks, and lockout/tagout) apply that cover all industries (25). Also even if there is not a specific standard, OSHA can cite a

facility under the “general duty clause” [Sec. 5(a)(1) of the OSH Act], since the OSH Act requires the employer to maintain a safe and healthful workplace.

1. Air Contaminants Standard (29 CFR 1910.1000)

Air contaminant standards are intended to reduce risk of occupational illness for workers by reducing permissible exposure limits (PELs) for chemicals. [Table 9](#) lists the PELs for *n*-hexane, hexane isomers, and some other solvents and chemicals. PELs are 8-h time-weighted average exposures. To achieve compliance with PEL, administrative or engineering controls must first be determined and implemented, whenever feasible. When such controls are not feasible to achieve full compliance, personal protective equipment, work practices, or any other protective measures are to be used to keep employee exposure below the PEL.

In the case of a mixture of contaminants, an employer has to compute the equivalent exposure when the components in the mixture pose a toxic effect on the same target organ to a worker's health (26, 27). The mixture calculation is expressed as:

$$E_m = (C_1/L_1) + (C_2/L_2) + \cdots + (C_n/L_n) \quad (1)$$

where:

E_m is equivalent exposure for the mixture (E_m should be ≤ 1 for compliance), C is concentration of a particular substance, and L is PEL (the exposure limit for that substance specified in 29 CFR 1910).

2. Hazard Communication Standard (HCS) (29 CFR 1910.1200)

The HCS requires all employers to provide information to their employees on the hazardous chemicals to which they are exposed through a written hazard communication program, labels and other forms of warning, material safety data sheet (MSDS), training programs, and record keeping.

A substance is a “hazardous chemical” if it is a “physical hazard” or a “health hazard” [29 CFR 1910.1200(c)]. A flammable or explosive liquid is a “physical hazard.” A flammable liquid means “any liquid having a flashpoint below 37.8°C (110°F), except any mixture having components with flashpoints of 37.8°C (110°F) or higher, the total of which make up 99% or more of the total volume of the mixture.” “Health hazard” means “a chemical for which there is statistically significant evidence based on at least one valid study that acute or chronic health effects may occur in exposed employees.” Hexane requires an MSDS, since all flammable liquids (physical hazard), as defined by OSHA and/or possible health hazards that have an U.S. OSHA PEL, require an MSDS. *n*-Hexane isomers (e.g., isohexane) do not have an OSHA PEL but do have an American Conference of Governmental Industrial Hygienists (ACGIH)

Table 9 U.S. Workplace Regulations,^a Air Contaminants

Chemical name (CAS no.)	Permissible exposure limit (PEL) [Health risk: basis for the PEL]
<i>n</i> -Hexane (110-54-3)	500 ppm-1800 mg/m ³ ; new PEL was 50 ppm-180 mg/m ³ same as ACGIH (TLV); [neuropathy]
Commercial hexane ^a (none)	(Same as <i>n</i> -hexane)
<i>n</i> Heptane (148-82-5)	500 ppm-2050 mg/m ³ ; new PEL was 400 ppm-1640 mg/m ³ , (500 ppm STEL) same as ACGIH (TLV); [narcosis]
Cyclohexane (110-82-7)	300 ppm-1050 mg/m ³ ; ACGH (TLV) 300 ppm-1030 mg/m ³ ; [sensory irritation]
Cyclopentane (287-92-3)	None; new PEL was 600 ppm, same as ACGIH (TLV); [narcosis]
Hexane isomers	None; new PEL was 500 ppm-1760 mg/m ³ (1000 ppm STEL) same as ACGIH (TLV); [narcosis]
Commercial isohexane ^a (none)	(Same as hexane isomer)
2-Methyl pentane (2-MP) (isohexane) (107-83-5)	(Same as hexane isomer)
3-Methyl pentane (3-MP) (96-14-0)	(Same as hexane isomer)
Methyl cyclopentane (MCP) (96-37-7)	(Same as hexane isomer)
2,2 Dimethyl butane (2,2-DMB) (neo-hexane) (75-83-2)	(Same as hexane isomer)
2,3 Dimethyl butane (2,3-DMB) (79-29-8)	(Same as hexane isomer)
Methyl cyclohexane (107-87-2)	500 ppm; new PEL was 400 ppm/1610 mg/m ³ , same as ACGIH (TLV); [narcosis]
Isopropyl alcohol (IPA) (2-propanol) (67-17-5)	400 ppm-980 mg/m ³ ; ACGIH (TLV) same plus 500 ppm-1230 mg/m ³ STEL; [sensory irritation]
Ethyl alcohol (ethanol) (64-17-5)	1000 ppm-1880 mg/m ³ ; ACGIH (TLV) same; [narcosis, irritation]
Acetone (67-64-1)	1000 ppm/2400 mg/m ³ ; ACGIH (TLV) 750 ppm (1000 ppm STEL); [sensory irritation]
Particulate not otherwise regulated (PNOR):	
Total dust	15 mg/m ³
Respirable dust	5 mg/m ³ ; [physical irritation]
Phosphoric acid (7664-36-2)	1 mg/m ³ ; [sensory irritation]
Sodium hydroxide (1310-73-2)	2 mg/m ³ ; [sensory irritation]
Sulfuric acid (7664-93-9)	1 mg/m ³ ; [sensory irritation]

^aCAS No. is the Chemical Abstracts Service Registry Number; PEL is from 29 CFR 1910.1000, Table Z-1; American Conference of Governmental Industrial Hygienists (ACGIH), threshold limit value (TLV); under the HCS, a MSDS is required for all of the compounds (physical and/or chemical hazard); all of the solvents are flammable liquids or gasses, under the OSHA definition, and are regulated under the PSM standard.

^bCommercial hexane as used in the U.S. is usually about 64% *n*-hexane, and the rest is hexane isomers [e.g., methyl cyclopentane (MCP), 2-methyl pentane (2-MP), and 3-methyl pentane (3-MP)], and it contains less than 10 ppm benzene.

^cMixture of 2-MP (45-50%), 3-MP, 2,2-DMB, and 2,3-DMB (3).

threshold limit value (TLV) (28) of 500 ppm (Table 9), which many states and countries enforce as a mandatory standard.

Chemical manufacturers and importers are required to review the available scientific evidence concerning the hazards of chemicals they produce or import, and to report the information to manufacturing employers who use their products [29 CFR 1910.1200(b)]. If a chemical mixture has not been tested as a whole to determine whether it is a hazardous chemical, the mixture is assumed to present the same hazards as the components that comprise 1% or more of the mixture or a carcinogenic hazard if it contains a component in concentration of 0.1% or more that is a carcinogen [29 CFR 1910.1200(a)(5)]. Commercial hexane, containing 52% *n*-hexane, has been tested and found not to be neurotoxic, unlike pure *n*-hexane (7, 29, 30). So mixtures with less than 52% *n*-hexane should not be considered neurotoxic, although *n*-hexane would have to be listed on the MSDS if present in greater quantity than 1% of the mixture.

3. Process Safety Management Standard (29 CFR 1910.119)

Process safety management (PSM) is for the prevention or minimization of the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. This regulation applies to all processes that involve one or more of 137 listed chemicals (29 CFR 1910.119, Appendix A) above their threshold quantities or have 4.5 t (10,000 lb) or more of a flammable liquid or gas, as defined by the OSHA HCS [29 CFR 1910.1200(c)]. This includes *n*-hexane, hexane isomers, and the other solvents listed in Table 9. The requirements for meeting this regulation are described in more detail by Lajeunesse (31) and Strube (32).

In addition to the PSM standard, OSHA has been enforcing two other regulations for operations/processes with flammable liquids. First, under Personal Protective Equipment—General Requirements (29 CFR 1910.132), OSHA has cited or obtained voluntary agreement from organizations relative to flame-resistant (FR) clothing. Operators and other employees working in the area of a flammable process are being required to wear flame-resistant work clothing. For facilities that use commercial hexane and other flammable solvents, it would be prudent to require FR clothing for all personnel working in areas where there is an exposure to a flammable liquid. Second, OSHA has cited organizations for failure to meet related safety regulations under Fire Brigades (29 CFR 1910.156), specifically for standards such as training, both initial and annual refresher training; protective equipment availability and testing; and fitness for duty including periodic physicals. If an on-site fire brigade is part of the site's emergency response plan (29 CFR 1910.38), then these requirements must also be met. In addition, the requirement of the PSM standard for an emergency response plan triggers the requirements of emergency action plan [29 CFR 1910.38(a)].

C. Food Safety

Oilseed extraction solvents and food processing substances, to be legally used in the United States, must have been subject to an approval by the U.S. Food and Drug Administration (FDA), which regulates all aspects of food, including food ingredients and labeling, or the U.S. Department of Agriculture (USDA) during 1938–1958 for this use (“prior sanction”); be generally recognized as safe (GRAS) for this use; or be used in accordance with food additive regulations promulgated by the FDA.

Many prior sanctions and GRAS determinations are not codified in the FDA regulations. However, extracting solvents used in food manufacturing, such as *n*-hexane, have been labeled as food additives, solvents, defoaming agents, component of a secondary food and color additives, minor constituent, or incidental additives (i.e., “additives that are present in a food at significantly low levels and do not have any technical or functional effect in that food”) depending on the application. Incidental additives can be “processing aids,” (i.e., “substances that are added to a food during processing but removed from the food before it is packaged”). Most food processing substances, including solvents, can be regarded as “incidental additives” and thus are exempt from label declaration in the finished food product. Even if exempt from label declaration, all extraction solvents must be used in accordance with the FDA good manufacturing practice (GMP; 21 CFR 100).

Commercial hexane, containing about 50–85% *n*-hexane, has been in major use since the 1940s as an oilseed extraction solvent on the determination that it is GRAS and it may also be subject to a prior sanction. Like many other food processing substances, there is no FDA regulation specifically listing *n*-hexane as GRAS or prior sanctioned. However, under FDA regulations hexane has been cleared as a solvent in the manufacture of food additives and has been cleared as a minor constituent (not more than 5 ppm) of a cocoa butter substitute that is a direct food additive that has been affirmed by FDA as GRAS for food use (52 FR 47918, December 17, 1987; 21 CFR 184.1259). In Europe the maximum residue limit (MRL) in vegetable oils has been established as 5 ppm *n*-hexane [European Union (EU) Communittee Directive 88/344/EEC of 13 June 1988; Off. J. Eur. Commun. L 157, 24 June 1988, pp. 0028–0033].

The Flavor and Extract Manufacturers Association (FEMA) has conducted a program since 1958 using a panel of expert pharmacologists and toxicologists to determine substances that are GRAS. This safety assessment program (“FEMA GRAS”) is widely accepted and considered an industry/government partnership with the FDA (33). A number of papers published since 1961 (34–36) list the substances that the panel has determined to be GRAS and the average maximal levels in parts per million (ppm) at which each has been reported to be GRAS for different categories of food. The FDA has not incorporated these substances

in their regulations but recognizes the findings of the Expert Panel of FEMA as GRAS substances.

Since vegetable oil and other human food grade oils undergo deodorization (steam distillation) and other purification processes (i.e., refining and bleaching) as part of the manufacturing process prior to being used as a food product, they should not contain any of the extraction solvent, if proper manufacturing practices are followed. Refining removes nonglyceride materials (e.g., phospholipids, color, and trace metals) and free fatty acids; bleaching with acid-activated bleaching earth or clay (e.g., bentonite), removes color-producing substances; and deodorization, the last major processing step in edible oils refining, removes volatile compounds (undesirable ingredients occurring in natural oils and those that may be imparted by prior unit processes or even storage, many of which are associated with undesirable flavors and odors) (37, 38). Most commercial deodorizers operate at a temperature of 245–275°C (475–525°F) under a negative pressure of 2–10 mm Hg (37, 38). It has been reported that no *n*-hexane residue remains in the finished oil after processing due to its high volatility (39). In addition, animal feeding studies with expeller and solvent-extracted meals have not indicated any adverse health effects related to the extraction solvent (40).

In summary, GRAS status may be determined by a company (“GRAS self-determination”), an industry, an independent scientific organization (e.g., FEMA GRAS), or the FDA. The Federal Food, Drug and Cosmetic Act (FFDCA; 21 U.S. Code 321 et seq.) does not provide for the FDA to approve all ingredients used in food, and the FDA explicitly recognizes that its published GRAS list is not meant to be a complete listing of all substances that are in fact GRAS food substances. Although there is no requirement to inform the FDA of a GRAS self-determination or to request FDA review or approval on the matter, the FDA has established a voluntary GRAS affirmation program under which such advice will be provided by the agency. If a facility is considering changing its extracting solvent for the extraction of the various edible biological materials, solvents that do not have prior sanction, a GRAS determination, or a tolerance set probably should be evaluated for compliance under food safety requirements.

V. SUMMARY

In summary, there most likely will be new demands for highly specialized extraction solvents as newly domesticated species that make useful novel oils (41) and other products and new or altered biological products with enhanced nutritional and industrial properties will be developed through conventional breeding and genetic engineering for use as “functional foods” (42) (e.g., phytosterols to achieve cholesterol lowering); as oils with altered lipid profiles (43) (e.g., for

lower saturated fat) or with more vitamin E; new drugs/nutraceuticals, industrial chemicals (e.g., fatty acids for lubricants, as cosmetics, coatings, detergents, surfactants, flavors, polymers, etc.); as sources for specialty chemicals; as value-added products; and so forth (42–49). There will be demands for solvent systems for simultaneous removal of undesirable meal components (e.g., mycotoxins, gossypol, flavors, and odors) that offer the potential for upgrading meal for use as higher value animal feeds and human foods. Solvents that offer energy savings and that pose lower health, environmental, and fire hazards will also be sought. However, it will be more necessary than ever to be aware of regulatory requirements for and the toxicity of the solvents used.

GLOSSARY

ACGIH	American Conference of Governmental Industrial Hygienists, an independent standards setting organization.
BACM	best available control measures.
BACT	best available control technology.
CAA	Clean Air Act, 42 U.S. Code 1251 et seq.
CERCLA (Superfund)	Comprehensive Environmental Response, Compensation, and Liability Act, 42 U.S. Code 9601 et seq.
CFR	Code of Federal Regulations. This is where the U.S. federal regulations after promulgation are codified. The preceding number is the Title, the succeeding number (after CFR) is the Part of Section (e.g., 29 CFR 1910 is Title 29 Code of Federal Regulations at Part 1910).
CWA	Clean Water Act (Federal Water Pollution Control Act), 33 U.S. Code 1251 et seq.
EPA	Environmental Protection Agency, 42 U.S. Code 4321 et seq.
EPCRA	Emergency Planning and Community Right-to-Know Act, part of CERCLA/Superfund, Title III of SARA, the 1986 amended Superfund.
FR	Federal Register. This is where regulatory announcements and new rules and their justification are published. The preceding number is the volume; the succeeding number (after FR) is the page, usually followed by the date when it appeared (e.g., 51 FR 27956 is Volume 51 Federal Register, page 27956).
GRAS	generally recognized as safe.

HAP	hazardous air pollutant, 40 CFR 61.
HCS	Hazard Communication Standard, 29 CFR 1910.1200.
IUR	Inventory Update Rule, 40 CFR 710.
LAER	lowest achievable emission rate.
MACT	maximum achievable control technology.
MSDS	material safety data sheet, required under OSHA HCS.
NAAQS	National Ambient Air Quality Standard, 40 CFR 50.
NESHAP	National Emission Standard for Hazardous Air Pollutants under the CAA.
Nonattainment	Areas that do not meet NAAQS, 40 CFR 51.100 et seq.
NPDES	National Pollution Discharge Elimination System. The national permit program under the CWA, 40 CFR 122.
NSR	new source review.
OPA-90	Oil Pollution Act of 1990.
OSHA	Occupational Safety and Health Administration (part of the U.S. Dept. of Labor), 29 U.S. Code 651 et seq.
Ozone (O ₃)	One of the compounds on the NAAQS list that is formed through chemical reaction in the atmosphere involving VOC, NO _x , and sunlight; also a primary constituent of smog.
NO _x	nitrogen oxides.
PEL	permissible exposure limit for an air contaminant under OSHA standards.
PM	particulate matter. One of the NAAQS; denotes the amount of solid or liquid matter suspended in the atmosphere. The EPA regulates PM as PM ₁₀ ("coarse" particulate 10 µm and less) and PM _{2.5} ("fine" particulate 2.5 µm or less).
POTW	publicly owned treatment works, for indirect wastewater discharge.
PSD	prevention of significant deterioration, a requirement of NSR.
PSM	process safety management standard.
RACM	reasonably achievable control measures.
RACT	reasonably available control technology.
RCRA	Resource Conservation and Recovery Act, 42 U.S. Code 6901 et seq.

RCRA-Characteristic Wastes	hazardous wastes that are ignitable, corrosive, reactive, or toxic, 40 CFR 260.64.
RCRA-Listed Wastes	Specially listed hazardous wastes in 40 CFR 261.30-33.
SARA	Superfund Amendments and Reauthorization Act.
TCLP	toxic characteristic leaching potential under RCRA, 40 CFR 261.24.
Title V	The part of the Clean Air Act that deals with federal permits, 40 CFR 70.
TLV	threshold limit value for an air contaminant under ACGIH regulations.
TRI	toxic release inventory, under section 313 of EPCRA.
TSCA	Toxic Substances Control Act.
TWA	time weighted average.
U.S. Code	The United States Code where legislation, including health, safety, and environmental legislation, is codified once passed by Congress (e.g., 42 U.S. Code 7401 is Title 42 U.S. Code at paragraph 7401).
UST	Underground storage tank (any tank completely covered with earth); Technical Standards and Corrective Action Requirements for Owners and Operators of UST (40 CFR 280).
VOC	volatile organic compounds. A group of chemicals that react in the atmosphere with nitrogen oxides (NO _x) in the presence of heat and sunlight to form ozone; does not include compounds determined by EPA to have negligible photochemical reactivity.

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