DRYING OILS

1. Introduction

Among the oldest binders for paints and printing inks are *drying oils*, which are liquid vegetable or fish oils that react with oxygen to form solid films. They have been used since prehistoric times; in the nineteenth and early twentieth centuries, binders of most paints and printing inks were drying oils. Their use has decreased; however, they still have applications. Most importantly, they are raw materials for other binders such as alkyd resins, epoxy esters, and uralkyds (see ALKYD RESINS.). These resins can be considered to be synthetic drying oils.

2. Composition of Natural Oils

Naturally occurring oils are *triglycerides*, triesters of glycerol (1,2,3-propanetriol)[56-81-5], and fatty acids. Some triglycerides are drying oils, but many are not. The reactivity of drying oils with oxygen results from the presence of diallylic groups (ie, two double bonds separated by methylene groups, $—CH{=}CHCH_2CH{=}CH—$, or conjugated double bonds. Esters of many different fatty acids occur in nature. Those present in drying oils are

- Stearic acid, CH_3- $(CH_2)_{16}COOH$, octadecanoic acid[57-11-4].
- Palmitic acid, $CH_3(CH_2)_{14}COOH$, hexadecanoic acid[57-10-3].
- Oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (9c), (*Z*)-9-octadecenoic acid[112-80-1].
- Linoleic acid, $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (9c 12c), (*Z,Z*)-9,12-octadecdienoic acid[60-33-3].
- Linolenic acid $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (9c 12c 15c), (*Z,Z,Z*)-9,12,15-octadectrienoic acid (α-linolenic acid)[463-40-1].
- Pinolenic acid, $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH_2CH{=}CH(CH_2)_3$ COOH (5c 9c 12c), (*Z,Z,Z*)-5,9,12-octadectrienoic acid.
- Ricinoleic acid, $CH_3(CH_2)_5CHCH_2CH{=}CH(CH_2)_7COOH$ (9c), (*Z*)−12-hydroxy-9-octadienoic acid.
- Ricinoic acid, $CH_3(CH_2)_7CH{=}CHCH{=}CH(CH_2)_7COOH$ (9c 11t), (*E,Z*)-9,11-octadienoic acid.
- α-Eleostearic acid $CH_3(CH_2)_3CH{=}CHCH{=}CHCH{=}CH(CH_2)_7COOH$ (9t 11c 13t), (*E,Z,E*)-9,11,13-octadectrienoic acid[506-23-0].

The letters c or *(Z)* and t or *(E)* represent cis and trans orientation, respectively, and the numbers designate the position of the first carbon of the double bond.

The oils are mixtures of mixed triglycerides with different fatty acids distributed among the triglyceride molecules. Separation of the tens or hundreds of different triglyceride molecules present in an oil borders on the impossible. Therefore, oils are characterized by high-performance liquid chromatography

(HPLC) or gas chromatography (GC) of the methyl esters obtained by transesterification (1,2).

Many oils have been used, some of the most important are

> Linseed oil, which is obtained from the seeds of flax, *Linum usitatissimum*. Flax is grown in North Dakota, Minnesota, Texas, Argentina, Canada, India, and Russia.
>
> Soybean oil, a semidrying oil is obtained from soybeans, the seed of *Glycine max* (L) Merrill, produce in the United States, Brazil, and China.
>
> Tung oil, also called wood oil and chinawood oil, is obtained from the seed kernels of the tung tree, *Aleurites fordii*. The principal source is China.
>
> Castor oil is not a drying oil but drying oils are prepared from it. It is obtained from castor beans, the seeds of *Ricinus communis*. It is widely grown.

Particularly in less developed nations, oils are used that have plentiful supplies there but are minor as far as the world market. A recent example of studies of such possible sources is rubber seed oil. Rubber seeds from *hevea* have been investigated in Nigeria in cooperation with India (3). Rubber seed contains 18.9% saturated aids, 24.6% oleic acid, 39.6% linoleic acid, and 16.3% linolenic acid. Rubber seed oil is a semidrying oil but heat treated rubber seed oil will dry to a solid film. Oxidizing alkyds were also prepared from rubber seed oil.

2.1. Tall Oil Fatty Acids.

Tall is the Swedish word for pine. Tall oil fatty acids (TOFA) are obtained as a byproduct of the sulfate pulping process for making paper. Oils present in the trees are saponified to soaps in the process. Tall oil fatty acids are obtained by acidification, followed by fractional distillation to separate the fatty acids from rosin acids and other byproducts also present. These acids have a range of compositions, especially between acids of North American and European origin as shown. They are often chemically modified to give conjugated bonds. They are widely used as raw materials to synthesize oils.

The only significant animal drying oils are marine fish oils, primarily from menhaden, pilchard, and sardines. Fish oil is isolated by steam treatment of the fish. For use as drying oil, the fraction of saturated acids is reduced by cooling followed by filtering off of the solid, primarily saturated, triglycerides that freeze out. The refined fish oils contain triglycerides of a wide spectrum of fatty acids, including C_{18}–C_{26} fatty acids with up to five nonconjugated double bonds separated by single methylene groups.

Typical fatty acid contents of some oils are given in Table 1 (4–6). Compositions of the oils vary, sometimes quite widely, with variations in plant strain, climate, soil, and other growth conditions. Differences in sunflower oils are especially large, as illustrated in Table 1 for sunflower oils from Minnesota and Texas. In general, oils derived from seeds grown in colder climates contain larger fractions of more highly unsaturated fatty acids as triglyceride esters. A review of drying oil sources and compositions that includes a variety of other specialized oils is available (7).

Table 1. **Typical Fatty Acid Compositions of Selected Oils**

	Fatty acids				
Oil	Saturated[a]	Oleic	Linoleic	Linolenic	Other
linseed	10	22	16	52	
safflower	11	13	75	1	
soybean	15	25	51	9	
sunflower, mn	13	26	61	trace	
sunflower, tax.	11	51	38	trace	
tung	5	8	4	3	80[b]
tall oil fatty acids[c]	8	46	41[d]	3	2[e]
tall oil fatty acids[f]	2.5	30	45	1	14[g]
castor	3	7	3		87[h]

[a] Saturated fatty acids are mainly mixtures of stearic (C_{18}) and palmitic (C_{16}) acids.
[b] α-Eleostearic acid.
[c] North American origin.
[d] Linoleic plus geometric and conjugated isomers.
[e] Rosin.
[f] European origin.
[g] Pinolenic acid.
[h] Ricinoleic acid.

3. Autoxidation and Cross-Linking

Drying, semidrying, and nondrying oils are often defined based on their *iodine value*, that is, grams of iodine required to saturate the double bonds of 100 g of an oil. Some authors classify oils as follows: drying oils, iodine value >140; semidrying oils, iodine value, 125–140; and nondrying oils, iodine value <125 (4). Although iodine values can serve as satisfactory quality control specifications, they are not useful and can be misleading in defining a drying oil or for predicting reactivity.

3.1. Nonconjugated Drying Oils. A useful empirical relationship is that nonconjugated oils that have a *drying index* >70 are drying oils (8). Drying index is calculated as follows:

$$\text{Drying index} = (\%\ \text{linoleic acid}) + 2(\%\ \text{linolenic acid})$$

If we use this formula with the data from Table 1, the drying index of linseed oil is 120, it is a drying oil; the drying index of soybean oil is 69, it is a semidrying oil. The active group initiating drying is the diallylic group ($\text{—CH=CHCH}_2\text{CH=CH—}$). Linoleic and linolenic acids have one and two diallylic groups per molecule, respectively. Criteria for predicting drying capacity can be stated more generally: Drying is related to the average number of diallylic groups per molecule. If this number is greater than ~2.2, the oil is a drying oil; if it is moderately <2.2, the oil is a semidrying oil; there is no sharp dividing line between semidrying oils and nondrying oils. These statements apply to synthetic drying oils as well as to natural oils. Since diallylic groups are the sites for cross-linking, it is convenient to relate the average number of such groups per molecule to the number average functionality $\bar{f}_n$ of the triglyceride or synthetic drying oil. This facilitates the ensuing discussion, although it is possible that some of the sites are involved in more than one cross-linking reaction.

As previously indicated, the reactivity of nonconjugated drying oils is related to the average number of diallylic groups per molecule. The methylene groups are activated by their allylic relationship to two double bonds and are much more reactive than methylene groups allylic to only one double bond. Evidence for these assertions is provided by the relative rates of autoxidation of synthetic triolein (glyceryl trioleate), trilinolein, and trilinolenein, which are 1:120:330, respectively, (9). The number of diallylic groups (f_n) of the three triglycerides are 0, 3, and 6, respectively; the theoretical iodine values are 86, 173, and 262. The autoxidation rates are more closely related to the number of diallylic groups between double bonds, $\bar{f}_n$, than to iodine values, which are proportional to the average number of double bonds per molecule. Based on the data in Table 1, the $\bar{f}_n$ of the linseed oil is 3.6; it is a drying oil. The $\bar{f}_n$ of soybean oil is 2.07; it is a semidrying oil. The higher the $\bar{f}_n$ of a drying oil, the more rapidly a solvent-resistant, cross-linked film forms on exposure to air.

Cross-linked films form from linseed oil in the following stages:

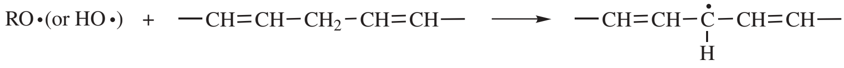
1. An induction period during which naturally present antioxidants (mainly tocopherols) are consumed.
2. A period of rapid oxygen uptake with a weight gain of about 10% [Fourier transform infrared (FTIR)] shows an increase in hydroperoxides and appearance of conjugated dienes during this stage).
3. A complex sequence of autocatalytic reactions in which hydroperoxides are consumed and cross-linked film is formed.

In one study, steps 1–3 for linseed oil films were far along in 4, 10, and 50 h, respectively, when catalyzed by a *drier* (10). Cleavage reactions to form low molecular weight byproducts also occur during the latter stages of film formation. Slow continuing cleavage and cross-linking reactions through the lifetime of the film lead to embrittlement, discoloration, and slow formation of volatile byproducts. Oils with significant quantities of fatty acids with three double bonds, such as linolenic acid, discolor to a particularly marked degree.

The following scheme illustrates some of the many reactions that occur during cross-linking. Initially, naturally present hydroperoxides decompose to form free radicals:

$$\mathrm{ROOH} \longrightarrow \mathrm{HO}\cdot + \mathrm{RO}\cdot$$

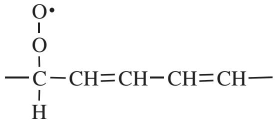
At first, these highly reactive free radicals react mainly with the antioxidant, but as the antioxidant is consumed, the free radicals react with other compounds. Hydrogens on methylene groups between double bonds are particularly susceptible to abstraction, yielding the resonance stabilized free radical (**1**):



$$\mathrm{RO}\cdot(\text{or } \mathrm{HO}\cdot) + -\mathrm{CH{=}CH{-}CH_2{-}CH{=}CH}- \longrightarrow -\mathrm{CH{=}CH{-}}\underset{\mathrm{H}}{\overset{\bullet}{\mathrm{C}}}\mathrm{{-}CH{=}CH}-$$

(1)

Free radical (**1**) exists as three resonance contributors and reacts with oxygen to give predominantly a conjugated peroxy free radical such as (**2**):



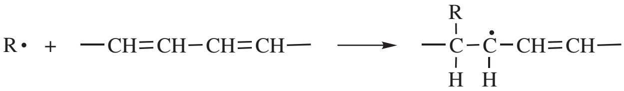
$$-\underset{\substack{|\\ H}}{\overset{\substack{O\cdot\\ |\\ O\\ |}}{C}}-CH=CH-CH=CH-$$

(2)

The peroxy free radicals can abstract hydrogens from other methylene groups between double bonds to form additional hydroperoxides and generate free radicals like (**1**). Thus, a chain reaction is established, resulting in autoxidation. At least part of the cross-linking occurs by radical–radical combination reactions forming C—C, ether, and peroxide bonds. These reactions correspond to termination by combination reactions in free-radical chain-growth polymerization.

$$\begin{aligned} R\cdot + R\cdot &\longrightarrow R—R \\ RO\cdot + R\cdot &\longrightarrow R—O—R \\ RO\cdot + RO\cdot &\longrightarrow R—O—O—R \end{aligned}$$

Reactions analogous to the addition step in chain-growth polymerization could also produce cross-links. For example, the residual conjugated double bonds after intermediate (**2**) has cross-linked may undergo addition reactions:



$$R\cdot + -CH=CH-CH=CH- \longrightarrow -\underset{\substack{|\\ H}}{\overset{\substack{R\\ |}}{C}}-\underset{\substack{|\\ H}}{\overset{\bullet}{C}}-CH=CH-$$

(3)

Such reactions could yield C—C or C—O linkages depending on the structure of R•. Subsequently, free radical (**3**) can rearrange, add oxygen to form a peroxy free radical, abstract a hydrogen from a methylene between double bonds, combine with another free radical, or add to a conjugated double-bond system.

The reactions taking place during drying are more complex than discussed above. Early studies of the chemistry of drying were done without benefit of modern analytical instrumentation, which has recently been brought to bear on this complex problem (10–13). The results of recent research are summarized in the next two paragraphs and in the section on catalysis.

Studies of the reactions of ethyl linoleate with oxygen in the presence of driers by proton and C-13 nuclear magnetic resonance (^{1}H and ^{13}C NMR) showed that the predominant cross-linking reactions were those that formed ether and peroxy cross-links (11,12). A further study confirmed that the cross-linking of linoleates occurred by radical combination leading primarily to C—O—C and C—O—O—C bonds (14). However, with an ester with conjugated double bonds, methyl ricinoate, cross-linking resulted from addition to double bonds. Fourier transform ir spectroscopy and FT Raman analysis of the drying of linseed oil have been reported (15). It is reported that the cross-links were only

C—O—C and C—C bonds. Mass spectroscopic studies showed that only ∼5% of the cross-links were new C—C bonds (11). Substantial levels of epoxy groups were detected in the reaction mixture, rising to a maximum in ∼5 days and virtually disappearing in 100 days; it is suggested that epoxy groups may react with carboxyl groups to form ester cross-links. Rearrangement and cleavage of hydroperoxides to aldehydes and ketones, among other products, lead to low molecular weight byproducts. An analytical technique has been developed to determine the extent of formation of free carboxylic acids in films of linseed oil paints as they age (16). The amount of free acid increases with age. The characteristic odor of oil and alkyd paints during drying is attributable to such volatile byproducts, as well as to the odor of organic solvents.

In a study of the reactions of (*Z*,*Z*)-3,6-nonadiene, a model compound for drying oils, it was found that in addition to hydroperoxides and oxirane substituted products, endo-peroxy compounds were produced (17). The authors propose that these latter were formed by photoxidation in which singlet oxygen is the reactive species. Under these conditions, oleic acid esters are almost as reactive as linoleic esters toward singlet oxygen generating hydroperoxides. It was shown that by adding colored dyes, such as methylene blue or rose bengal, drying of alkyds can be accelerated by light. The dye functions as a photosensitizer converting oxygen to singlet oxygen. In white paints, the color from the dyes fades completely within 6 days presumably by photoxidative bleaching.

The drying of oils is inhibited by SO_2 pollution, It has been shown that SO_2 reacts with the methylene groups between two double bonds to form sulfate esters (18). Thus, the functionality for autoxidative cross-linking is reduced.

Undesirable odor has been a factor motivating replacement of oil and alkyds in paints with latex, particularly for interior applications. The reactions leading to these odors have been extensively studied in connection with flavor changes of vegetable cooking oils (13). Aldehydes have been shown to be major byproducts from the catalyzed autoxidation of methyl oleate, linoleate, and linolenate, as well as from curing of drying oil-modified alkyd resins (9,19). It has also been shown that C_9 acid esters remain in the nonvolatile reaction mixture (19). It has been proposed that formation of aldehydes, ketones, and carboxylic acids in the aging of films of linseed oil result from photoxidation (20).

Dried films, especially of oils with three double bonds, yellow with aging. The yellow color bleaches significantly when exposed to light; hence, yellowing is most severe when films are covered, such as by a picture hanging on a wall. The reactions leading to color are complex and are not fully understood. Yellowing has been shown to result from incorporation of nitrogen compounds and is markedly increased by exposure to ammonia. It has been proposed that ammonia reacts with 1,4-diketones formed in autoxidation to yield pyrroles, which oxidize to yield highly colored products (21).

3.2. Catalysis of Autoxidation and Cross-Linking. The rates at which uncatalyzed nonconjugated drying oils dry are slow. Many years ago, it was found that metal salts (*driers*) catalyze drying. The most widely used driers are oil-soluble cobalt, manganese, lead, zirconium, and calcium salts of octanoic or naphthenic acids. Salts of other metals, including rare earths, are also used. Cobalt and manganese salts, so-called *top driers* or *surface driers*, primarily catalyze drying at the film surface. Lead and zirconium salts catalyze drying throughout the film and are called *through driers*. Mixtures of lead with cobalt and/or manganese are particularly effective, but, as a result of toxicity control regulations, lead driers can no longer be used in consumer paints sold in interstate commerce in the United States. Combinations of cobalt and/or manganese with zirconium, frequently with calcium, are commonly used. Neither lead nor zirconium alone catalyze drying. Calcium does not undergo redox reactions; it has been suggested that it may promote drying by preferentially adsorbing on pigment surfaces, minimizing adsorption of active driers. The amounts of driers needed are system specific. Their use should be kept to the minimum possible level, since they not only catalyze drying, but also catalyze the reactions that cause postdrying embrittlement, discoloration, and cleavage.

It has been proposed that cobalt driers primarily accelerate the reaction of oxygen with methylene groups leading to formation of hydroperoxides and that manganese primarily accelerates the decomposition of the hydroperoxides to free radicals (22). It has been reported that cobalt drier promotes surface cure but after this initial acceleration becomes inactive and other metals are required for through dry (23). A cobalt–zirconium combination was particularly effective for promoting through dry. It was suggested that the zirconium inhibits the cobalt deactivation by carboxylic acids. It has been reported that rate of polymerization at 60°C as a function of Co content goes through a maximum at 6.0 mmol/500-g linseed oil (24). (*Note*: There were only four concentrations used: 0, 3.0, 6.0, and 12.0 mmol.) It was said that Co primarily catalyzed oxidation rather than polymerization. Mixtures of Co and Zr were more effective than Co alone. It was proposed that a 1:3 molar Co/Zr complex formed that increased both oxidation and polymerization. Lead was reported to be less effective than zirconium.

3.3. Conjugated Drying Oils. Oils containing conjugated double bonds, such as tung oil, dry more rapidly than any nonconjugated drying oil. Free radical polymerization of the conjugated diene systems can lead to chain-growth polymerization, rather than just a combination of free radicals to form cross-links. High degrees of polymerization are unlikely because of the high concentration of abstractable hydrogens acting as chain-transfer agents. However, the free radicals formed by chain transfer also yield cross-links. In general, the water and alkali resistance of films derived from conjugated oils are superior, presumably because more of the cross-links are stable carbon–carbon bonds. However, since the α-eleostearic acid in tung oil has three double bonds, discoloration on baking and aging is severe.

4. Synthetic and Modified Drying Oils

Several types of chemical modification of drying oils are practiced. In addition to those discussed here, drying oil-modified alkyds, epoxy esters, and uralkyds (see ALKYD RESINS).

4.1. Heat Bodied Oils, Blown Oils, and Dimer Acids. Both nonconjugated and conjugated drying oils can be thermally polymerized by heating under an inert atmosphere to form *bodied oils*. Bodied oils have higher viscosities and are used in oil paints to improve application and performance characteristics. Process temperatures may be as high as 300–320°C for nonconjugated oils and 225–240°C for conjugated oils, although the reactions occur at an appreciable rate at somewhat lower temperatures (4). At least in part, bodying results from thermal decomposition of hydroperoxides, always present in natural oils, to yield free radicals, resulting in a limited degree of cross-linking. It has also been shown that thermal rearrangement to conjugated systems occurs followed by Diels–Alder reactions, which lead to formation of dimers (25). The effect of Mn, Zr, and Ti(isopropoxide)$_4$ on the temperature of bodying reactions, differential scanning calorimetry (DSC) curves, and film hardness of linseed oil have been studied (26). It was found that calcium driers had no effect on rate of viscosity increase. Since tung oil has a high concentration of conjugated double bonds, it undergoes thermal polymerization more rapidly than nonconjugated oils (eg, linseed oil). One must be careful to control the heating of tung oil or the polymerization will lead to gelation.

A study of the most appropriate surfactants to prepare oil–water emulsions of bodied linseed oil for waterborne paints is available (27).

Viscosity of drying oils can also be increased by passing air through oil at relatively moderate temperatures, 140–150°C, to produce *blown oils* (4). Presumably, reactions similar to those involved in cross-linking cause autoxidative oligomerization of the oil. The oligomerization increases functionality, and hence accelerates the drying of linseed oil and makes a drying oil from soybean oil. Preparation of blown soybean oil almost to the stage of gelation by passing oxygen through the oil heated to 137°C for 3 h, reducing the heat to 77°C for a total of 72 h (28).

Polyunsaturated acids dimerize or oligomerize by heat treatment; the reactions are acid catalyzed. For example, the doubly unsaturated fatty acids of TOFA can be dimerized or oligomerized followed by removal of the residual monobasic acids by distillation. Under the high reaction temperatures, some decarboxylation occurs. Decarboxylation can be minimized by heating under pressure in the presence of a small percentage of water and activated clay. The products obtained are called *dimer acids*. They are predominantly C_{36} dicarboxylic acids, with small fractions of monocarboxylic acid and some C_{54} tricarboxylic acids. For some uses, it is desirable to eliminate residual double bonds by hydrogenation. Dimer acids are used to make polyesters and aminoamides.

4.2. Varnishes. The drying rate of drying oils can be increased by dissolving a solid resin in the oil and diluting with a hydrocarbon solvent. Such a solution is called a *varnish*. The solid resin serves to increase the T_g of the solvent-free film so that film hardness is achieved more rapidly. The rate of cross-linking does not increase so the time required for the film to become solvent resistant is not shortened. Any high melting thermoplastic resin soluble in drying oil will serve the purpose. The higher the "melt point" of the resin, the greater the effect on drying time. Naturally occurring resins, such as congo, copal, damar, and kauri resins, synthetic resins, such as ester gum (glyceryl esters of rosin), phenolic resins, and coumarone-indene resins, have been used.

In varnish manufacture, the drying oil (usually linseed oil, tung oil, or mixtures of the two) and the resin are cooked together to high temperature to obtain a homogeneous solution of the proper viscosity. The varnish is then thinned with hydrocarbon solvents to application viscosity. During cooking, some dimerization or oligomerization of the drying oil occurs; in some cases, reaction between the oil and resin (particularly with phenolic resins) has been demonstrated. Varnishes were widely used in the nineteenth and early twentieth centuries, but have been almost completely replaced by a variety of other products, especially alkyds, epoxy esters, and uralkyds. The term varnish has come to be used more generally for transparent coatings, even though few of them today are varnishes in the original meaning of the word.

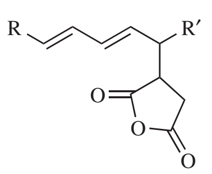
4.3. Synthetic Conjugated Oils. Tung oil dries rapidly, but is expensive and its films discolor rapidly due to the presence of three double bonds. These shortcomings led to efforts to synthesize conjugated oils, especially those containing esters of fatty acids with two conjugated double bonds. One approach is to dehydrate castor oil using acid catalysis. A major component (87%) of the fatty acid content of castor oil triglycerides is ricinoleic acid, 12-hydroxy-(*Z*)-9-octadecenoic acid, which dehydrates to mixed geometric isomers of 9,11-conjugated and 9,12-nonconjugated fatty acid esters. *Dehydrated castor oil* dries relatively rapidly at room temperature, but on further exposure to air, the surface becomes tacky. This *aftertack* has been attributed to the presence of various geometric isomers formed during the dehydration. Dehydrated castor oil and its fatty acids are mainly used to prepare alkyds and epoxy esters for baking coatings, in which aftertack does not occur.

Nonconjugated oils can be partially isomerized to conjugated oils by heating with a variety of catalysts, mostly alkaline hydroxides. Some cis–trans isomerization occurs in the process but the extent is apparently not great enough to result in aftertack. A similar process can be used to partially conjugate double bonds of TOFAs. Synthesis of conjugated fatty acids by treatment of oils at high temperature with aqueous alkali hydroxides accomplishes isomerization and saponification simultaneously (29). The principal use of such conjugated oils and fatty acids has been to make alkyds and epoxy esters.

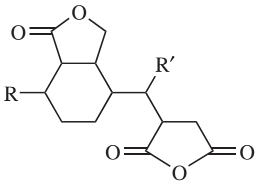
4.4. Esters of Higher Functionality Polyols. As mentioned earlier, the time required for nonconjugated oils to form a solvent-resistant, cross-linked film decreases as the average number of diallylic groups, $\bar{f}_n$, increases. When oil-derived fatty acids are reacted with polyols with more than three hydroxyl groups per molecule, the number of cross-linking sites per molecule increases relative to the corresponding natural triglyceride oil. While soybean oil is a semi-drying oil since $\bar{f}_n$ is 2.07, the pentaerythritol (PE) 2,2-bis(hydroxymethyl)-1,3-pentanediol [115-77-5] tetraester of soybean fatty acids has an $\bar{f}_n$ of 2.76 and is a drying oil. The PE ester of linseed fatty acids has an $\bar{f}_n$ of $\sim$5 and gives dry, solvent-resistant films more rapidly than linseed oil. Still faster drying rates can be achieved with still higher functionality polyols, such as dipentaerythritol (2,2'-[oxybis(methylene)]-bis[2-hydroxymethyl]-1,3-propanediol)[126-58-9] and tripentaerythritol (2,2-bis([3-hydroxy-2,2-bis(hydroxymethyl)propoxy]methyl-1,3-propanediol)[78-24-0]. Alkyds, epoxy esters, and uralkyds made with fatty acids from such oils as soybean and linseed oils can be considered as higher functionality synthetic drying oils (see ALKYD RESINS).

4.5. Maleated Oils. Both conjugated and nonconjugated oils react with maleic anhydride (2,5-furandione)[108-31-6] to form adducts. Conjugated oils, such as dehydrated castor oil, react at moderate temperatures by a Diels–Alder reaction:

Nonconjugated oils, such as soybean and linseed oils, require higher temperatures (>100°C) and form a variety of adduct structures. Model compound studies using methyl linoleate demonstrate that maleic anhydride undergoes an ene reaction to give succinyl anhydride adducts. The ene reaction results in conjugated bonds, as shown in general structure (**4**) subsequent Diels–Alder reaction with a second maleic anhydride gives a dianhydride, as shown in general structure (**5**) (30).



(**4**)



(**5**)

The products of these reactions, termed *maleated oils*, or sometimes, *maleinized oils*, react with polyols to give moderate molecular weight derivatives that dry faster than the unmodified drying oils. For example, maleated soybean oil esterified with glycerol dries at a rate comparable to that of a bodied linseed oil with a similar viscosity. It has been used as an alternative to linseed oil in printing inks depending on the cost differences from time to time.

Maleated linseed oil can be made water reducible by hydrolysis with aqueous ammonia to convert the anhydride groups to the ammonium salts of the diacid. Such products have not found significant commercial use, but the process is used to make water-reducible alkyds and epoxy esters.

4.6. Vinylated Oils. Both conjugated and nonconjugated drying oils react in the presence of a free-radical initiator, usually benzoyl peroxide, with such unsaturated monomers as styrene, vinyltoluene, and acrylic esters. High degrees of chain transfer result in the formation of a variety of products, for example, low molecular weight homopolymer of the monomer, short-chain graft copolymers, and dimerized drying oil molecules. The reaction of drying oils with such monomers is no longer commercially important, but the same principle is used to make modified alkyds. Linseed oil modified with cyclopentadiene has found fairly sizeable commercial use. This product is made by heating a mixture of linseed oil and dicyclopentadiene above 170°C, the temperature above which the reverse Diels–Alder reaction liberates monomeric cyclopentadiene at an appreciable rate. The product is inexpensive and dries faster than linseed oil. However, its odor and dark color limit its applications.

The side reaction encountered with use of benzoyl peroxide, formation of homopolymer of styrene, can be avoided by using a glyceryl ester with a chemically bound azo initiator bound to it (31). Partial glyceryl esters of linseed oil (or other oils) were reacted with 4,4′-azobis(4cyanopentanoyl chloride) and the product was reacted with styrene to give a graft copolymer. The length of the styrene side chains can be controlled by including diethyl malonate in the reaction mixture. These styrenated oils are said to be more alkali resistant and have better flexibility as compared to styrenated oils prepared conventionally, Hybrid oil–alkyd–acrylic latexes have been prepared by emulsion polymerization (32).

Hydroperoxidized sunflower oil was used as the initiator to polymerize a combination of sunflower oil, a long oil alkyd, and ethyl methacrylate. The use of the hydroperoxidized sunflower led to homogeneous polymerization in contrast to use of *tert*-butyl hydroperoxide. Films formed from the latex gave the fast dry expected from a latex followed by autoxidation to give cross-linked films.

4.7. Epoxidized Oils.

Epoxidized soybean oil, that is soybean oils whose double bonds have been converted to epoxy (oxirane) groups are used as plasticizers for poly(vinyl chloride) (PVC) polymers and copolymers that also serve to stabilize the vinyl resin. Epoxidized linseed oil is used with bisphenol epoxy resins to increase the flexibility of amine cured epoxy polymers. Epoxidized linseed oil can be reacted with acrylic acid. The acrylated oil is used in ultraviolet (uv) curing inks.

5. Economic Aspects

The data in Table 2 on consumption of drying oils were abstracted from Bureau of Census reports on consumption of Fat and Oils (33). Many fats and oils are used in both edible and inedible uses. The data in Table 2 includes data for linseed oil, tung oil, tall oil, safflower oil, sunflower oil, fish oil, and soy bean oil in inedible uses after deducting the amount of oil consumed in animal feed. At least some of the fatty acids reported are used in making modified drying oils, alkyds, epoxy esters, and uralkyds. A significant part of the tall oil fatty acids reported are converted to conjugated tall oil acids and dimer acids. Consumption of dehydrated castor oil and dehydrated castor oil acids are not given in the report. Soybean oil is a semidrying oil but it is widely used in making modified drying oils and alkyd resins that are drying oils.

There are inconsistencies between the data in various tables covering the same data. Further complicating analysis of the data is the need to protect confidentiality by not including data that could disclose the consumption by individual companies, designated (D). Such data is included in totals of the

Table 2. **Consumption of Selected Oils Consumed in Inedible Products in 2000 from U.S. Census Bureau Reports**[a]

Oil	Paint and varnish[b]	Resins and plastics[b]	Lubricants[b]	Fatty acids[b]	Other inedible[b]	Total inedible
linseed	14.5	15.0	(D)	(D)	(D)	37.0
tung	0.8	3.6	(D)	0.9		5.8
tall	23.7	7.7	3.1	458.6	(D)	508.6
safflower	(D)	(D)	(D)	(D)	(D)	0.3
sunflower	(D)	1.0	(D)	(D)	(D)	1.9
fish	(D)	(D)	(D)	(D)	(D)	15.0
soybean	33.0	5.5	(D)	27.4	152.7	267.6

[a] Where amounts for feed uses were given they have been subtracted to obtain the numbers in this table. Figures have been converted from lbs. × 10^6 to kg × 10^6.

[b] The D = consumption of individual companies.

consumption of inedible use consumption but not broken down by individual end use. Furthermore, data includes other unidentified uses. The attempt has been made here to select those values that seem to best reflect actual consumption but, obviously, the precision of the data is unknown.

6. Uses

The use of drying oils has decreased substantially since the early part of the twentieth century. Some formerly large uses have been completely replaced with other materials: Oil cloth and linoleum have been completely converted to vinyl resins or other polymers. Drying oil vehicles for putty have been virtually completely replaced by acrylic latexes. Use of oils in paints and coatings, printing inks, and artists' colors have been substantially reduced. The largest use for drying oils now is in the manufacture of alkyd resins, epoxy esters, uralkyds, and modified drying oils.

In the paint and coatings industry, relatively small amounts of drying oils are used in the manufacture of penetrating stains. These stains are made with an oil such as linseed oil. They have been replaced to a large extent with stains formulated with latexes but oil stains give greater penetration and more clarity. Tung oil is used as a penetrating finish for wood furniture by the do-it-yourself trade. It protects the wood against staining without leaving an apparent film on the surface. Some red-lead-in-oil corrosion protective primers are still used in applications where there is no risk of lead poisoning. Linseed oil and modified linseed oils have been used as concrete coatings to protect against spalling. Very little drying oil is used in wall paints or exterior house paints now. They have been replaced with either alkyd resins or latexes.

Drying oils and oxidizing alkyds have been studied as binders for organic/inorganic (ceramer) coatings (28). (see also the references cited therein). The inorganic phase was formed by the gelation of tetraethyl orthosilicate (TEOS). Blown soybean oil, TEOS oligomer, a sol–gel precursor (titanium-tetra-*i*-propoxide), and Co/Zr drier gave ceramer coatings with good properties. A proposed use for such coatings is a corrosion protection primer for steel rebars.

Some drying oils are used in printing inks, particularly sheet fed lithographic printing primarily after being converted to alkyds resins. Drying oils and modified drying oils are so-called renewable resources. Publicity of the renewability of soybean oil based printing inks is being used to promote their use.

Dimer acids are prepared by heat oligomerizing fatty acids such as tall oil fatty acids. Amide-terminated resins prepared by reacting dimer acids with a diamine are used as binder in flexographic inks. Amine-terminated polyamides from dimer acids are used as cross-linkers for bisphenol epoxy resin primers. Polyesters prepared with dimer acids are used in making vehicles for coil coating with exceptional flexibility and formability.

Linseed oil has been used as a binder for replacement brake linings. Linseed oil has been used as core oil to bond sand for metal casting molds. The Census reports list lubricants as a significant consumer of oils.

BIBLIOGRAPHY

"Drying Oils" in *ECT* 1st ed., Vol. 4, pp. 277–299, by O. Grummitt, Western Reserve University, H. J. Lanson, Mastercraft Paint Manufacturing Co., and A. E. Rheineck, Hercules Powder Co.; in *ECT* 2nd ed., Vol. 7, pp. 398–428, by O. Grummitt, Western Reserve University, J. Mehaffy, Sherwin-Williams Co., A. E. Rheineck, North Dakota State University, and H. J. Lanson, Lanson Chemicals Corp.; in *ECT* 3rd ed., Vol. 8, pp. 130–150, by J. C. Cowan, Bradley University, in *ECT* 4th ed., Vol. 8, pp. 519–532, by Zeno W. Wicks, Jr., Consultant; "Drying Oils" in *ECT* (online), posting date, December 4, 2000, by Zeno W. Wicks, Jr., Consultant.

CITED PUBLICATIONS

1. G. R. Khan and F. Scheinmann, *Prog. Chem. Fats Other Lipids* **15**, 343 (1977).
2. J. W. King, E. C. Adams, and B. A. Bidlingmeyer, *J. Liq. Chromatogr.* **5**, 275 (1982).
3. A. I. Aigbodion and C. K. S. Pillai, *Prog. Org. Coat.* **38**, 187 (2000).
4. A. E. Rheineck and R. O. Austin, in R. R. Myers and J. S. Long, eds., *Treatise on Coatings*, Vol. 1, No. 2, Marcel Dekker, New York, 1968, pp. 181–248.
5. F. L. Fox, *Oils for Organic Coatings*, Federation of Societies for Coatings Technology, Blue Bell, Pa., 1965.
6. K. S. Ennor and J. Oxley, *J. Oil Colour Chem. Assoc.* **50**, 577 (1967)
7. J. T. P. Derksen, F. P. Cuperus, and P. Kolster, *Prog. Org. Coat.* **27**, 45 (1996).
8. J. H. Greaves, *Oil Colour Trades J.* **113**, 949 (1948).
9. J. R. Chipault, E. E. Nickell, and W. O. Lundberg, *Off. Digest* **23**, 740 (1951).
10. J. H. Hartshorn, *J. Coat. Technol.* **54**(687) 53 (1982).
11. W. J. Muizebelt and co-workers, *J. Coat. Technol.* **70**(876) 83 (1998).
12. N. A. R. Falla, *J. Coat. Technol.* **64**(815) 55 (1992).
13. E. N. Frankel, *Prog. Lipid. Res.* **19**, 1 (1980).
14. W. J. Muizebelt and co-workers, *J. Coat, Technol.* **70**(876) 83 (1998).
15. J. Mallegol, J.-L. Gardette, and J. Lemaire, *JAOCS* **76**, 967 (1999) and *JAOCS* **77**, 249 (2000).
16. J. D. J. van den Berg, K. J. van den Berg, and J. J. Boon, *Prog. Org. Coat.* **41**, 143 (2001).
17. J. C. Hubert and co-workers, *J. Coat. Technol.* **69**(869) 59 (1997).
18. W. H. Simendinger and C. M. Balik, *J. Coat. Technol.* **66**(831) 39 (1994).
19. R. A. Hancock, N. J. Leeves, and P. F. Nicks, *Prog. Org. Coat.* **17**, 321, 337 (1989).
20. J. Mallegot, J. -L. Gardette, and J. Lemaire, *JAOCS* **77**, 257 (2000).
21. T. L. T. Robey and S. M. Rybicka, *Paint Research Station Technical Papers No. 217*, Vol. 13, No. 1, 1962, p. 2.
22. V. Verholantsev, *Eur. Coat. J.* (1–2) 120 (2000).
23. J. Mallegot, J. Lemaire, and J. -L. Gardette, *Prog. Org. Coat.* **39**, 107 (2000).
24. S. M. P. Meneghetti, R. F. de Souza, A. L. Monteiro, and M. O. de Souza, *Prog. Org. Coat.* **33**, 219 (1998).
25. D. H. Wheeler and J. White, *J. Am. Chem. Soc.* **44**, 298 (1967).
26. S. J. Tuman, D. Chamberlin, K. M. Scholsky, and M. D. Soucek, *Prog. Org. Coat.* **28**, 251 (1995).
27. E. Makarewicz, *Prog. Org. Coat.* **28**, 125 (1996).
28. D. Deffar and M. D. Soucek, *J. Coat. Technol.* **73**(919) 95 (2001).
29. T. F. Bradley and G. H. Richardson, *Ind. Eng. Chem.* **34**, 237 (1942).
30. A. E. Rheineck and T. H. Khoe, Fette Seifen Anstrichm. **71**, 644 (1969).

31. F. S. Erkal, A. T. Erciyes, and Y. Yaggi, *J. Coat. Technol.* **65**(827) 37 (1993).
32. E. M. S. Van Hamersfeld and coworkers, *Prog. Org. Coat.* **35**, 235 (1999).
33. http://www.census.gov/ftp/pub/industry/1/m20k0013.pdf.

GENERAL REFERENCES

F. L. Fox, *Oils for Organic Coatings*, Federation of Societies for Coatings Technology, Blue Bell, Pa., 1965.

A. E. Rheineck and R. O. Austin, in R. R. Myers and J. S. Long, eds., *Treatise on Coatings*, Vol. I, No. 2, Marcel Dekker, New York, 1968, pp. 181–248.

ZENO W. WICKS, JR.
Consultant