ALKYD RESINS

1. Introduction

While no longer the largest volume vehicles in coatings, alkyds still are of major importance. Alkyds are prepared from polyols, dibasic acids, and fatty acids. They are polyesters, but in the coatings field the term polyester is reserved for “oil-free polyesters”. The term *alkyd* is derived from *alcohol* and *acid*. Alkyds tend to be lower in cost than most other vehicles and tend to give coatings

Kirk-Othmer Encyclopedia of Chemical Technology.

that exhibit fewer film defects during application. However, durability of alkyd films, especially outdoors, tends to be poorer than films from acrylics, polyesters, and polyurethanes. In a comparison of resistance to acid rain among coconut alkyd-MF, polyester-MF, and silicone-modified polyester-MF (MF = melamine–formaldehyde) coatings at five locations in the United States and Canada, the alkyd coating showed the poorest resistance (1).

There are several types of alkyds. One classification is into *oxidizing* and *nonoxidizing* types. Oxidizing alkyds cross-link by the same mechanism as drying oils. Nonoxidizing alkyds are used as polymeric plasticizers or as hydroxy-functional resins, which are cross-linked by MF resins, by urea–formaldehyde (UF) resins, or by isocyanate cross-linkers. A second classification is based on the ratio of monobasic fatty acids to dibasic acids utilized in their preparation. The terminology used was adapted from terminology used to classify varnishes. Varnishes with high ratios of oil to resin were called long oil varnishes; those with a lower ratio, medium oil varnishes; and those with an even lower ratio, short oil varnishes. Oil length of an alkyd is calculated by dividing the amount of "oil" in the final alkyd by the total weight of the alkyd solids, expressed as a percentage, as shown in equation 1. The amount of oil is defined as the triglyceride equivalent to the amount of fatty acids in the alkyd. The 1.04 factor in equation 2 converts the weight of fatty acids to the corresponding weight of triglyceride oil. Alkyds with oil lengths >60 are *long oil alkyds*; those with oil lengths from 40 to 60, *medium oil alkyds*, and those with oil lengths <40, *short oil alkyds*. There is some variation in the dividing lines between these classes in the literature.

$$\text{Oil length} = \frac{\text{Weight of oil}}{\text{Weight of alkyd} - \text{water evolved}} \times 100 \tag{1}$$

$$\text{Oil length} = \frac{1.04 \times \text{Weight of fatty acids}}{\text{Weight of alkyd} - \text{water evolved}} \times 100 \tag{2}$$

Another classification is *unmodified* or *modified alkyds*. Modified alkyds contain other monomers in addition to polyols, polybasic acids, and fatty acids. Examples are *styrenated alkyds* and *silicone alkyds*. Since they are closely related to alkyd resins, uralkyds and epoxy esters are also discussed.

2. Oxidizing Alkyds

Oxidizing alkyds can be considered as synthetic drying oils. They are polyesters of one or more polyols, one or more dibasic acids, and fatty acids from one or more drying or semidrying oils.

2.1. Film Formation. Most of the studies of the chemistry of cross-linking have been with drying oils and not the alkyds derived from them but the mechanisms are applicable to both (see DRYING OILS). Films exposed to air undergo autoxidative cross-linking. In nonconjugated unsaturated oils, the active group initiating drying is the diallylic group ($-CH{=}CHCH_2CH{=}CH-$) from esters of (Z,Z)-9,12-octadecadienoic acid [60-33-3] (linoleic acid) and

(*Z*,*Z*,*Z*)-9,12,15-octadecatrienoic acid [463-40-1] (linolenic acid). They have one and two diallylic groups per molecule, respectively. Drying is related to the average number of diallylic groups per molecule. If this number is greater than $\sim$2.2, the oil is a drying oil and if it is moderately $<$2.2, the oil is a semidrying oil; there is no sharp dividing line between semidrying oils and nondrying 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 f_n of the triglyceride or synthetic drying oil. It is probable that some of the sites are involved in more than one cross-linking reaction.

When a film is applied, initially naturally present hydroperoxides decompose to form free radicals. Hydrogens on methylene groups between double bonds are particularly susceptible to abstraction, yielding a resonance stabilized free radical that reacts with oxygen to give predominantly a conjugated peroxy free radicals. The peroxy free radicals can abstract hydrogens from other methylene groups between double bonds to form additional hydroperoxides and generate free radicals like. 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. Reactions analogous to the addition step in chain-growth polymerization could also produce cross-links (see DRYING OILS for further discussion).

Rearrangement and cleavage of hydroperoxides to aldehydes and ketones, among other products, lead to low molecular weight byproducts. 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. Undesirable odor has been a factor motivating replacement of oil and alkyds in paints with latex, particularly for interior applications.

Dried films, especially of alkyds with three double-bond fatty acids, 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 (2).

The autoxidation rates of uncatalyzed nonconjugated oxidizing alkyds 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*. The surface-drying catalysis by cobalt and manganese salts results from the catalysis of hydroperoxide decomposition. The cobalt or manganese cycle between the two oxidation states. The activity of through driers has not been adequately explained.

Combinations of metal salts are almost always used. 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. 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. For further discussion see section on catalysis in 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 (*E*,*Z*,*E*)-9,11,13-octadecatrienoic acid [506-23-0] (α-eleostearic acid) in tung oil has three double bonds, discoloration on baking and aging is severe.

The most commonly used polyol in preparing alkyds is glycerol (1,2,3-propanetriol) [56-81-5], the most commonly used dibasic acid is phthalic anhydride (PA) (1,3-isobenzofurandione) [85-44-9], and a widely used oil is soybean oil. Let us consider a simple, idealized example of the alkyd prepared from 1 mol of PA, 2 mol of glycerol, and 4 mol of soybean fatty acids. A typical fatty acid composition data for soybean oil is as follows saturated fatty acids, palmitic acid (hexadecanoic acid) [57-10-3] and stearic acid (octadecanoic acid) [57-11-4], 15%; oleic acid (*Z*)-9-octadecenoic acid [112-80-1], 25%; linoleic acid, 51%; and linolenic acid, 9%. Any oil with an $\bar{f}_n$ higher than 2.2 is a drying oil. Although soybean oil is a semidrying oil, this alkyd would have an $\bar{f}_n$ of 2.76 per molecule and, therefore, would dry to a solid film. The alkyd would form a solvent-resistant film in about the same time as a pentaerythritol (PE) (2,2-bis(hydroxymethyl)-1,3-pentanediol) [115-77-5] ester of soybean fatty acids, since they have the same $\bar{f}_n$. However, the alkyd would form a tack-free film faster because the rigid aromatic rings from PA increase the T_g of the film.

If the mole ratio of PA to glycerol were 2–3, 5 mol of soybean fatty acid could be esterified to yield an alkyd with an $\bar{f}_n$ of 3.45. This alkyd would cross-link more rapidly than the 1:2:4 mol ratio alkyd and would also form tack-free films even faster because the ratio of aromatic rings to long aliphatic chains would be 2:5 instead of 1:4. As the ratio of PA to glycerol is increased further, the average functionality for autoxidation increases and the T_g after solvent evaporation increases because of the increasing ratio of aromatic to long aliphatic chains. For both reasons, films dry faster.

A theoretical alkyd prepared from 1 mol each of glycerol, PA, and fatty acid would have an oil length of ~60. However, if one were to try to prepare such an alkyd, the resin would gel prior to complete reaction. Gelation would result from reaction of a sufficient number of trifunctional glycerol molecules with three difunctional PA molecules to form cross-linked polymer molecules, swollen with partially reacted components. Gelation can be avoided by using a sufficient excess of glycerol to reduce the extent of cross-linking. When the reaction is carried to near completion with excess glycerol, there are few unreacted carboxylic acid groups, but many unreacted hydroxyl groups.

There have been many attempts, none fully successful, to calculate the ratios of functional groups and the extent of reaction that can be reached without encountering gelation. The problem is complex. The reactivity of the hydroxyl groups can be different; for example, glycerol contains both primary and secondary alcohol groups. Under esterification conditions, polyol molecules can self-condense to form ethers and, in some cases, can dehydrate to form volatile aldehydes. Reactivity of the carboxylic acids also varies. The rate of formation of the first ester from a cyclic anhydride is more rapid than formation of the second ester. Aliphatic acids esterify more rapidly than aromatic acids. Polyunsaturated fatty acids and their esters can dimerize or oligomerize to form cross-links. Of the many papers in the field, that by Blackinton recognizes the complexities best (3). In addition to the above complexities, particular emphasis is placed on the extent of formation of cyclic compounds by intramolecular esterification reactions. Equations have been developed that permit calculation of ratios of ingredients theoretically needed to prepare an alkyd of any desired oil length, number average molecular weight, and hydroxy content (4). Just like in other equations, the important effect of dimerization of fatty acids is not included as a factor in these equations. In practice, alkyd resin formulators have found that the mole ratio of dibasic acid to polyol should be <1 to avoid gelation. How much <1 depends on many variables.

For medium oil alkyds, the ratio of dibasic acid to polyol is not generally changed much relative to alkyds with an oil length of $\sim$60, but the fatty acid content is reduced to the extent desired. This results in a larger excess of hydroxyl groups in the final alkyd. It is commonly said that as the oil length of an oxidizing alkyd is reduced <60, the drying time decreases to a minimum at an oil length of $\sim$50. However, this conventional wisdom must be viewed cautiously. The ratio of aromatic rings to aliphatic chains continues to increase, increasing T_g after the solvent evaporates from the film tending to shorten the time to form a tack-free film. However, at the same molecular weight, the number of fatty acid ester groups per molecule decreases as the oil length decreases <60, since more hydroxyl groups are left unesterified. Therefore, the time required to achieve sufficient cross-linking for solvent resistance increases.

Long oil alkyds are soluble in aliphatic hydrocarbon solvents. As the oil length decreases, mixtures of aliphatic and aromatic solvents are required, and oil lengths below $\sim$50 require aromatic solvents, which are more expensive than aliphatics. The viscosity of solutions of long oil alkyds, especially of those with oil lengths <65, is higher in aliphatic than in aromatic solvents; in medium oil alkyds, which require mixtures of aliphatic and aromatic solvents, viscosity decreases as the proportion of aromatic solvents increases. In former days, and to some extent still today, it was considered desirable to use a solvent mixture that gave the highest possible viscosity; then, at application viscosity, the solids were lower and the raw material cost per unit volume was less. Accordingly, alkyds were designed to have high dilutability with aliphatic solvents. This was false economy, but it was a common practice and is still being practiced to some extent. Increasingly, the emphasis is on reducing volatile organic compound (VOC) emissions and so the question becomes how to design alkyds with low solvent requirements rather than high dilutability potential. Furthermore, the aromatic solvents are on the hazardous air pollutants (HAP) list. High solids alkyds are discussed in a later section.

2.2. Monobasic Acid Selection.

Drying alkyds can be made with fatty acids from semidrying oils, since the $\bar{f}_n$ can be well >2.2. For alkyds made by the monoglyceride process, soybean oil is used in the largest volume. Soybean oil is economical and supplies are dependable because it is a large scale agricultural commodity; alkyd production takes only a few percent of the world supply. For alkyds made by the fatty acid process, tall oil fatty acids (TOFA) are more economical than soybean fatty acids. Both soybean oil and TOFA contain roughly 40–60% linoleic acid and significant amounts of linolenic acid. White coatings containing linolenic acid esters gradually turn yellow. Premium cost "nonyellowing" alkyds are made with safflower or sunflower oils, which are high in linoleic acid but contain very little linolenic acid.

Applications in which fast drying and high cross-link density are important require alkyds made with drying oils. The rate of oxidative cross-linking is affected by the functionality of the drying oils used. At the same oil length and molecular weight, the time required to achieve a specific degree of cross-linking decreases as the average number of diallylic groups ($\bar{f}_n$) increases. Linseed long oil alkyds therefore cross-link more rapidly than soybean long oil alkyds. The effect is especially large in very long oil alkyds and less noticeable in alkyds with oil lengths ~60, where $\bar{f}_n$ is very high even with soybean oil and the effect of further increase in functionality by using linseed oil is small. Because of the large fraction of esters of fatty acids with three double bonds in linseed alkyds, their color and color retention are poorer than that of soybean alkyds. Tung oil based alkyds, because of the high proportion of esters with three conjugated double bonds, dry still faster. Tung oil alkyds also exhibit a high degree of yellowing. Dehydrated castor alkyds have fairly good color retention and cure more rapidly than those made with nonconjugated fatty acids. Since they contain only a small proportion of esters of fatty acids with three double bonds; they are used primarily in baking coatings. Conjugated acids made by isomerizing tall oil acids give similar results to those obtained with dehydrated castor oil acids.

Drying oils and drying oil fatty acids undergo dimerization at elevated temperatures. Dimerization occurs concurrently with esterification during alkyd synthesis; it generates difunctional acids, increasing the mole ratio of dibasic acids to polyol. The rate of dimerization is faster with drying oils having a higher average number of diallylic groups per molecule and with those having conjugated double bonds. Thus, the molecular weight, and therefore the viscosity of an alkyd, made with the same ratio of reactants depends on the fatty acid composition. The higher the degree of unsaturation, the higher the viscosity because of the greater extent of dimerization. Linseed alkyds have higher viscosities than soybean alkyds made with the same monomer ratios under the same conditions. The effect is particularly marked with tung oil. It is difficult to prepare straight tung alkyds because of the risk of gelation; commonly, mixed linseed–tung alkyds are used when high oxidative cross-linking functionality is desired.

A critical factor involved in the choice of fatty acid is cost. Drying oils are agricultural products and, hence, tend to be volatile in price. By far, the major use of vegetable oils is for foods. Depending on relative prices, one drying oil is often substituted for another in certain alkyds. By adjusting for functionality differences, substitutions can frequently be made without significant changes in properties.

Fatty acids are not the only monobasic acids used in making alkyds. Benzoic acid is also used, especially to esterify some of the excess hydroxyl groups remaining in the preparation of medium oil alkyds. The benzoic acid [65-85-0] increases the ratio of aromatic to aliphatic chains in the alkyd, thus contributing to a higher T_g of the solvent-free alkyd and more rapid formation of a tack-free film. At the same time, the reduction in the free hydroxyl content may somewhat reduce water sensitivity of the dried films. Rosin can also be used in the same fashion. Although rosin is not an aromatic acid, its polynuclear ring structure is rigid enough to increase T_g. If the critical requirement in drying is rapid development of solvent resistance, such benzoic acid and rosin modifications do not serve the purpose; they only reduce tack-free time. Frequently, benzoic acid modified alkyds are called *chain-stopped* alkyds. The implication of the terminology is that the benzoic acid stops chain growth, which is not the case; the benzoic acid simply esterifies hydroxyl groups that would not have been esterified if the benzoic acid were absent. The effect on degree of polymerization is negligible.

2.3. Polyol Selection.

Glycerol is the most widely used polyol because it is present in naturally occurring oils from which alkyds are commonly synthesized. The next most widely used polyol is PE. In order to avoid gelation, the tetrafunctionality of PE must be taken into account when replacing glycerol with PE. If the substitution is made on a mole basis, rather than an equivalent basis, chances for gelation are minimized. As mentioned earlier, the ratio of moles of dibasic acid to polyol should be <1, and generally, a slightly lower mole ratio is required with PE than with glycerol. At the same mole ratio of dibasic acid to polyol, more moles of fatty acid can be esterified with PE. Hence, in long oil alkyds, the average functionality for cross-linking is higher, and the time to reach a given degree of solvent resistance is shorter for a PE alkyd as compared to a glycerol alkyd. Because of this difference, one must be careful in comparing oil lengths of glycerol and PE alkyds. Films from PE based alkyds generally are superior to their glycerol counterparts in drying, hardness, and humidity resistance.

When PE is synthesized, 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] are byproducts, and commercial PE contains some of these higher polyols. Consequently, care must be exercised in changing sources of PE, since the amount of the higher polyols may differ. Because of the very high functionality, diPE and triPE ($F = 6$ and 8, respectively) are useful in making fast drying low molecular weight alkyds.

To reduce cost, it is sometimes desirable to use mixtures of PE and ethylene glycol (1,2-ethanediol) [107-21-1] or propylene glycol (1,3-propanediol). A 1:1 mole ratio of tetrafunctional and difunctional polyols gives an average functionality of 3, corresponding to glycerol. The corresponding alkyds can be expected to be similar, but not identical. Trimethylolpropane (TMP) (2-ethyl-2-(hydroxymethyl)-1,3-propanediol) [77-99-6] can also be used, but the rate of esterification is slower than with glycerol. Although all of TMPs alcohol groups are primary, they are somewhat sterically hindered by the neopentyl structure (5). Trimethylolpropane, however, gives a narrower molecular weight distribution, which provides alkyds with a somewhat lower viscosity than the comparable glycerol-based alkyd. A kinetic study demonstrated that esterification of one or two of the hydroxyl groups of TMP has little effect on the rate constant for esterification of the third hydroxyl group (6). It can be speculated that PE behaves similarly.

2.4. Dibasic Acid Selection. Dibasic acids used to prepare alkyds are usually aromatic. Their rigid aromatic rings increase the T_g of the resin. Cycloaliphatic anhydrides, such as hexahydrophthalic anhydride, are also used. While they are not as rigid as aromatic rings, the cycloaliphatic rings also increase T_g.

By far, the most widely used dibasic acid is PA. It has the advantage that the first esterification reaction proceeds rapidly by opening the anhydride ring. The amount of water evolved is lower, which also reduces reaction time. The relatively low melting point (the pure compound melts at 131°C) is desirable, since the crystals melt and dissolve readily in the reaction mixture. In large-scale manufacturing, molten PA is used, which reduces packaging, shipping, and handling costs.

The next most widely used dibasic acid is isophthalic acid (IPA) (1,3-benzenedicarboxylic acid) [121-91-5]. Esters of IPA are more resistant to hydrolysis than are those of PA in the pH range of 4–8, the most important range for exterior durability. On the other hand, under alkaline conditions esters of phthalic acid are more resistant to hydrolysis than isophthalic esters. The raw material cost for IPA is not particularly different from PA (even after adjusting for the extra mole of water that is lost), but the manufacturing cost is higher. The high melting point of IPA (330°C) leads to problems getting it to dissolve in the reaction mixture so that it can react. High temperatures are required for longer times than with PA; hence more dimerization of fatty acids occurs with IPA resulting in higher viscosity. The longer time at higher temperature also leads to greater extents of side reactions of the polyol components (7). Thus, when substituting IPA for PA, one must use a lower mole ratio of IPA to polyol in order to make an alkyd of similar viscosity.

Maleic anhydride (2,5-furandione) [108-31-6] is sometimes used with PA to give faster drying with improved adhesion and water resistance alkyds. Aliphatic acids, such as adipic acid (1,6-hexanedioic acid) [124-04-9], are sometimes used as partial replacements for PA to give more flexible alkyds.

Chlorinated dibasic acids, such as chlorendic anhydride (3,4,5,6,7,7-hexachloroendomethylene-1,2,3,6-tetrahydrophthalic anhydride), are used in making alkyds for fire retardant coatings (8).

2.5. High Solids Oxidizing Alkyds. The need to minimize VOC emissions has led to efforts to increase solids content of alkyd resin coatings. Since xylene is on the HAP list, its use is being reduced. Some increase in solids can be realized by a change of solvents. Aliphatic (and to a somewhat lesser degree, aromatic) hydrocarbon solvents promote intermolecular hydrogen bonding, especially between carboxylic acids, but also between hydroxyl groups, thereby increasing viscosity. Use of at least some hydrogen-bond acceptor solvent, such as an ester or ketone, or hydrogen-bond acceptor–donor solvent such as an alcohol, gives a significant reduction in viscosity at equal solids.

The molecular weight of conventional alkyds is usually $>50,000$. Solids can be increased by decreasing molecular weight, which is easily accomplished by decreasing the dibasic acid to polyol ratio. Alkyds with solids in the range of 60–80% are commercially available with molecular weights in the range of 12,000–20,000 (9). High solids alkyds tend to have lower functionality for cross-linking and a lower ratio of aromatic to aliphatic chains. Both changes increase the time for drying. There is also a decrease in branching with the higher hydroxyl excess.

The effect of longer oil length on functionality can be minimized by using drying oils with higher average functionality. Use of oils containing linolenic or α-eleostearic acid is limited by their tendency to discolor. One can use safflower oil, which has a higher linoleic acid content and less linolenic acid than soybean oil. Proprietary fatty acids with 78% linoleic acid are commercially available. Early hardness of the films can be improved by using some benzoic acid to esterify part of the free hydroxy groups. As noted earlier, the rigid rings of benzoic acid increase T_g to increase hardness after solvent evaporation.

Different drier combinations are recommended for use with high solids alkyds. A study of a variety of driers and drier combinations with high solids coatings has been published (10). Cobalt, neodymium, aluminum, and barium carboxylic acid salts were of particular interest. Performance was enhanced by adding bipyridyl as an accelerator. The author reports that the best drier system was 0.04% Co, 0.3% Nd with 0.07% bipyridyl (percentages based on the vehicle solids). Reference (11) reports studies of mechanisms of action of cobalt and mixed cobalt–zirconium driers.

By using optimized resins, good quality air dry and baking alkyd coatings can be formulated with VOC levels of 280–350 g/L of coating. A 250-g/L level is attainable only with some sacrifice of application and film properties; still lower limits of permissible VOC are projected.

Solids can be increased by making resins with narrower molecular weight distributions. For example, one can add a transesterification catalyst near the end of the alkyd cook; this gives more uniform molecular weight and a lower viscosity product. To study the effect of molecular weight distribution, model alkyds with very narrow molecular weight distribution were synthesized by using dicyclohexylcarbodiimide, which allows low temperature esterification (5). With the same ratio of reactants, the $\bar{M}_n$ and polydispersity were lower than that of the conventional alkyd control. These differences resulted from less dimerization through reactions of the double-bond systems of the fatty acids and avoidance of self-etherification of polyol in the low temperature preparation. It was found that the solids could be 2–10% higher than with the conventionally prepared alkyd of the same raw material composition. The model alkyds dried more rapidly, but their film properties, especially impact resistance, were inferior to those obtained with control resins with the usual broad molecular weight distribution (12). Conventionally prepared TMP alkyds had lower molecular weights and viscosities than the glycerol alkyds. This difference may result from less self-etherification of TMP as compared to glycerol.

High solids alkyds for baking applications have been made using tripentaerythritol. The high functionality obtained using this polyol ($F = 8$) gives alkyds that cross-link as rapidly as shorter oil length, higher viscosity glycerol alkyds (13). However, for air dry applications, the lower aromatic to aliphatic ratio lengthens the tack-free time. Presumably, progress could be made using a high functionality polyol with some combination of phthalic and benzoic acid, together with fatty acids with as high functionality fatty acids as possible. The cost of such an alkyd would be high.

Another approach to high solids alkyds is to use *reactive diluents* in place of part of the solvent. The idea is to have a component of lower molecular weight and that lower viscosity than the alkyd resin, which reacts with the alkyd during drying, so that it is not part of the VOC emissions. This permits the use of somewhat higher molecular weight alkyds that improves performance. The use of reactive diluents is reviewed in (14), the authors give a list of the key properties of a reactive diluent: low viscosity, good compatibility with alkyds, low volatility (bp >300°C), nontoxic, low color, and economic replacement for solvent. A variety of possible reactive diluents were studied. A combination of 2,7-octadienyl maleate and fumarate and 2-(2,7-octadienyloxy)succinate was reported to be particularly effective. The mechanism of reactions between this combination with alkyds has been studied (15). The use of esters prepared from ricinoic acid (9,11-octadecdienoic acid) and polyols gave faster drying reactive diluents.

Several other types of reactive diluents have been used to formulate high solids alkyd coatings. Polyfunctional acrylate monomers (eg, trimethylolpropane trimethacrylate) have been used in force dry coatings (coatings designed to be cured in the range of 60–80°C) (16). Another example is use of dicyclopentadienyloxyethyl methacrylate [70191-60-5] as a reactive diluent (17). It is difunctional, because of the easily abstractable allylic hydrogen on the dicyclopentadiene ring structure and the methacrylate double bond. The compound coreacts with drying oil groups in the alkyd. Mixed acrylic and drying oil fatty acid amides of hexa(aminomethoxymethyl)melamine have been recommended as reactive diluents (18,19). They contain high functionalities of $>NCH_2NHCOCH{=}CH_2$ and $>NCH_2NHCOC_{17}H_x$ moieties and promote fast drying. A recent patent discloses use of a reactive diluent prepared by reacting drying oil fatty acids with excess dipentaerythritol and then with isophorone diisocyanate (20).

3. Waterborne Alkyds

As with almost all other resin classes, work has been done to make alkyd resins for coatings that can be reduced with water. One approach that has been more extensively used in Europe than in the United States is the use of alkyd emulsions (21–23). The emulsions are stabilized with surfactants and can be prepared with little, if any, volatile solvent. Some problems limit use of alkyd emulsions (24). Coatings prepared using alkyd emulsion loose dry time on storage because of absorption of cobalt drier on the surface of pigments and precipitation of cobalt hydroxide. Best results were obtained with a combination of cobalt neodecanoate and 2,2′-bipyridyl (bpy). Incorporation of driers in the alkyd resin can adversely affect emulsion stability. It has been recommended to emulsify the driers separately and mix the emulsions so that the drier and the alkyd are in separate phases (25). It was shown that the surfactant tends to bloom to the surface of films formed from emulsions of long oil alkyds, washing a dry film tends to leave pits in the film showing a hexagonal pattern.

It is common to add a few percent of an alkyd–surfactant blend to latex paints to improve adhesion to chalky surfaces and, in some cases, to improve adhesion to metals. It is important to use alkyds that are as resistant as possible to hydrolysis. Hybrid alkyd–acrylic latexes have been prepared by dissolving an oxidizing alkyd in the monomers used in emulsion polymerization, yielding a latex with an alkyd grafted on the acrylic polymer (26,27). Nonyellowing waterborne alkyds based on rosin–fatty acid modified acrylic latexes have been reported (28). Hybrid alkyd–acrylic latexes have been prepared by emulsion polymerization (29). Hydroperoxidized sunflower oil was used as the initiator to polymerize a combination of 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 to fast dry expected from a latex followed by autoxidation to give crosslinked films.

Another approach has been to make alkyds with an acid number in the range of 50, using secondary alcohols or ether alcohols as solvents. The acid groups are neutralized with ammonia or an amine. The resultant solution can be diluted with water to form a dispersion of solvent swollen aggregates in water. Molecular weight can be higher than in the case of high solids alkyd because the major factor affecting viscosity at application solids is the volume fraction of internal phase of the dispersion rather than the molecular weight of the polymer. Use of primary alcohol solvents should be avoided because they can more readily transesterify with the alkyd during resin production and storage, leading to reduction in molecular weight and $\bar{f}_n$ (30). Hydrolytic stability can be a problem with water-reducible alkyds. If the carboxylic acid groups are half esters from PA or trimellitic acid anhydride (1,3-dihydro-1,3-dioxo-5-isobenzofurancarboxylic acid) [552-30-7], the hydrolytic stability will be poor and probably inadequate for paints that require a shelf life of more than a few months. Because of the anchimeric effect of the neighboring carboxylic acid group, such esters are relatively easily hydrolyzed. As hydrolysis occurs, the solubilizing acid salt is detached from the resin molecules, and the aqueous dispersion loses stability. A more satisfactory way to introduce free carboxylic acid groups is by reacting a completed alkyd with maleic anhydride. Part of the maleic anhydride adds to the unsaturated fatty acid esters. The anhydride groups are then hydrolyzed with amine and water to give the desired carboxylate salt groups, which are attached to resin molecules with C–C bonds and cannot be hydrolyzed off. There is still a hydrolytic stability problem with the alkyd backbone, but hydrolysis does not result in destabilization of the dispersion. Similarly acrylated fatty acids can be used to synthesize water-reducible alkyds with improved hydrolytic stability (31). Another approach to improving package stability is to react some of the free hydroxyl groups of an alkyd with isophorone diisocyanate (IPDI) [(1-isocyanato-3-isocyanatomethyl)-3,5,5-trimethylcyclohexane) [4098-71-9] and dimethylolpropionic acid, (DMPA) (3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid) [4767-03-7] (32) or with α,α-tetramethylxylylene diisocyanate (TMXDI) (1,3-bis(2,2-dimethyl-2-isocyanato)benzene] [2778-42-9] and DMPA (33).

After the film is applied, the water, solvent, and amine evaporate, and the film cross-links by autoxidation. Since there are a fairly large number of residual carboxylic acid groups left in the cross-linked binder, the water resistance and particularly the alkali resistance of the films are reduced, but are still satisfactory for some applications (34). *Early water resistance* can be a problem if, for example, a freshly painted surface is rained on before all the amine has evaporated from the film. Commonly, ammonia is used as the neutralizing amine because it is assumed that ammonia volatilizes faster than any other amine. This assumption is not necessarily valid; if the T_g of the alkyd film is sufficiently high before all of the amine has volatilized, loss of amine becomes controlled by diffusion rate. The rate of diffusion of amine through the carboxylic acid-functional film is affected by the base strength of the amine. A less basic amine, such as morpholine, may leave the film before ammonia even though its volatility is considerably lower.

4. Modified Alkyds

Oxidizing alkyds have been modified by reacting with a variety of other components; vinyl-, silicone-, phenolic-, and polyamide-modified alkyds are the most common examples.

Oxidizing alkyds can be modified by reaction with vinyl monomers. The most widely used monomers are styrene (ethenylbenzene) [100-42-5], vinyl toluene (1-ethenyl-2-methylbenzene), and methyl methacrylate (2-methyl-2-propenoic acid methyl ester), but essentially any vinyl monomer can be reacted in the presence of an alkyd to give a modified alkyd. Methyl methacrylate imparts better heat resistance than styrene but at higher cost.

In making styrenated alkyds, an oxidizing alkyd is prepared in the usual way and cooled to about 130°C in the reactor; then styrene and a free-radical initiator such as dibenzoyl peroxide [94-36-0] are added. The resulting free-radical chain process leads to a variety of reactions, including formation of low molecular weight homopolymer of styrene, grafting of polystyrene onto the alkyd, and dimerization of alkyd molecules. The reaction is generally carried out at ~130°C, which favors decomposition of benzoyl peroxide to form phenyl free radicals; phenyl radicals have a greater tendency to abstract hydrogen, which favors grafting. After the reaction is complete, the resin is diluted with solvent. Alkyds made with some maleic anhydride as one of the dibasic acids give a higher ratio of grafting. The ratio of alkyd to styrene can be varied over a wide range; commonly 50% alkyd and 50% styrene is used. The ratio of aromatic rings to aliphatic chains is greatly increased, and as a result, the T_g of styrenated alkyd films is higher and tack-free time is shorter. Styrenated alkyds give a "dry" film in 1 h or less versus 4–6 h for the counterpart nonstyrenated alkyd. However, the average functionality for oxidative cross-linking is reduced, not just by dilution with styrene, but also because the free-radical reactions involved in the styrenation consume some activated methylene groups. As a result, the time required to develop solvent resistance is longer than for the counterpart alkyd. The fast drying and low cost make styrenated alkyds very attractive for some applications, but in other cases, the longer time required for cross-linking is more critical, in which case styrenated alkyds are not appropriate.

Styrenated alkyd vehicles are often used for air dry primers. One must be careful to apply top coat almost immediately or not until after the film has had ample time to cross-link. During the intermediate time interval, application of top coat is likely to cause nonuniform swelling of the primer, leading to what is called *lifting* of the primer. The result of lifting is the development of wrinkled areas in the surface of the dried film. End users who are accustomed to using alkyd primers, which do not give a hard film until a significant degree of cross-linking has occurred, are particularly likely to encounter problems of lifting if they switch to styrenated alkyd primers.

Graft copolymers prepared from anhydride-functional acrylic resins and hydroxyamides of soybean–conjugated tall oil acids are another approach to making acrylic resins that undergo oxidative curing (35).

Silicone resins have exceptional exterior durability but are expensive. Silicone modification of alkyd resins improves their exterior curability. The earliest approach was simply to add a silicone resin to an alkyd resin in the reactor at the end of the alkyd cook. While some covalent bonds between silicone resin and alkyd might form, probably most of the silicone resin simply dissolves in the alkyd. Exterior durability of silicone-modified alkyd coatings is significantly better than unmodified alkyd coatings. The improvement in durability is roughly proportional to the amount of added silicone resin; 30% silicone resin is a common degree of modification. Further improvements in exterior durability are obtained by coreacting a silicone intermediate during synthesis of the alkyd. Such intermediates react readily with free hydroxyl groups of the alkyd resin. Silicone resins designed for this purpose may contain higher alkyl, as well as methyl and phenyl, groups to improve compatibility. Alkyd coatings modified with high-phenyl silicone resins are reported to have greater thermoplasticity, faster air drying, and higher solubility than high methyl silicone-modified alkyds. These differences result from the higher rigidity of the aromatic rings, which leads to a “solid” film at an earlier stage of cross-linking. Less cross-linking in the phenylsilicone-modified coatings makes them more thermoplastic and soluble. Since IPA based alkyd resins have better exterior durability than PA alkyds, they are generally used as the alkyd component. Silicone-modified alkyds are used mainly in outdoor air dry coatings for which application is expensive (eg, in a topcoat for steel petroleum storage tanks).

Phenolic-modified alkyds are made by heating the alkyd with a low molecular weight resole phenolic resin based on *p*-alkylphenols. Presumably, the methylol groups on the phenols react with some of the unsaturated groups of the alkyd to form chroman structures. The resins give harder films with improved water and chemical resistance as compared to the unmodified alkyd.

Ceramer (organic–inorganic hybrid) coatings prepared with long oil linseed alkyds and titanium tetraisopropoxide gave films with excellent hardness, tensile strength, flexibility, and impact resistance (36).

Polyamide-modified alkyds are used as thixotropic agents to increase the low shear viscosity of alkyd resin based paints. Typically, $\sim$10% of a polyamide resin made from diamines such as ethylenediamine (1,2-ethanediamine) with dimer acids is reacted with an alkyd resin. High solids thixotropic alkyds based on polyamides made with aromatic diamines have been developed, which give superior performance in high solids alkyd coatings (37).

5. Nonoxidizing Alkyds

Certain low molecular weight short-medium and short oil alkyds are compatible with such polymers as nitrocellulose and thermoplastic polyacrylates. Therefore, such alkyds can be used as plasticizers for these polymers. They have the advantage over monomeric plasticizers (eg, dibutyl or dioctyl phthalate) in that they do not volatilize appreciably when films are baked. It is generally not desirable to use oxidizing alkyds, which would cross-link and lead to embrittlement of the films, especially on exterior exposure. Therefore, nondrying oil fatty acids (or oils) are used in the preparation of alkyds for such applications. For exterior acrylic lacquers, pelargonic acid (nonanoic acid) alkyds combine excellent resistance to photodegradation with good compatibility with the thermoplastic acrylic resins. An interesting sidelight on terminology is that these pelargonic alkyds have been called polyesters rather than alkyds because the word polyester connotes higher quality than the word alkyd. Castor oil derived alkyds are particularly appropriate for nitrocellulose lacquers for interior applications, since the hydroxyl groups on the ricinoleic acid (12-hydroxy-(*Z*)-9-octadecenoic acid [141-22-0] promote compatibility.

All alkyds, particularly short-medium oil and short oil alkyds, are made with a large excess of hydroxyl groups to avoid gelation. These hydroxyl groups can be cross-linked with MF resins or with polyisocyanates. In some cases, relatively small amounts of MF resin are used to supplement the cross-linking during baking of medium oil oxidizing alkyds. To achieve compatibility, butylated MF resins are used. Such coatings provide somewhat better durability and faster curing than alkyd resins alone, with little increase in cost. The important advantage of relative freedom from film defects common to alkyd coatings can be retained. However, the high levels of unsaturation remaining in the cured films reduce resistance to discoloration on overbake and exterior exposure and cause loss of gloss and embrittlement on exterior exposure. These difficulties can be reduced by using nondrying oils with minimal levels of unsaturated fatty acids. Coconut oil has been widely used; its performance can be further enhanced by hydrogenation of the small amount of unsaturated acids present in it.

Since isophthalic (IPA) esters are more stable to hydrolysis in the pH range of 4–8 than phthalate esters, the highest performance exterior alkyd-MF enamels use nonoxidizing IPA alkyds. Exterior durability of such coatings is satisfactory for automobile topcoats with opaque pigmentation. The films have an appearance of greater “depth” than acrylic-MF coatings. The films are perceived to be thicker than films of acrylic-MF coatings of comparable thickness and pigmentation. However, for many applications, alkyd-MF coatings have been replaced with acrylic-MF or polyester-MF coatings to improve the overall balance of film properties.

6. Synthesis of Alkyd Resins

Various synthetic procedures, each with many variables, are used to produce alkyd resins. The general reference and (38) and (39) provide useful reviews of manufacturing procedures. Alkyds can be made directly from oils or by using free fatty acids as raw materials.

6.1. Synthesis from Oils or Fatty Acids.

Monoglyceride Process. In the case of glycerol alkyds, it would be absurd to first saponify an oil to obtain fatty acids and glycerol, and then reesterify the same groups in a different combination. Rather, the oil is first reacted with sufficient glycerol to give the total desired glycerol content, including the glycerol in the oil. Since PA is not soluble in the oil, but is soluble in the glycerol, transesterification of oil with glycerol must be carried out as a separate step before the PA is added; otherwise, glyceryl phthalate gel particles would form early in the process. This two-stage procedure is often called the monoglyceride process. The transesterification reaction is run at 230–250°C in the presence of a catalyst; many catalysts have been used. Before the strict regulation of lead in coatings, litharge (PbO) was widely used; the residual transesterification catalyst also acted as a drier. Examples of catalysts now used in the United States are tetraisopropyl titanate, lithium hydroxide, and lithium ricinoleate. The reaction is run under an inert atmosphere such as CO_2 or N_2 to minimize discoloration and dimerization of drying oils.

While the process is called the monoglyceride process, the transesterification reaction actually results in a mixture of unreacted glycerol, monoglycerides, diglycerides, and unconverted drying oil. The composition depends on the ratio of glycerol to oil and on catalyst, time, and temperature. In general, the reaction is not taken to equilibrium. At some relatively arbitrary point, the PA is added, beginning the second stage. The viscosity and properties of the alkyd can be affected by the extent of reaction before the PA addition. While many tests have been devised to evaluate the extent of transesterification, none is very general because the starting ratio of glycerol to oil varies over a considerable range, depending on the oil length of the alkyd being made. (In calculating the mole ratio of dibasic acid to polyol, the glycerol already esterified in the oil must also be counted.) A useful empirical test is to follow the solubility of molten PA in the reaction mixture. This test has the advantage that it is directly related to a major requirement that must be met. In the first stage, it is common to transesterify the oil with PE to obtain mixed partial esters. The second stage, esterification of the “monoglyceride” with PA, is carried out at a temperature of 220–255°C.

Fatty Acid Process. It is often desirable to base an alkyd on a polyol (eg, PE) other than glycerol. In this case, fatty acids must be used instead of oils, and the process can be performed in a single step with reduced time in the reactor. Any drying, semidrying, or nondrying oil can be saponified to yield fatty acids, but the cost of separating fatty acids from the reaction mixture increases the cost of the alkyd. A more economical alternative is to use TOFA, which have the advantage that they are produced as fatty acids. Tall oil fatty acid composition is fairly similar to that of soybean fatty acids. Specially refined tall oils with higher linoleic acid content are available, as are other grades that have been treated with alkaline catalysts to isomerize the double bonds partially to conjugated structures. Generally, when fatty acids are used, the polyol, fatty acids, and dibasic acid are all added at the start of the reaction, and the esterification of both aliphatic and aromatic acids is carried out simultaneously in the range of 220–255°C.

6.2. Process Variations. Esterification is a reversible reaction; therefore, an important factor affecting the rate of esterification is the rate of removal of water from the reactor. Most alkyds are produced using a reflux solvent, such as xylene, to promote the removal of water by azeotroping. Since the reaction is run at a temperature far above the boiling point of xylene, $<5\%$ of xylene is used. The amount is dependent on the reactor and is set empirically such that there is enough to reflux vigorously, but not so much as to cause flooding of the condenser. Some of the xylene is distilled off along with the water; water is separated and xylene is returned to the reactor. The presence of solvent is desirable for other reasons: vapor serves as an inert atmosphere, reducing the amount of inert gas needed, and the solvent serves to avoid accumulation of sublimed solid monomers, mainly PA, in the reflux condenser.

Reaction time is affected by reaction temperature. Higher temperatures obviously accelerate the reaction. If the reaction is carried too far, there is a major risk of gelation. There are economic advantages to short reaction times. Operating costs are reduced, and the shorter times permit more batches of alkyd to be produced in a year, increasing capacity without capital investment in more reactors. Therefore, it is desirable to operate at as high a temperature as possible without risking gelation.

A critical aspect of alkyd synthesis is deciding when the reaction is completed. Disappearance of carboxylic acid is followed by titration, and increase in molecular weight is followed by viscosity. Determination of acid number and viscosity both take some time. Meanwhile, in the reactor, the reaction is continuing. After it is decided that the extent of reaction is sufficient, the reaction mixture must be “dropped” into a larger tank containing solvent. When a 40,000-L batch of alkyd is being made, a significant time is required to get the resin out of the reactor into the reducing tank; meanwhile, the reaction is continuing. The decision to start dropping the batch must be made so that the acid number and viscosity of the batch will be right after the continuing reaction that occurs between the time of sampling, determination of acid number and viscosity, and discharging of the reactor. The time for these determinations becomes the rate-controlling step in production. If they can be done rapidly enough, the reaction can be carried out at 240°C or even higher without overshooting the target acid number and viscosity. On the other hand, if the control tests are done slowly, it may be necessary to run the reaction at only 220°C, which may require 2 h or more of additional reaction time. Automatic titration instruments permit rapid determination of acid number, so the usual limit on time required is viscosity determination. While attempts have been made to use viscosity of the resin at reaction temperature to monitor change in molecular weight, the dependence of viscosity on molecular weight at that high temperature is not sensitive enough to be very useful. The viscosity must be determined on a solution at some lower standard temperature. Since viscosity depends strongly on solution concentration and temperature, these variables must be carefully controlled.

In alkyd production, viscosity is commonly determined using Gardner bubble tubes. The cook is continued until the viscosity is high enough so that by the time the resin batch is dropped into the solvent and the batch cooled, its viscosity will be what is called for in the specification. This means starting to discharge the reactor when the test sample is at some lower viscosity. It is not possible to generalize how large this difference should be; it depends on the specific alkyd composition, the temperature at which the reaction is being run, the time required to do the determination, the time required to empty the reactor, and so on. Viscosities can be determined more rapidly using a cone and plate viscometer than with bubble tubes; the very small sample required for a cone and plate viscometer can be cooled and equilibrated at the measurement temperature more quickly.

Many variables affect the acid number and viscosity of alkyds. One is the ratio of reactants: The closer the ratio of moles of dibasic acid to polyol approaches 1, the higher the molecular weight of the backbone of the resin, but also the greater the likelihood of gelation. A useful rule of thumb for a starting point is to use a mole ratio of 0.95. The final ratio is determined by adjustments such that the combination of acid number and solution viscosity come out at the desired levels. The greater the ratio of hydroxyl groups to carboxylic acid groups, the faster the acid groups are reduced to a low level. The degree of completion of the reaction is an important factor controlling the viscosity, as well as the acid number. It is usually desirable to have a low acid number, typically in the range of 5–10.

The composition of the fatty acids is a major factor affecting the viscosity, and compositions of an oil or grade of TOFA can be expected to vary somewhat from lot to lot. Dimerization and oligomerization of the unsaturated fatty acids occur in the same temperature range at which the esterification is carried out. Fatty acids with conjugated double bonds dimerize more rapidly than those with nonconjugated bonds, and dimerization rates increase with the level of unsaturation. At the same ratio of phthalic to polyol to fatty acids, alkyds of the same acid number and solution concentration will increase in viscosity in the order soybean < linseed < tung.

Some volatilization of polyol, PA, and fatty acids out of the reactor will occur depending on the design of the reactor, the rate of reflux of the azeotroping solvent, the rate of inert gas flow, and the reaction temperature, among other variables; the amount and ratio of these losses affect the viscosity at the standard acid number. The exact ratio of reactants must be established in the reactor that is actually used for synthesis. Since gelation can occur if the ratio of dibasic acid to polyol is too high, it is better not to put all the PA into the reactor in the beginning. If the viscosity is too low when the acid number is getting down near the standard, more PA can easily be added. The amount of PA held back can be reduced as experience is gained cooking a particular alkyd in a particular reactor.

Side reactions can affect the viscosity–acid number relationship. Glycerol and other polyols form ethers to some degree during the reaction. Glycerol can also form acrolein by successive dehydrations. When these reactions occur, the mole ratio of dibasic acid to polyol increases and the number of hydroxyl groups decreases; therefore, at the same acid number, the molecular weight will be higher. Excessively high viscosity and even gelation can result. Ether formation is catalyzed by strong protonic acids; therefore, it is desirable to avoid them as catalysts for the esterification. Monobutyltin oxide has been used as an esterification catalyst; presumably, it does not significantly catalyze ether formation. As noted earlier, PE and TMP seem less vulnerable than glycerol to undesirable side reactions such as ether formation, and glycerol is the only polyol that can decompose to form acrolein. A hydroxyl group on one end of a growing polyester chain can react with a carboxylic acid group on another end of the same molecule, leading to ring formation. Transesterification of chain linkages can have the same result. Since cyclization reactions reduce chain length, their net effect is to reduce viscosity.

Many alkyd resins have broad, uneven molecular weight distributions. It has been shown that even modest changes in reaction conditions can cause large differences in molecular weight distribution, which can have significant effects on final film properties (40). In many alkyds, very small gel particles (microgels) are formed. It has been shown that these microgels play an important role in giving greater strength properties to final films (40). Process changes that may make the alkyd more uniform may be undesirable. For example, allowing glycerolysis to approach equilibrium before addition of PA and using transesterification catalysts in the final stages of esterification both favor narrower molecular weight distributions and lower viscosities, but films made from the more uniform alkyds may exhibit inferior mechanical properties.

7. Urethane Derivatives

Uralkyds are also called *urethane alkyds* or *urethane oils*. They are alkyd resins in which a diisocyanate, usually 2,4(6)-toluene diisocyanate [584-84-9] (TDI) or bis(4-isocyanatophenyl)methane (MDI), has fully or partly replaced the PA usually used in the preparation of alkyds. One transesterifies a drying oil with a polyol such as glycerol or PE to make a "monoglyceride" and reacts it with some PA (if desired) and then with somewhat less diisocyanate than the equivalent amount of N=C=O based on the free OH content. To assure that no N=C=O groups remain unreacted, methanol is added at the end of the process. Just like alkyds, uralkyds dry faster than the drying oil from which they were made, since they have a higher average functionality (more activated diallylic groups per average molecule). The rigidity of the aromatic rings also speeds up the drying by increasing the T_g of the resin.

Two principal advantages of uralkyd over alkyd coatings are superior abrasion resistance and resistance to hydrolysis. Disadvantages are inferior color retention (when aromatic isocyanates used) of the films, higher viscosity of resin solutions at the same percent solids, and higher cost. Uralkyds made with aliphatic diisocyanates have better color retention, but are more expensive and have lower T_g. The largest use of uralkyds is in architectural coatings. Many so-called varnishes sold to the consumer today are based on uralkyds; they are not really varnishes in the original sense of the word. They are used as transparent coatings for furniture, woodwork, and floors: applications in which good abrasion resistance is important. Since they are generally made with aromatic isocyanates, they tend to turn yellow and then light brown with age; yellowing is acceptable in clear varnishes, but would be a substantial drawback in light colored pigmented paints.

Water-reducible polyunsaturated acid substituted aqueous polyurethane dispersions are also being used (41). They can be made by reacting an diisocyanate with a polyol, monoglyceride of a drying oil, and dimethylolpropionic acid. The carboxylic acid groups are neutralized with a tertiary amine and dispersed in water. If aliphatic isocyanates are used, good color retention can be obtained. They are much more resistant to hydrolysis than conventional alkyd resins. Films also have excellent abrasion resistance. Cost can be reduced by blending in 10–20% of acrylic latex.

8. Epoxy Esters

Bisphenol A (BPA) [4,4′-(1-methylethylidene)bisphenol] [80-05-7] epoxy resins can be converted to what are commonly called *epoxy esters* by reacting with fatty acids. Drying or semidrying oil fatty acids are used so that the products cross-link by autoxidation. The epoxy groups undergo a ring-opening reaction with carboxylic acids to generate an ester and a hydroxyl group. These hydroxyl groups, as well as the hydroxyl groups originally present on the epoxy resin, can esterify with fatty acids. They are generally made by starting with a low molecular weight epoxy resin (ie, the standard liquid resin, $n = 0.13$) and extending with BPA by the advancement process to the desired molecular weight. Off-specification epoxy resin is often used to reduce cost. The fatty acids are added to the molten, hot resin, and the esterification reaction is continued until the acid number is low, usually <7 mg of KOH/g of resin. In the esterification reaction with fatty acids, the average number of sites for reaction is the n value, corresponding to the number of hydroxyl groups on the resin, plus twice the number of epoxy groups. The esterification is carried out at high temperatures (220–240°C). The rate of esterification slows as the concentration of hydroxyl groups diminishes, and side reactions occur, especially dimerization of the drying oil fatty acids (or their esters). It is not practical to esterify more than ~90% of the potential hydroxyl groups, including those from ring opening the epoxy groups. The lower useful limit of the extent of esterification is ~50%. This is required to ensure sufficient fatty acid groups for oxidative cross-linking.

Tall oil fatty acids are commonly used because of their low cost. Linseed fatty acids give faster cross-linking coatings because of higher average functionality. However, their viscosity is higher because of the greater extent of dimerization during esterification, and their cost is higher. For still faster cross-linking, part of the linseed fatty acids can be replaced with tung fatty acids, but the viscosity and cost are still higher. The color of epoxy esters from linseed and linseed–tung fatty acids is darker than the tall oil esters. Dehydrated castor oil fatty acids give faster curing epoxy esters for baked coatings. The rate of formation of a dry film from epoxy esters depends on two factors: the average number of diallylic groups $\bar{f}_n$ and the ratio of aromatic rings to long aliphatic chains. The $\bar{f}_n$ can be maximized by using higher molecular weight BPA epoxy resin and by using enough fatty acid to react with a large fraction of the epoxy and hydroxyl groups. The ratio of aromatic rings to fatty acids can be maximized by using high molecular weight epoxy resin and esterifying a smaller fraction of epoxy and hydroxyl groups.

Epoxy esters are used in coatings in which adhesion to metal is important. While the reasons are not completely understood, it is common for epoxy coatings, including epoxy esters, to have good adhesion to metals and to retain adhesion after exposure of the coated metal to high humidity, a critical factor in corrosion protection. A distinct advantage of epoxy esters over alkyd resins is their greater resistance to hydrolysis and saponification. The backbone of alkyds is held together with esters from PA and the polyol, whereas in epoxy esters, the backbone is held together with C–C and ether bonds. Of course, the fatty acids are bonded to the backbone with ester groups in both cases, but the fraction of polymer bonds in a dry film subject to hydrolysis is substantially lower in the case of epoxy esters. On the other hand, exterior durability of epoxy ester coatings is poor, as is the case with all films made with BPA epoxy resins. As a result of these advantages and disadvantages, the major uses for epoxy resins are in primers for metal and in can coatings, such as for crowns (bottle caps), in which the important requirements are adhesion and hydrolytic stability. In baking primers, it is sometimes desirable to supplement the cross-linking through oxidation by including a small amount of MF resin in the formulation to cross-link with part of the free hydroxyl groups on the epoxy ester.

Epoxy ester resins with good exterior durability (better than alkyds) can be prepared by reacting epoxy-functional acrylic copolymers (made with glycidyl methacrylate) with fatty acids. The product is an acrylic resin with multiple fatty acid ester side chains. By appropriate selection of acrylate ester comonomers and molecular weight, the T_g of the resin can be designed so that a tack-free film is obtained by solvent evaporation; then the coating cross-links by autoxidation. For an application like repainting an automobile at ambient temperatures, the cross-linking can proceed relatively slowly and need not be catalyzed by metal salt driers. The rate of cross-linking is slower without driers, but exterior durability is better.

Epoxy esters can also be made water reducible. The most widely used water-reducible epoxy esters have been made by reacting maleic anhydride with epoxy esters prepared from dehydrated castor oil fatty acids. Subsequent addition of a tertiary amine, such as 2-(dimethylamino)ethanol [108-01-0], in water results in ring opening of the anhydride to give amine salts. Like other water-reducible resins, these resins are not soluble in water but form a dispersion of resin aggregates swollen with water and solvent in an aqueous continuous phase. The hydrolytic stability of these epoxy esters is better than corresponding alkyds and sufficient for use in electrodeposition primers until anionic primers were replaced by cationic primers. Water-reducible epoxy esters are still used in spray applied baking primers and primer surfacers. They are also used in dip coating primers in which nonflammability is an advantage. Their performance equals that of solvent–soluble epoxy ester primers.

9. Uses

In 1997, the U.S. consumption of alkyds was ~310 metric tons (t) and projected use in 5 years is estimated to be 280–290 t (42). Coatings are the largest market with use in 1997 of $\sim$250 t (43). European consumption of alkyd coating resins in 1996 has been reported to be 360 t (43). Use of alkyds has been declining at $\sim$2%/year and is projected to decline further as they are replaced with resins with higher performance and lower volatile emissions. Higher solids alkyds have been replacing conventional solids alkyds. In 1997, $\sim$81,000 t with solids of 50–60% and 16,000 t of >60% were used in the United States, in comparison with 150,000 t of alkyds with <50% solids. 10,000 t of waterborne alkyds were used (42).

The principal advantages of alkyds are low cost, low toxicity, and low surface tension. The low surface tension permits wetting of most surfaces including oily steel. Also, the low surface tension minimizes application defects such as cratering. The principal limitations are generally poorer exterior durability and corrosion protection than alternative coating resins. While high solids and waterborne alkyd resins are manufactured, their properties are generally somewhat inferior to conventional solventborne alkyds.

The largest use for alkyds in coatings is in architectural paints, particularly in gloss enamels for application by contractors. Contractors tend to prefer alkyd enamels over latex enamels because coverage can be achieved with a single coat. Also alkyd paints can be applied at low temperatures whereas latex paints can only be applied at temperatures above $\sim$5°C. The do-it-yourself market is served primarily with latex paints because of ease of cleanup and lower odor. While initial gloss of alkyd enamels is higher than of latex enamels, the latex enamels exhibit far superior gloss retention especially in exterior applications. Alkyd primers provide better adhesion to chalky surfaces than most latex paints.

The largest uses of alkyds in industrial applications is in general industrial coatings for such applications as machinery and metal furniture. Significant amounts are used with UF resins in coatings for wood furniture. Alkyd resin–chlorinated rubber based coatings are used in traffic paints, but use is decreasing because of high VOC content. An approach to overcoming this problem is the use of solvent free alkyds in hot melt traffic paints (44). Some alkyds are still used in refinish paints for automobiles since they give high gloss coatings with a minimum of polishing. Soy alkyds are used in topcoats for complete refinishing of cheap old cars, where the primary requirement is for low cost. For intermediate performance and cost refinish enamels for painting whole cars, drying oil functional acrylic resins are still used. Higher grades of coatings are urethane coatings. Some nitrocellulose primers with nonoxidizing alkyd plasticizers and some alkyd underbody sealers are still used in the United States but will undoubtedly be phased out completely in the next few years. Alkyds are still fairly widely used for refinish coatings in some underdeveloped countries. An example of recent work in formulating refinish coatings is preparing an alkyd by reacting tris(hydroxyethyl)isocyanurate with drying oil fatty acids and formulating with trimethylolpropane trimethacrylate as a reactive diluent (45).

About 39,000 t of uralkyds were used in the United States in 1997 (42). The largest use for uralkyds is as the vehicle for so-called urethane varnishes for the do-it-yourself market. The abrasion resistance of such coatings is greatly superior to that obtained with conventional varnishes or alkyd resins. Epoxy esters give coatings with markedly superior corrosion protection as compared with alkyd resins while retaining the advantage of low surface tension. However, as with any BPA epoxy system, exterior durability is poor. They are used primarily in primers for steel and in flexible coatings such as for metal crowns. Maleated epoxy esters give primers with equivalent properties of solvent borne epoxy ester coatings and are widely used in formulating waterborne primers for steel.

Noncoatings applications include foundry core binders and printing inks, especially lithographic inks.

BIBLIOGRAPHY

"Alkyd Resins" in *ECT* 1st ed., Vol. 1, pp. 517–532, by W. Howlett Gardner, National Aniline Division, Allied Chemical & Dye Corporation; in *ECT* 2nd ed., Vol. 1, pp. 851–882, by Richard G. Mraz and Raymond P. Silver, Hercules Powder Company; in *ECT* 3rd ed., Vol. 2, pp. 18–48, by H. J. Lanson, Poly-Chem Resin Corporation; "Alkyd Resins" in *ECT* 4th ed., Vol. 2, pp. 53–85, by K. F. Lin Hercules Incorporated; "Alkyd Resins" in *ECT* (online), posting date: December 4, 2000, by K. F. Lin, Hercules Incorporated.

CITED PUBLICATIONS

1. Northwest and Montreal Sections of FSCT, *J. Coat. Technol.*, **67**(850) 19 (1995).
2. T. L. T. Robey and S. M. Rybicka, *Paint Research Station Technical Papers No. 217*, Vol. 13, No. 1, 1962, p. 2.
3. R. J. Blackinton, *J. Paint Technol.*, **39**(513) 606 (1967).
4. T. A. Misev, *Prog. Org. Coat.*, **21**, 79 (1992).
5. S. L. Kangas and F. N. Jones, *J. Coat. Technol.*, **59**(744) 89 (1987).
6. R. Bacaloglu and co-workers, *Angew. Makromol. Chem.*, **164**, 1 (1988).
7. R. Brown, H. Ashjian, and W. Levine, *Off. Digest*, **33**, 539 (1961).
8. *Tech. Bull. No. 524-5*, Velsicol Chemical Corp., Chicago Ill.
9. D. Ryer, *Paint Coat. Ind.*, **14**(1) 76 (1998).
10. R. W. Hein, *J. Coat. Technol.*, **71**(898) 21 (1999).
11. J. Mallegol, J. Lemaire, and J.-L. Gardette, *Prog. Org. Coat.*, **39**, 107 (2000).
12. S. L. Kangas and F. N. Jones, *J. Coat. Technol.*, **59**(744) 99 (1987).
13. U.S. Patent 2,577,770 (Dec. 11, 1951), P. Kass and Z. W. Wicks, Jr. (to Interchemical Corporation).
14. K. H. Zabel and co-workers, *Prog. Org. Coat.*, **35**, 255 (1999).
15. W. J. Muizebelt and co-workers, *Prog. Org. Coat.*, **40**, 121 (2000).
16. E. Levine, *Proc. Water-Borne Higher-Solids Coat. Symp.*, New Orleans, La., 1977, p. 155.
17. D. B. Larson and W. D. Emmons, *J. Coat. Technol.*, **55**(702) 49 (1983).
18. *Tech. Bull., Resimene AM-300 and AM-325*, Monsanto Chemical Co., (now Solutia, Inc.), January 1986.
19. U.S. Patent 4,293,461 (Oct. 6, 1981), W. F. Strazik, J. O. Santer, and J. R. LeBlanc (to Monsanto Company).
20. U.S. Patent 6,075,088 (June 13, 2000), J. Braeken, (to Fina Research, S. A.).
21. G. Osterberg, M. Hulden, B. Bergenstahl, and K. Holmberg, *Prog. Org. Coat.*, **24**, 281 (1994); G. Ostberg and B. Bergenstahl, *J. Coat. Technol.*, **68**(858), 39 (1996).
22. A. Hofland, in J. E. Glass, ed., *Technology for Waterborne Coatings*, American Chemical Society, Washington, D.C. 1997, p. 183.
23. E. Makarewicz, *Prog. Org. Coat.*, **28**, 125 (1996).
24. P. K. Weissenborn and A. Motiejauskaite, *Prog. Org. Coat.*, **40**, 253 (2000).
25. V. Verkholantsev, *Eur. Coat. J.*, (1–2) 120 (2000).

26. T. Nabuurs, R. A. Baijards, and A. L. Germna, *Prog. Org. Coat.*, **27**, 163 (1996).
27. J. W. Gooch, S. T. Wang, F. J. Schork, and G. W. Poehlein, *Proc. Waterborne, High Solids, Powder Coat. Symp.*, New Orleans, La., 1997, p. 366.
28. W. S. Sisson and R. J. Shah, *Proc. Waterborne, High Solids, Powder Coat. Symp.*, New Orleans, La., 2001, pp. 329–336.
29. E. M. S. Van Hamersfeld and co-workers, *Prog. Org. Coat.*, **35**, 235 (1999).
30. C. J. Bouboulis, *Proc. Water-Borne Higher-Solids Coat. Symp.*, New Orleans, La., 1982, p. 18.
31. B. Zuchert and H. Biemann, *Farg och Lack Scandinavia*, (2) 9 (1993); W. Weger, *Fitture e Vernici*, **B66**(9), 25 (1990).
32. U.S. Patent 5,004,779 (Apr. 2, 1991), H. Blum and co-workers, (to Bayer Aktiengesellschaft).
33. U.S. Patent 6,187,384 (Feb. 13, 2001), G. Wilke, D. Grapatin, and H.-P. Rink, (to BASF Coatings A. G).
34. R. Hurley and F. Buona, *J. Coat. Technol.*, **54**(694), 55 (1982).
35. U.S. Patent 5,223,582 (June 29, 1993), H. Blum and L. Fleiter, (to Bayer Aktiengesellschaft).
36. R. A. Sailer and co-workers, *Prog. Org. Coat.*, **33**, 117 (1998).
37. P. J. Bakker and co-workers, *Water-borne High-Solids, Powder Coating Symposium*, New Orleans, La, 2001, pp. 439–453.
38. J. Kaska and F. Lesek, *Prog. Org. Coat.*, **19**, 283 (1991).
39. Anonymous, *The Chemistry and Processing of Alkyd Resins*, Monsanto Chemical Co. (now Solutia, Inc.), 1962.
40. J. Kumanotani, H. Hironori, and H. Masuda, *Adv. Org. Coat. Sci. Tech. Ser.*, **6**, 35 (1984).
41. W. Liu, S. Wang, and T. Rende, *Western Coat. Symp.*, Reno, Nv. (1999).
42. Skeist Report VI, Skeist Inc., Whippany, NJ, 1998, pp. 805–826.
43. E. Connolly, E. Anderson, and Y. Sakuma, *Alkyd/Polyester Surface Coatings*, SRI International, Pasadena, Calif., 1998.
44. U.S. Patent 6,011,085 (Jan. 4, 2000), B. A. Maxwell, M. A. Weaver, G. R. Robe, and R. A. Miller, (to Eastman Chemical Co.).
45. U.S. Patent 6,083,312 (July 4, 2000), G. L. Bajc, (to BASF Corporation).
46. R. A. Sailer and M. D. Soucek, *Prog. Org. Coat.*, **33**, 36 (1998).

GENERAL REFERENCE

T. C. Patton, *Alkyd Resin Technology*, John Wiley & Sons, New York, 1962.

Zeno W. Wicks, Jr.
Consultant