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REVIEW

Waterborne Coatings Based on Renewable Oil Resources: an Overview

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Abstract Polyurethane dispersions are gaining in importance due to their environmentally friendly coating system, versatile coating properties and ease of application. An enormous amount of research is focused on waterborne coatings such as waterborne alkyds, water-reducible alkyds, alkyd–acrylic hybrids, oil modified polyurethane dispersions and their composite latexes. This review gives a comprehensive compilation of recent studies on the synthesis and applications of waterborne coatings. The article specifically covers all of the research work carried out in the field of waterborne alkyd–acrylics, polyurethane dispersions and their hybrid latexes systematically.

Keywords Alkyd acrylic dispersion · Polyurethane dispersion · Waterborne alkyd · Waterborne coatings water reducible alkyd

Abbreviations

AIBN	Azobisisobutyronitrile
AMP95	2-Amino-2-methyl-1-propanol containing 5% water
CPUA	Castor oil modified polyurethane-acrylate
DCO	Dehydrated castor oil
DMAE	Dimethylethanolamine
KPS	Potassium persulfate
GES	(2,3-Dihydroxypropoxy)-4-oxobut-2-enoic acid
GPC	Gel permeation chromatography
HAP	Hazardous air pollutants
HEMA	Hydroxylethylmethacrylate
H12MDI	Hydrogenated diphenylmethane diisocyanate
HMMM	Hexmethoxymelamine
HMDI	Hexamethylene diisocyanate
MA	Maleic anhydride
MCO	Modified castor oil
SBR	Styrene butadiene latexes
PA	Phthalic anhydride
PBA	Polybutylacrylate
PBTDI	Poly(1,4-butanediol)
PPG	Polypropylene glycol (PPG)
PEG	Polyethylene glycol
PEA	Polyethylacrylate
PMDA	Pyromellitic dianhydride
PTMG	Polytetramethylene glycol
PUD	Polyurethane dispersions
PUA	Polyurethane-polyacrylate
NMP	*N*-methylpyrrolidone
NPG	Neopentylglycol
TEA	Triethylamine
TPGDA	Tripropylene glycol dimethacrylate
TMA	Trimellitic anhydride
TMP	Trimethylolpropane
TMPTA	Trimethylolpropane triacrylate
TDI	Toluene 2,4-diisocyanate
MMA	Methyl methacrylate
VT	Vinyltoluene
VOC	Volatile organic components

Introduction

Several attempts have been made from scientific and technological viewpoints to develop waterborne coating systems that are environmentally friendly and easily diluted with

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water. These waterborne coatings using the evaporation of water should exhibit almost similar performance properties as solvent borne systems. In this respect, polyurethane dispersions [1, 2] (PUD) are a recent class of binders that are easily diluted with water and air-dried, stoved or crosslinked with hexmethoxymelamine (HMMM) resin to produce volatile organic components (VOC) compliant coatings. PUD processed from renewable and cheaper natural oil resources are gaining more importance due to cost advantages. This article summarizes the research work carried out in the field of PUD based on renewable oil resources.

Previously, PUD gained importance because of their use in VOC compliant coatings; however, in recent years, only small amounts of research work or literature that compiles all the developments in the field of waterborne coatings have been available. Hence, we undertook a systematic compilation of all the research work carried out in the field of alkyd acrylic and polyurethane dispersions under major headings, such as (1) synthesis and (2) application of the coating systems. The development of high quality coatings with zero or low VOC is one of the most difficult challenges facing the coating industries today. Research on waterborne coatings has been stimulated by economic and ecological pressures. The higher costs of solvents as well as federal regulations on solvent emissions are forcing several industries to use waterborne polymer coating systems.

Most of the waterborne coatings used today contain one of the following four types of polymers: (a) water-reducible binders, (b) water soluble binders, (c) emulsion polymers and (d) polyurethane dispersions.

(a) Water-reducible binders Alkyd resins with high acid values upon neutralization of their carboxylic acids with amines are used as water reducible binders. These water reducible alkyd resin films dry slowly and remain tacky due to the presence of amines. The drawbacks of slow drying and tackiness can be overcome by curing with melamine formaldehyde or urea formaldehyde while baking at 150 °C for 2 h [2].

(b) Water soluble binders Water solubility is achieved by introducing non-ionic groups, such as polyether or hydroxyl groups, on the polymer backbone. Dried films were found to be water sensitive and poor in adhesion. Water resistance and the adhesion of water soluble binders can be improved by controlling the hydrophilic content, e.g., the ethylene oxide (EO) content, or by crosslinking with melamine resins.

(c) Emulsion polymers An emulsion polymer system contains four components: water, water insoluble monomers, emulsifiers and initiators. These are the major class of binders that are commercially available and used in water-based paints, mainly distemper and high-gloss acrylic emulsion paints.

(d) Polyurethane dispersions (PUD) are an increasingly important and very versatile class of binders used in inks, adhesives and various protective or decorative coatings. The technical quality of PUD has improved dramatically during the past decade as a result of many innovations in basic chemistry, dispersion technology, formulations and application techniques, which have been fueled by consumer awareness and legislation to reduce VOC levels. PUD are produced by employing conventional surfactants under high speed shear mixing. Such procedures result in large particle size dispersions with poor colloidal stability. The most elegant approach to synthesize PUD is by the introduction of monomers, which contain inbuilt dispersing functional groups in the polymer backbone. The functional groups may be cationic, non-ionic or anionic in nature. There are several synthetic processes used for the preparation of high molecular weight polyurethane dispersions, as follows: (1) the acetone process (solution process), (2) the prepolymer mixing process, (3) the hot melt process and (4) the ketamine/ketazinine process. However, only the acetone and pre-polymer mixing processes are widely used in industries [3, 4]. The schematic of PUD synthesis is given in Fig. 1. The synthesis involves formation of polyurethane prepolymer followed by neutralization, dispersion in water and chain extension to obtain PUD [5].

Historical Development of Waterborne Coatings

Alkyds were first synthesized in 1901 by J. Smith and later patented by General Electric (GE) in 1914. The first commercialized alkyd paint was Glyptal, made by GE in 1926. Alkyd resins have been used as a major binder since the start of the nineteenth century due to their excellent autooxidative, chemical and mechanical properties. The special class of polyesters are derived from naturally occurring oils, including soybean, sunflower and linseed oils, polyols and dibasic acids as shown in Fig. 2. Polyvinyl acetate was the first important vinyl resin, available by about 1912. Air drying and baking enamel were introduced in the years 1928–1930. Automotive finishes were made based on non-drying oils that were baked and that exhibited excellent coating properties. Aldehyde-treated polyvinyl acetate resins were used as varnish; copolymers of vinyl acetate and vinyl chloride were also used for coatings. Waterborne coatings were introduced in the late 1950s with the development of polyvinyl acetate dispersions. Later on, styrene butadiene latexes (SBR) were introduced; these found applications in paper and paper boards. SBR were used in paint as binders in those days, but they did not gain much importance due to their high yellowing tendency and low UV resistance. Acrylic resins were first used in 1935 for surface coatings; since then, hundreds of different acrylic resins have been made commercially available. In 1945, urea formaldehyde resins were used as crosslinking

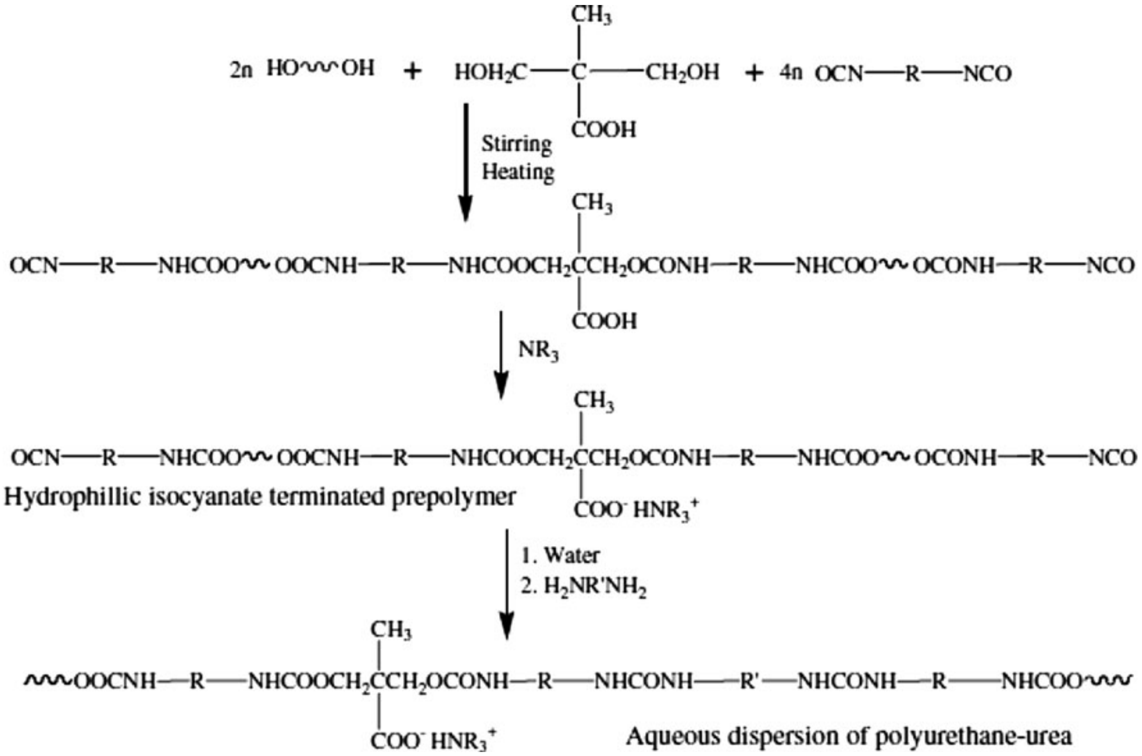
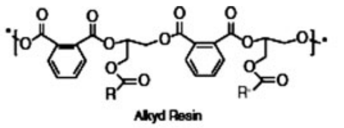


Fig. 1 Schematic of aqueous polyurethane dispersion

agents with other resins. Epoxy resins were introduced in 1947 on a commercial scale. They are available as two pack systems and are mainly used in marine applications such as ships and storage tanks for food, oil and chemicals due to their high performance coating. Polyurethane resins were introduced by Bayer in the 1980s based on isocyanates and hydroxyl functional polyols that found use in a wide range of applications.

Stringent VOC content rules for architectural and industrial maintenance coatings have recently been enacted by government, regional and state regulatory agencies. These new rules effectively ban the use of solvent-borne alkyd resins, despite their excellent properties. Current VOC-exempted solvents such as acetone and methyl acetate are expected to find limited use in alkyd-based coatings due to their odor, cost, and flammability. Traditional alkyd coatings contain mineral spirits or aromatic solvents such as xylene or toluene. However, stringent VOC regulations have driven producers away from xylene and toluene, leaving mineral spirits as the main solvent for future alkyd coatings. To design higher performance surface coatings, formulators must choose from a multitude of polymer processes. The polymers used in the paint hold the coating cohesively (internally) together and adhere (externally) to the substrate to which they are applied. The proper selection of polymers can be the most important factor in determining their physical and chemical properties. Each polymer typically has some merits and some demerits. It is necessary to combine the polymers and explore the blend of properties; hence, polymer manufacturers have developed a hybrid polymer technology to combine the advantages of one polymer species with another, offsetting their shortcomings in a synergistic manner to create a higher performance class of polymers. The most common acrylic hybrids with alkyd modifications are physical blends of hard acrylic copolymers with short or medium oil alkyd resins for general industrial spray coating. The acrylic system provides quick drying, low tackiness, toughness and durability, whereas the alkyd system provides self-priming and air drying to enhance the solvent and chemical resistance compared to thermoplastic binders. Current versions



Where R and R' are different combinations of these acids depending on oil choice

Stearic acid	$CH_3(CH_2)_{16}COOH$
Palmitic acid	$CH_3(CH_2)_{14}COOH$
Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (9c)
Linoleic acid	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (9c 12c)
Linolenic acid	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$ (9c 12c 15c)

Fig. 2 General structure of Alkyd resin

of this technology appear to suffer from the unfortunate combination of limited compatibility and extended hard-dry times. However, improved drying has been claimed as a modification in which secondary hydroxyl groups are present in the ester linkages of the alkyds. Today, almost all the solvent-borne systems have been transformed in one way or another into waterborne versions. Waterborne and high solids coatings [6, 7] are used in the furniture and automotive industries. A waterborne anticorrosive dip priming system of cathodic electrodeposition is extremely effective in protecting even the most inaccessible areas of vehicle bodies. However, water-based coatings synthesized from single polymers suffer from inferior performance properties, requiring the combination of two or more polymers to form hybrid systems. Hybrid systems in which more than two generic classes of polymers are combined or mixed physically or by chemical reaction for their dual coating properties have been widely explored in industries, e.g., urethane acrylics, epoxy acrylics, alkyd acrylics and polyurethane modified alkyd acrylic emulsions.

Waterborne Resins

The waterborne resins are of four types: (1) waterborne alkyds, (2) alkyd emulsions, (3) waterborne urethanes and (4) hybrid dispersions.

Waterborne Alkyds

Alkyd, polyesters, polyurethanes and epoxy resins are diluted with various solvents. These solvents are released into the environment, polluting the atmosphere [1]. The increase in the need to reduce the emission of volatile organic compounds (VOC) and hazardous air pollutants (HAP) has led to increased efforts to formulate a coating system with minimum VOC, or solvent-free and high-solid-content binders [2]. The coating industry recently started using different terminologies such as water-soluble resins, water-reducible binders and latexes. Water-borne coatings contain very low levels of organic solvents. The coatings cure in a similar manner as solvent-borne systems, i.e., either through oxidative or thermosetting (cross linking) reactions.

Synthesis of Water Soluble Maleinized Oils

A water-soluble polymer is a polymer that can be diluted with or without the assistance of co-solvents and a neutralizing agent to form a transparent solution. It has been known for many years that maleinized drying oils produce water-soluble coatings. In 1971, Balakrishna et al. treated dehydrated castor oil (DCO) or isomerized linseed and safflower oils with 5–12% maleic anhydride (MA). The resultant alkyd resin films exhibited good hardness, flexibility and water resistance [8]. Alkyd resins synthesized from monoglycerides using soybean oil, maleic anhydride (MA), phthalic anhydride (PA), trimellitic anhydride (TMA) and maleopimaric acid were cured using methylated melamine formaldehyde. The coatings based on TMA and maleopimaric acid crosslinked with melamine resin showed good results. [9] Similar results were reported by Shukla and coworkers [10] with DCO fatty acid. Kusefoglu studied the simultaneous copolymerization of bromine and acrylate to the double bonds of fatty acids in triglycerides. In the first part of the study, methyl oleate was bromoacrylated in the presence of acrylic acid and *N*-bromosuccinimide (NBS) as a model compound for application with the triglycerides. Next, soybean oil and high oleic sunflower oil were bromoacrylated by using the same procedure. The products were characterized by GC, IR, ^{1}H NMR, and ^{13}C NMR. The radical copolymerization of bromoacrylated soybean oil with styrene and the bromoacrylated sunflower oil–styrene copolymer were examined. The crosslinked network structure of the copolymers was examined by their swelling behavior in different solvents [11]. Vaszilcsin and coworkers [12] filed a patent on the process of malleated water soluble alkyd resins based on castor and linseed oils; however, Paar et al. [13] also synthesized water-dilutable malleated alkyd based on linseed oil and blended it with an acrylic dispersion (Mowilith LDM 6621) to produce a lacquer binder with an excellent gloss and shelf-life stability of more than 8 weeks. Water-based organic coatings are ecologically friendly materials and more economic than solvent-based coatings. Alkyd resins with high acid numbers neutralized with amines and alkyd emulsions were discussed by different authors [14–16]. Aigbodion et al. [17] used rubber seed oil in the production of alkyd emulsion. The oil was initially treated with different amounts of 2–20% of MA. Then, maleinized rubber seed oils were used to prepare water-soluble alkyd samples. In another set of experiments, rubber seed oil (RSO) was also modified with different amounts of maleic anhydride, and RSO alkyds (50% oil length) were modified to various extents by the incorporation of different amounts of maleic anhydride and fumaric acid [18]. All the resins were evaluated as water-reducible binders. Modification with maleic anhydride increased the acid and saponification values of RSO but reduced the iodine values. RSO modified with maleic anhydride exhibited lower amounts of volatile organic compounds (<20 g/L) than the corresponding RSO alkyds (34–87 g/L). The alkyd samples were superior to the modified RSO in terms of chemical resistance. Nakayama [19] explained that the resin-blend technique is a simple and useful method for improving paint properties. It is more important for waterborne paints in which the design of resins requires more sophisticated techniques. Combinations of special emulsions, microgels and water-soluble resins have yielded excellent aqueous binders for various coatings. The concept of a resin blend in our research is based on (1) the blending of resins to reinforce their advantages and (2) the blending of minor resin components to compensate for the weakness of the major resin.

Modification of Oils and Alkyd Resins with Functional Monomers

Alkyd resins can also be modified with vinyl and/or acrylic resins to obtain a combination of the properties of both the resins. The wetting and flexibility of alkyd resin can be preferentially combined with hardness, chemical and weather resistance properties associated with vinyl or acrylic resins.

Modification can be carried out in the following three different ways: (a) mechanical blending, (b) copolymerization through the unsaturated fatty acid chain and (c) condensation reactions involving the functional groups present in each of the individual resins. In the 1940s, attempts were made to polymerize the oils by treating conjugated and non-conjugated fatty acids and oils with different chemicals. At low temperatures, non-conjugated, unsaturated fatty acids react with styrene radicals by the free radical transfer mechanism. Mono- and disubstituted unsaturated fatty acids are formed at higher temperatures by the addition reaction. At low temperatures, conjugated fatty acids react readily with styrene to give Diels–Alder adducts, whereas at higher temperatures, mixed polymerization products are more likely. To minimize the formation of incompatible polystyrene, the concentration of styrene is kept low by the stepwise addition of the same [20]. The reactions at 60 °C of styrene with olefins at a total pressure of 1 atm and the addition of either *tert*-butyl or α-tetralyl hydroperoxide were examined by Mayo et al. *tert*-Butyl hydroperoxide has a half-life of only about 100 min under these conditions. Several lines of evidence indicate that the hydroperoxide reacts mostly by chain transfer with the peroxy radicals by oxidizing styrene to produce styrene polyperoxide as shown in Fig. 3. Both chain initiation and peroxide disappearance are initially autocatalytic; the oxidation later becomes slower, but does not stop, as the original free hydroperoxide is exhausted. Formaldehyde forms addition compounds with hydroperoxides and complicates analytical problems and the interpretation of the results [21]. Equal weights of styrene and methyl esters of different acids such as stearic, oleic, linoleic, *trans*-10,12-octadecadienoic, conjugated linoleic, and linolenic were mixed and polymerized using benzoyl peroxide as the initiator by Tolberg and co-workers. The polymerization rate, molecular weight and compounds of the polymer were determined. The numbers of fatty esters per polymer mol were respectively 0.64, 1.7, 3.0, 14.5, 12.1, and 1.1. The data indicate that styrene does copolymerize with fatty esters that have conjugated unsaturation and non-conjugated fatty esters; however, both saturated and monounsaturated esters behave in a neutral fashion, serving as solvents for the monomers and polymers, with only small amounts of the esters being included in the polymer [22]. Certain catalysts are effectively used for the isomerization of vegetable oils to conjugated forms. Figures 4 and 5 show the structure and reaction of a cobalt catalyst. These catalysts include active surface materials such as diatomaceous earth and carbon black, nickel on kieselguhr, and nickel–carbon black. Because these catalysts are neutral, they do not split ester linkages, and no further chemical treatment of the isomerized oil is required. The nickel–carbon catalyst is the

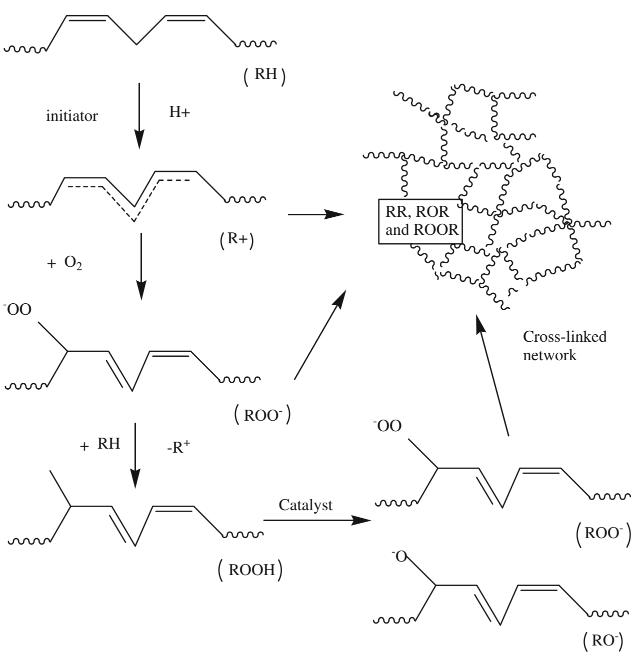


Fig. 3 The catalyst decomposes hydroperoxides to form alkoxyl and peroxyl radicals. Termination reactions create the crosslinked network

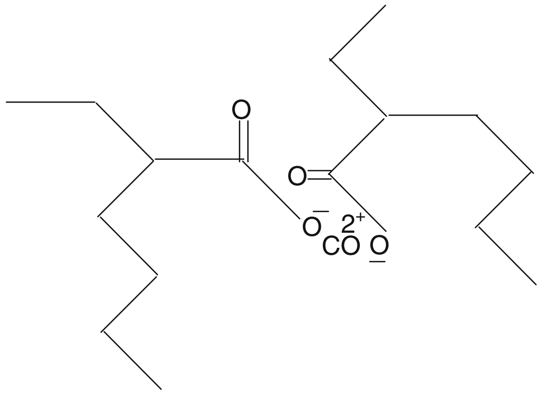


Fig. 4 The structure of the cobalt drier

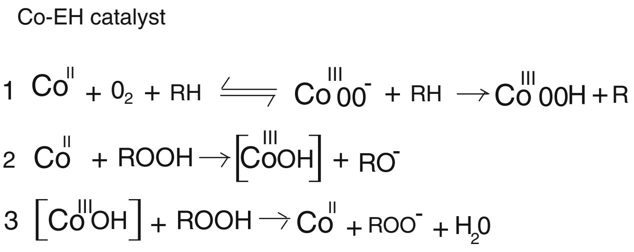


Fig. 5 The reaction of the cobalt catalyst

most effective, particularly when it is prepared by the reduction of a suitable nickel salt. When 6–8% of reduced catalyst was heated for 6 h at 170 °C with alkali-refined soybean or linseed oil, 30–45% conjugation was obtained. The following total % conjugation resulted when nickel–carbon catalysts were used with typical oils, and their neutral derivatives are methyl esters of soybean fat acids (40.9%), methyl esters of linseed fat acids (45.9%), methyl esters of dehydrated castor oil (43.8%), methyl linoleate (64.0%), alkali-refined soybean oil (32.1%), alkali-refined linseed oil (33.1%), and dehydrated castor oil (38.8%). A sample of catalyst can be used to isomerize 5–10 batches of oil before its activity is lost. The treated oils dry in substantially less time than the untreated oils, and the water and alkali resistances of their films are appreciably improved [23]. The addition of phenol to fatty acid in the presence of sulfur dioxide and sulfuric acid produces a viscous product. Considerable heat is evolved when tung oil reacts with phenol in the presence of hydrochloric acid, sulfur dioxide or sulfuric acid to form a viscous product. The increase in viscosity may be due to the reaction of the phenol-conjugated double bonds of tung oil [24]. In the mechanical blending of acrylic monomers with unsaturated fatty acids, compatibility was a major problem between these two polymers. However, copolymerization of acrylic monomers with unsaturated fatty acids resulted in stable polymers with a blend of beneficial properties of both of the polymers. The synthesis of acrylate modified alkyd resins was reported by D.H. Solomon and co-workers in 1962 [25]. Vinyl- and acrylic-modified non-drying oil alkyd resins cannot be prepared by the usual methods. Non-drying oil alkyd resins can be esterified with epoxide groups in an unnamed addition polymer. Some of the batches gelled, however, by using a monoglyceride process followed by reaction with polyols and polybasic acid, which resulted in resins with promising properties that could be used as air-drying or stoving enamels [26]. To blend the advantages and avoid the disadvantages of thermoplastic acrylic lacquers and thermosetting alkyd enamel automotive finishes, alkyd resins polymerized by monoglyceride processes were grafted with acrylate monomers by Solomon et al. Alkyds with 30–40% acrylic content were capable of further modifications. Paints made with these media had suitable properties for automotive finishes [27]. Roller-coating enamels based on acrylics have better properties and cost more than alkyds. Cost reduction by direct blends was successful but revealed a slight gloss-reducing incompatibility. This was overcome by the use of the monoglyceride process, which yielded cheaper but very satisfactory acrylated alkyds. Fletcher et al. [28] suggested a method involving a reaction between a carboxylic acid group containing acrylic copolymer and a monoglyceride followed by glycol and dibasic acid to achieve further condensation. Methacrylated alkyd based on a 36.5:63.5 mol% of adipic acid: phthalic anhydride exhibited performance properties similar to those of an epoxy ester except for chip resistance. Optimal conditions for the oxidation of refined sunflower oil and its copolymerization with styrene were studied. Oxidized samples of refined sunflower oil were copolymerized with styrene in various ratios in xylene solutions. Only highly viscous resins were produced at the temperature range of 80–100 °C. Oxidation of refined sunflower oil gave homogeneous copolymers, which could form transparent films [29]. Forty percent oil-length coconut oil-based alkyd resins containing 0.5–5% fumaric acid was grafted individually and in various ratios with different monomers such as acrylic acid, 2-ethylhexyl acrylate, methyl methacrylate, and ethyl acrylate. All the grafted polymers were blended with butylated melamine–formaldehyde resin in 5–150% (based on the alkyd resins) and were studied for their coating properties. Saturated lauric acid–isophthalic acid alkyd resins could not be grafted with acrylic acid. It was observed that styrene radicals as well as activated CH_2 groups may react with resin, which helps the polymer chain to grow. Resins diluted in xylene (50% solid content) showed clear films. These resins were tinted with 1:1 TiO_2, which was subsequently coated onto steel, tin plate, and glass panels and examined for their gloss, hardness, and flexibility properties [30]. The production of full-gloss water-thinnable paints from polymer emulsions and the advantages and disadvantages of water soluble resins as media for water-thinned gloss paints were described by Hunt et al. in 1970 [31]. Water-based clear stove coating materials were prepared by mixing the water-reducible palm stearin alkyds with a methylated formaldehyde–melamine copolymer at ratios of 1–9. Thermogravimetric analysis was used to establish the solid content of each of the coatings as well as the curing temperature that could be used to prevent thermal degradation. The gloss of the coating after cure was affected by the oil length, alkyd–melamine ratio and curing temperature [32]. In 1987, Steven et al. [33, 34] synthesized high-solid-content alkyd resins using trimethylol propane (TMP) and dicyclohexylcarbodiimide by esterification using *p*-toluene sulfonic acid (*p*-TSA) as a catalyst. The resultant resins had solid contents 2–10% greater than the conventional alkyd resins and possessed lower molecular weight. The low reactivity of TMP may be the cause of the low molecular

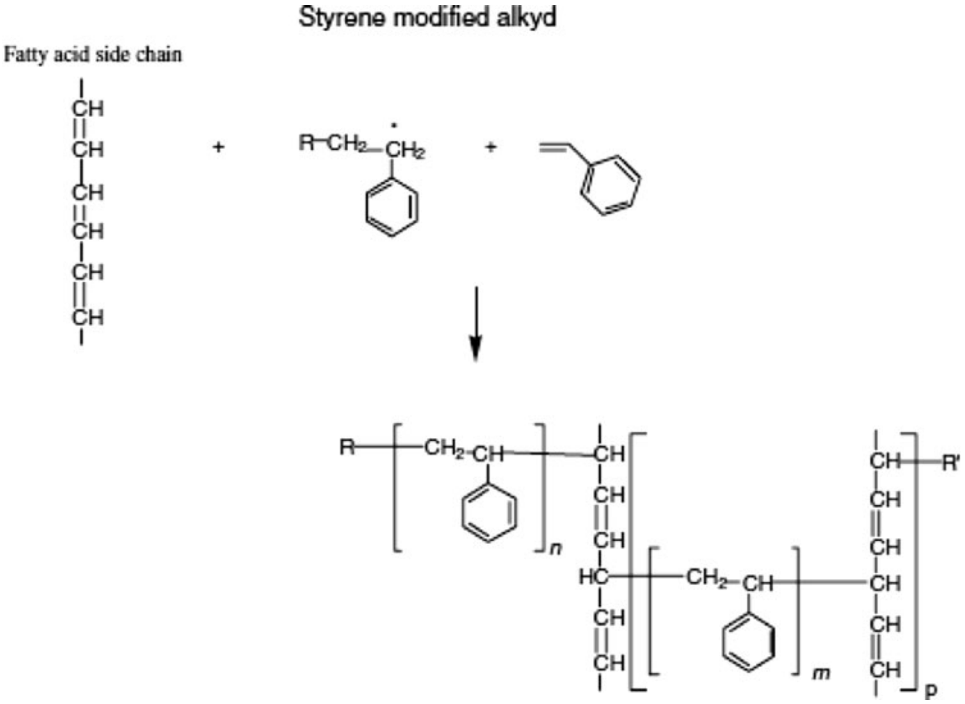


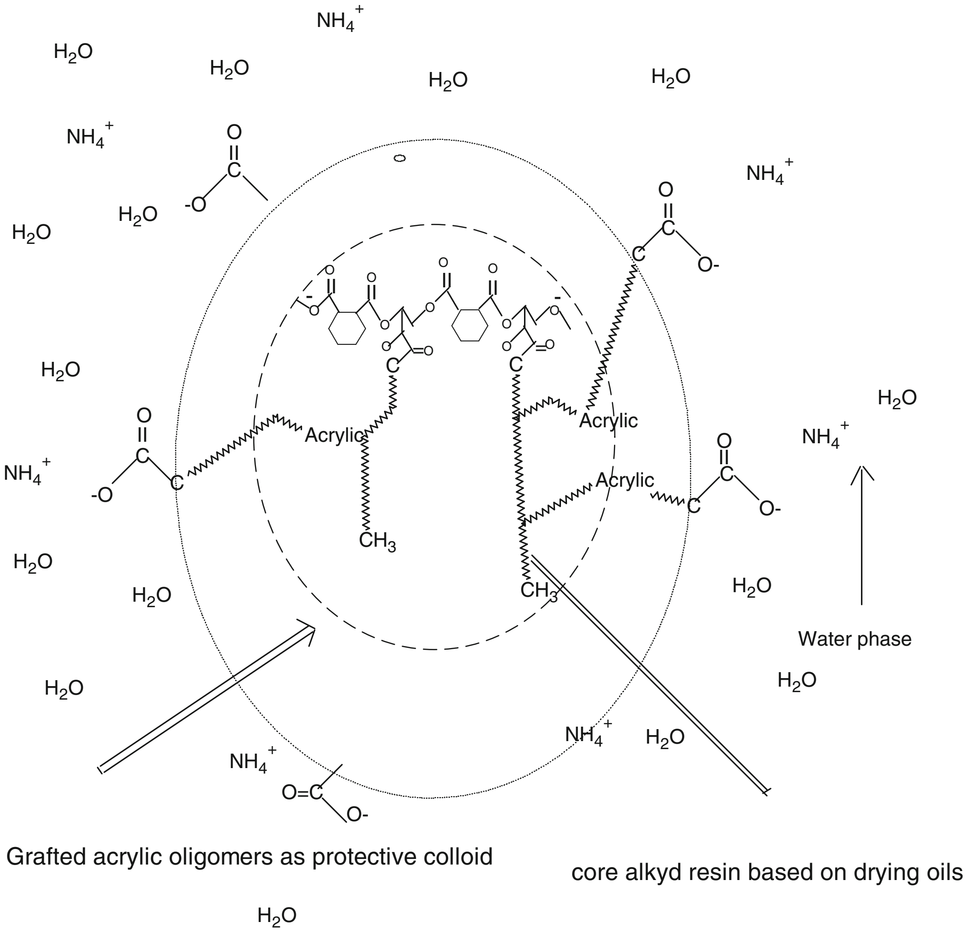
Fig. 6 The styrene-modified alkyd resin (*m* and *n* are typically 4–7 units)

weight. The replacement of trimethylolpropane by glycerol significantly reduced the average molecular weight (M_n) and the polydispersity index (PDI) of alkyds prepared by a conventional process. This substitution was expected to reduce the resin viscosity. Peterson et al. [35] worked out different methods for making styrene react with all varieties of drying oils to produce products that were fast drying, light colored, durable at any reasonable viscosity, resistant to water and chemicals, and low cost. Tucker [36] copolymerized styrene with tung oil (1:1) in xylene in the absence of polymerization catalysts. About 60% of the styrene was not reacted, and none formed a homopolymer. It was suggested that the 1:1 portion of the product was formed by a Diels–Alder mechanism. Copolymerization in bulk between styrene and the fatty acids of tung, oiticica, dehydrated castor, and isomerized linseed oil was conducted at 145 °C in the presence of 3% benzoyl peroxide by Payne et al. [37]. No appreciable reaction occurred with standard linseed oil fatty acids. The rate of reaction increased with higher styrene ratios. The fastest rate was obtained with dehydrated castor oil fatty acids followed by that of the acids of oiticica and tung oil. The styrenated alkyds displayed excellent air drying and baking characteristics as well as better chemical resistance than conventional phthalic alkyds. Hoogsten et al. [38] evaluated more extensively the relation between the properties of dehydrated castor oil and the styrenated product based on the oil. Oils were prepared under different conditions and made to react with styrene by both the mass and solvent methods of polymerization. A relation exists between the viscosity and degree of dehydration of the castor oil and the homogeneity and film properties of the styrenated product. Crofts [39] styrenated methyl esters of fatty acids (Fig. 6) in xylene or dipentene at 140 °C in a nitrogen atmosphere or in evacuated sealed glass tubes. It was concluded that styrene forms true high-molecular copolymers with conjugated triene and conjugated diene esters, as well as Diels–Alder adducts; methyl α-eleostearate did not react substantially with nonconjugated compounds. The results and their applications to triglycerides are discussed in detail. Rinse [40] made a distinction between the solvent and solventless processes for combining drying oils with styrene. Various theories of the mechanism of the drying oil–styrene reaction were explained and discussed. Chand et al. [41] styrenated tobacco seed oil, which gave non-yellowing paint films with better resistance to corrosion, water, acid and alkali compared with unstyrenated oil. The best results were obtained by styrenating a 3:1 mixture of tobacco seed oil and tung oil. Styrenated alkyds based on isomerized tobacco seed oil [42] are fast-drying, resistant to water and chemicals and nonyellowing. Isomerization in the presence of anthraquinone is a good method for improving the conjugation of the oil for styrenation, post-styrenation, and general purpose binders. Falkenburg et al. [43] suggested that considerable amounts of conjugation can be induced in linseed and soybean oils without appreciable polymerization by heating the oils at 260–300 °C in the presence of anthraquinone or related compounds. The amount of conjugation reaches a maximum depending on the concentration of catalyst and the temperature and then drops off due to polymerization. The ability of oil to polymerize is related to its unsaturation. The drying of films or the preparation of blown oil is representative of polymerization in the presence of oxygen.

Excellent drying oils of good polymerization properties can now be obtained from dehydrated castor oil. Vegetable oils are hydroxylated by blowing with air, followed by dehydroxylation in the presence of dehydrating agents (for linseed and soybean oils). Physical processes such as solvent segregation, which depends on the known solvency difference of similar molecular species having different molecular weights, were studied by Terril et al. [44]. Maleopimaric acid was treated with vinyl acetate, and the adduct was radically copolymerized with styrene. The polymer was incorporated into alkyd resins using ethylene glycol and dehydrated castor oil fatty acid. The alkyds had coating properties superior to those obtained from phthalic anhydride in terms of hardness and chemical resistance; the coatings were also anticorrosive [45]. A number of reactive vinyl monomers such as styrene, vinyl toluene, methylmethacrylate, butyl acrylate, ethyl acrylate and acrylonitrile have been used to modify the alkyd resins. Styrene polymerization with oils involves free radical initiated polymerization in the classical method. Generally, free radical-type initiators, such as benzoyl peroxide and di-tertiary butyl peroxide, have been used to accelerate the copolymerization reaction. Hewitt [46] proposed two types of reaction mechanisms for conjugated and non-conjugated oils. According to these authors, styrene chains are propagated across the conjugated dienes as in the styrene–butadiene reaction, while non-conjugated fatty acid radicals serve to modify the growth of styrene chains by a chain transfer mechanism. Styrene–oil copolymerization has been investigated by several other researchers [47–51]. Saxena et al. discussed the polymerization in view of reaction mechanisms, preparation techniques, raw materials and analysis and properties of the products [52, 53]. Linseed, tung, soybean, sunflower and oiticica oils and dehydrated castor oil (DCO) and DCO modified with vinyl are mainly used in the paint industry; in recent years, there has been an increasing trend towards their use as biopolymers [54]. Li et al. [55, 56] reported the preparation of tung oil–styrene–divinylbenzene copolymers by thermal polymerization. The resulting polymers were a light yellow color, transparent, rigid, tough and thermally stable below 300 °C. The same research group prepared thermosetting polymers by cationic polymerization of tung, soybean and fish oils. The polymerization was initiated by boron trifluoride diethyl etherate. Different experiments on styrenated alkyd resins prepared by the polymerization of styrene, vinyltoluene, and *p*-methyl styrene in the presence of middle-oil alkyd resins, containing 5–50% styrene with varying oil lengths from 28 to 60%, were carried out by several authors [57–61]. The coating properties were excellent when resins were styrenated up to 50% only. However, styrenation leads to yellowing of the film; maleic acid modified styrenated alkyd resin produced a non-yellowing binder [62]. If styrene is [63] partly replaced by acrylonitrile, the resultant resin shows improved resistance to oil and greases and has a lower chalking rate. Styrenated alkyds are used in screen printing, lithographic inks [64], primers and enamel paints [65]. Film properties are correlated with the compounds of vinyl-hydrocarbon-modified alkyd resins. The two types of alkyd resins containing linseed (85%) and tung oil (15%) and tobacco-seed oil (70%) and dehydrated castor oil (30%) were studied for grafting with vinyltoluene. The oil length of both alkyds was 57%. Vinyltoluene gives [66] better dilution tolerance with aliphatic hydrocarbon solvents. A decrease in vinyl hydrocarbon content gives a decrease in viscosity. An increase in vinyl hydrocarbon content gives a paler color. Coatings based on drying oil aldehydes and hydroxyl-bearing resins were studied by Sampath et al. in 1969 [67]. The films generally had good flexibility, gloss and acid resistance for 1 week, but all the products resisted 5% sodium hydroxide (NaOH) for only 40–90 min. Modifications of alkyd resins with vinyl, acrylic resins, and styrene maleic anhydride by reacting hydroxyl or carboxyl acid groups were studied by several co-workers [68, 69]. Styrenated and methacrylated alkyds dried faster and recoated better than similar vehicles made by a conventional method [68]. A comparison of the inverted styrenated alkyds with the conventional styrenated alkyds showed that the former had a better compatibility with mineral spirits, indicating a higher level of bound vinyl monomers and lower ester contents, resulting in improved alkali resistance [69]. Influence of catalysts on the glycerolysis of linseed oil was studied by Solomon et al. using the chromatographic method. The series of glycerol/linseed oil alkyd resins synthesized using NaOH as the catalyst showed higher triglyceride:diglyceride ratios than those prepared by lead oxide (PbO) or lead naphthenate catalysts [70]. Vinyl groups were first introduced by reacting with 12-hydroxystearic acid to form vinyl 12-hydroxystearate, which was subsequently polymerized using potassium persulfate to give a product that was soluble in benzene and insoluble in methanol [71]. In another method, variables affecting the use of tin chloride ($SnCl_4$) as a catalyst for initiating the polymerization of conjugated and nonconjugated soybean vinyl ether were studied. The molecular weight of the polymers increased with an increase in catalyst and a decrease in initiation temperature, and it decreased when the amount of moisture in the solvent, the amount of free fatty alcohol in the monomer, or the ratio of solvent to monomer was increased. Ferric chloride ($FeCl_3{\cdot}6H_2O$) initiated polymerization at 25 °C, but polymerization was incomplete, and the polymers had a relatively low molecular weight [72]. Polymers and copolymers of nonconjugated linseed vinyl ether were prepared in benzene (C_6H_6) by using $SnCl_4$ as a catalyst and initiating polymerization at room temperature. The comonomers of vinyl ethers and non-conjugated linseed homopolymer dried tack-free in <1 h and dried fully in

3–4 h [73]. Baked films of the polymers and copolymers were wrinkle-free, moderately hard, and flexible, and they had excellent adhesion to glass, black iron, and aluminium [74]. A process is described for the copolymerization of alkyl vinyl ethers in the presence of a $SnCl_4$ catalyst [75]. The resultant films showed good resistance to acids, alkalis, and ordinary solvents. Hurley et al. [76] discussed the differences in drying characteristics of solvent-based and water-reducible alkyds with precomplexed cobalt metal and cobalt zirconium complexes. The problem of slow drying is attributed to both drier adsorption on pigments and hydrolytic degradation of the resin. The latter can be controlled by controlling pH. A literature survey revealed that the water-soluble composition of dehydrated castor-oil alkyd was synthesized by Ghanem et al. [77] in 1972 using trimellitic anhydride and various ethylene glycols via an alcoholysis process. In another set of experiments, drying alkyds were prepared by the use of monoglycerides of castor oil and dehydrated castor oil. Polydispersity increased with increases in oil-length and reaction temperature. The hardest alkyd films were obtained when castor oil was first dehydrated separately [78]. Edward et al. [79, 80] used a multifunctional monomer, 5% trimethylolpropane triacrylate, in a water-reducible alkyd resin formulation, which gave paints with improved drying rates, water resistance, color retention, outdoor durability, and salt spray resistance. The best results were obtained by adding trimethylolpropane triacrylate toward the end of the process. A soya-fatty acid alkyd (alkyd–melamine resin ratio 8:2) containing 5% trimethylolpropane triacrylate (TMPTA) reached a tack-free state faster than that without (TMPTA) and had a higher Tukon hardness. The color, drying rate, water resistance, and long-term flexibility of waterborne air-drying alkyd resins (Fig. 7) are improved by the reaction of the alkyds with low molecular weight acrylic resins based in part on hydroxyethyl acrylate and methacrylic acid. The use of polyacrylates high in ethyl or butyl acrylate monomer units as internal plasticizers for alkyds was also discussed by Edward et al. [81]. Low, medium, and high isophthalic acid alkyds were studied, and low and medium isophthalic acid alkyds benefitted the most from the polyacrylate modification. The hardness profiles of the test paint films during the first 4 weeks after application confirmed that reactive acrylic polymers with high glass transition temperatures (tgs) acted

Fig. 7 A waterborne air drying alkyd resin



as hardening agents, whereas reactive acrylic polymers with low tgs acted as internally bound plasticizers [82].

Synthesis of Alkyd Emulsions

Water-based organic coatings are ecologically friendly materials and more economic than solvent-based coatings. The increase in restrictive legislation concerning VOC emissions has stimulated research in alkyd emulsions. An alkyd emulsion is a dispersion of alkyd resin in water. The possibility of using mono-, di- and triethanolamine as emulsifiers in the preparation of an emulsion glyptal drying oil was studied by Smirnova in 1965. All the amines had identical effects on the stability of the emulsion, foam formation was inhibited, and the water resistance of the films was not impaired by the addition of monoethanolamine. The viscosity of the emulsion increased with increases in the concentrations of amines. The best results were obtained with monoethanolamine [83]. Paints with reduced flammability and reduced solvent contents were prepared using water-based vehicles containing anionic, cationic, or hydrophilic polymers. Typical systems contained an adduct of maleic anhydride with fatty acids or polybutadiene and epoxy resins crosslinked with amines (Fig. 8) or boric acid. The water-based systems were formulated with >50% solids [84]. In 1979, Brugger et al. [85] discussed the development of emulsifier-free, aqueous suspensions of polyester-epoxy powder coatings and their manufacturing processes. They also studied their application in paint formulations and compared them with conventional waterborne and powder coatings. Paints based on Resydrols M471 (melamine type) and P411 (phenolic alkyd type) were diluted with NH_4OH as simple methylol derivatives, which cross-linked upon stoving. Some modifications of the usual techniques were required because water needs more heat to evaporate and boils below normal stoving temperatures [86]. A medium-oil pentaerythritol-ethylene glycol was prepared by heating a mixture of phthalic anhydride and ethylene glycol at 150 °C for 30 min. Then, after the addition of phthalic anhydride, pentaerythritol, tall oil fatty acids, and xylene, heating was continued for 1 h at 190 °C and thereafter at 245 °C until an acid number <10 was reached. Then, Igepal CO-880 (a water soluble nonyl phenoxy polyethylene ethanol) and Igepal CO-430 (an oil-soluble nonyl phenoxy polyethylene ethanol) were added, and the mixture was stirred at 350 rpm. As the aqueous phase was added, the viscosity of the resulting water-in-resin emulsion gradually increased. When sufficient water had been added to cause inversion of the phases of the emulsion, the viscosity decreased suddenly, and the product became a thick, white cream [87]. This emulsion was then diluted and pigmented to form paint. Emulsions of alkyd resins modified with oleic, linoleic, and linolenic acids have good storage stability [88]. The storage stability of emulsions containing an anionic emulsifier, such as sodium dodecylbenzenesulfonate, was less than that of emulsions containing a mixture of sodium dodecylbenzenesulfonate and a nonionic emulsifier, such as sorbitol monooleate. The nature of the fatty acids used in the preparation of the alkyds does not affect emulsion stability. The combination of emulsifying agents produces a stable oil modified resin emulsion. Thus, a long oil phthalic soya alkyd was heated with alkylphenylpolyethylene glycol (Tergitol NP-14) to 70 °C. The solution was stirred and diluted with water containing 2-amino-2-methyl-1-propanol also at 70 °C to produce an emulsion. The paint dried tack-free in 2–3 h and was still stable after 29 months of storage [89]. Harold et al. [90] employed a method of mixing casein peptized in ammonia solution with a drying oil-modified alkyd resin so as to form an oil-in-water type emulsion. Stable emulsifiable polyester resins that did not gel, become discolored or become difficult to cure were prepared for use as binders for glass fibre mats [91]. Vinyl monomers were polymerized in the presence of an oil-modified, unsaturated alkyd resin and an oil-soluble free-radical catalyst until 40–70% of the monomer had polymerized. After the addition of water, an emulsifying agent and a hydroxylic-base pH-control agent, the polymerization was continued until 60–85% of the monomer

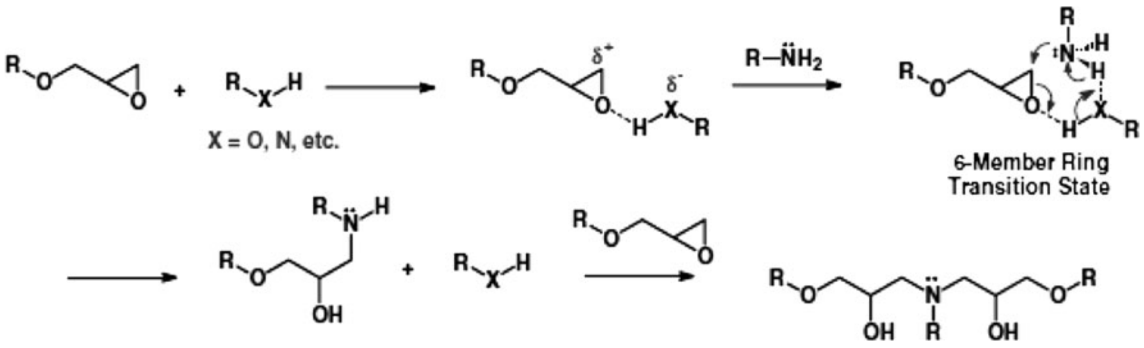


Fig. 8 The mechanism for the catalyzed reaction of amines and epoxides

had reacted. A stable oil-in-water emulsion having an alkyd–styrene ratio of 60:40, a pH of 6.5, and a 48.3% H_2O content was obtained. Similar oil-modified alkyd resins are treated with *p*-vinyltoluene or methyl methacrylate [92]. A self-emulsifying alkyd resin is produced by modification with ethylene glycol and ethylene/propylene oxide asymmetric block copolymer. The product has better frost resistance and storage stability than the unmodified material [93]. Alkyd resin modified by styrene, vinyltoluene, methyl methacrylate, butyl acrylate, methacrylic acid, or acrylic acid is neutralized by a water-dilutable amine. The resultant resin is used as an air-drying, anticorrosive primer for metals and wood [94]. Alkyds resins diluted with water produce stable dispersions with low viscosity. Dispersion of alkyd resins gives varnishes that exhibit fast-drying elastic films with increased hardness. [95]. Boltorn W3000, a nonionic, self-emulsifying cross-linkable dendritic polymer, is used to disperse conventional alkyd resins. The emulsions are obtained through the EIP (emulsion inversion point) method. The emulsions are typically characterized by good shelf life stability and are made at solid contents of about 50% with a viscosity of 50–150 mPa s [96]. The complexity of the rheological behavior of the binders was explained using core–shell dispersions [97]. Polyurethane thickeners, nonionic associative thickeners, water emulsifiable driers, polymeric dispersants, antifoaming agents, polymerizable surfactants and film-building corrosion inhibitors for use in waterborne paints were discussed by various authors [98–100]. The colloidal stability of water-based paints is predominantly governed by osmotic and electrostatic repulsion of both the binder and the pigment particles. The stability of drying properties of alkyd emulsion paints upon storage can be strongly improved by preventing the use of ketoximes as anti-skinning agents and by selecting the proper driers. Properties of the dried paints depend strongly on the process of film formation. The protective and aesthetic quality of films based on binder dispersions is governed by the key parameters of the resin that are within the droplets: viscosity, miscibility and the ability of the binder to undergo crosslinking. To obtain the total package of desired properties of water-based paints, it is necessary that all of the paint components are adjusted to each other [101]. Solvent-free water based alkyds are environment-friendly alternatives, which could replace solvent based systems without deficits in quality and performance. This is demonstrated by practical examples like brushable house paints, stain blocking wall paints and wood stains [102]. Characteristics of various alkyd emulsions and their blends with acrylic resin binder were investigated for wall-finishing applications [103]. In 2006, Raval and Parmar [104] studied alkyd emulsions for their coating characteristics and shelf life and revealed that alkyd emulsions are low VOC surface coating binders. Alkyd emulsions are relatively low molecular weight polymers. They do not present the same complex multi-stage process of film formation as that of an acrylic dispersion (i.e., the water-evaporation stage) with the particles coming into contact (I), the deformation stage (II) and then the coalescence step with interdiffusion of the polymer chains to form a continuous film (III) [105, 106]. In particular, as soon as the water evaporates from an alkyd emulsion-based film, a phase inversion takes place. The high viscosity of the acrylics prevents such a phase inversion, and the particle interfaces disappear slowly, resulting in slow drying, and a homogeneous film is formed. The final step consists of the reaction of the alkyd chains with the oxygen from the air to form a cross-linked system. The drying of the alkyd emulsion was studied by Oyman et al. [107, 108] in the presence of a manganese complex (MnMeT can), which exhibited comparable drying time to a cobalt drier. The acrylate and the phosphate-based dispersing agent deactivated the cobalt by the formation of cobalt precipitate, which resulted in loss of the polymer upon drying. In another set of experiments, an emulsifiable containing 2,2′-bipyridyl (a complexing agent for cobalt) showed the best resistance to loss on drying [109]. Alkyd emulsions are used in making red oxide primers, washable distempers and metal primers [110]. Recently, the synthesis of an alkyd emulsion containing a sulfur complex coating that controls the release of fertilizer was reported by Wan Lianbu [111]. Hashimoto et al. [112, 113] used an amino- and epoxy-based varnish of an alkyd emulsion for the exterior coatings of cans. Alkyd emulsions were electrodeposited on leather. These processes were used for leather finishes by Joseph et al. in 1996 [114, 115].

Synthesis of Waterborne Oil Modified Urethanes

The major thrust of research and development work in recent years has been the preparation and use of autooxidizable PUD. They are non-toxic and non-flammable and do not pollute the atmosphere. Water-dispersed urethanes of different molecular weights with pendant-blocked isocyanate groups find a use where solvent-based systems are unacceptable. A range of diisocyanates and blocking agents were investigated. Wicks Jr. [116, 117] has extensively reviewed blocked isocyanates. Blocked urethanes can be easily dispersed in water. The type of blocked isocyanate functionality and the blocking agent determines the liability of the bond between the isocyanate and the blocking agent. Hydrolytic instability was observed for aromatic systems. Details of the synthesis of waterborne urethanes based on different oils such as sunflower, castor, linseed, soybean and tall oil are described below.

Synthesis of Waterborne Sunflower Oil Modified Urethane

Sunflower oil has been used in the synthesis of alkyd resins for decades. Sunflower oil alkyd was used as the polyol component to study the effects of the amount and type of diisocyanate components on the film properties of polymers. Depending on the polyol structure used, polymers showed various film properties. Polymers are prepared from drying and semi-drying oils, such as sunflower, soybean and linseed oils. These oils are used in paint formulation because of their good film properties. Polymers were prepared from the following three kinds of diisocyanates: toluene 2,4-diisocyanate (TDI), HMDI and poly(1,4-butanediol) TDI (PBTDI) [118]. Sunflower oil partial glycerides were used as the polyol component. In this study, the effects of the amount and type of diisocyanate component on the film properties of the polymer were investigated. Depending on the monomer structure used, the polymers showed various film properties. Polymers based on aromatic diisocyanates (TDI and PBTDI), for example, had good water resistance. Additionally, with greater amounts of diisocyanate components in the polyurethane formulation, a shorter drying time was achieved. The monomer structure also affects the flow properties. For investigating the effects of monomer ratio and type on the flow properties, polymers were prepared from two different diisocyanates at three different monomer concentrations [119]. TDI and PBTDI were used as diisocyanate components, and sunflower oil partial glycerides were used as the polyol component. In the polymer preparation, the lowest diisocyanate concentration was 6.38×10^{-4} mol/g polyol, and the highest diisocyanate concentration was 12.61×10^{-4} mol/g polyol. Although both diisocyanates have aromatic structure, for the same monomer concentration, PBTDI-based samples have a higher viscosity than TDI-based samples. Because of the existence of two aromatic rings per molecule in PBTDI, the chain of the polymer is not flexible. Apparently, this causes an increase in viscosity. Oil from the seeds of *Ecballium elaterium* and *Prunus mahaleb* were used as the oil component for the preparation of oil-modified polyurethanes [120]. Since these oils contain conjugated trienoic acids, polymers prepared from them have good film properties such as a short drying time and good water, alkali and acid resistances. Oil-modified polyurethane films were prepared from HMDI and/or MDI for wound-dressing applications [121]. It was found that the amount and type of diisocyanates affected the mechanical properties and gas permeabilities of polymeric membranes. For the preparation of millable polyurethane elastomers, difunctional castor oil or its blends with poly(propylene glycol) with two different ratios of 1,4-butanediol as chain extender and TDI were used as reactants [122]. Investigation of the physical, mechanical and thermal properties showed that the elastomers obtained could be used for industrial applications.

Synthesis of Waterborne Castor Oil Modified Urethane

Castor oil (Fig. 9) used for the preparation of various coating formulations. Polymers of cyclopentadiene and its copolymers with vegetable oils obtained at 260–320 °C gave brittle films. Copolymerization in the presence of tin (IV) chloride with sunflower, castor, or tung oil gave quick drying, wrinkled and brittle films. Copolymerization with linseed oil gave films with satisfactory properties. The films of the polymers so obtained had good adhesion and excellent stability under ultraviolet light and remained elastic, hard, and strong. They were recommended for interior and exterior applications [123]. Multifunctional acrylates were evaluated in clear ultraviolet curable topcoat formulations based on acrylated polyester, alkyd and epoxy resins; pentaerythritol triacrylate provided the maximum crosslinking density and exhibited the best chemical resistance. In 1958, Shahidi et al. studied the performance properties of trimethylolpropane triacrylate (TMPTA) and hexanediol diacrylate. TMPTA produced a balance set of performance properties, whereas hexanediol diacrylate was superior in flexibility and adhesion. The polyester system showed low viscosity with good flexibility. The coating displayed excellent gloss, flow and adhesion [124]. Alkali-soluble polyester resins useful as insulating coatings for wires were prepared containing trimellitic anhydride, dipropylene glycol, glycerol, castor oil and neopentyl glycol. The resultant resin coated wires that were formed and subjected to currents exhibited superior thermal aging characteristics [125]. A fast-curing polyurethane prepolymer tissue adhesive composed of castor oil, toluene diisocyanate and 6-chloro-2,4,5-trifluoro-1,3-phenylene diisocyanate was evaluated for bonding strength and setting time and compared with a slow curing prepolymer composed of castor oil and toluene diisocyanate alone. Figure 10 shows the copolymerization reaction of the hard and soft segments using TDI. Dilution of the prepolymer

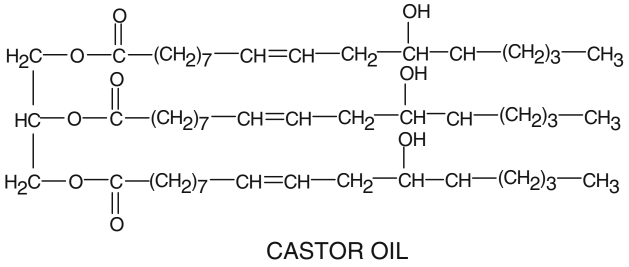


Fig. 9 The structure of castor oil

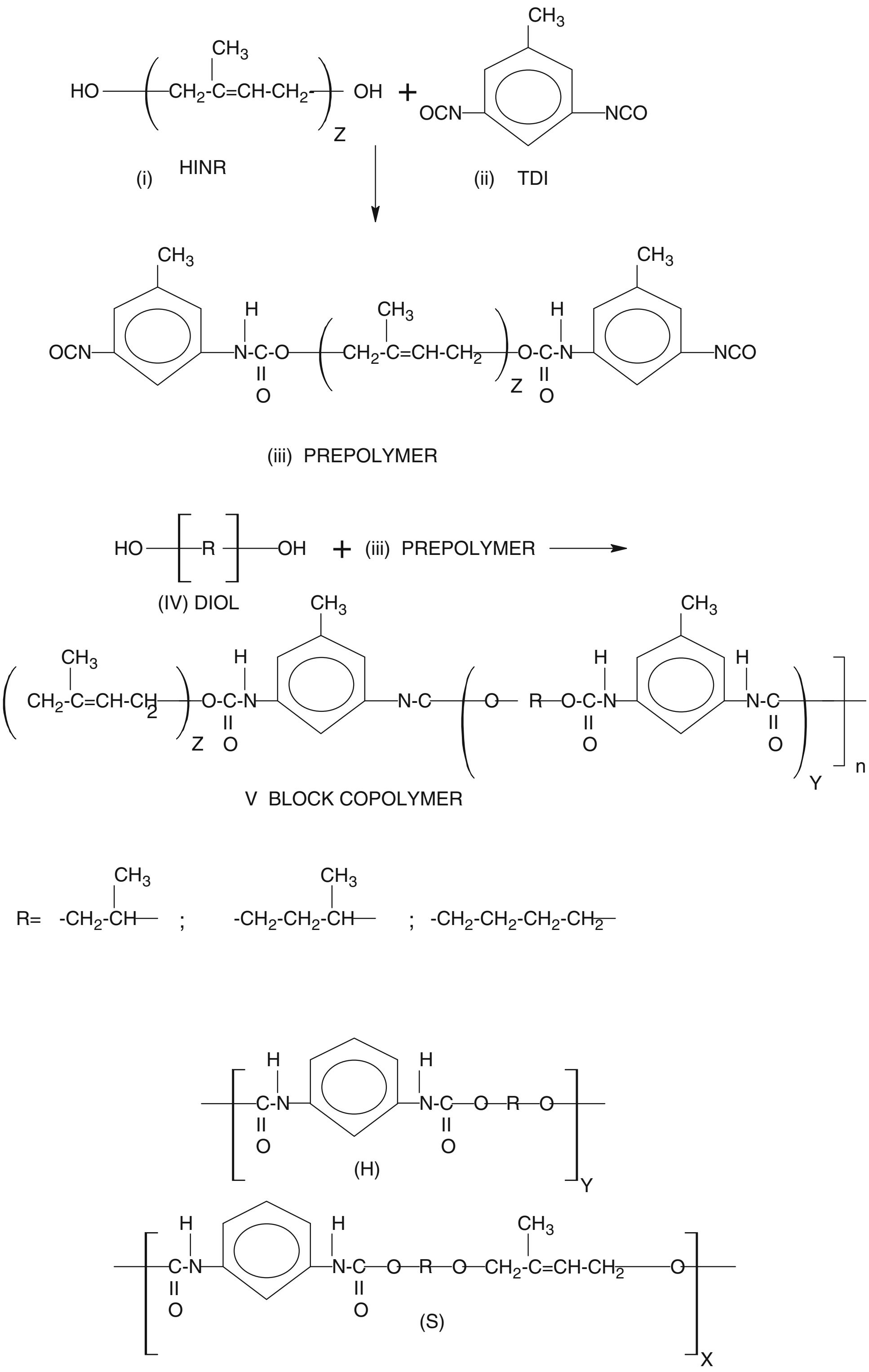


Fig. 10 Copolymerization reactions of the hard and soft segments using TDI

with tetrahydrofuran (THF) and the addition of pyridine to an optimum concentration that improved the adhesion was reported by Thomas et al. [126]. Water-soluble epoxy resins derived from maleopimaric acid, linseed fatty acids, and epoxy resin were prepared under specific conditions. Methylated urea–formaldehyde resin and melamine–formaldehyde resin were also prepared for the purpose of curing. Coatings had good film properties, such as scratch hardness, flexibility, impact resistance, corrosion resistance, and resistance to water, acid, and alkali [127]. In another set of experiments, Mishra et al. synthesized epoxy resins from maleopimaric acid for electrodeposition. The resins were

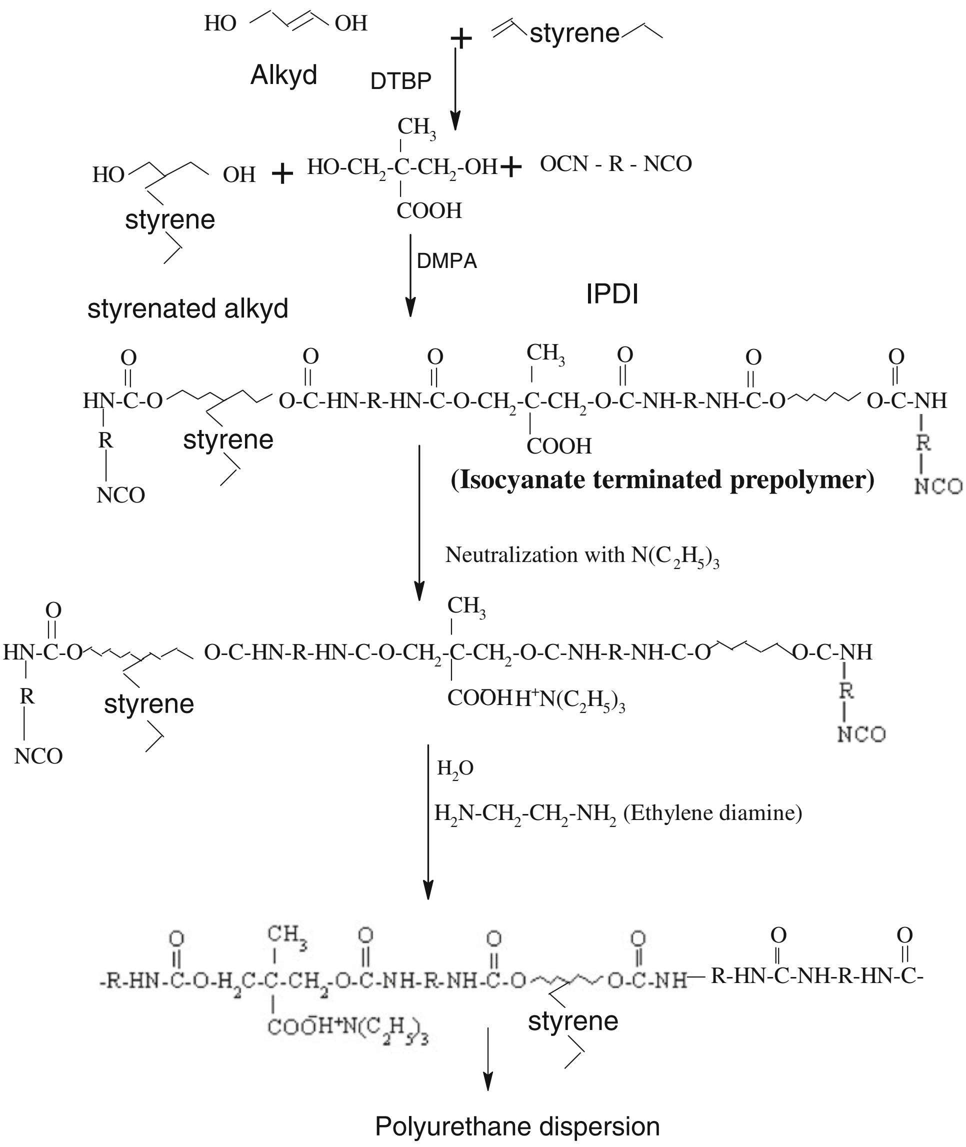


Fig. 11 Synthesis of a polyurethane dispersion containing styrene

cured with methylated urea–formaldehyde resin and melamine–formaldehyde resin. These anodic electrocoatings had good film properties such as scratch hardness, flexibility, impact, water, acid, alkali, and solvent resistance [128].

The polyol/polyisocyanate composition improves abrasion resistance and hence can be used as undercoat for automotive parts. The polyol component is unmodified castor oil or castor oil modified with cyclohexanone-formaldehyde condensate. The modified castor oil may be further modified by adding the reaction product of neopentyl glycol and adipic acid. The polyisocyanate component comprises an MDI-based mixture containing polyisocyanate prepolymers based on alkylene oxides [129]. A series of waterborne polyurethane dispersions (PUD) were synthesized using castor oil, polypropylene glycol, toluene diisocyanate, and (2,3-dihydroxypropoxy)-4-oxobut-2-enoic acid (GES). These PUD can be crosslinked spontaneously upon drying without extra additives or processing steps. Results reveal that the particle size of PUD mainly depends on the concentrations of castor oil, GSE, and polymer. With an increase in GSE concentration and a decrease in castor oil and polymer concentrations, the particle size decreases. Furthermore, an increased amount of castor oil, GSE, and polymer concentration results in an increased viscosity of PUD because of the increase of the effective volume for the dispersed phase [130]. A castor oil-modified polyurethane-acrylate (CPUA) hybrid emulsion was synthesized with isophorone diisocyanate (IPDI), polyether diol (N220), castor oil (CO) and methyl methacrylate (MMA) used as the main raw materials. Synthesis of styrene modified PUD is shown in Fig. 11. The effects of castor oil content on the properties of CPUA and its coating films were investigated by Luo et al. It was found that the properties of the emulsions and films, such as viscosity, film flexibility, moisture absorption and mechanical properties, improved when the molar ratio of OH groups in castor oil and polyether diol was between 1.5 and 1.3 [131]. A maleic anhydride-modified castor oil (MCO) was used to prepare aqueous polyurethane dispersions with ionic groups in the soft segments according to the prepolymer mixing process. The aliphatic polyether PU prepolymer was prepared with MCO and polyether glycol (N210) as the polymeric glycol component. The prepolymer was dispersed under vigorous agitation by adding water and by chain extension with ethylene diamine. The effects of the mass ratio of MCO and N210 on the properties of the resultant waterborne polyurethanes were studied [132]. Drying alkyds, modified with dewatered castor oil, are prepared without alcoholysis. The castor oil is dewatered with excess trimellitic anhydride, giving an oil containing combined carboxyl groups that react with diols and glycerol. Further reactions with trimellitic anhydride (or phthalic anhydride) gives water soluble resins [133]. Dispersions were prepared from castor oil, soya oil, polypropylene glycol and DMPA and neutralized with ethylenediamine to form PUD of 36% solid content. The resultant pigmented films showed good film-forming properties [134].

Synthesis of Waterborne Linseed Oil Modified Urethanes

Linseed oil and its fatty acids have been used for the synthesis of air-drying alkyds. Water-dispersible binders with air-drying properties were prepared from unsaturated fatty amide diols (amides of unsaturated fatty acids and dialkanolamines), diisocyanates, and acids containing two active H groups (other than COOH groups) by Arora in 1992 [135]. Polymers containing organic sulfonate-containing groups are capable of being dissolved or dispersed in a liquid medium. The polymer is useful as a pigment dispersant and as a film-forming polymer in coatings [136]. Various modified polyester-amide varnishes were prepared and evaluated as water thinnable binders for surface coatings. The resins were prepared from one of two amine itaconyl derivatives, namely *N*,*N*-di(itaconyl)aniline (DIA) and *N*,*N*-di(itaconyl)-*p*-aminobenzoic acid (DIAB), linseed oil fatty amides, and phthalic anhydride. This modification was expected to improve the film performance and durability [137]. Phenolic resins were modified with maleic anhydride-linseed oil reaction products to give anticorrosive coatings with good water solution and storage stability. The amount of phenol is recommended as being <10% of the total resin. The coatings can be applied on the metal surfaces immediately after phosphating treatment without drying [138].

Synthesis of Waterborne Soya Oil Modified Urethane

Soya oil and its fatty acid are the second most used raw materials in the paint industry due their autooxidative drying and the fact that they are a readily available renewable resource. A urethane alkyd was synthesized by Eckhoff et al. in 1978 [139] from soya oil, pentaerythirol ethylene glycol and PA by reacting it with TDI. The resultant resin was emulsified with a surfactant and mixed with vinyl acetate copolymer latex. A uralkyd emulsified in a aqueous dispersion of maleinized polybutadiene was used as a binder in wood coatings [140]. A thixotropic uralkyd was synthesized from dimeric acid polyesteramide, stearic acid, ethylene diamine, soya oil, TMP and TDI pre-polymer [141]. A series of waterborne alkyd resins was prepared by a fatty acid process with soybean fatty acid, trimellitic anhydride, various polyols and polybasic carboxylic acids that were used as raw materials. The alkyd resin was modified with benzoic acid, maleic anhydride and oleic acid. The effects of heating on the final acid value, nature of polyols, polybasic carboxylic acids, particle size, hardness, adhesion, water resistance and gasoline resistance of the coating film of the alkyd resin were studied [142]. The high-solid-content binders for waterborne coatings, their uses and challenges have been discussed at various symposia [143–145] held in New Orleans.

Crosslinking Polyurethane Dispersions

Various crosslinking agents are used to cure PUD. Crosslinking agents react with hydroxyl or carboxyl acid groups

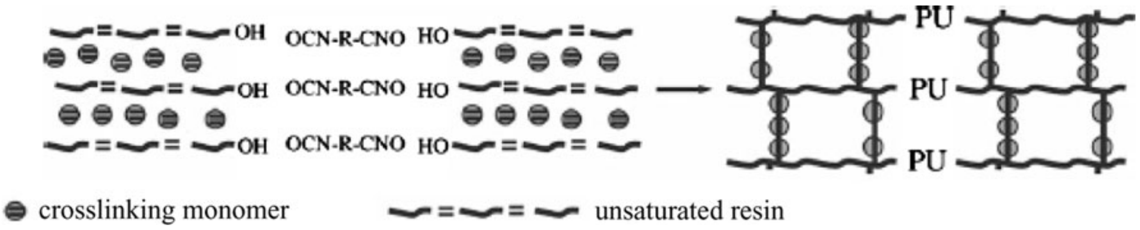


Fig. 12 The crosslinking pattern of a PUD resin

of PUD that cure at elevated temperatures. The crosslinking pattern of a PUD resin is shown in Fig. 12. The improvement of the resistance properties of polyurethane dispersions crosslinked with amino-formaldehyde resins was studied. To investigate the effect of crosslinking on properties, the functional group content was varied in several polyurethane dispersions from low carboxyl functionality to high hydroxyl and carboxyl functionality. The mechanical and chemical resistance properties of the polyurethane films at different crosslinking densities were compared along with the effect of self-condensation of the amino formaldehyde crosslinker [146]. Novel cosolvent-free waterborne polyurethane dispersions have been prepared and crosslinked with a variety of polyisocyanates to yield coatings that cure at ambient temperature. The polyisocyanates can be dispersed in the polyurethane dispersion with almost complete elimination of the foaming problem that is typically associated with the reaction of polyisocyanates with water. The ambient-cured coatings exhibit excellent gloss and flexibility and are solvent resistant. The optimum type and level of crosslinker were determined in each case [147]. A dispersion of an organic polyol component that can be diluted with water was mixed with another polyester resin containing urethane, carboxylate, and hydroxyl groups with a polyisocyanate component; the resulting mixture has a viscosity of 50–10,000 mPa s. Hexamethylene diisocyanate dimer/trimer was mixed and emulsified with the above polyesters at a NCO/OH ratio of 1.2:1, giving a two-component polyurethane having a pot life of 5–8 h and films with good chemical resistance properties [148]. The dispersions, with extended pot life, contain sufficient polyurethane-bearing anionic substituents to permit its dispersion in water. A water-emulsifiable polyisocyanate with 0.04–1.5 equiv. NCO/kg of dispersion and a tertiary alkanolamine in the amount of 0.05–40 equivalent tertiary amine per equivalent NCO group gives a water emulsifiable polyisocyanate. This polyurethane was prepared by the reaction of poly (butylene adipate) with TDI and then hexamethylene diisocyanate and treated (0.54% NCO) with an aqueous solution of the sodium salt of acrylic acid–ethylenediamine to form a Michael adduct [149]. Potter et al. [150] prepared two-component aqueous polyurethane or polyurea–polyurethane dispersions for coatings. Blum et al. [151, 152] filed patents for two component polyurethane coatings based on polyester–polyisocyanate. Several crosslinkers were evaluated at room temperature. The cured waterborne urethane latexes are used in the production of abrasion-resistant and chemical resistant coatings. The crosslinkers studied include a polyaziridine, a water-dispersible isocyanate, two carbodiimides, two epoxy-silanes, and methoxymethyl melamine as a control. Post-crosslinking improved the performance of the coatings. For carboxylic urethanes, the aziridine CX-100 gives the overall best improvement in mechanical and solvent resistance properties. The carbodiimides CDS-43 and XL-29SE and the epoxy-silane MAGAS afford 80–90% of the properties obtained with the aziridine. The water-dispersed isocyanate XP-7063 gives large improvements in physical properties but less so with solvent resistance. An epoxy-silane, Z-6040, while still offering improvements, is the least effective [153]. Aqueous dispersions of polyester–polyurethanes having acid numbers of 5–60 and containing 0.25–6.5% OH groups and 2–25% urethane groups were prepared for use in the formation of crosslinked coatings having a soft feel and good solvent resistance [154]. Polymers were prepared that contained carboxy, OH, ester, urethane, and carbonate groups and formed stable aqueous dispersions. The polymers were curable with amino resins and blocked polyisocyanates. These were used as automobile clear coats and showed good chemical and solvent resistance [155]. Solvent-free urethane acrylic hybrid polymers for coatings were synthesized by Hegedus et al. [156]. Preparation of polyisocyanates containing uretidione and isocyanurate groups for use in polyurethane coatings were discussed by Winfried [157]. Several reviews on polyurethane ionomers used in aqueous dispersion and as a block polymers have been discussed [158–160]. Polyurethane (PU) cationomers were synthesized from poly(tetramethylene adipate glycol), isophorone diisocyanate, and *N*-methyldiethanolamine according to a prepolymer mixing process. The basic structure–property behaviors of the emulsion (obtained by adding water to the ionomer solution.) and emulsion cast film were studied with respect to their molecular weight (M_n). The amount of poly (tetramethylene adipate glycol) and *N*-methyldiethanolamine content, degree of neutralization, and extender functionality affect the stability of the emulsions. [161] Various amounts of fluorine-containing polyol (mol. wt. = 3,700) were introduced into the soft segments of anionic aqueous polyurethanes (PU) to examine the effect of the fluorine on the properties of the anionic aqueous PU. Both the mechanical and water resistance properties of the anionic aqueous PU were improved [162]. Elastomeric polyurethane anionomer dispersions were prepared from hydrogenated diphenylmethane diisocyanate (H12MDI) or isophorone diisocyanate (IPDI), poly(caprolactone) (PCL) diol, 1,4-butanediol (BD), and dimethylolpropionic acid (DMPA). Polyurethanes from H12MDI showed coarser dispersion and better tensile properties over those from IPDI. When some of the PCL diol was replaced by DMPA or BD, the tensile strength increased, and ductility decreased due mainly to the increased chain rigidity and intermolecular forces [163]. Aqueous dispersions of anionic polyester–polyurethanes containing sulfonate groups with Na^+ counterions were ion-exchanged with H^+ Ag^+, Ca^{2+}, Ba^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Al^{3+}. The unstabilized dispersion was coagulated by the exchange process in all cases except H^+ and Ag^+. The addition of a nonionic surfactant gave stable dispersions. The stress–strain properties of films from the ion-exchanged polymer indicated that a crosslinking effect occurred in the presence of both monovalent and divalent cations, with Ca^{2+} and Ba^{2+} giving the strongest effect. Ion exchange strongly reduced the water swelling of the film, except in the case of aluminium [164]. Polyurethane ionomers based on polyoxyalkylene (polypropylene glycol or polyethylene glycol), bis(4-isocyanatophenyl)methane, butane-1,4-diol and *cis*-2-butene-1,4-diol were synthesized and characterized. Attempts were made by Egboh et al. [165] to convert the unsaturated polyurethanes directly to ionomers by reaction with *N*-chlorosulfonyl isocyanate. These ionic diol intermediates were used for the preparation of polyurethane ionomers. Unsaturated polyurethanes were prepared from polypropylene glycol, 1,4-butanediol, and *cis*-2-butene-1,4-diol by heating them at 80 °C with *N*-vinyl-2-pyrrolidone in DMF in the presence of AIBN [166]. A new ionic diol was prepared by the addition of sodium bisulfite across the double bond of the diester diol based on maleic anhydride, and 1,4-butanediol was used to make a PU ionomer [167]. Crosslinked ionic polyurethane membranes were synthesized and were mechanically strong enough for pervaporation experiments. The crosslinked ionic polyurethane membranes were selective towards water over the entire range of liquid mixtures. Swelling measurements were also carried out using the membranes, varying the ethanol–water compounds and ionic contents [168]. Adipic acid-ethylenediamine-hexamethylene diisocyanate-1,6-hexanediol-neopentyl glycol-pyromellitic dianhydride polymer were prepared by polymerization of NCO-terminated prepolymers with diamines and dianhydrides. Analysis of NCO contents indicated that 2:1 diamine–dianhydride adducts, which were formed in situ, acted as chain-extenders [169]. The sulfur vulcanization of polyester or polyether urethane rubber chains extended with 3-(allyloxy)-1,2-propanediol and inhibited by bases (amines, ZnO) as well as accelerated by acids ($ZnCl_2$ complexes) were studied [170]. Poly(2,6-dimethyl-1,4-phenylene oxide) was crosslinked in the presence of large di-methyl siloxane cyclics (92 repeating units). Approximately 26% by weight of the cyclics were threaded and permanently captured by the polymer network, forming a polymeric catenane [171]. Aqueous polyurethane (PU) dispersions were prepared from isophorone diisocyanate (IPDI), polytetramethylene glycol (PTMG), polypropylene glycol (PPG), polyethylene glycol (PEG), and dimethylol propionic acid (DMPA) as an anionic center. PTMG-based PU generally showed superior mechanical properties. With increasing hard segment contents, the particle size, storage modulus (*E*), and tensile strength increased. At the lowest hard segment content (36 wt%) tested in this experiment, soft segments crystalized, and water swell decreased [172]. Water dispersions of polyurethaneurea anionomers, based on polyurethane synthesized by using a one-step process, and the water dispersion of polyurethaneurea anionomers, based on polyurethane synthesized by using a two-step process, were prepared. A uniform distribution of hydrophilic monomer units led to smaller average sizes and polydispersity of the polyurethaneurea particles dispersed in water, as well as higher stability of the water dispersion [173]. A polyurethane was prepared using poly(oxytetramethylene) as soft segments, 4,4′-methylenebis(phenol isocyanate), and 2,2-bis(hydroxymethyl)propionic acid as a chain-extender and then ionized with KOH to yield the K ion-based anionomer. Compared with other polyurethane anionomers, the present system was branched rather than linear, as reflected in the good mechanical properties of the present system [174]. Polyurethane (PU) anionomer dispersions were formulated from polytetramethylene ether glycol (PTMG), polypropylene glycol (PPG), dimethylol propionic acid (DMPA), and isophorone diisocyanate by a prepolymer mixing process. The glass transition temperature of the soft segment was almost independent of the DMPA content and the molecular weight of PTMG but increased with PPG content in the mixed polyol system, probably due to the increased phase mixing between soft and hard segments [175].

Applications of Oil Modified Urethane

Water-borne polyurethanes are in great demand and widely accepted as environmentally friendly coatings. Polyurethane dispersions have been used in book binding, adhesives, coating, flexible/rigid foams, waterproofing binders in construction and innumerably various applications of textiles (finishing and printing process). Two-component waterborne polyurethane (2K WBPU) coatings were prepared using a silicone-modified acrylic emulsion as the hydroxyl component and a hydrophilically modified polyisocyanate as the curing agent. The effects of the levels of silicone monomer and hydroxyl values on the film properties of the 2K WBPU coatings were studied by Kim et al. in 1995 [176]. Polyurethanes based on MDI, bis(hydroxymethyl) propanoic acid and poly (tetramethylene oxide) were prepared, and their morphologies and physical properties were investigated. The polyurethanes had very poor phase separation and mechanical properties; upon neutralization with alkali metals, the phase separation improved dramatically, and the materials resembled tough elastomers [177]. Water-borne polyurethanes (PU) were hydrophobically modified using various types of acrylate monomers. PU having 2-hydroxyethyl acrylate terminal groups were first obtained by following a prepolymer mixing process.

These PU-based polymers were then chain extended with acrylate monomers via a radical polymerization mechanism [178]. UV-curable polyurethane (PU) acrylates have been synthesized from polypropylene glycol (PPG), isophoron diisocyanate (IPDI), and three types of reactive diluents, i.e., 2-hydroxyethyl acrylate (HEA), tripropyleneglycol diacrylate (TPGDA), and trimethylolpropane triacrylate (TMPTA). The effects of soft segment length, type, and concentration of reactive diluent on the mechanical and dynamic mechanical properties were determined [179]. Liquid–crystal polyurethanes were prepared from 4,4′-bis(2-hydroxyethoxy)biphenyl and 2,4-TDI. The effect of partial replacement of 4,4′-bis(2-hydroxyethoxy)biphenyl by 25–75 mol% poly(oxytetramethylene) diol on the liquid–crystal properties was studied [180]. Wood coatings are prepared from malleated drying oils such as dehydrated castor, linseed oil, linseed fatty acids and safflower acids by reacting with acrylate and TDI. The anhydride ring opening was carried out using diethylene glycol [181]. Huelsman et al. [182] suggested the use of uralkyd in printing inks. Trimellitic anhydride modified urethanes were used to coat steel anodes [183]. Eckhoff et al. suggested the application for stain resistant [184] and corrosion resistant coatings on metals [185]. Aqueous polyurethane (PU) adhesives are non-toxic and non-flammable and do not pollute the air. However, they have low adhesive strengths compared to solvent-based PU adhesives because of a low affinity with rubber substrates. The polyol was modified with hydroxyl-terminated polybutadiene (HTPB) and hydroxyl-terminated acrylonitrile-butadiene copolymer (HTBN). The effect of the HTPB and HTBN content on the adhesive strength was investigated [186]. Polyfluoroethane oil was used as an additive for the curable composition to produce oil and water repellent binders [187]. The durability and weather resistance of fibrous materials (e.g., ropes and fish nets) were increased by a coating mixture of urethane–alkyd resins [188]. Park et al. [189] synthesized water-based UV-curable paint by mixing PUD with nitrocellulose lacquer. Yan et al. [190, 191] suggested the use of fluorochemicals and lecithin as additives for coatings, which act as thickening agents and dispersants in decorative paints. The use of novel dispersants and thickening agents in decorative coating compounds is presented. The dispersion rates for a variety of pigments, as well as the viscosity, gloss and storage stability of alkyd resins and urethane-modified alkyd resins, were determined [192].

Synthesis of Hybrid Systems

Hybrid systems prepared by sequential polymerization can provide superior properties to those obtained from the corresponding polymer blends. The most widely utilized technique is free-radical polymerization, which is the combination of monomers in the presence of a base polymer (alkyd resin) that may or may not be intrinsically water-dispersible. If the base polymer is water-dispersible, then it can be used directly as a seed for subsequent free-radical emulsion polymerization; however, if the base polymer is not intrinsically water-dispersible, then it can either be emulsified in water by using a combination of surfactants and high shear, or it can be dissolved in monomers that are further polymerized to form an emulsion. In some instances, the polymer may have pendant or terminal functional groups that can participate in the subsequent emulsion polymerization, grafting the two polymers.

Synthesis of Alkyd Acrylic/Urethane Hybrid Systems

Every polymer has certain disadvantages; these can be overcome by combining two or more polymers. Non-conjugated tall oil fatty acids-based alkyd resins were synthesized and further copolymerized via miniemulsion polymerization with acrylates (butyl acrylate and methyl methacrylate) to prepare stable hybrids. An increase in alkyd resin content resulted in a decrease in the polymerization rate, and the steric hindrance of MMA affected the degree of grafting and monomer conversion compared to butyl acrylate [193]. Two kinds of hybrid acrylic-polyurethane (PUA) latexes were compared according to their synthesis and properties. The acrylic part is a copolymer of styrene, methyl methacrylate, and butyl acrylate. The PUA is based on the polycondensation of isophorone diisocyanate and poly(propylene glycol) using butanediol and ethylene diamine as chain extenders. The first class of PU is a result of the polymerization of mini emulsions of solutions of PU in the mixture of monomers using benzoyl peroxide as an initiator at 80 °C. The second class of PU was modified by neutralized dimethylol propionic acid and used as seed along with emulsifiers for emulsion polymerization of the monomer mixtures initiated with azobisisobutyronitrile at 75 °C [194]. Film formation in waterborne coatings [195] was discussed at a symposium held at the 210th National Meeting of the American Chemical Society, Chicago, in 1995. A new technology has been developed to achieve enhanced properties of aqueous urethanes and urethane–acrylics through the design of unique (self) crosslinkable polyols. The synthesis and properties of a wide range of urethanes and urethane–acrylics with varying crosslinking densities and structures were discussed [196]. Observation of multiple glass temperatures in a series of polyurethanes for coatings revealed a two phase morphology arising from the existence of hard and soft segments [197]. Three types of core–shell type acrylic–

polyurethane hybrid aqueous emulsions were prepared by soap-free emulsion polymerization techniques. The size and the distribution of emulsion particles were found to vary drastically depending on the chemical composition of core and shell parts and the core–shell ratio [198]. The hybrid miniemulsion polymerization of acrylates in the presence of alkyd resin was carried out. The polymers obtained were characterized via gel permeation chromatography, ^{13}C NMR, and differential scanning calorimetry. The final product contained some free alkyd resins, though the predominant form was grafted polymer (poly(acrylate-graft-alkyd). This confirmed that monomer droplet nucleation is the predominant nucleation mechanism for this hybrid miniemulsion system [199]. As a part of a wider effort to develop a new class of waterborne coatings, hybrid miniemulsion polymerization was carried out with acrylic monomers (MMA, butyl acrylate and acrylic acid) in the presence of alkyd and oil-modified polyurethane resins. Latexes with different ratios of resin to acrylic monomers were synthesized. Alkyd/acrylate coatings are targeted as a replacement for solvent-based architectural coatings, and oil-modified polyurethane/acrylate coatings may provide a low VOC alternative to solvent-based clear coats [200]. The ultimate objective of the hybrid miniemulsion process is to produce a water-based crosslinkable coating through in-situ grafting of a free-radical growing acrylic polymer with an unsaturated resin. Some authors have reported low incidence of grafting, while others have reported higher. For hybrid systems involving an acrylate monomer such as butyl acrylate (BA), virtually complete grafting with alkyd was observed. This is due to the uninhibited BA radical center that allows the molecule to be directly added through a resin double bond [201]. Emulsion and miniemulsion copolymerizations were carried out with acrylic monomers (MMA, BA, and acrylic acid) in the presence of an alkyd resin. The results demonstrate that the miniemulsion process is the preferred process, probably because of mass transport limitations of the alkyd in the conventional emulsion polymerization reactions [202]. Water-based crosslinkable coatings via miniemulsion polymerization of acrylic monomers in the presence of unsaturated polyester resin was studied by Schork et al. [203]. Schork et al. also synthesized hybrid acrylic–polyurethane latexes by miniemulsion polymerization [204]. Alkyd–acrylic hybrids having final solid contents of 75–80% were prepared by dropping alkyd resin into an acrylic dispersion. Different liquid structures were obtained depending on how the surfactant was added to the system [205]. The morphology of high-solid-content acrylic alkyd hybrid binders were studied by Karlsson et al. [206]. Several reviews about the synthesis and properties of alkyd acrylic emulsions are available in the literature [207–209]. The invention of acrylated modified fatty acid-based hybrid polymers finds its applications in water-based coatings, adhesives and composites [210–212].

Use of Crosslinkers in a Hybrid System

A waterborne polyurethane–polyacrylate (PUA) hybrid emulsion was prepared by using crosslinkers (TPGDA and TMPTA). Results showed that the properties of the films were optimum when TMPTA and TPGDA were used at 0.9% and 0.6%, respectively [213]. With the use of seed emulsion polymerization and in-situ emulsion polymerization, multiple-crosslinkable polyurethane–acrylate hybrid emulsions were prepared via introducing intra- and inter-molecular crosslinking structures. The effects of the addition methods and content of crosslinkable groups on the properties of the emulsions and their films have been studied [214]. A double self-crosslinked polyurethane–acrylate (PUA) hybrid emulsion crosslinked not only by ketone and hydrazide groups but also by epoxy and carboxyl groups. The emulsion polymerization was carried out in situ with toluene diisocyanate (TDI-80), polyether binary alcohol (Diol-1000), butanediol (BDO), dimethylol propionic acid (DMPA), methyl methacrylate (MMA), glycidyl methacrylate (GMA), adipic dihydrazide (ADH) and diacetone acrylamide (DAAM) as reactants. The mass fractions of ADH, DAAM, COOH in DMPA and GMA in PUA were, respectively, 4.1, 2.2, 1.6, and 4.0%. The emulsion and film both exhibited excellent properties [215].

Acrylate Modified PU Hybrid System

The polyurethane–acrylate (PUA) hybrid emulsion is synthesized by in-situ polymerization with toluene diisocyanate, polyethylene glycol, 1,4-butanediol, dimethylol propionic acid, methyl methacrylate, triethylamine and potassium persulfate as the main materials [216]. PU/poly[ethyl(butyl)acrylate] [PU/PE(B)A] hybrid emulsions were synthesized by the method of seed emulsion polymerization, and the influence of the composition was investigated on the properties of emulsions [217]. Aqueous acrylic–polyurethane (AC-PU) hybrid emulsions were prepared through the semibatch emulsion polymerization of acrylic monomer mixtures MMA, BA and acrylic acid, using a polyester-based polyurethane dispersion as a seed. The PU dispersion was synthesized through a prepolymer mixing method using isophorone diisocyanate, an aliphatic, polyester polyol, dimethylol propionic acid and hexamethylene diamine with triethyl amine as the neutralizing base and *N*-methyl pyrrolidone as the co-solvent [218]. Contact angle measurements indicated an increase in the surface energy of AC–PU hybrid films with increasing acrylic components. The waterborne polyurethane prepolymer (PU) was prepared with the method of emulsion polymerization in situ, through the free-radical polymerization of polyurethane resin and methylmethacrylate to form a hybrid emulsion. A product prepared with a 1.3–1.4 of NCO/OH ratio, approximately 2.6% of –COOH content, 20–30% of MMA content, and 90–100% of the mole ratio of TEA/DMPA, produced PUA emulsions with satisfactory coating properties [219]. Aqueous acrylic–polyurethane hybrid emulsions were prepared by the semibatch emulsion copolymerization of MMA and BA in the presence of eight polyurethane dispersions. The interactions between the acrylic and polyurethane components in hybrid particles and the particle structures were studied with IR spectroscopy and NMR spectroscopy. Mechanical properties such as the Koenig hardness, tensile strength, elongation at break, and Young's modulus were improved [220].

Silicon and Fluorine Modified Hybrid Emulsions

The incorporation of silicon in the polymer network enhances exterior durability, hardness, water and solvent resistance. Light and solvent resistance was improved by using 1% γ-methacryloxypropyltriethoxysilane and tetraethoxysilane in hybrid emulsions. The result suggested the formation of the 3-dimensional crosslinking network between the acrylic polymer chain and silica [221]. A new core–shell fluorinated acrylic silicon PU hybrid emulsion was synthesized using siliconated polyurethane as a seed and copolymerized with BA and trifluoroethyl methacryalte (TFEMA). TEM data confirmed the core–shell structure [222]. The water and oil repellency of films were improved significantly with a suitable fluorine and siloxane content. The synthesized acrylic silica hybrid emulsion, which exhibited pollution resistance and fire proof properties, was used in paint preparation. A new type of polysiloxane modified PUA hybrid emulsion was prepared by using dihydroxybutyl-terminated polydimethylsiloxane (PDMS) [223]. The improved water resistance and mechanical properties were measured. The physicochemical properties of silica powder and the stability of the organic–inorganic hybrid emulsion were investigated by Chen et al. [224]. Figure 13 shows the synthesis of hybrid emulsion containing fluorine and siloxane. The acrylic polyurethane modified with 12% siloxane and 20% fluorine exhibited excellent oil and water resistance [225].

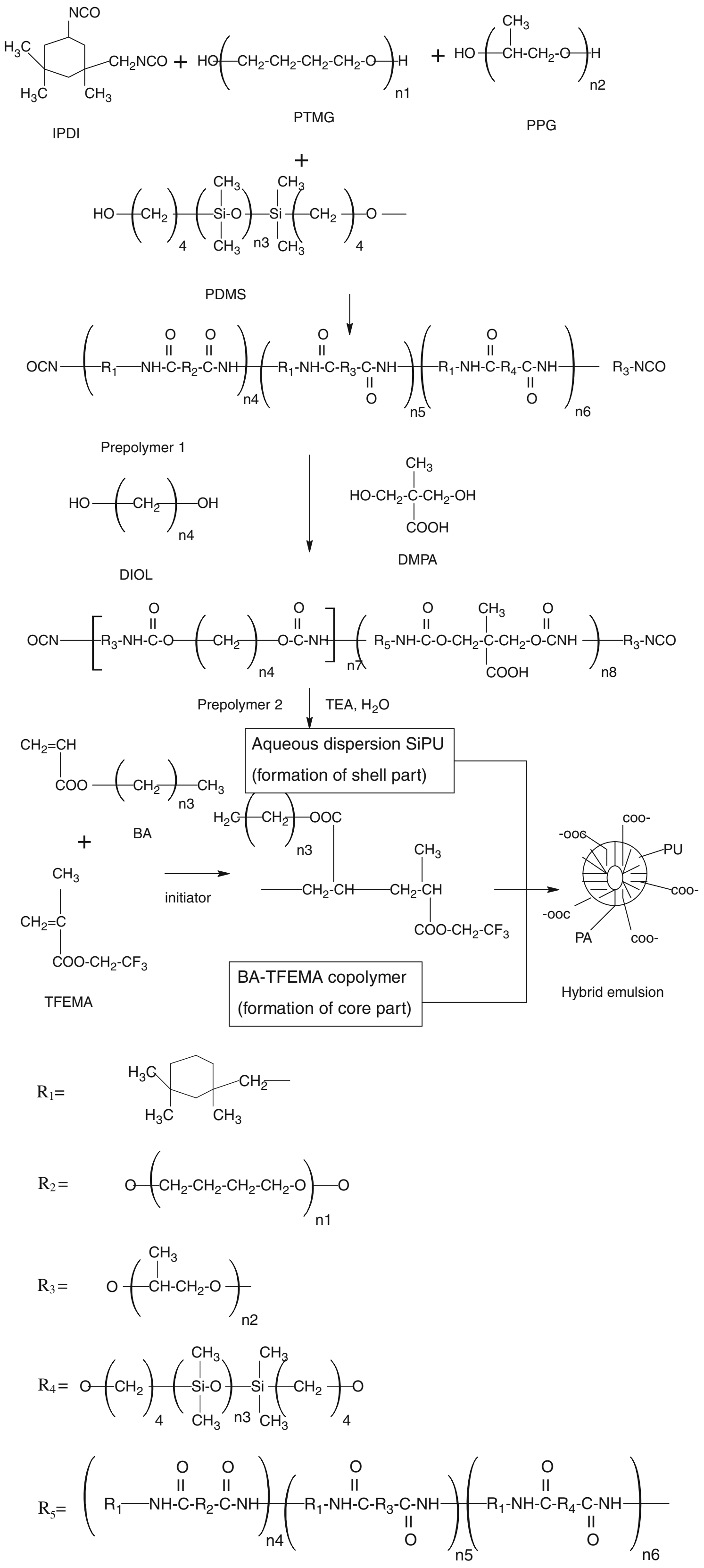
The Clean Air Act (United States) was passed in 1970, which was not targeted at the coating industry, but it did mandate that coatings could only contain VOC (volatile organic compounds) levels of 3.5 lb (lbs)/gallon of water. However, the most commonly used solvent-based paints ranged up to 6.0 lbs/gallon of water. The VOC content of solvent-based paint can range from 2.5 lbs/gallon of water up to 6.0 lbs/gallon of water, depending on the formulation of the paint. By excluding water from the calculation, the results reflect only the volume of VOC and non-volatile solids. During the production of waterborne paint, however, the organic solvents are, in part, replaced by water, resulting in VOC levels between 1.5 and 3.5 lbs/gallon of water. Industrial manufacturers realized that reducing the coating-related VOC in their factories (in compliance with the Clean Air Act) can improve conditions in their factories. If they have to comply with VOC requirements without sacrificing their significant investment in liquid paint, which often includes integrated wash lines, spray paint booths, and drying ovens, then they need to use waterborne coatings. They saw other advantages of water-based coatings; paint booths equipped with filters that absorb any over-spray were replaced and discarded, and solvent paint-laden filters were treated as hazardous waste. However, when waterborne paints were used, the filters were less hazardous, as long as spontaneous combustion of the oxidizing vehicle was prevented. In addition, the risk of fire with solvent-based coatings disappears with waterborne coatings, providing both a practical advantage and a financial incentive in the form of reduced insurance premiums. Water-borne coating manufacturers reached the same conclusions and began making significant research and production investments to create high-performance, low-VOC, waterborne liquid coatings that would empower manufacturers to meet market requirements and improve working conditions.

Underlying this trend in low-VOC coatings was a mutual understanding by industrial and coating manufacturers that any new coating also had to meet all the necessary economic and field performance requirements. No company could afford to adopt a coating that made a poor impression on the market, failed during use, or was too expensive to apply. For example, colors had to match that of the solvent paint being replaced, and color consistency had to be exact from batch to batch. Some companies market products that feature metallic appearance as a key focal point. This product category had to be filled by waterborne companies as well.

Conclusions

Stringent VOC regulations have stimulated the tremendous research in waterborne coatings. Various chemistry theories and experiments have been carried out to achieve coating performances on par with solvent-borne systems, focusing more on environmentally friendly products. Different types of hydrophilic agents, stabilizers, viscosity modifiers and

Fig. 13 Synthesis of a hybrid emulsion containing fluorine and siloxane



emulsifiers are used to combine two or more different polymers to form hybrid systems. It has been found that the hybrid systems give optimum coating properties. Polyurethanes embedded in polyesters and copolymerized with acrylate monomers by emulsion polymerization is an area of recent research. Alkyds modified with urethane are gaining importance due to their autooxidative properties and flexibility. Copolymerizations with acrylates give weatherability and toughness, while emulsion polymerization results in a stable aqueous dispersion with a fine particle size. The paint industry in the future will be using renewable resources of oils obtained from plants to formulate waterborne coatings, which are likely to replace the solvent-borne systems completely.

Prognosis

The overall market share of environmentally friendly waterborne coatings is still relatively small compared to solvent-borne alternatives. However, waterborne coatings are becoming increasingly important as a technology to reduce VOC emissions and thus cost. Water-borne coatings are being pushed worldwide by regulatory bodies for higher market shares. Today, they are used in a wide selection of market segments, such as wood and furniture, but also on non-wood substrates such as metals and plastics for industrial maintenance coatings, coatings for machines and equipment, and metal cans. One obstacle that still limits the use of waterborne coatings in various applications is the sometimes poor solvent and humidity resistance of waterborne coatings. In order to overcome these drawbacks, different additives are available, mainly based on silicones or paraffin waxes. However, these additives are not universally applicable and can be used only in specific formulations. In addition, they may cause problems later when coated parts have to be over-coated or refurbished. With today's evolving technology, one thing to look for in water-based coatings is a multifunctional additive. Multifunctional additives allow paint formulators to achieve a number of different benefits with just one product. Many amines on the market claim to be multifunctional, but there are very few that offer a full range of capabilities. When selecting a multifunctional amine for waterborne coatings, there are some key properties to seek. Excellent co-dispersion, viscosity stability, film performance, physical properties and additive optimization are all important considerations when using a multifunctional amine. An efficient dispersion lays the groundwork for the highest quality optical and film performance of the end product. There are various desirable film properties, but one of the most important is achieved through the ability to reduce water-sensitive components from the film. Most dispersants and surfactants contain 25–50% non-volatile, hygroscopic components that remain in the dried paint film and contribute to poor scrub resistance and water spotting. With a multifunctional amine that disperses efficiently and allows for the reduction of these hygroscopic components, customers can realize improved scrub resistance, water resistance and reduced water spotting of the film. Blocking is another unwanted characteristic that an efficient multifunctional amine can help to reduce. Blocking is the tendency of painted surfaces to adhere to one another, creating deficient performance of the final film. When using a multifunctional amine that has balanced physical properties, one can achieve a controlled release such that the additive will remain in the film long enough to offer a range of advantages but will not remain in the film for a prolonged period of time. Bases that remain latent in the dried film are the ones that contribute to lower block performance. Maintaining excellent film properties also requires that additives do not contribute to yellowing. As they age, many paint components become subject to this unwanted variation in color because of their exposure to light and other factors related to the environmental conditions in which they exist. A multifunctional additive that remains stable in the formulation will not go through this yellowing color shift. In an industry where there are thousands of tinted colors on the market, prevention of yellowing is paramount, as any slight change in undertone can lead to customer complaints. High gloss is an important attribute of paint as well, and a multifunctional amine that provides complete dispersion and stabilization of the prime pigments will maximize optical performance. In an extremely competitive industry, it is this performance that helps coating manufacturers stay ahead of the competition.

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