

2

Organic film formers

J Bentley

2.1 Introduction

The first chapter has indicated the major types of surface-coating resins used, and this chapter will describe their chemistry in more detail, including their preparation.

In this introductory section an outline is presented of the theory of polymer formation and curing; the mechanism specific to each type of resin is then covered more fully in the subsequent sections of the chapter. The classes of resins available and the factors that decide the choice of resin for a particular use are also indicated. The properties and uses of each type of resin, again, are detailed more fully in the later relevant sections.

A number of terms are used interchangeably to describe the film-forming component of paint, as will already be apparent. 'Film former', 'vehicle', or 'binder' relates to the evident fact that this component carries and then binds any particulate components together, and that this provides the continuous film-forming portion of the coating. Resin or varnish are older terms relating to the previous more prevalent use of natural resins in solution or 'dissolved' in oils as the film former; they date from the time when the chemistry and composition of these components were far less well understood. Nowadays, with our better knowledge of the materials used, along with the wide application of the sophisticated polymers used also in the plastics and adhesives industries but tailored to our own use, it is strictly more correct to refer to this component as the polymeric film-forming component. The interchangeable use of old and new nomenclature is also found in the manufacture of film formers where 'kettle' refers to the polymerization reactor, and 'churn' to the thinning tank normally part of the manufacturing plant.

Film-forming polymers may or may not be made in the presence of solvent; however, since the polymers in solvent-free form generally range from highly viscous liquids to hard brittle solids, they are practically always handled in storage and in the paint-making process in solution (or in dispersion) with significant quantities of solvent or diluent included (and here the terms solvent and diluent include the full range of organic solvents and water). The exceptions are where unsaturated

monomers and liquid oligomeric materials are used in place of solvent as diluents in high solids finishes. Solid resins are also used alone for the specialized application of powder coatings.

Many polymers used will be in true solution, with solvent being the other component. However, in other cases, either for reasons connected with the polymer preparation or with its final use, the polymer will exist in the form of a fine-particle dispersion in non-solvent (diluent); this is true for aqueous emulsions, non-aqueous dispersions, and for the emulsified materials used in electrodeposition and other water-borne applications. In some cases the system may be mixed solution/dispersion, for example a solution containing micellar polymer dispersion, micro-emulsion or microgel. A particular striking consequence of whether the polymer is dissolved or dispersed is the viscosity; dispersions are invariably more fluid at comparable solids contents than solutions. Most significantly while solution viscosity increases as molecular weight rises, the viscosity of emulsions or dispersions is independent of molecular weight. For any given polymer in solution or dispersion, viscosity will broadly increase as the solids increases (though water-borne solutions often exhibit unusual behaviour); the viscosity will decrease if the temperature rises.

As with any utility product, the paint user is concerned mostly with the ability of the material to provide final protective and decorative effects; he or she has little regards for composition, except in so far as it guides him or her to the ability of the material to satisfy those needs. Table 1.1 in Chapter 1 has listed the function of paint components and Table 2.1 shows the contribution that the three major components — resin, pigment, and solvent — make to the most important properties of a typical gloss paint. Informed readers will see limitations in the above, but it is primarily intended to highlight the broader binder/solvent contributions.

Generally all polymer types can provide a spectrum of compositions covering a span of properties at varying cost, and so given user criteria may be satisfied by selection from a number of resin types. The principal final choice for the user, whose application and cure conditions will probably have been determined by scale and now possibly environmental considerations, ultimately would appear to concern balancing performance and cost; true cost includes the total of paint cost, labour and equipment cost, and energy for cure.

The industry is constantly striving for higher performance and novel products. Factors influencing system design may well include a need to guarantee performance in such diverse applications as decorative maintenance paints and in automobile and coated coil products, and to apply total quality management concepts

Table 2.1 — Contribution of major paint components to final paint properties

Property	Film former	Pigment	Solvent
Application	Major	Minor	Major
Cure rate	Major	None	Significant
Cost	Major	Major	Minor
Mechanical properties	Major	Minor	—
Durability	Major	Major	—
Colour	Minor	Major	—

as enacted in the ISO 9002 standards required of suppliers. Other forces that increasingly apply are legislation to control usage and pollution, availability and cost of energy supplies, and periodic abundance or shortage of natural and oil-based materials. Most recent developments are the carrying out of life-cycle assessments (LCAs) on paints in connection with eco-labelling studies, along with needs to apply environmental management systems (EMSs) in manufacture [1, 2]. LCA carries through to ultimate disposal including consideration of recycling of paint, paint waste, and packaging. Eco-labelling is now a major issue and can drive the choice of all components of the paint system; compliant coatings are those fully meeting both legislation and voluntary agreements. These issues present many challenges to the resin formulator [3, 4].

The choice and amount of solvent or diluent used will be constrained by hazard and eco-labelling and then will depend on the nature of the polymer and the method of application; the quantity of solvent (solids) and final viscosity will then depend on the latter. The method of application generally imposes constraints regarding solvent boiling point and evaporation rate, for example, to ensure good spray or brush application. If the polymer can be prepared in the presence of little or no solvent, the solvent required by the method of paint application has little practical significance to the resin chemist, i.e. an alkyd or polyester may easily be thinned at end point with high or low boiling solvent. However, for an acrylic resin it is usually necessary to use a solvent or solvent blend of low chain transfer properties; the boiling point must be such that the reaction mixture can be refluxed to remove heat of polymerization and such that an initiator system is available at that temperature capable of efficient conversion of monomer to polymer. The enduring market trend is in reducing quantities of all organic solvent (particularly hydrocarbon solvent) used and in an increase in the use of water as a major part of the solvent/diluent system.

The mechanical properties of any given polymer 'improve' as molecular weight increases up to a value at which no change is seen with a further increase. In contrast the viscosity of the solution of a polymer continues to increase with molecular weight without a break. This imposes the constraint in designing a surface-coating system that if the polymer is to be made for optimum application and final properties, then molecular weight needs careful specification and control. Furthermore, since for many polymer systems the molecular weight necessary for good mechanical properties and durability will be high, considerable amounts of solvent will be needed to obtain good application properties, if the polymer is to be applied in solution at that molecular weight. The kind of system this describes is a lacquer, drying by solvent evaporation alone to leave a film of the polymer with useful properties, with no subsequent change of molecular weight or further reaction occurring. Practically this system, initially used with varnishes such as Shellac and French polish, continues with plasticized nitrocellulose and with thermoplastic acrylic lacquer systems used in automotive refinishing systems.

The simplest way of avoiding the molecular weight/viscosity conflict is the use of dispersion rather than solution systems. Examples are the decorative aqueous emulsions now made in high volume, the dispersed polymer used in water-borne systems, non-aqueous dispersion (NAD) systems, and organosols. The use of dispersions can also allow the use of cheaper, less polluting diluents, and was particularly useful when the Californian Rule 66 legislation controlling the VOC (volatile organic content) of factory exhaust emissions was first introduced. Dispersed polymers are,

however, more complex to formulate, and more restricted in composition than solution polymers.

Most surface-coating systems avoid the molecular weight constraint by using 'crosslinking' or 'curing' reactions; the system is assembled with one or more reactive polymer components of relatively low molecular weight, capable of further reaction after application to high or infinite molecular weight. Crosslinking implies a multifunctionality such that each initial component molecule links to a number of other molecules, so that an infinite network is formed in the final coating.

Methods used for film formation with typical polymer systems are shown in Table 2.2. In every case except the lacquer system, the polymer system assembled includes free reactive groups in its architecture appropriate to the method of curing chosen. The curing reactions are discussed later in this chapter under the appropriate resin types. Apparent overlap of techniques may be found; for example, stoving may be used to accelerate solvent evaporation so blurring the distinction between thermoplastic and thermosetting acrylics; equally, stoving may accelerate curing of an alkyd capable of slower but ultimately satisfactory air-drying unaided.

Electrodeposited films normally require a subsequent heat cure; electrodeposition insolubilizes the polymer on deposition, but the film is soft and not fully resistant to other agents until crosslinking occurs. Electrostatic spraying of powder coating lightly adheres the powder to the substrate, but this may be brushed off until fused and possibly cured by stoving.

Polymers are conveniently categorized by their method of polymerization from monomers, which may be by stepwise or functional group polymerization, or by chain addition polymerization. These terms are more satisfactory than the older common terms, condensation and addition polymerization, being both more precise and more generally applicable.

Stepwise or *condensation* polymerization is identified where the monomer units initially present are nearly all incorporated into larger molecules at an early stage in the reaction; these larger molecules remain reactive and continue to join together so that the average molecular weight increases with time, but once the reaction is under way the yield of polymer species does not vary with reaction time. The reaction usually involves two separate monomer species with different but co-reactive groups. Most usually, though not invariably, some small molecule such as water will be eliminated as each step occurs. Alkyds and polyesters are typical stepwise polymers. The concept of functionality is particularly relevant to this type of polymerization in that a minimum requirement of each 'monomer' molecule is that it shall

Table 2.2 — Methods of film formation for typical polymer systems

Method	External agent	Typical polymer system
Solvent evaporation	None or heat	Lacquer systems
Environmental cure	Oxygen	Oil-modified alkyd
	Moisture	Moisture-curing urethane
Vapour phase curing	Amine	Hydroxy acrylic/isocyanate blend
2-pack	None or heat	2-pack epoxy/amine
Radiation	Infrared/ultraviolet/electron beam cure	Photocuring unsaturated polyester
Thermosetting	Stoving oven	Alkyd/nitrogen resin blend
		Thermosetting acrylic

Table 2.3 — Classification of polymer types used in coatings

Type	Subgroup
Natural resins	Resins, gums, rosin
Modified natural resins	Cellulose, starch, nitrocellulose
Stepwise (condensation) polymers	Polyester, alkyd resins
	Formaldehyde resins (urea, melamine, phenol)
	Epoxy resins
Chain addition polymers	Acrylic polymers and copolymers
	Vinyl polymers
Ether polymers	Polyethylene oxides and glycols

possess two reactive functional groups, if the product of each reaction step is to be able to participate in further reactions.

Chain addition polymerization has the characteristic that high molecular weight polymer is formed from the start by a chain reaction, and monomer concentration decreases steadily throughout the polymerization period; thus the yield of polymer increases with time, unlike stepwise polymerization. Polymerization is initiated by some active species capable of rupturing one of the bonds in the monomer, and may be radical, electrophilic, or nucleophilic in character. Only free radical chain addition polymerization is generally practised in production by surface-coating manufacturers though they may purchase polymers made by other techniques. Acrylic polymers are the best known chain addition polymers.

Group transfer polymerization is one special technique [5], enabling polymers of varied and controlled architecture and functionality to be prepared. Other investigations into structure control techniques [6] have provided star, hyperbranched, and dendritic structures [7, 8] finding application in high solids finishes (see Section 2.18). A further new technique, giving low molecular weight polymers of narrow distribution, also with potential for high solids applications, is catalytic chain transfer polymerization (CCTP) [9].

Table 2.3 shows the broad types of polymers used in coatings, partly in terms of the above classification. Ether polymers are separated into a group of their own, in part to acknowledge that materials such as polyethylene glycol can be prepared by both stepwise and addition polymerization, and also to avoid further confusion. Epoxy resins are formed by stepwise polymerization, but it should be noted that the epoxide group may take part in both stepwise and chain addition polymerization.

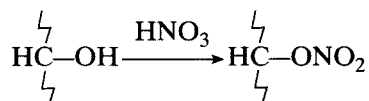
Finally, while the polymer phase has been referred to as the continuous phase, it should not be assumed that this phase is always homogeneous. Providing the bulk of the phase is continuous, there are many instances, a number described later in this chapter, where identifiable polymer inclusions are present, altering the properties of the final film. These inclusions are invariably of sub-micron size. Often these are rubbery, toughening the film, but there are also instances where these are hard affecting pigment distribution, or voided providing additional opacity.

2.2 Natural polymers

The vehicles used as surface coatings were originally based on natural oils, gums, and resins, giving, when combined, a range of both lacquer and autoxidatively drying

products. The naturally occurring triglyceride oils still find considerable use in oil-modified alkyds and to a lesser extent in other fatty acid-modified products such as epoxy esters, and these are described under separate headings. The use of other natural products has now diminished to very minor amounts, in part owing to limited availability; some mention of those natural resins still used is made in the section on oleoresinous vehicles.

Under the description of modified natural products mention must be made of cellulose derivatives, particularly 'nitrocellulose', which is the major binder in cellulose lacquers which still find use. Nitrocellulose, more accurately named cellulose nitrate, is obtained by the nitration of cellulose under carefully specified conditions, which control the amount of chain degradation and the extent of nitration of the hydroxyl groups of the cellulose. The nitration reaction in essence is



Organic esters of cellulose can also be produced, and the mixed ester cellulose acetate butyrate is used as a modifying resin additive, particularly for acrylic lacquers. The mixed ester is used in preference to the softer higher esters, or the acetate which has poorer dimensional stability (see Section 2.7.4). Sucrose esters are now available, finding similar uses.

Cellulose derivatives such as hydroxy ethyl cellulose and the salts of carboxy methyl cellulose also find use as protective colloids in the emulsion polymerization of vinyl monomers (see Section 2.8).

2.3 Oils and fatty acids

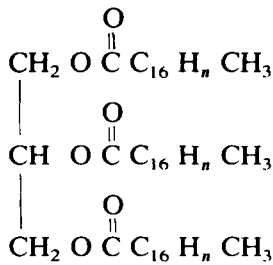
Vegetable oils and their derived fatty acids still play an important role in surface coatings today because of their availability as a renewable resource, their variety and their versatility.

Oils are mixed glycerol esters of the long chain (generally C₁₈) monocarboxylic acids known as fatty acids (Fig. 2.1); unrefined oils also contain free fatty acids, lecithins, and other constituents, the first two finding their own application in coatings.

Oils useful in coatings (Table 2.4) include linseed oil, soya bean oil, coconut oil, and 'tall oil'. Many countries will find some application for their own indigenous oils as well as those detailed here. When chemically combined into resins, oils contribute flexibility and, with many oils, oxidative crosslinking potential, one of the properties most exploited in paint.

It should be added that in searches for a synthetic alternative to drying oils, only allyl ethers have been found to be both accessible and possess similar and useful autoxidative abilities. These have found limited application in high solids finishes and unsaturated polyesters (see Sections 2.6.4 and 2.18).

Oils are classified as drying, semi-drying, or non-drying, and this is related to the behaviour of the unmodified oil, depending on whether it is, on its own, able to oxidize and crosslink to a dry film. This behaviour is directly related to the concentrations of the various fatty acids (Table 2.5) contained in the structure. These fatty



n may be 32, 30, 28, or 26

Fig. 2.1 — Representative structure of naturally occurring oil.

Table 2.4 — Composition of major oils used in surface coatings

	Saturated acids	Oleic acid	9,12-Linoleic acid	9,12,15-Linolenic acid	Conjugated acid
Tung	6	7	4	3	80 ^d
Linseed	10	20–24	14–19	48–54	0
Soya bean	14	22–28	52–55	5–9	0
Castor oil	2–4	90–92 ^a	3–6	0	0
Dehydrated castor oil	2–4	6–8	48–50	0	40–42 ^b
Tall	3	30–35	35–40	2–5	10–15 ^c
Coconut	89–94	6–8	0–2	0	0

^a Principally ricinoleic acid, not oleic.

^b Conjugated 9,11 linoleic acid.

^c Conjugated linoleic acid and octadeca 5,9,12-trienoic (pinolenic) acid, proportions dependent on source and refinement.

^d α -Eleostearic acid.

Table 2.5 — Structures of the commonly occurring unsaturated fatty acids

Octadeca-9-enoic (oleic)	$\text{CH}_3 \cdot (\text{CH}_2)_7 \cdot \text{CH}=\text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOH}$
Octadeca-12-hydroxy-9-enoic (ricinoleic)	$\text{CH}_3 \cdot (\text{CH}_2)_4 \cdot \text{CH}_2 \cdot \text{CHOH} \cdot \text{CH}_2 \cdot \text{CH}=\text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOH}$
Octadeca-9,12-dienoic (linoleic)	$\text{CH}_3 \cdot (\text{CH}_2)_4 \cdot \text{CH}=\text{CH} \cdot \text{CH}_2 \cdot \text{CH}=\text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOH}$
Octadeca-9,11-dienoic (conjugated linoleic)	$\text{CH}_3 \cdot (\text{CH}_2)_5 \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOH}$
Octadeca-9,12,15-trienoic (linolenic)	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}=\text{CH} \cdot \text{CH}_2 \cdot \text{CH}=\text{CH} \cdot \text{CH}_2 \cdot \text{CH}=\text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOH}$
Octadeca-5,9,12-trienoic (pinolenic)	$\text{CH}_3 \cdot (\text{CH}_2)_4 \cdot \text{CH}=\text{CH} \cdot \text{CH}_2 \cdot \text{CH}=\text{CH} \cdot (\text{CH}_2)_2 \cdot \text{CH}=\text{CH} \cdot (\text{CH}_2)_3 \cdot \text{COOH}$
Octadeca-9,11,13-trienoic (α -eleostearic)	$\text{CH}_3 \cdot (\text{CH}_2)_3 \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot (\text{CH}_2)_7 \cdot \text{COOH}$

acids contain, with few exceptions, 18 carbon atoms including the terminal carboxyl. Fatty acids may be saturated (no double bonds), mono-unsaturated (one double bond) or polyunsaturated (two or more double bonds); to be considered 'drying' an oil must contain at least 50% of polyunsaturated acids. The fully saturated C_{18} fatty acid is stearic acid, of which some is found in all oils. The C_{12} saturated fatty acid, lauric acid, is the predominant component of coconut oil, where it constitutes 90% of its composition.

Thus linseed oil, a good drying oil contains over 60% of the polyunsaturated linoleic and linolenic acids, while soya bean oil, usually classified as semi-drying, contains just over 50% of linoleic acid. By contrast, coconut oil, a non-drying oil contains 90% saturated lauric acid and less than 10% unsaturated fatty acid.

Polyunsaturated fatty acids may be conjugated or non-conjugated, and tung oil, now in short supply and little used, contains nearly 80% of the conjugated α -eleostearic acid. By contrast 9,12,15-linolenic acid has three non-conjugated double bonds, while 9,12-linoleic acid has two non-conjugated double bonds. High conjugation is reflected in higher drying ability and greater tendency to heat body over that expected from the double bond content; thus, tung oil can in fact readily be gelled by heating, and for this reason — if incorporated into an alkyd resin — would not be processed by the monoglyceride process, this being considered too risky.

The drying oils, tung and linseed, may find application either unmodified or only heat bodied in coating compositions in simple blends with other resins. In contrast, most other oils find little application alone but only after chemical modification; soya bean oil, for example, finds its major application in chemically combined form in long oil alkyds. Oils such as coconut oil do not dry or heat body and have no application alone, but only find use when reacted into alkyds. In this case the oil component provides plasticization. Coconut alkyds have good colour and are used for stoving finishes and appliance enamels.

The two most important oils to the industry nowadays are probably soya bean oil and 'tall oil', the latter misnamed, as it is a fatty acid mixture containing over 50% polyunsaturated fatty acid, principally 9,11-linoleic acid. Tall oil is a by-product of the paper industry, and to be useful in coatings must be refined to reduce its rosin content to 4% or less from the higher concentration in the crude product. However, it is the fractionally distilled form [10, 11], which can now be interchanged with soya fatty acids (and in alkyds where soya bean oil is replaced with tall oil and polyol) depending on seasonal fluctuations of availability and price. Tall oil of Scandinavian origin may be more favoured than that from America owing to its higher unsaturated fatty acid content, which includes the triply unsaturated pinolenic acid. Tall oil is probably more variable in quality, dependent on source and refinement, than any other oil or fatty acid, and so needs careful evaluation and specification for any critical use.

An oil with a more distinctive fatty acid is castor oil which contains nearly 90% of ricinoleic acid, or 12-hydroxy oleic acid. It has some use as a polyol for polyurethane preparation; a major use exploiting the hydroxyl content is in the preparation of higher hydroxyl containing alkyds for crosslinking with nitrogen resins or isocyanates, and for use as plasticizing alkyds for nitrocellulose where high polarity is necessary for compatibility.

Oils are generally purified by acid or alkali refining for the coatings industry in order to remove materials such as free fatty acids and lecithins, to give a neutral clear product and to improve colour. When further reaction is required, oils may be

separated into constituent fatty acids and glycerol, and though more expensive than oil, the free fatty acids of all the common oils are currently available to the coatings industry.

2.3.1 Modified oils

Drying oils may be heat-bodied at temperatures in the region of 290°C to produce 'stand oils', where the viscosity increase is due principally to dimerization reactions through double bonds of unsaturated fatty acid moieties. This reaction may be followed through decrease in the iodine value. 'Stand oils' find application in oleo-resinous vehicles and in alkyd resins. The separated dimer fatty acids also find specialized uses, for example in polyamide resin manufacture.

So-called boiled oils were once prepared by heating metal oxides in oil until fatty acids released during bodying solubilized the oxides as soaps. Nowadays a 'boiled oil' may be prepared more conveniently by blending commercial driers with a 'stand oil'.

Dehydration of castor oil is important, since the removal of the hydroxy group and an adjacent hydrogen atom creates an additional double bond, so increasing the residual unsaturation. Dehydrated castor oil (DCO) has distinctive characteristics since the second double bond generated is generally positioned relative to the original one to give both conjugated as well as non-conjugated polyunsaturation. Some bodying may occur on dehydration, although this can be minimized by use of a good vacuum and suitable catalysts, thus reducing the time necessary for the reaction. By virtue of its unsaturated fatty acid content DCO is classed as a drying oil. DCO finds major application in stoving alkyds and in alkyds required for further modification by vinylation; it is little used in air-drying finishes because of the incidence of surface 'nip' (tackiness) in dried films. DCO fatty acids are also available to resin formulators.

Castor oil may also be hydrogenated, and hydrogenated castor oil (HCO) has some application in alkyd resins for stoving application with MF resins; HCO fatty acid, more usually named 12-hydroxy stearic acid, finds application particularly for graft copolymers [12] for use in dispersants and surfactants (see Section 2.9).

Isomerization of oils and fatty acids is used to improve the drying properties particularly of medium oil length alkyds. These processes includes transformation of the double bonds of non-conjugated fatty acids (principally linoleic) to conjugated form, and in certain cases from the *cis* to the *trans* isomer; a number of processes exist for carrying this out [13]. Improvements from using these oils/fatty acids include better colour, initial dry, and resistance to water, acid, and alkali. Weathering and gloss retention are also said to be improved.

Oils and fatty acids containing unsaturation can be reacted with maleic anhydride. Where conjugated double bonds are present a Diels–Alder reaction (Fig. 2.2) is possible, and this proceeds exothermically. Where the bonds are non-conjugated (linolenic or linoleic) the first addition is by the Ene reaction; this has the consequence of moving the double bonds from a non-conjugated to a conjugated configuration. There is then the possible side effect that a sluggish first Ene reaction (Fig. 2.3) may be followed by a faster exothermic Diels–Alder second reaction.

Maleinization is carried out to increase acid functionality of fatty acids, for example for subsequent water solubilization (see Sections 2.5.7 and 2.16). It also occurs *in situ* in alkyd preparations where maleic anhydride is included in the for-

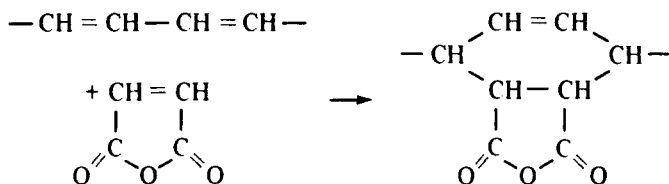


Fig. 2.2 — Diels–Alder reaction.

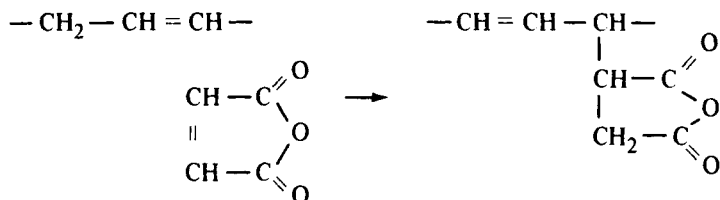


Fig. 2.3 — Ene reaction.

mulation, and its effect is to increase viscosity by increasing acid functionality. Care is needed in formulation since a small maleic addition can for this reason have an unexpectedly large effect.

True ‘urethane oils’ are obtained where a monoglyceride produced by reaction of an oil with glycerol (see Section 2.5.8) is reacted with a diisocyanate; most ‘polyurethanes’ of this type are, however, urethane alkyds where some condensation of monoglyceride with dibasic acid is first carried out prior to diisocyanate reaction.

Oils and fatty acids may be vinylated, but this alone has little application, though it may be a first step in the preparation of a water soluble or a vinylated alkyd (see Sections 2.5.7 and 2.5.8).

2.3.2 Drying oil polymerization

As previously stated, drying oil fatty acids may dimerize under heat treatment by Diels–Alder or Ene reaction of unsaturated groups. However, the most exploited reaction of these unsaturated groups is autoxidative crosslinking, accelerated by the presence of heavy metal driers and also with the aid of heat in stoving compositions.

The theories of autoxidative dry have been well reviewed [14], and the mechanisms recently further investigated [15, 16]; only an outline is given here. It is now accepted that the first steps in autoxidative drying are free radical in nature and involve hydroperoxide formation. It is believed that in the process double bonds may shift from the *cis* to the *trans* structure; for linoleates hydroperoxidation can lead to a movement in the double bond adjacent to the position of attachment of the hydroperoxide leading to a conjugated structure that stabilizes the product. While Khan [17] explained this by a non-radical reaction transition state, Fig. 2.4 shows a more likely mechanism with a delocalized radical transition state [18].

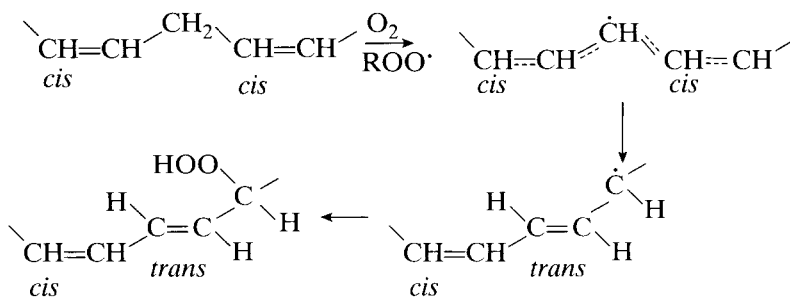
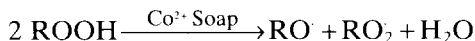


Fig. 2.4 — Oxidation of 9, 12-*cis-cis*-linoleate to conjugated *cis-trans*-linoleate hydroperoxide.

It is unclear whether added metal drier effects hydroperoxide formation. It is, however, well established that further decomposition and crosslinking reactions of hydroperoxides are accelerated by the presence of metallic driers (particularly cobalt). The use of a hydroperoxide with cobalt drier to initiate the cure of unsaturated polyesters is an example of this reaction being used elsewhere. Just as this latter reaction is identifiable as free radical in nature, so the autoxidative crosslinking reaction is also largely free radical in mechanism. This may be exploited by the copolymerization of high boiling or involatile vinyl monomers into an autoxidatively drying system to modify final properties [19, 20] (see also 2.18):



The actual crosslinking reactions following radical formation are complex, and as well as the desired high molecular weight compounds, scission products with aldehydes prominent [21, 22] are also produced, giving characteristic drying smells. Yellowing is also a feature [23]. Polymerization reactions certainly involve both radical dimerizations and reactions further involving residual unsaturation. Recent evidence also indicates the transient presence of epoxides and endoperoxides [15].

Metallic catalysts or accelerators used are principally derivatives of heavy metals, particularly cobalt, with added calcium, zirconium and aluminium and other transition metals to enhance through drying properties in paint compositions; metals are normally added as soaps of long chain acids so that they are fully soluble in the media.

Synthetic branched acids have now displaced the use of naphthenates. Lead has been almost entirely eliminated because of its toxicity, and replaced with zirconium and aluminium, as above [24].

2.3.3 Characterizing oils

The iodine value of an oil is the number of grams of iodine absorbed by 100g of oil; since iodine adds across double bonds this is a measure of the unsaturation present. The Wijs method is the most commonly used, though this can be inaccurate with conjugated systems.

The saponification value gives an indication of the molecular weight of the component fatty acid chains, assuming the original oil is intact and entirely triglyceride.

It must be noted that oils, being derived from annual crops of typically leguminous plants, can vary from season to season in quality (that is in fatty acid distribution); crop yields also vary, causing supply and price fluctuations. Geographical variations also occur as cited earlier in the difference between Scandinavian and American tall oils.

2.4 Oleoresinous media

Oleoresinous vehicles are those manufactured by heating together oils and either natural or certain preformed synthetic resins. In the process, the resin dissolves or disperses in the oil portion of the vehicle. The equipment for preparing this type of product may be essentially simple, and these vehicles were among the first used in the coatings industry after the exploitation of simple gum solutions and natural oils in either unmodified or bodied state. The manufacturing process involves heating oil and resin together until the product becomes clear (this may be tested by cooling a small sample 'pill' of material on a cold plate) and of the required viscosity.

The temperatures used are frequently those at which oil bodying occurs, that is around 240°C or higher, and the best performance is often obtained when the resin is taken close to gelation point; for this reason great skill is required of the maker of this type of vehicle. Reaction near to end point may be rapid, and thus quick though subjective tests such as bodying to 'a short string' may have to be employed. Following attainment of end point the product may be cooled and thinned, often in one operation.

Oleoresinous vehicles continue in use for a number of applications, though they have been displaced by alkyds and other synthetic resins for many other uses. For example, clear varnishes such as can lacquers, primers and undercoats, aluminium paints, and marine coatings may still use oleoresinous vehicles to advantage. A high residual use persists in printing inks, though this is not a topic considered further in this chapter.

Oils used are exclusively drying and semi-drying oils, with the more highly unsaturated oils, i.e. tung and linseed, preferred. The resins used have included a number of natural 'fossil' resins such as rosins, copals, shellac, etc., of which only 'tall' rosin is now in good supply. (Rosin consists of a mixture of acids including abietic acid.) Bitumen is a natural resin, and black japan which contains bitumen is, in fact, an oleoresinous vehicle prepared as described above. Synthetic resins now used include rosin derivatives, and phenolic and epoxy resins. The latter two retain considerable importance for oleoresinous marine and insulating varnishes.

An important concept first used in oleoresinous vehicles and then used in defining alkyd formulations is that of oil length. In this context it refers to the oil content of the final resin; different nomenclatures may be used, either US gallons of oil per 100lb of resin or in a more precise definition, the weight of oil % in the total non-volatile varnish produced. Short oil vehicles contain less than 67% oil and are fast drying, giving hard films but that lack flexibility; they are used for floor varnishes and gold size. Long oil vehicles (more than 67% oil) are slower drying but more flexible and are used for exterior varnishes and undercoats.

2.5 Alkyd resins

The alkyd resin was one of the first applications of synthetic polymers in surface coatings technology; it was successful in chemically combining oil or oil-derived fatty acids into a polyester polymer structure. Benefits were the enhancement of the mechanical properties, drying speed and durability of these vehicles over and above those of the oils themselves and the oleoresinous vehicles then available. Though now surpassed by more sophisticated polymers for the more exacting applications, the alkyd, because of its partial reliance on renewable natural resource, and especially because of the enormous variety of compositions possible, still accounts for a considerable volume of total surface-coating resins produced. The long oil alkyd, optionally blended with other modified alkyds to increase toughness or alter rheology, remains the major resin used in brush-applied solvent-based decorative coatings. Recent application has extended into higher solids and use in emulsified form, as ways of solvent reduction, in producing eco-labelled products. High solids compositions are covered later in this chapter (see Section 2.18). Short oil alkyds still have use in some automotive and general industrial stoving compositions where they are combined with melamine/formaldehyde hardening resins.

Oils are not directly reactive with polyester components and therefore cannot be incorporated into an alkyd structure without prior modification. We can, however, start with fatty acids saponified from the oil, though for many applications this will be an expensive route, especially if glycerol is intended to be included in the formulation. The method evolved to achieve oil modification is to carry out, as a first stage, a so-called monoglyceride preparation. In this process glycerol (or other polyol) and oil in the molar ratio of 2:1 are reacted at around 240°C in the presence of a basic catalyst (sodium hydroxide, lithium hydroxide, etc.) forming 'monoglyceride', the mono fatty acid ester of glycerol (Fig. 2.5).

Practically, the reaction does not go to completion, and an equilibrium distribution of species is present including oil, polyol, and mono- and diglycerides. If polyols other than glycerol are to be used, such as pentaerythritol (PE) in long oil alkyds, a 'monoglyceride' stage may still be carried out using the appropriate amount of polyol to give a notional dihydroxy functional product. The satisfactory attainment of sufficient randomization of structure may be tested for by an alcohol tolerance test, when no separation of free oil should be observed. Sometimes with polyols such as PE the alcohol test is not satisfactory. In that case, reaction is carried out on a small scale in a wide-necked tube with the correct proportions of 'monoglyceride' sample and polybasic acid to test for the ability to derive a clear final product without gelation resulting. With some oils it is important not to prolong the time at

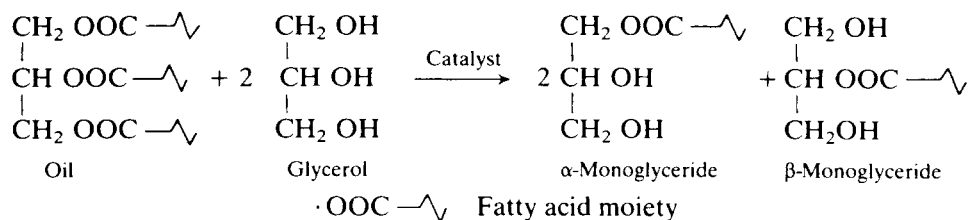


Fig. 2.5 — Schematic representation of monoglyceride formation.

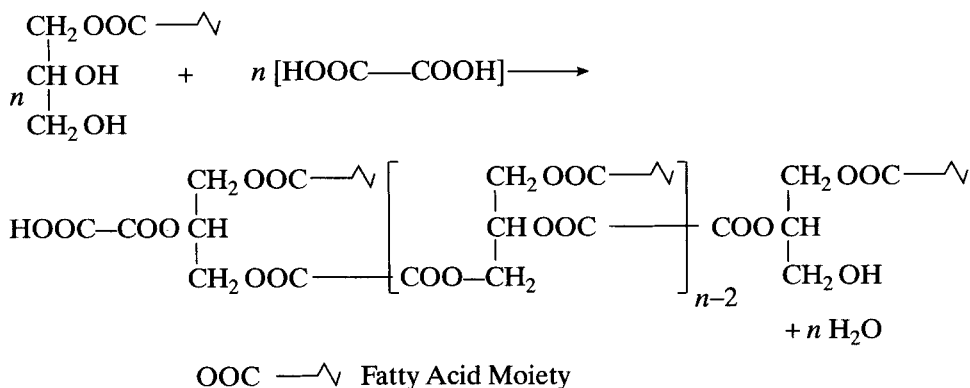


Fig. 2.6 — Schematic representation of glycerol alkyd polymer formation.

temperature for this stage in order to minimize oil bodying; for the same reason it is good practice to standardize on heat-up rate and time for the normal reaction, to ensure reproducible and predictable behaviour in the following stage.

Preparation of the final resin is carried out by the addition of further polyol and dibasic acid in the so-called bodying stage; in this stage, multiple esterification reactions occur (Fig. 2.6) and water formed as a by-product of reaction must be removed. Esterification results in the steady building-up of polymer structure and hence viscosity increases; the stage is taken to a degree of reaction at which the desired viscosity at a specified concentration (in solvent) and temperature has been attained.

While the monoglyceride method as described is used for long oil alkyds, the simpler so-called 'fatty acid process' is also practised; here, all ingredients including fatty acid (not oil) are charged together, and the process is frequently used for shorter oil alkyds where polyols other than glycerol are required. Other techniques are possible, for example an acidolysis route where oil is first equilibrated with polybasic acid prior to reaction with polyol in an apparent reversal of the monoglyceride process; this method is not widely favoured. Where it is necessary to incorporate tung oil into an alkyd, when to carry out a monoglyceride stage would risk excessive bodying, a variant is the fatty acid/oil process. Here the tung oil is taken along with a good proportion of fatty acid, polyol, and dibasic acid, and a one-stage reaction carried out. Providing the oil concentration is not high, transesterification of sufficient magnitude takes place during processing to react the oil into the resin and ensure a clear final product. Another technique proposed for alkyd manufacture is the 'high polymer' technique [25, 26], where by stepwise addition of ingredients, more favourable molecular weight and reactive group distributions are said to be obtained and certain properties enhanced; this is claimed to be particularly effective with tall oil alkyds. This technique has recently been examined theoretically [27, 28].

2.5.1 Composition

Each of the main ingredients of an alkyd contributes to its properties in a predictable manner [29]. Oil content is expressed as 'oil length' where long oil alkyds

contain over 60% oil, medium oil between 40 and 60%, and short oil below 40%. Long oil alkyds are generally made with drying oils and are soluble in aliphatic solvents. They are low viscosity resins that air-dry slowly to give soft flexible films with poorer gloss retention and durability.

Shorter oil length generally results in the need for aromatic solvent, giving higher viscosity resins at lower solids. If formulated with drying or semi-drying oils, and of medium or long oil length, the alkyd can air-dry oxidatively at room temperature. Otherwise it will not do so, and to form hard films it must be stoved with a crosslinking resin. Medium and short oil alkyds give hard films with good gloss retention and chemical resistance; they are less flexible than long oil alkyds and are normally dried by stoving.

Aromatic acids such as phthalic anhydride or isophthalic acid, and maleic anhydride contribute hardness, chemical resistance, and durability to alkyds; in contrast long chain dibasic acids such as adipic, sebacic, and azelaic acids, are sometimes used to plasticize alkyds and provide flexibility, not hardness. Phthalic anhydride dominates in conventional alkyd formulations because of its low cost and ready availability. It should be noted that it has added economy in use, in that by virtue of its anhydride structure, water evolution is halved compared with a dibasic acid; the first stage of its reaction is exothermic, with so-called 'half ester' formation.

Polyols used are generally at least trifunctional to permit branching or crosslinking and can provide the alkyd with hydroxyl groups for further reaction. In general they contribute good colour and colour retention, but vary in their chemical and weathering resistance (see also Section 2.6). Most general-purpose alkyds are formulated using phthalic anhydride with properties modified by polyol variation. The effects of polyol change may be readily related to structure so that in a series where glycerol is replaced by trimethylol ethane and then by trimethylolpropane, aliphatic solubility increases, viscosity falls, and flexibility increases, contributed to by increased side chain length; otherwise varying the polyol component may have a significant effect, not least because with varying polyol molecular weight the phthalic content of the final resin is affected, and hence the hardness of the final alkyd.

Rosin was originally included in alkyds as a modifier because of its low cost. However, it may also be added, as may other monobasic acids such as benzoic acid, to enable oil length to be shortened without causing increased viscosity. Rosin itself contributes to faster drying and film hardness, but degrades weathering performance; its use is restricted to alkyds for primer applications.

Where short oil length and aliphatic solubility present conflicting requirements, trimethylol propane can be used as polyol, though with some penalty of increasing softness. *Para* tertiary butyl benzoic acid can also be used as a monobasic acid to modify solubility, and both are effective because of the contribution of their aliphatic side groups.

Isophthalic acid gives higher molecular weight resins than orthophthalic, with better drying characteristics and harder, more durable films. Its use can narrow molecular weight distribution and enable lower viscosity/higher solids resins to be made [30]. However, it is more difficult to incorporate, remaining solid in the reaction mixture until at least one of its acid groups has reacted. Like orthophthalic anhydride it can sublime, but unlike orthophthalic anhydride, it can lead to overhead blockages in manufacturing plant because of its lower solubility in xylene which is used as the entraining solvent for the removal of water of reaction. Special

understanding is necessary to formulate high solids alkyds with longer oil length [31], and these principles are discussed further in section 2.18. Terephthalic acid has little use in alkyds because of its extremely low solubility in reaction mixtures and its very slow reactivity.

Mention must be made of Cardura E10 (Fig. 2.7; Shell Chemicals) which is the glycidyl ester of the branched Versatic Acid (Shell Chemicals), the latter being a 'tertiary' or trialkyl acetic acid with a total of ten carbon atoms. By virtue of the epoxide group, it reacts rapidly and completely with carboxyl groups at temperatures above 150°C; when incorporated into an alkyd, the effect is that which would be contributed by a non-drying oil or fatty acid component. Cardura E10 contributes special properties of good colour, gloss retention, and very good resistance to yellowing and staining [32–34]. Derived alkyds can be used in stoving enamels and in nitrocellulose lacquers. Care should be taken in the manufacture of alkyds which include both Cardura E10 and phthalic anhydride since the reaction is both rapid and exothermic (around 110 kJ per epoxy equivalent). Special formulating techniques are available for this type of alkyd that also allow control of polymer architecture [35]. Cardura E10 has special use for reducing the acid value in resins as a final treatment, for example where zero acid value is required for resins for use with photocatalyst, in metallic paints or with certain drier systems:

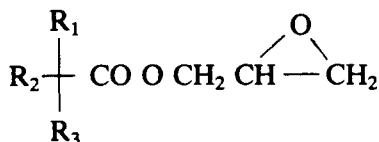


Fig. 2.7 — Cardura E10 (Shell Chemicals). R₁, R₂, R₃ are alkyl, one of which is methyl.

Epoxy resin may be used as polyol in alkyd compositions in combination with the more usual polyols. Epoxy resin addition improves water and chemical resistance and contributes to hardness and toughness; however, it adds to cost and can lead to chalking on exterior exposure.

Since alkyds are soluble in either aromatic or aliphatic solvent dependent on their oil length, they are tolerant of additional stronger alcohol, ester, or ketone solvents for special applications.

2.5.2 Alkyd reactions and structure

The major polymer-forming reaction in alkyd preparation is the esterification reaction between acid and alcohol, and hence the mechanism is through a type of stepwise polymerization (Fig. 2.6). In alkyds this reaction is generally not catalysed. Side reactions that can occur include etherification of polyol especially in prolonged monoglyceride stages.

Pentaerythritol is particularly prone to etherification, and grades should be chosen with low dipentaerythritol content.

A reason for lower molecular weight with orthophthalic alkyds compared with those prepared with iso- or terephthalic acids is the tendency to form intramolecu-

lar ring structures in *o*-phthalate esters. Because of this, the effective functionality of phthalic anhydride is practically less than two.

It has been claimed that alkyds owe some of their special properties, including application and dry, to the presence of 'microgel' in the alkyd [36]. While this seems to be proven, it would appear difficult to exploit in formulating for a microgel content unless a 'microgel' prepared separately were to be deliberately blended with the composition [37]. It has been suggested that gelation of an alkyd occurs through separation of microgel particles, until particles become crowded enough to coalesce into a 'macrogel'.

2.5.3 Alkyd reaction control

Alkyd preparations must be controlled to a viscosity end point by sampling, with acid value also monitored. Viscosity measurement may be simply achieved by using Gardner bubble tubes with thinned samples; however, improved speed of measurement and higher accuracy may be achieved by using a heated cone and plate viscometer [38]. The sampling interval will often need to be reduced as the end point is approached, owing to an increased rate of rise in viscosity, especially with short oil alkyds.

Where behaviour has been characterized from previous batches, a 'flare path' guide may be provided to follow the viscosity and acid value change; if reference to this shows deviation from normal progress, adjustment may be made by a small addition of acid or polyol. Where solvent process and oil bodying is occurring, adjustment may be made by changing the reflux rate, providing this is carried out at an early enough stage in the process. It is also possible to make temperature changes during processing to modify the bodying rate.

On attainment of end point, cooling and thinning are necessary to halt the reaction; thinning is also essential since the alkyd resin, in the absence of thinning solvent, will either be extremely viscous or solid when cold.

For new formulations, process temperature will be established by consideration of the need for higher temperatures for oil bodying and faster reaction in long oil alkyds, or for lower temperature for easier control of end point in shorter oil alkyds. Acid value at gelation (AV gel) prediction may be possible as the preparation proceeds (see Section 2.5.4). The results of experiments will allow modification in both composition and processing conditions.

2.5.4 Describing alkyds

In specifications for alkyds, oil type, oil length, and solvent will be stated, and sometimes the dibasic acid and its % in the composition.

Oil length refers to the % weight of glyceride oil calculated on the theoretical yield of solid alkyd; fatty acid content for non-glycerol-containing compositions may alternatively be quoted. In both cases this is the major indication of the flexibility, solubility, and — where containing drying oil — drying potential to be expected for the resin.

Solids, viscosity, and acid value (AV) will be determined as for other resins, and hydroxyl value (OHV) may also be measured. Both the latter are quoted in units of weight of potassium hydroxide in milligrams, equivalent to 1 g of solid resin.

Excess hydroxyl content, in contrast to OHV, which can be found experimentally, is calculated from the molar formula and expressed as the excess hydroxyl % over that required to react completely with the polybasic acid moieties present. Excess hydroxyl % may be used as a formulating parameter to derive formulations with a required AV gel or average functionality.

Acid value at gelation (AV gel) may be calculated theoretically, and may also be determined practically by extrapolation of a graph of acid value against 1/viscosity as an alkyd preparation proceeds to its end point.

2.5.5 Alkyd formulating

Practical alkyd formulating involves a process of calculation, application of previous practical experience, and trial preparation to arrive at the desired product. Principally oil length and oil/fatty acid type will be specified for the application, and polyol and dibasic acid dictated by a combination of other considerations including solubility, availability, and cost.

The average functionality concept is one method of formulating as first proposed by Carothers:

$$F_{\text{average}} = 2 \times \frac{\text{total acid equivalents}}{\text{total mol}} \quad (\text{hydroxyl in excess})$$

where for gelation to occur F should be two or more. This is the basis of the well-respected scheme by Patton, except that his constant $k = 2/F$. The basic functionality approach is recognized to require correction and Patton recommends appropriate factors for various ingredients.

An alternative method useful in arriving at a trial formulation involves calculating the extent of reaction at gelation, most usefully expressed as AV gel, which for example might be around five units below that desired in the final resin. It will be found necessary to vary the hydroxyl content, expressed as excess OH in order to alter the AV gel. Various equations have been produced as gelation theory has been developed, by for example Flory and Stockmeyer, and formulating guides are available which review the whole field of alkyd calculation [39, 40].

Frequently, one of the forms of the Stockmeyer equation will be used, such as:

$$p^2 = \frac{(\sum gB)^2}{(\sum f^2A - \sum fA)(\sum g^2 - \sum gB)}$$

where p = degree of reaction of acid groups at gelation, f, g = functionality of carboxyl and hydroxyl moieties respectively, and A, B = mols of carboxyl and hydroxyl moieties present. Before applying this equation to oil-containing formulations, the mols of oil should be split into constituent fatty acids and glycerol.

It is recognized that to formulate accurately, the true picture invariably lies between the two approaches. While the Flory – Stockmeyer approach is statistically correct, its inaccuracy is due to the actual formation of a number of cyclic rather than long chain polyesters through intramolecular reaction. The effect is more pronounced with the anhydrides such as phthalic anhydride, a very common ingredient. While the simplest correction can be to consider phthalic anhydride as having a functionality of less than 2 (e.g. 1.85), Kilb developed the best theoretical solution, applied practically by Bernado and Bruins [41].

As a simpler alternative to some quite complicated calculations, those offered by Weiderhorn [42] may be found a simpler and equally practical alternative, being less complex to use in the circumstances to which they apply.

In formulating short oil alkyds, monobasic acid may need to be included, dictated by solubility and hydroxyl content requirements. The use of bodied oil in long oil alkyds will be determined by the need to increase molecular weight and obtain higher viscosity, when this is not attainable by other means; the effect will be to raise the practical AV gel above that calculated.

With microcomputers being generally available, people formulating alkyds (and polyesters) regularly are likely to use computer programs to calculate both stoichiometry and gelation parameters. Programs of high functionality have been written [43]. However, writing one's own program is quite feasible; alternatively simpler programs are available from raw material suppliers [44, 45].

Some further comments on alkyd and polyester formulating are included in Chapter 20 on modelling.

2.5.6 Alkyd preparation equipment

Alkyds may be prepared on both laboratory and production scales by both the so-called 'fusion' and 'solvent' process techniques. In the former, ingredients are heated in vented stirred pots; problems encountered are mainly due to variable losses of reactant, particularly phthalic anhydride which is volatilized along with the water of reaction. In the latter process, more sophisticated equipment is needed, namely reactors fitted with condensers, water separation equipment, and solvent return systems. Organic solvent, typically xylene, is added to the resin in the bodying stage (2–5%) and recycled via the overheads, water being removed by azeotropic distillation. It can be of advantage to fit a solvent process plant with a vacuum facility which, besides providing assistance with loading, can be used, for example, to reduce the residual solvent content at the end of processing a batch.

Problems of phthalic anhydride sublimation in the solvent process may be minimized by careful plant design or avoided by using bubble cap scrubbers or fractionating equipment [46]. Inert gas is normally supplied in all alkyd processing to improve colour and to increase safety. Process temperatures may be between 180°C and 260°C. Where consistent practice such as heating rate, gas flow, and ventilation can be achieved, it must be stressed that the fusion process can be satisfactory for almost all classes of alkyd, provided that environmental problems caused by fume can be controlled.

2.5.7 Water-soluble and dispersed alkyds

Water-soluble resins are discussed more generally in section 2.16. This section specifically concerns alkyd resins. One issue is the current inability of emulsion polymer systems (section 2.8) to provide traditional high gloss decorative coatings; for this reason, alkyd systems continue to be used. While high solids systems have been developed to satisfy eco-labelling requirements, emulsified alkyd systems have also evolved for glossy decorative applications.

The usual route to water solubility is to formulate to acid value in the region 40–60, followed by partial neutralization with alkali, ammonia, or amine. Since phthalate-based alkyds have poor hydrolysis resistance and hence poor storage

stability, isophthalic acid (IPA) alkyds may be preferred. Alternatively, alkyds will be formulated using trimellitic anhydride (TMA) or dimethylol propionic acid (DMPA). The most common method in processing water-soluble alkyds containing TMA is first to react all the ingredients except the anhydride to form a polymer with an acid number below 10; and then to add the TMA at a reduced temperature of around 175 °C. Under these conditions the TMA is attached by a single ester link to hydroxyl groups on the preformed polymer, and the two remaining carboxyls are available for salt formation and subsequent water solubilization. This is termed the 'ring-opening' technique from the single stage reaction of the anhydride group of the TMA.

Water-soluble alkyds of this type find application in stoving compositions with water soluble melamine/formaldehyde resins as crosslinker. They may be supplied thinned in water-miscible solvent (e.g. butyl glycol) and water thinned at a late stage to gain maximum storage stability.

Water solubility can be conferred by incorporating water-soluble polymer. Thus, polyethylene glycols confer water solubility or dispersibility to the alkyd which may be exploited in the manufacture of gloss paints with easy brush-clean properties (as well as other use as surfactant) [47].

Alkyd emulsions may be prepared by emulsifying using surfactants [48]; polymeric non-ionic surfactants give advantages over normal anionic surfactants, especially when they contain autoxidizable reactivity [49]. All resin emulsification processes produce better results when using inversion, and in the case of alkyd emulsions, special techniques using the phase inversion temperature (PIT) have been developed [50]. The various problems additional to stability, found in the use of alkyd emulsions have been discussed in depth [51]. These include pigmentation, drier distribution, and system rheology. In the preparation of more stable emulsions, mixed ionic/non-ionic stabilization is now favoured.

To overcome deficiencies further, techniques have evolved to prepare alkyd emulsions with core/shell-like structures. One technique has been to use as a component, fatty acid grafted with copolymer rich in methacrylic acid [52]. Another is to use emulsified alkyd as the seed for growth of an acrylic polymer shell.

2.5.8 Modified alkyds

Urethane alkyds may be prepared by replacing part of the dibasic acid in the alkyd formulation with a diisocyanate such as toluene diisocyanate (TDI); the formulating calculations applicable are those used for alkyds. Long oil urethane alkyds are used in decorative paint formulations to impart greater toughness and quicker drying characteristics. While total replacement of dibasic acid is possible (thus producing a urethane oil), it is more normal to formulate an alkyd with a reduced dibasic acid content. This is processed to a low acid value, but a high residual hydroxyl content and the thinned resin is then treated with diisocyanate. The isocyanate groups react with hydroxyl groups to form urethane links, but, unlike acids in ester formation, do so exothermically at lower temperatures and without by-product evolution. It is essential to complete the reaction of all isocyanate groups present because of the high toxicity associated with free isocyanates. In-process testing may be by titration with amine, with final verification being by infrared spectroscopy. Small remaining residues of isocyanate may be removed by deliberate

addition of low molecular weight alcohol. For the preparation of urethane alkyds, a monoglyceride catalyst should be chosen for the alkyd stage that does not promote unwanted isocyanate reactions, e.g. allophanate formation, and such catalysts as calcium oxide or a soluble calcium soap should be used.

Another modification of long oil alkyd is that with polyamide resin, used to impart thixotropy in the final resin solution. Polyamide resins used are typically those derived from dimer fatty acid and a diamine. The physical properties of these alkyds are very delicately balanced. Such characteristics as gel strength, gel recovery rate, and non-drip properties of derived paints are intimately connected with both the composition and the processing of the alkyd, along with the proportion and type of polyamide and degree of reaction [53]. If this type of alkyd is being prepared, or when formulating paint compositions containing such an alkyd, care should be taken to avoid the use of, or contamination with, polar, e.g. alcoholic, diluents; these destroy the rheological structure to which hydrogen bonding almost certainly provides a considerable contribution. Typical levels of polyamide modification are around 5%, and care in processing is necessary to stop the reaction in its final stage at such a point as to achieve clarity and the optimum and desired gel properties [54].

Silicone modification of long oil alkyds imparts much improved gloss retention for their use in structural maintenance and marine paints. The same hydroxy or methoxy functional silicone resins are applicable (Section 2.14) as used for modification of polyesters. In general, the degree of enhancement in properties is in proportion to the level of modification with these expensive materials, and formulators need to weigh carefully the balance of cost versus durability enhancement achieved.

Phenol formaldehyde resins of both reactive and non-reactive oil-soluble types can be used as alkyd modifiers. They increase film hardness and improve resistance to water and chemicals, but cause yellowing. Such modified alkyds are useful in primer systems as cheaper but less chemically resistant alternatives to epoxy resins.

Vinyl modification of alkyds is used to impart faster dry, increase hardness, and give better colour, water, and alkali resistance. However, decreased gloss retention and poorer resistance to solvents result, the latter making formulation for early recoatability difficult to achieve. Vinylated alkyds are typically used for metal finishes. Styrene and vinyl toluene are the usual modifiers, methyl methacrylate being much less common. The modification stage involves free radical chain addition polymerization of the monomer in the presence of the alkyd under conditions where grafting to the unsaturated oil component of the alkyd is encouraged. This is typically by using at least some dehydrated castor oil in the alkyd composition since the conjugated fatty acid moieties then present encourage the necessary co-reaction; the typical use of peroxide catalysts such as di-*tert*-butyl peroxide also encourage grafting by hydrogen abstraction.

A number of techniques for preparing vinylated alkyds are possible; most common is post-vinylation of the thinned alkyd by feeding monomer and initiator into the resin held at 150–160°C. Less common alternatives are to vinylate the oil prior to alkyd manufacture or to vinylate the monoglyceride before esterification with dibasic acid. These latter techniques can allow final dilution in low boiling or reactive solvents in which the vinylation reaction would have been impossible. Where difficulties in achieving adequate grafting are experienced,

resulting in cloudy resin preparations, possibilities exist of including maleic anhydride or methacrylic acid in the alkyd polyester structure to provide additional grafting sites.

To the list of modifications must be included the possibility of precondensation with melamine/formaldehyde (MF) resins. Normally for a coating composition that is multicomponent, viscosity will be minimized by keeping the components unreacted until the curing stages; however, for some systems, advantages of increased stability, compatibility, or improvement in cure properties are seen by partial pre-reaction, even as here where the two polymers are compatible. For low bake curing alkyd/MF systems, precondensation of alkyd and MF can enhance final cure properties, while reducing the tendency of the MF component to self-condense when highly acidic catalyst systems are used.

2.6 Polyester resins

In the chemical sense, the term polyester embraces saturated polyesters, unsaturated polyesters, and alkyds. However, the term alkyd is normally reserved for the oil-modified alkyd discussed above. Similarly, unsaturated polyesters containing vinyl unsaturation, which most typically are maleic-containing resins partially or totally thinned with a vinyl or acrylic monomer, are referred to as such; hence the term polyester is generally reserved for oil-free, acid, or hydroxy functional polyester resins. Polyester resins are typically composed mainly of co-reacted di- or polyhydric alcohols and di- or tri-basic acid or anhydride, and will be thinned with normal solvents. Much of the following applies nonetheless to both saturated and unsaturated polymers, the special features of unsaturated polyesters being referred to at the end of this section. The use of monobasic acids is not excluded from our definition of polyester. It is convenient to call a polyester containing lauric or stearic acid an alkyd, but to consider as polyesters those containing only shorter chain aliphatic acids, including lower molecular weight branched synthetic fatty acids, and monobasic aromatic acids, such as benzoic acid.

Polyesters can be formulated both at low molecular weight for use in high solids compositions, and at higher molecular weight, and can be both hydroxy and acid functional. Since they exclude the cheaper oil or fatty acid components of the alkyd and are so normally intrinsically more expensive, much effort has gone into understanding their formulation, to exploit the higher performance of which they are capable; also, effort has gone into the development of new raw materials. The latter are in the main new polyols to suit high-durability applications such as automotive clearcoats and the painting of steel coil strip.

In choosing polyols, three factors affect durability. Both steric factors and the 'neighbouring group' or 'anchimeric' effects affect resistance to hydrolysis [55]. The absence of hydrogen atoms on the carbon atom beta to the hydroxyl group and subsequent ester group is a principal factor determining resistance of the ester link to break down under the influence of heat or radiation. These requirements are met by such polyols as 1,4-cyclohexane dimethanol (CHDM) and 2,2,4-trimethyl-1,3-pentane diol (TMPD) where the beta hydrogen content is reduced or hindered, and in materials such as trimethylol propane (TMP), neopentyl glycol (NPG), hydroxypivalyl hydroxy pivalate (HPPH), and 2-butyl-2-ethyl propane diol (BEPD) (Fig. 2.8).

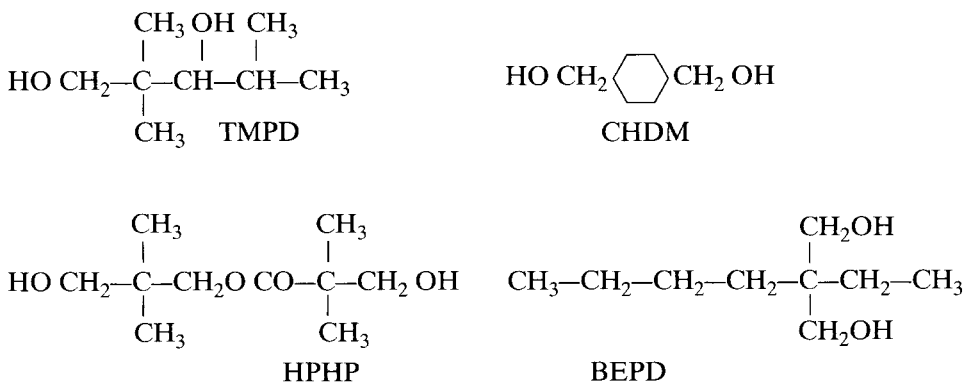


Fig. 2.8 — Typical polyol structures with hindered β positions relative to OH group.

2.6.1 Formulation

Polyesters are formulated in similar fashion to alkyds by making calculations of average functionality, supplemented by calculation of acid value of gelation by the Stockmeyer method [41]. In addition, for a theoretical hydroxy functional polyester, number average molecular weight can be calculated from the formula

$$M_n = \frac{\text{formula weight}}{\sum M - \sum E_a + \left(\frac{\text{formula weight} \times \text{AV}}{56100} \right)}$$

where M = mols of acid, hydroxy components; E_a = equivalents of acid.

The hardness/flexibility of polyesters may be adjusted by either blending 'softer' aliphatic dibasic acids with the 'harder' aromatic acids or by the inclusion in the polyol blend of the more rigid CHDM in place of 'softer' aliphatic polyols. With the general use of IPA rather than orthophthalic anhydride, crystallization problems can occur with the final polyester solutions. One technique of controlling this is to include a small proportion of terephthalic acid (TPA) to disrupt chain symmetry.

Solvent-borne polyesters for such applications as coil coating, automotive basecoat or clearcoat, and wood finish may be formulated from a blend of the 'hard' and 'soft' acids, IPA and adipic acid, with diols and triols such as NPG and TMP. Formulation variants can include phthalic anhydride for cheapness, and longer chain glycols added for extra flexibility. Monobasic acids such as pelargonic or benzoic acid may be included. These polyesters will generally be crosslinked by MF resin in stoving applications or in non-bake applications as a 2-pack formulation with polyfunctional isocyanate adduct. The triol included can contribute to branching and to in-chain hydroxy/functionality depending on the formulation; for some applications such as coil coating where high molecular weight may be an advantage, triol content will be minimized.

With polyesters for high solids coatings, the total polyol in the composition is increased, and the resin processed to lower molecular weight and higher hydroxyl content. Water-soluble polyesters are formulated to a high acid value, often by a 2-stage technique, as described for the preparation of water-borne alkyds, where ring opening with trimellitic anhydride is carried out as a stage subsequent to

polymerization. Dimethylol propionic acid has also been used to prepare high acid value water-soluble polyesters.

Polyesters for powder coatings, since they must have a softening point typically $>40^{\circ}\text{C}$, will generally not contain long chain plasticizing dibasic acids, but one or more aromatic acids with possibly a simple diol. They may be of high acid value for epoxy resin cure or low acid value and high hydroxyl content for melamine/formaldehyde or masked isocyanate resin curing.

2.6.2 Polyester preparation

For polyesters the general techniques used in alkyd manufacture are used, but with refinements appropriate to the materials used. All-solid initial charges will arise with many formulations, requiring careful initial melting. Difficulties in achieving clarity, even with complete reaction, can be encountered when isophthalic acid is present, and this may be exacerbated when the even less soluble and less reactive terephthalic acid is present. Since a number of the glycols used in polyester manufacture are volatile (e.g. ethylene glycol, neopentyl glycol) and are easily lost with the water of reaction, any serious attempts to prepare polyesters containing these components reproducibly demand a reactor fitted with a fractionating column [56, 57]. Pressure processing has been advocated as a means of raising reaction temperatures and hence reaction rates, without serious loss of glycol, particularly where ethylene and propylene glycols are included in the formulations. Where high molecular weight polyesters are desired, it can also be useful to have vacuum available for use later in the reaction to strip final residual water of reaction and achieve increased molecular weight (the technique is that used in the manufacture of polyesters of fibre-forming molecular weight [58]). For high molecular weight polyesters, particular care needs to be taken regarding glycol loss, since small losses can cause a sufficient imbalance in the formulation to restrict the molecular weight.

Catalysts are frequently used to increase reaction rate in polyester preparation, although the choice of catalyst needs care since colour may be adversely affected. Tin catalysts are particularly useful [59].

2.6.3 Modification

Silicone modification is used to enhance the properties of polyesters, particularly with respect to durability. Modification of both solvent-borne [60] and water-borne [61] polyesters is possible, and the former has become firmly established practice for coil application. In solvent-borne compositions, siliconization is carried out as a second stage following polyester preparation, using a silicone level of typically 20% to 50%; with high AV water-borne resins, the siliconization stage may be carried out after esterification and before the TMA addition stage. Silicone resins in common use are methoxy functional (Section 2.14), and methanol evolution occurs in reaction, which under some conditions may be used to monitor the reaction. The degree of reaction in terms of methoxy functionality may be of the order of 70–80%.

2.6.4 Unsaturated polyesters

The established unsaturated polyester resins are polyesters derived from polyols and dibasic acids, which also include some constituent containing a double bond,

and thinned in a polymerizable monomer. By far the majority of these polyesters are linear and contain co-condensed maleic anhydride as the source of unsaturation. In surface coatings these resins have been used mainly in wood finish and refinish two-pack finishes, including a significant use in refinish surfacers and putties. In thin-film coatings, difficulties were found in controlling air inhibition of the curing reaction at the surface of the film, which limited their use. Expansion of the monomer range available, and increased use of radiation curing, has enabled this problem to be overcome to a large extent, and their use has risen.

For radiation curing, polyesters are of the post-acrylated type rather than the maleic type described below. For this application they are, however, in competition with acrylic and urethane oligomers (see Section 2.19).

Generally, unsaturated polyesters are formulated with ortho and isophthalic acids along with maleic anhydride, with appropriate aliphatic glycols, such as diethylene glycol, chosen as co-reactants to control flexibility. The actual amount of maleic in proportion to other acids present may be from 25% to 75% molar. During preparation, a degree of isomerization of *cis* maleate residues to *trans* fumarate occurs (Fig. 2.9), this being important to final curing, as copolymerization with styrene in particular is favoured with the *trans* configured fumarate. This isomerization can be virtually 100%, but varies with reaction mixture composition and reaction conditions. The post-acrylation method referred to above involves the preparation of a saturated polyester with excess hydroxyl groups which are esterified with acrylic acid as a final stage in the preparative process.

Preparation of unsaturated polyesters is straightforward and is carried out in a similar manner to saturated polyesters [57]. However, where the slower reacting iso and terephthalic acids are used rather than *o*-phthalic anhydride it is claimed that multistage processing, reacting the aromatic acid in a first stage with subsequent reaction of maleic anhydride, gives better performing products [62]. Since unsaturated polyesters are thinned in monomers capable of polymerizing thermally, care needs to be taken in this stage and as low a thinning temperature used as possible. For additional safety in thinning, and stability on storage, adding an inhibitor such

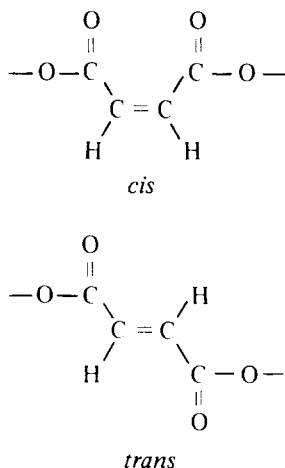


Fig. 2.9 — *Cis* and *trans* configurations of maleate and fumarate.

as *para-tert*-butyl catechol to the monomers in the thinning tank is necessary before resin dissolution. Alternatively, the resin may be allowed to solidify and the broken up solid subsequently dissolved in the monomer.

The monomer traditionally used is styrene, but vinyl toluene, methyl methacrylate, and some allyl ethers and esters such as diallyl phthalate are also used. The ultimate polymerization mechanism is most commonly a redox-initiated chain addition polymerization operating at ambient temperature, though thermal initiation is possible. The redox system is two-pack, where an organic peroxide or hydroperoxide is used as the second component, with the reducing component (amine or metal soap) mixed with the resin (see next section).

Oxygen is an inhibitor for styrene polymerizations, and exposed styrene thinned unsaturated polyester films suffer air inhibition which shows up as surface tack. This can be minimized by either the mechanical exclusion of oxygen by wax incorporation, or by the introduction into the composition of chemical groups which react with oxygen. Allyl ether groups have been used in such a role either through the addition of allylated monomers [63] or by reacting allylated materials such as allyl glycidyl ether or trimethyl propane diallyl ether into the backbone of the polyester [64]. (The allyl ether grouping can hydroperoxidize and then break down and oxidatively crosslink, in a similar manner to drying oils [65].)

Radiation curing unsaturated polyester compositions probably suffer less from air inhibition because the higher radical flux allows the reaction to proceed faster than the rate at which oxygen dissolves in the film. However, typical radiation curing compositions now use acrylated resins along with higher functionality and lower volatility monomers than styrene. The polyester resins used hence have acrylic acid attached at their end, replacing in-chain maleate/fumarate residues (see Section 2.19).

2.7 Acrylic polymers

Acrylic polymers are widely used for their excellent properties of clarity, strength, and chemical and weather resistance. The term acrylic has come to represent those polymers containing acrylate and methacrylate esters in their structure along with certain other vinyl unsaturated compounds. Both thermoplastic and thermosetting systems are possible, the latter formulated to include monomers possessing additional functional groups that can further react to give crosslinks following the formation of the initial polymer structure. Vinyl/acrylic polymerization is particularly versatile, in that possibilities are far wider than in condensation polymerization, of controlling polymer architecture and in introducing special features; for example, by using modification stages following the initial formation. Various references in the literature fully discuss the formulation and use of acrylic polymers in coatings [66, 67].

2.7.1 Radical polymerization

The kinetics and mechanism of radical-initiated chain addition polymerization [68] are important in all those processes where unsaturated vinyl monomers are used, either in the resin preparation or in the final cure mechanism. In resin preparation, processes discussed in this chapter include preparation of solution acrylic thermo-

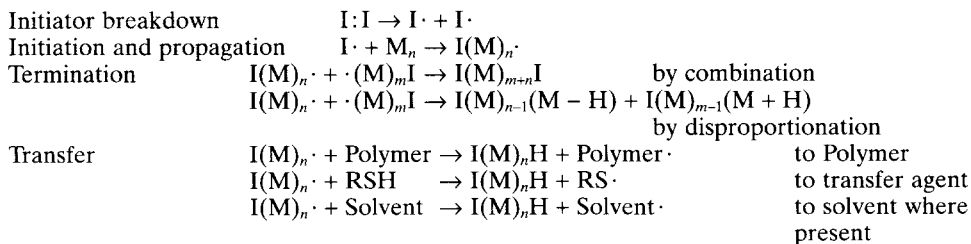


Fig. 2.10 — Representation of main reactions occurring in free radical chain addition polymerization.

plastic and thermosetting resins, emulsion and dispersion polymers, and the vinylation of alkyds. These reactions are also involved in the cure of unsaturated polyesters and of radiation-curable polymers. Autoxidative curing of oils and alkyds also occurs by a free radical mechanism, but not in the simple manner described below. Radical polymerization is the most widespread form of chain addition polymerization.

The main polymer-forming reaction is a chain propagation step which follows an initial initiation step (Fig. 2.10). A variety of chain transfer reactions are possible before chain growth ceases by a termination step.

Radicals produced by transfer, if sufficiently active, can initiate new polymer chains where a monomer is present which is readily polymerized. Radicals produced by so-called chain transfer agents are designed to initiate new polymer chains; these agents are introduced to control molecular weight and are usually low molecular weight mercaptans, e.g. primary octyl mercaptan.

Transfer to polymer is not normally a useful feature. At extremes such as with vinyl acetate polymerization, transfer at methyl groups on the acetate leads to grafted polymer side chains being present which are relatively easily hydrolysed, leading to undesirable structural breakdown of the polymer in use. Grafting to epoxy resin is used to prepare water-based can lacquers (see Section 2.16).

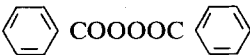
Transfer to solvent generally does not occur to a very significant extent and does not lead to radicals initiating new polymer chains. However, polymerization systems for high solids applications may be designed with, for example, alcohol solvent present where its chain-terminating effect can assist with molecular weight control. The nature of the solvents present can significantly affect the decomposition rates of most peroxy initiators.

Initiators (Table 2.6) used to give free radicals, are compounds typically breaking down under the influence of heat; two types predominate, those with an azo link ($-N=N-$) and those with a peroxy link ($-O-O-$). Initiator breakdown is characterized by 'half-life' which varies with temperature.

The 'half-life' of an initiator is the time within which 50% of the material has decomposed at a specified temperature. For many processes an initiator/temperature combination will be chosen so that the half-life under reaction conditions is in the region of 5–30 minutes. This ensures the steady generation of radicals at such a rate that the heat of reaction can be safely contained and high conversion of monomer to polymer ensured.

Despite the handling problems caused by its solid nature and poor solubility, azo-di-isobutyronitrile (AIBN) is often used for its non-grafting characteristics; di-

Table 2.6 — Typical initiators used in polymer preparation

Name	Formula	Half life 30 min
Azo-di-isobutyronitrile (AIBN)	$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ \text{CH}_3-\text{C}-\text{N}=\text{N}-\text{C}-\text{CH}_3 \\ \qquad \quad \\ \text{CN} \qquad \text{CN} \end{array}$	89°C
<i>t</i> -Butyl-per-2-ethylhexanoate	<i>t</i> -BuOOCOCH(CH ₂ CH ₃)(CH ₂) ₃ CH ₃	96°C
Di-benzoyl peroxide		99°C
<i>t</i> -Butyl perbenzoate	<i>t</i> -BuOOCO 	130°C
Di- <i>t</i> -butyl peroxide	<i>t</i> -BuOO <i>t</i> -Bu	156°C

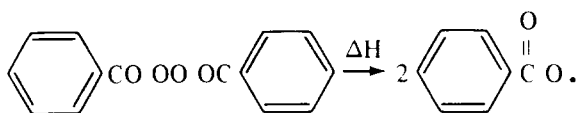
benzoyl peroxide, though of only a slightly higher half-life temperature, conversely has a strong grafting tendency, a fact that may be deliberately exploited, for example to produce acrylic grafts onto other polymers such as epoxides. (Grafting is where the radical extracts a hydrogen atom from a site on the polymer chain, leaving a radical site onto which further polymer growth occurs.) This latter initiator is also a solid, normally supplied as a paste in plasticizer; for many uses it must first be dissolved and the solution assayed. It is therefore another less than ideal initiator. *t*-Butyl perbenzoate and *t*-butyl per-2-ethyl hexanoate are, however, liquid initiators which are more readily handled and may now be preferred. Many peroxide initiators produce acidic breakdown products that may have adverse effects in formulations. Dibenzoyl peroxide and perbenzoates can also leave benzene among the residues from side reactions.

It has been stated above that initiator decomposition may be affected by (solvent) environment. Reducing agents may in fact be deliberately added along with the initiator to produce *redox* (reduction–oxidation) systems where initiator decomposition is induced at far lower temperatures than would otherwise be the case. These systems have a number of specialist applications in both polymerization and curing reactions. Figure 2.11 shows the manner of decomposition of benzoyl peroxide by both thermal and amine-induced redox initiation routes to produce initiating benzoyl radicals. Redox initiation is frequently used in emulsion polymerization (see Section 2.8), and for cure of unsaturated polyesters.

2.7.2 Monomers and copolymerization

Monomers may be classified as ‘hard’, ‘soft’, or ‘reactive’, based on the properties they confer on the final polymer or copolymer. Hard monomers are, for example, methyl methacrylate, styrene, and vinyl acetate. The acrylates are ‘softer’ than methacrylates, and useful ‘soft’ monomers include ethyl acrylate and 2-ethyl hexyl acrylate, and also the long chain methacrylates. Reactive monomers may have hydroxy groups, for example hydroxy ethyl acrylate. Acrylamide and glycidyl methacrylate possess exploitable reactivity, the latter being particularly versatile. Acidic monomers such as methacrylic acid are also reactive and they are often included in small amounts so that the acid groups may enhance pigment dispersion and provide catalysis for cure of the derived polymer (Table 2.7).

Thermal



Amine induced

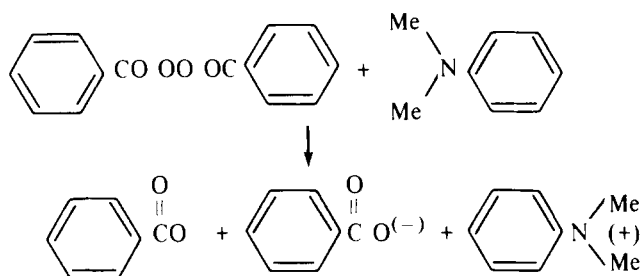


Fig. 2.11 — Thermal and amine-induced decomposition of benzoyl peroxide.

Table 2.7 — Typical unsaturated monomers

Monomer	Structure	Polymer $T_g(^{\circ}\text{C})$
Butyl methacrylate	$n \text{ Bu}-\text{O}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$	22
Ethyl acrylate	$\text{CH}_3-\text{CH}_2\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2$	-22
2-Ethyl hexyl acrylate	$\text{C}_4\text{H}_9-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2$	-70
2-Hydroxy propyl methacrylate	$\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2\text{O}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$	76
Methacrylic acid	$\text{HO}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$	210
Methyl methacrylate	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$	105
Styrene	$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	100
Vinyl acetate	$\text{CH}_2=\text{CH}-\text{O}-\text{C}(=\text{O})-\text{CH}_3$	30

Methyl methacrylate as a hard monomer imparts resistance to petrol, UV resistance, and gloss retention. It is therefore used in copolymers for topcoats, particularly for automotive application. Butyl methacrylate is a softer monomer imparting excellent low-bake humidity resistance, but its plasticizing effect is limited. It gives

good intercoat adhesion and solvent resistance and excellent UV resistance and gloss retention. Ethyl acrylate has good plasticizing properties but as a monomer has a highly unpleasant and toxic vapour. Its copolymers are fairly resistant to UV and give good gloss retention.

Practical coating polymer systems are rarely homopolymer but are copolymers of hard and soft monomers. Polymer hardness is characterized by glass transition temperature (T_g) and for any given copolymer the T_g of the copolymer may be estimated by the equation

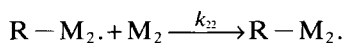
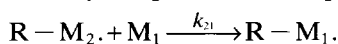
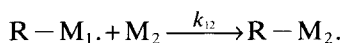
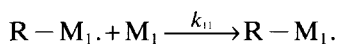
$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \text{ etc.}$$

where T_{g1} , etc. are the T_g 's of homopolymers of the component monomers in K, and W_1 , etc. their weight fraction present. (The calculated T_g will not be the final film T_g if the polymer is thermosetting since crosslinking will further raise the T_g , and this should be taken into account where appropriate.)

While monomers can combine during copolymerization in a variety of configurations (random, alternating, block, or graft), the vast majority of acrylic polymers actually used in coatings are random. This randomness also has the effect that the tacticity and crystallization phenomena so important in bulk polymer properties are generally not apparent or important in coating polymers. The most common structural effects actually experienced are phase separation and domain effects occurring either by accident or design.

The way different monomers react in copolymerization with other monomers depends on both their own structure and the nature of other monomers present [69]. Monomers of similar structure generally copolymerize readily and randomly. Thus all acrylates and methacrylates, including the parent acids, can be copolymerized together satisfactorily in almost any composition, though the longer chain monomers may be slower to polymerize and hinder attainment of complete conversion. Styrene can be included up to certain levels in acrylic polymers to reduce cost, and raise hardness and refractive index, but can be difficult to convert in higher concentrations. Maleic anhydride and maleate esters, though apparently able to copolymerize satisfactorily with other monomers when included in small amounts, do not homopolymerize but can form alternating structures with certain other monomers, notably styrene; they should be used with circumspection unless there is good understanding of this behaviour. Vinyl acetate and other vinyl esters are difficult to polymerize except in disperse systems.

When two monomers copolymerize, the rate may generally be slower than that of either polymerizing alone. The polymer radicals may react more readily with one monomer than another, and in fact four growth reactions can be envisaged, proceeding at different rates as shown by the following scheme:



where k_{11} and k_{22} are the reaction rate constants for chain ends with one monomer radical adding the same monomer, while k_{12} and k_{21} are for chain ends with one monomer radical adding the other monomer. The ratios k_{11}/k_{12} and k_{22}/k_{21} are referred to as the reactivity ratios, r_1 and r_2 , and characterize the relative rates of

reaction of the monomers with each other. Thus $r > 1$ indicates a polymer radical reacting more rapidly with its own monomer, and $r < 1$ indicates a polymer radical reacting selectively with the comonomer.

The product $r_1 r_2$ has interest in that if, for example, $r_1 r_2 = 1$ the monomers copolymerize truly randomly, while if $r_1 r_2$ approaches zero the monomers trend strongly towards alternating in an equimolar manner. The kinetics of copolymerization has had considerable attention, and comprehensive tables of r_1 and r_2 values have been published [70]. Hence successful analytical and predictive modelling of simpler chain addition processes is now possible (see Section 20.5).

A more general scheme, which can be used to explore the copolymerisation behaviour of multi-monomer systems, is the Q - e scheme [71]. The Q parameter refers to the degree of resonance stabilization of the growing polymer chain, whereas the e value represents its polarity. Unfortunately, this scheme is rarely precise enough in practice, so its use is limited to gaining first approximations of reactivity. The recently disclosed Revised Patterns of Reactivity Scheme [72] is a four parameter scheme that is claimed to enable more reliable reactivity ratios to be calculated. Here parameters for monomer and radical reactivities and polarity are used.

Since monomers can polymerize thermally and by exposure to light, it is necessary to store monomers in opaque containers in cool conditions and to ensure that an adequate inhibitor level is maintained to prevent adventitious polymerization. Inhibitors are typically phenolic, and for some monomers checks on levels may be necessary on prolonged storage. Monomers also have toxicity ratings ranging from the mild to very severe, and many are highly flammable.

2.7.3 Formulation and preparation

When formulating acrylic resins, monomer composition may be determined by durability and cost requirements, and by functionality [66]. Hard and soft monomer ratios will be adjusted for T_g , which along with molecular weight may have a fairly rigid definition for the intended application of the coating. The major task of the formulator may be to achieve these and to obtain conversion. The major factors affecting molecular weight in preparation are the choice of the initiator and its concentration, temperature, and monomer concentration, and the concentration present of chain transfer species, if any. Normally polymerization will be carried out with up to 50% of solvent present and at reflux, the temperature thus defined by the solvents used. Initiator contents vary between 0.1 and 5% and polymerization temperatures for thermal initiator from 90 to 150°C. The molecular weight (number average) is often found to vary inversely with the square root of initiator concentration at a given temperature.

Polymerization of acrylic monomers may be by bulk, suspension, emulsion, dispersion, or solution polymerization techniques; for surface coating applications solution, emulsion, and dispersion techniques are most common. The first of these is discussed below, and the others elsewhere in this chapter.

Solution polymerization has a number of possible modes, the simplest being the one-shot technique where solvent, monomer, and catalyst are heated together until conversion is achieved. However, vinyl polymerization is highly exothermic (50–70 kJ/mol) and this heat is generally removed in a refluxing system by the condenser. The one-shot process may give rise to dangerously high exotherm peaks. Thus

processes where monomer and initiator, or initiator alone, are fed to the other refluxing reactants over 1–5 hours, moderate the reaction and the heat evolution rate, enabling the heat to be removed in a more controlled fashion. The process, where monomer and initiator are fed into refluxing solvent, also serves to give better control of molecular weight and molecular weight distribution, and is most favoured on technical as well as safety grounds. Mixed monomer and initiator can be fed together, or for ultimate safety, from separate vessels, provided good control of the two concurrent feeds can be achieved. While post-reaction thinning can be carried out, polymerization is always in the presence of at least 30–40% solvent so that the viscosity of the polymerizing mixture can be low enough to allow good mixing and heat transfer. Having a separator after the condenser in most processes is not essential, though useful to remove adventitious water. However, it is essential for resins where a condensation reaction proceeds concurrently with the addition polymerization, e.g. with some acrylamide-containing polymers.

The solvent present will depend on the exact nature of the acrylic polymer. Acrylic polymer solubility is affected by the nature of the side group, and shorter side chain polymers are relatively polar and require ketone, ester, or ether–alcohol solvents. As the side chain length increases, aromatic solvent can be introduced. In the choice of solvent composition it may also be necessary to consider the crosslinking method and any additional crosslinking agent which may be introduced, and any requirements dictated by the method of application.

Acrylic processes are usually followed by measuring the viscosity and solids of the reactor contents, principally to monitor conversion. In these processes no correction is possible once reaction has commenced, if molecular weight is found incorrect at any stage. For many formulations conversion does not continue unaided to completion after the end of the feed period, and one or more ‘spikes’ (or more preferably a feed) [73] of initiator will be necessary to complete the process. Accurate measurement of molecular weight may be by gel permeation chromatography (GPC) or may be deduced from reduced viscosity measurement in a U-tube viscometer using a dilute solution of the polymer in dichloroethane.

2.7.4 Thermoplastic acrylic resins

Thermoplastic acrylic resins have found application particularly for automotive topcoats both for factory application, and currently still for refinishing following accident damage repair. Molecular weight and molecular weight distribution need careful specification and control for lacquers, particularly with metallic formulations where rheological behaviour affects the orientation of the aluminium flakes in the paint film, so necessary for the flip tone effects required. Too high a molecular weight gives low spraying solids, and very high molecular weight ‘tails’ can result in cobwebbing on spraying; low molecular weight degrades film strength, mechanical properties, and durability. It has been found that the optimum molecular weight is in the region of 80 000 for polymethyl methacrylate lacquers [74].

Polymethyl methacrylate homo- or copolymers for these applications can be prepared using a peroxide initiator in hydrocarbon/ketone blends, the reaction optionally being carried out at above atmospheric pressure by a one-shot process [75]. Polymethyl methacrylate films require plasticization to improve cold crack resistance, adhesion, and flexibility, and early compositions used such external plasticizers as butyl benzyl phthalate or a low molecular weight polyester. Phthalate

plasticizers can be volatile, causing film embrittlement. Since problems of repair crazing and cracking are also found in externally plasticized films and post-polishing is necessary, further development became necessary. The use of cellulose acetate butyrate allowed the use of the bake-sand-bake process, but the most dramatic improvement was found when two-phase polymer films were designed [76]. These could be achieved, for example, by the blending of a methyl methacrylate/butyl acrylate (MMA/BA) copolymer with homopolymer polymethyl methacrylate solution when apparently clear but two-phase films with enhanced resistance to crazing resulted.

In lacquer formulations containing MMA, plasticizing monomers are introduced to tailor flexibility and hardness to application requirements. Also, small amounts of an acid monomer such as methacrylic acid may be included to introduce a degree of polarity to help pigment wetting and adhesion; for adhesion improvement amino monomers such as dimethyl amino methacrylate may alternatively be included, though these may introduce slight yellow coloration to otherwise colorless formulations.

Thermoplastic resins may be blended with nitrocellulose and plasticizing alkyl for use in low-bake automotive finishes, both for use by low volume motor manufacturers and for repair.

2.7.5 Thermosetting acrylic resins

Thermosetting acrylic resins were formulated to overcome the defects of thermoplastic compositions, particularly apparent in industrial applications. Advantages from thermosetting resins accrue in improved chemical and alkali resistance, higher application solids in cheaper solvents, and less softening at higher service temperatures. Thermosetting resins can be self-crosslinking or may require a co-reacting polymer or hardener to be blended with them; most fall into the latter category.

Normal thermosetting acrylics may have molecular weights of 10000–30000, with high solids formulations lower, and the hardeners and resins themselves will typically be polyfunctional (>2). The concentration of functional monomers used in the backbone will be in the range 5–25% by weight. The overriding principle in design of the complete curing system is that on crosslinking, an infinite network of crosslinks between polymer chains will be created. Thus, polymer of low molecular weight and low viscosity at the time of application is converted to infinite molecular weight and total insolubility after curing.

Hydroxy functional thermosetting acrylic resins are not self-reacting, but must be blended with, for example, nitrogen resins or blocked isocyanates for stoving applications or with isocyanate adducts for use as two-pack (2K) finishes for room temperature or low bake refinish paint application.

Hydroxy functionality is introduced by the incorporation of hydroxy alkyl (meth)acrylates such as hydroxy ethyl acrylate at up to 25% weight concentration in the total monomer blend [77]. A small percentage of an acidic monomer is usually introduced to give a final resin acid value of typically 5–10 in order to catalyse curing reactions with nitrogen resins. The constituents must be balanced to obtain the desired hardness, flexibility, and durability, and care must be taken to achieve the necessary compatibility and storage stability with the chosen amino resin. This type of resin along with a melamine formaldehyde (MF) resin is used, for example, in automotive topcoats and clearcoats, the ratio of acrylic to melamine/formaldehyde

being typically between 80–20 and 70–30. The crosslinking reactions observed are those typical for amino resins with hydroxy-containing materials (see Section 2.10). Acrylic/MF compositions are superior to alkyd/MF for colour and exterior durability, but not necessarily for gloss. Acrylic/polyester/MF blends may be used for clearcoats. For repair of automotive topcoats in the factory, acid catalysts such as the half esters of dicarboxylic acid anhydrides or acid phosphates, are added to reduce the stoving temperature necessary, and acrylic/MFs are superior to alkyd/MFs under these conditions.

Hydroxy acrylic resins are generally prepared by the techniques previously described, typically in aromatic or ester solvent, feeding the monomer blend along with a peroxy initiator such as *t*-butyl perbenzoate into the refluxing solvent. Chain transfer agents may be used to achieve better molecular weight control.

Hydroxy acrylics can also be prepared by *in situ* hydroxylation of acid-containing polymers with ethylene or propylene oxides. Added flexibility can be given to the crosslinks by extending the hydroxyl group away from the acrylic backbone by reaction of existing hydroxy residues from hydroxy monomers with caprolactone.

The most distinctive class of self-crosslinking thermosetting compositions are those from acrylamide interpolymers reacted with formaldehyde and then alkoxy-lated [78,79]. The ultimate reactive group is the alkoxy methyl derivative of acrylamide, typically the butyl or iso-butyl ether. This group, which reacts in a near identical manner to the groups in nitrogen resins, also improves the compatibility of the polymer with alkyd and epoxy resins and nitrocellulose. These resins may hence also be blended with the acrylic resin, and co-reaction can then occur. Typical curing reactions are shown in Fig. 2.12.

Three methods of polymerization are possible in the manufacture of these acrylic polymers. The monomers, including the acrylamide, may be copolymerized and the amide groups subsequently reacted with formaldehyde and then alcohol. Concurrent reaction may be carried out when solvents, including alcohol, monomers, and formaldehyde, are charged with polymerization and methylation taking place simultaneously. As a final possibility, *N*-alkoxy methyl acrylamide may be prepared as an intermediate prior to the polymerization stage. Formaldehyde in these compositions is most usually included in alcoholic rather than aqueous solution (e.g. 40% formaldehyde in butanol) or as paraformaldehyde. The amide/formaldehyde reaction may be acid or base catalysed. For the etherification reaction, it is necessary to remove water of reaction by azeotropic distillation. Excess of the alcohol, necessarily present for acrylamide solvation as well as being a reactant, should remain at the end as solvent to give stability to the resin. Polymerization may be initiated by a peroxide initiator, and a chain transfer agent will be present since the final polymer being crosslinking need only be of low molecular weight.

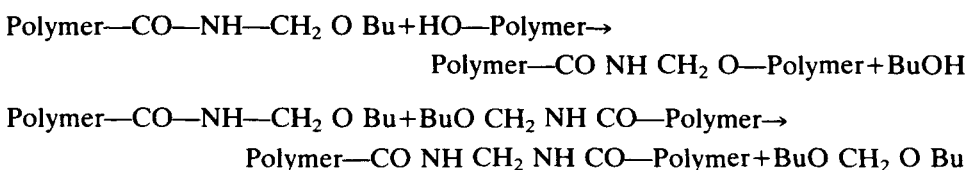
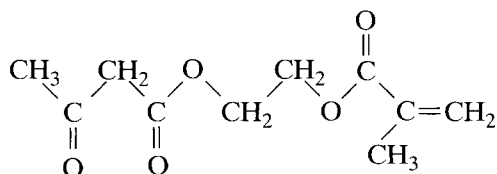


Fig. 2.12 — Typical curing reactions of *N*-butoxymethyl acrylamide copolymers.

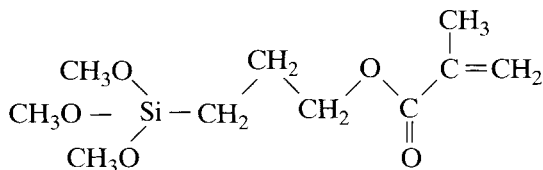
Thermosetting acrylamide polymers may contain styrene for alkali, detergent, and salt spray resistance, acrylate esters for flexibility, and acrylonitrile for improving toughness and solvent resistance. A wide range of compositions is therefore possible, for example, for domestic appliance, general industrial, or post-formed coil-coated strip application. An acid monomer is generally included to provide catalysis of curing. Epoxy addition has been used in appliance finishes to obtain extremely good detergent and stain resistance, and silicone modification can also be carried out to improve weathering performance. High AV variants are possible, which when amine-neutralized can be used in water-borne applications [80].

Carboxy functional thermosetting acrylic resins have been prepared which may be crosslinked with diepoxides. These were for a long time used for industrial finishes for appliances, coil coatings, and drums [81]. Their use has now been superseded in most of these applications by the hydroxy and acrylamide thermosetting acrylics.

Other functionalities may be introduced into acrylic resins (also emulsion polymers, section 2.8); for example, alkoxysilane functionality is provided by using trialkoxysilylalkyl methacrylate [82,83]. Coatings of this type find application in building exterior, automotive OEM and automotive refinishing. These resins cure through hydrolysis of the alkoxysilyl group, and exterior exposure properties are excellent. Acetoacetylated resins are made through copolymerization of acetoacetoxyethyl methacrylate [84,85]; a variety of subsequent curing reactions are possible, such as the Michael reaction shown in Fig. 2.13.



Acetoacetoxy ethyl methacrylate (AAEMA)



Trimethoxysilyl propyl methacrylate

Post-modification of acrylic resins is possible; for example acrylic resins with a high acid content may be condensed with the epoxy intermediate Cardura E10 (Shell Chemicals) to link plasticizing side chains to the polymer [32]. A reactive, though secondary hydroxyl group remains for possible crosslinking reactions. (The pre-prepared Cardura E10/unsaturated acid adducts may alternatively be used as monomers in preparation.) Saturated or unsaturated fatty acid modification has also been carried out on hydroxy functional acrylic resins for either plasticization purposes or to introduce air-drying functionality.

Water-soluble or dispersible acrylic resins will be prepared in a water-miscible solvent such as a glycol ether. They will be acid functional by the incorporation of, for example, acrylic acid; or amine functional by the incorporation of for example

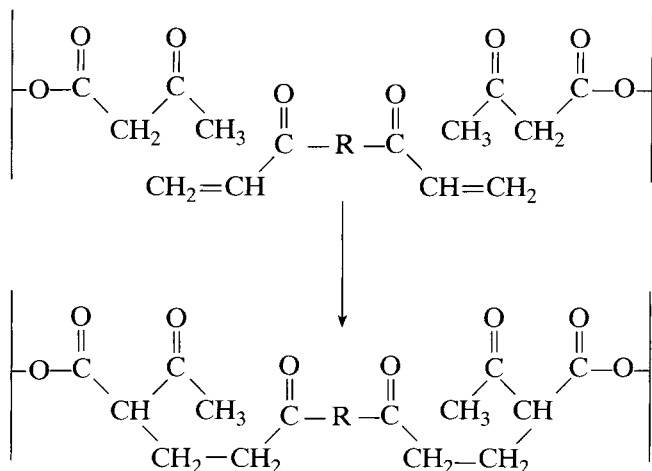


Fig. 2.13 — Michael addition reaction of resins containing incorporated AAEMA monomer.

dimethyl amino ethyl methacrylate, or glycidyl methacrylate which is reacted with amine (see Section 2.16).

2.8 Emulsion and dispersion polymers

This section will deal with fine particle addition polymers largely made by emulsion polymerization. Aqueous emulsion polymers are now probably the highest volume resins used by the coatings industry, principally because of the high usage of emulsion paints for home decoration; for this application the polymer is in the non-functional, room temperature coalescing, thermoplastic form. In parallel, other uses of more specialized emulsion formulations also exist, for example in industrial finishes where a hydroxy functional polymer is used, and in automotive and refinish basecoats where structurally engineered core/shell latexes are used [86,87].

It may be noted that high usage exists for emulsions in the adhesive and textile industries and emulsion polymerization is a route to poly (vinyl chloride) (PVC) and synthetic rubber polymer preparation.

The colloidal term 'emulsion' refers strictly to two-phase systems of immiscible liquids, where small droplets of one form the dispersed phase in the other, which is the continuous phase. In the terminology of the polymer industry, emulsion polymerization and emulsion polymer describe the process and end product of polymerizing addition monomers in water in the presence of surfactant, using water-soluble initiators to form fine-particle, stable dispersions. The term latex is also interchangeably used with emulsion for the final polymer dispersion. The polymer particles are typically sub-micrometre (0.1–0.5 μm) such that one litre of emulsion may contain 10¹⁶ individual particles of total surface area 2000 m². The monomers and fundamental chemistry of polymer formation are those of acrylic polymerization described earlier.

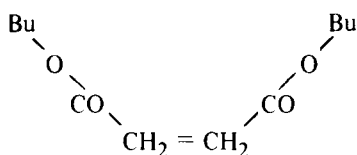
Emulsion polymerization is a member of the polymerization class known as dispersion polymerization, of which the other major member used in surface coatings

is NAD polymerization. Certain other disperse polymer classes also find application in the coatings industry [88–90]. Latexes stabilized by non-ionic rather than anionic surfactants may be mentioned as specialist emulsion polymers; the stabilizing groups may, for example, be polyethylene glycol chains [91, 92], providing steric stabilization in a like manner to non-aqueous dispersions (see Section 2.9). Polyurethane dispersions are mentioned later (Section 2.13.3).

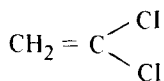
While suspension polymerization produces particles too coarse for coatings application, forms of micro suspension polymerization have been used to prepare composite particles incorporating preformed polymer with additional polymer polymerized *in situ*, for use in coatings [93, 94].

A typical emulsion polymerization formulation will contain, besides water, around 50% of monomers, blended for the required T_g , with surfactant, and often colloid, initiator, and usually pH buffer and fungicide [95]. Hard monomers used in emulsion polymerization may be vinyl acetate, methyl methacrylate, styrene, and the gaseous vinyl chloride. Soft monomers used include butyl acrylate, 2-ethylhexyl acrylate, Vinyl Versatate 10 or VeoVa 10 (Shell Chemicals), maleate esters, and the gaseous monomers ethylene and vinylidene chloride (see Table 2.7 and Fig. 2.14).

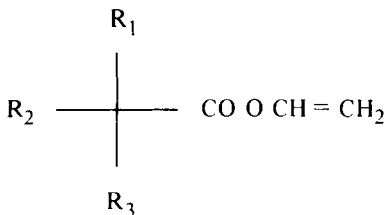
The most suitable monomers are those with low, but not very low, water solubility; monomers of very low solubility can be difficult to use satisfactorily. To use any of the gaseous monomers requires special plant; the techniques for handling these are briefly mentioned at the end of this section. Other monomers may be included in formulations, for example acids such as acrylic and methacrylic acids and adhesion-promoting monomers. It is important that films coalesce as the diluent evaporates, and the minimum film-forming temperature (MFFT) of the paint composition is a characteristic, closely related to T_g of the polymer. MFFT is also affected by materials present such as surfactant and by inhomogeneity of polymer



Dibutyl maleate



Vinylidene chloride



where R_1 , R_2 , R_3 are alkyl, one of which is methyl.

VeoVa 9 and 10 (Shell Chemicals)

Fig. 2.14 — Monomers particularly used in emulsion polymerization.

composition at the particle surface [96]. Higher T_g polymers that would not otherwise coalesce at room temperature may be induced to do so by incorporating a transient plasticizer or 'coalescing agent' such as Texanol (Eastman) into the paint composition. MFFT is normally determined in preference to T_g for emulsion compositions, since it is difficult to allow for these deviating effects; for the usual decorative applications it may typically be in the range 0–20°C. Lower MFFTs are required with more highly pigmented and extended finishes.

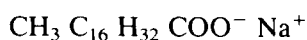
Available surfactants are anionic, cationic, and non-ionic, and essential characteristics of these surface-active materials are that their molecules possess two dissimilar structural groups; one will be a water-soluble or hydrophilic group and the other a water-insoluble hydrophobic moiety (Fig 2.15). The composition, solubility properties, location, and relative sizes of the dissimilar groups in relation to the overall structure determine the surface activity of the compound. It will be noted that reactive stabilizers now find increased use both in general and in specific uses [97].

The role of surfactants [98] is conventionally considered to be firstly to provide a locus for the monomer to polymerize in surfactant micelles and, secondly, to stabilize the polymer particles as they form. Anionic and cationic surfactants function as electrostatic stabilizers, preventing coagulation by electrostatic repulsion arising from the charges located at the particle surface. Polymeric non-ionic stabilizers function through steric stabilization described in Section 2.9 (see also Fig. 2.18). When surfactants are dissolved in water at concentrations above a certain level, the molecules associate to form 'micelles' instead of being present in true solution; these micelles can solubilize monomer.

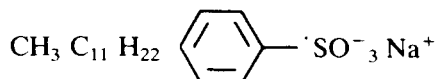
It is normal to use mixed anionic and non-ionic surfactants in emulsion polymerization; cationic surfactants are rarely used. The non-ionic nonyl phenol ethoxylates are being phased out on environmental toxicity grounds, with alkyl ethoxylates being found satisfactory replacements.

Anionic surfactants

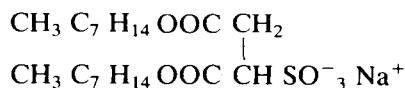
Stearate soaps



Dodecyl benzene sulphonate

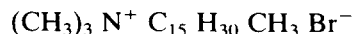


Sodium dioctyl sulpho succinate



Cationic surfactant

Cetyl trimethyl ammonium bromide



Nonionic surfactants

Polyethoxylated nonyl phenol



Polyethoxylated polypropylene glycol $\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{—}(\text{C}_3\text{H}_6\text{O})_m\text{—}(\text{C}_2\text{H}_4\text{O})_p \text{ H}$

Fig. 2.15 — Typical surfactants used in emulsion polymerization.

'Protective colloids' are water-soluble polymers such as poly(meth)acrylic acid or its copolymers, so-called polyvinyl alcohol (partly hydrolysed polyvinyl acetate), or substituted celluloses such as hydroxy ethyl cellulose. The properties of these colloids vary with molecular weight, degree of branching, and composition (proportion of water-soluble acid or hydroxy present). When used in emulsion polymerizations they may become grafted by growing chains of the polymer being formed, especially in the case of the celluloses, or may undergo chain scission. They assist in particle size control and in determining the rheology of the final paint, particularly in the derived gel structure and in the degree of thixotropy found.

A typical thermally initiated emulsion polymerization will involve two characteristic stages known as the seed stage and feed stage. In the seed stage, an aqueous charge of water, surfactant, and colloid will be raised to reaction temperature (80–90°C) and 5–10% of the monomer mixture will be added along with a portion of the initiator (typically a water-soluble persulphate). In this stage the first polymer particles are formed. If redox initiation is used (typically water-soluble persulphate again, but with a reductant such as sodium metabisulphite), the temperature will be in the region of 50°C or less.

The seed formulation contains monomer droplets stabilized by surfactant, initiator, and a small amount of monomer in solution, and surfactant, both in solution and micellar form. According to the micellar nucleation theory, radicals are formed in solution from initiator breakdown; these add monomer units dissolved in the water forming oligo-radicals, until the chain reaches such a size that the growing radical enters a micelle, where the monomer present within the micelle also polymerizes. Termination can occur when a further growing polymer radical enters the particle. Alternatively if coagulative nucleation is occurring, oligo-radicals coagulate together on their own to form nucleus particles which then become swollen with monomer and grow in like manner to micellar nuclei. In the seed stage, during which no reactants are added, initial monomer and initiator will largely be converted to polymer with the particle number roughly corresponding to the number of micelles of surfactant initially present (or until most of the surfactant present is mainly absorbed onto nuclear particles formed from coagulation processes). Monomer in droplets will diffuse through the aqueous phase into seed particles during this stage. At the end of the seed stage, monomer droplets will have disappeared. The concentration of surfactant remaining which is not associated with polymer particles will be small.

In the feed stage, remaining monomer and initiator solutions are fed together, the monomer being swollen into existing particles, or dissolved in the aqueous phase. Droplets temporarily formed as neat monomer is fed in, quickly diffuse. Polymer formation proceeds as monomer in particles polymerizes, being replenished by monomer in solution. At the same time radicals enter the monomer-swollen particles, causing both termination and re-initiation of polymerization. As the particles grow, remaining surfactant from the water phase is absorbed onto the surface of the particles to stabilize the dispersion. In the overall process the entities shown in Fig. 2.16 are believed to be involved. Particles are stabilized from flocculation and coalescence by mutual repulsion of surface charges from the anionic surfactant.

The final stage of polymerization may include a further shot of initiator, probably redox, to complete conversion, followed by cooling and addition of biocide if required.

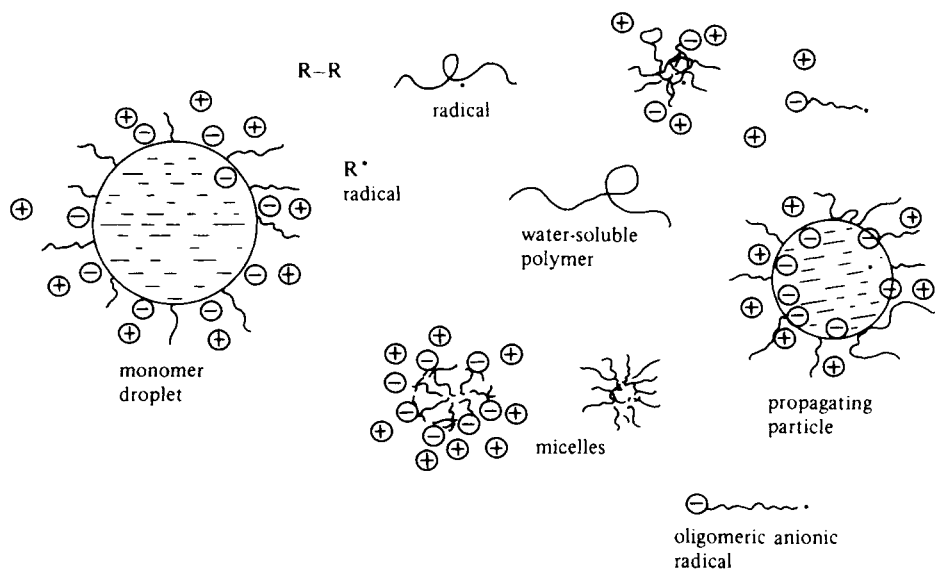


Fig. 2.16 — Entities involved in emulsion polymerization.

Various factors make emulsion polymerization more difficult to control than normal acrylic polymerizations. Agitation is critical in initial stages to get good dissolution/emulsification of seed reactants, and in the later stages to get heat extraction through the reactor cooling surfaces and good incorporation of added monomer. At the same time formulations may be shear-sensitive, and excess agitation is to be avoided. Reflux in latex processes generally has an adverse effect, hence initial heating followed by progressive application of cooling is necessary to hold a steady temperature. Bit content and polymer buildup on reactor walls can cause problems.

The kinetics of emulsion polymerization are complex, and efforts to understand the overall mechanism have been extensive [99, 100]. With better understanding, particularly of the thermodynamics involved, techniques are now established to control the internal structure of particles in many ways, so that they may for example contain voids or interpenetrating networks, or have separately distinguishable core and shell structures [101]. Larger particles have also been made which include both pigment and air filled voids in order to provide improved paint opacity. Particles may be rubbery 'microgels' for mechanical property modification, or engineered for rheology control, as with solvent-borne microgels [102, 103]. Typical structures are shown in Fig. 2.17. They are generally prepared by changing the monomer feed composition during the course of the feed stage. A striking example of their use is in water-borne metallic basecoats for both automotive and refinish applications. The use of a crosslinked core, with a mantle of acrylic polyelectrolyte containing hydroxyl and carboxyl groups [86], gives paint with low viscosity when sprayed, but high viscosity once applied. This prevents sagging and ensures alignment of aluminium flakes.

Though it is possible to prepare emulsions with hard monomer only, when so-called external plasticizer must be added to the paint formulation, virtually all emul-

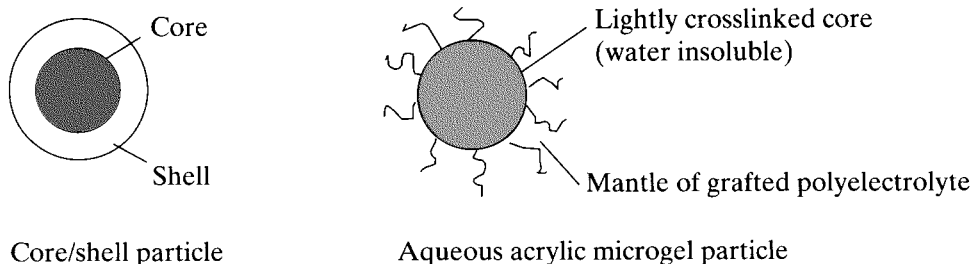


Fig. 2.17 — Structured particles preparable by emulsion polymerization.

sions used nowadays are internally plasticized with copolymerized soft monomer. Styrene-containing emulsions find little use in coatings in the UK though they are used in continental Europe. General-purpose emulsions are often formulated with vinyl acetate plasticized with an acrylate such as butyl or 2-ethyl-hexyl acrylate, or a dialkyl maleate. Formulations of this type have good chalking resistance but poor alkali resistance and hydrolysis resistance; to improve these latter properties VeoVa 10 (Shell Chemicals) and analogues [104, 105] may be used as plasticizing monomer. All-acrylic formulations containing methyl methacrylate and an acrylate plasticizing monomer generally give higher quality emulsions except for poorer chalking performance. VeoVa 9 (Shell Chemicals) may upgrade water resistance of acrylic formulations.

In order to use gaseous monomers, equipment is needed that is capable of working under pressure; these monomers can be used to give cheaper emulsions by copolymerizing vinyl chloride and ethylene with vinyl acetate. Ethylene in particular cheapens formulations but is so soft that typically vinyl chloride is incorporated as a hard monomer along with vinyl acetate. Polymers containing vinyl chloride and vinylidene chloride find particular application for anti-corrosive primers. Vinyl chloride monomer is carcinogenic, and final emulsions must be carefully treated by steam stripping to remove all traces of free monomer from the product.

Emulsions are characterized by solids and viscosity, by MFFT [106] and by freeze-thaw stability. Film tests are additionally carried out to assess freedom from bits. pH may also need control particularly with vinyl acetate-containing emulsions in order to prevent hydrolysis.

As well as the established use of autoclaves for the preparation of 'pressure' polymers, a technique capable of handling gaseous as well as liquid monomers is the loop reactor [107, 108]. This is a form of continuous reactor whereby the reacting mixture is pumped around a heated/cooled loop, monomers and initiator being pumped in at one point in the loop, and at another point product 'overflows' from the loop at a similar rate to the incoming feeds. Claimed advantages include low installation, capital, and running costs, while disadvantages include inability to exploit, for example, techniques for making products with core/shell morphology.

The polymer composition may include acids to modify rheology; monomers to improve adhesion, or monomers to provide crosslinking opportunities may be included. For primers to adhere well to wood and to old gloss paint, ureido [109, 110] monomers are used. For room temperature crosslinking, methoxy silane [83] functional monomers are used. Acetoacetate functional monomers provide a number of reaction possibilities [85, 111].

Polymers for thermosetting applications will be formulated and prepared similarly to those described above, but will contain hydroxy or modified acrylamide monomer and will generally be colloid-free.

2.9 Non-aqueous dispersion polymerization

Bearing many superficial similarities to emulsion polymers that exist in aqueous media, the other type of polymer dispersion used in the coatings industry is the non-aqueous dispersion (NAD). Here the polymer, normally acrylic, is dispersed in a non-aqueous solvent, typically aliphatic hydrocarbon [112]. Acrylic polymer NADs have found application chiefly in automotive systems and as modifiers in decorative systems [113, 114], though a range of other applications has been described; however, both condensation and addition polymer dispersions may be prepared, with a variety of particle structures including layered, heterogeneous, and vesiculated [90].

NAD polymer dispersions may typically be submicrometre, of size $0.1\text{--}0.5\mu\text{m}$ similar to aqueous polymers, and the chain addition polymerization mechanisms are again those earlier described under acrylic polymers. Unlike emulsion polymers, however, where particles are stabilized by charge-repulsion mechanisms derived from ionic surfactants, the only successful method available for stabilizing NADs is steric stabilization involving the presence at the particle-medium interface of an adsorbed solvated polymer layer. Charge stabilization has an inadequate effect in the media used in NAD polymerization because of their dielectric constant, one or two orders of magnitude lower than that for water. In steric stabilization, the repulsive forces that prevent flocculation when particles collide arise from the increase in local solvated polymer concentration arising at the point of contact; the system reacts to eliminate this local excess concentration by causing the particles to separate (Fig. 2.18). Steric stabilization is also effective in media of high dielectric constant where charge stabilization is normally used, this being the situation when non-ionic stabilizers are used [91].

The most successful stabilizers used in dispersion polymerization have been based on block or graft copolymers [115], and special techniques have been developed to prepare amphipathic graft copolymers suitable for use in NAD preparation [116]. Preformed graft stabilizers based on poly-12-hydroxystearic acid (PHS) are simple to prepare and effective in both addition and condensation NAD polymer-

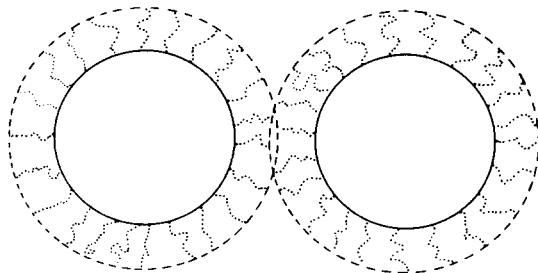


Fig. 2.18 — Representation of steric repulsion from soluble chains attached to dispersed particles.

izations. PHS oligomer may be converted to a 'macromonomer' by reacting the carboxy group with glycidyl methacrylate (GMA). The 'macromonomer' is then, in turn, copolymerized with an equal weight of methyl methacrylate or a similar monomer to give a polymer of molecular weight 10–20000, which is a 'comb' stabilizer with five to ten soluble chains, pendant from a polymeric anchor backbone (Fig. 2.19).

The formation of the graft, and its method of stabilization of dispersed particles by adsorption of the insoluble anchor component, is shown diagrammatically (Fig. 2.19). Poly-12-hydroxystearic acid derivatives also gain application more generally as dispersion agents [12]. The special techniques to prepare the 'macromonomers' necessary for preparing graft dispersants of defined structure have been reviewed [117].

Virtually the full range of addition polymers may be used in NAD polymerization. It is of note that those found more difficult to polymerize in solution may be more readily polymerized in dispersion (as with aqueous emulsion polymerization). The major limitation for monomer composition is that the polymer produced shall be insoluble in the medium used. Thus, when in aliphatic media, the proportion of longer chain plasticizing monomers included, must be limited to satisfy this condition.

Excellent control of particle size is achieved in NAD preparations and it is possible to prepare dispersions of uniform particle size, far more so than with emulsion polymerization. Similarly, by using the control differently, different sizes of particles can be produced giving a more efficient packing arrangement enabling dispersions of high solids of up to 85% by volume to be obtained [118, 119].

NAD acrylic polymers found major application in automotive thermosetting polymers, and here hydroxy monomers were included in the monomer blend used. The polymer initially formed in dispersion may be blended with stronger solvent to dissolve a portion or all of the dispersed polymer. Using this, it is possible to

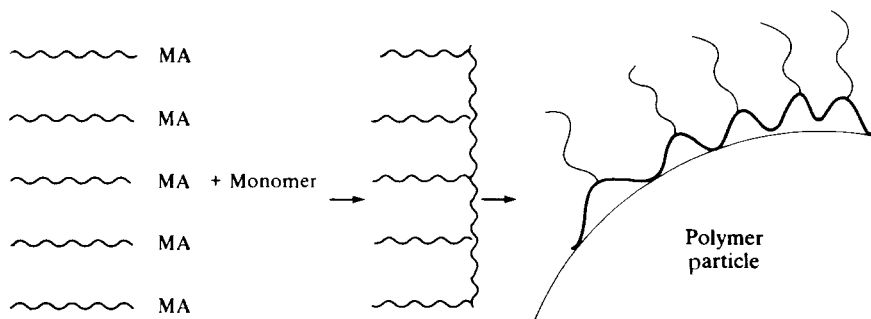
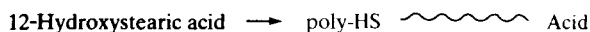


Fig. 2.19 — Schematic representation of poly-12-hydroxystearic acid 'comb' stabilizer preparation and use.

formulate particle compositions that range in state from the polymer being in true solution, through solvent swollen gel, to stable unswollen polymer particles. The reason for using this type of NAD is that the presence of swollen insoluble polymer has a profound effect on the evaporation rate of the solvents used and on the rate of increase of viscosity during evaporation. These effects give wide control over the formation of thicker coatings by spray application, with little sagging and good control of metallic pigment orientation. It was ultimately found most useful to prepare organic 'microgels' for blending with solution-prepared thermosetting hydroxy acrylic polymers to assist rheological control during application [102]. Monomers used include, for example, glycidyl methacrylate and methacrylic acid reacted *in situ* during the preparation, catalysed by added amine, such that the final particles become completely insoluble in organic solvents. These particles may be modified with an auxiliary polymer following the microgel core preparation, and finally diluted with a strong solvent blend. NADs continue in use in decorative systems as physical property modifiers [114] and for rheology control in high solids finishes.

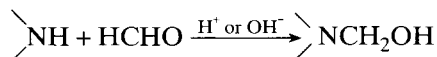
2.10 Amino resins

Amino or nitrogen resins are the condensation products of certain compounds with two or more amine groups, particularly urea and melamine, with formaldehyde. These condensation products are generally alkylated and may also be partly polymerized. The family of acrylamide-derived thermosetting acrylic resins bear considerable resemblance to amino resins in both their formation and crosslinking reactions.

Nitrogen resins are used as hardening or crosslinking resins with a range of hydroxy functional resins in both stoving and two-pack room temperature curing systems; as such they are normally the minor component by weight. The special properties they confer are excellent colour and colour retention, hardness, and chemical resistance. Certain of the family of nitrogen resins are water-soluble. It may be noted that nitrogen resins find considerable use outside the coatings industry for bonding chipboard, as laminating adhesives and as a provider of hard laminate worksurfaces.

The major amino resin types are those derived from melamine (MF) and urea (UF), with benzoguanamine also used. Resins based on glycoluril [120] find some use for cure of powder coatings [121] (Fig. 2.20).

In all cases the first reaction in preparation is the condensation of formaldehyde with an amino group, as represented by:



With melamine two molecules of formaldehyde can add on to each amino group; with urea only one molecule condenses under normal circumstances. Basic conditions are used for this stage for both urea and melamine resins, though for melamine resins acidic conditions are also effective. In all cases the reaction is exothermic. The preparation of both dimethylol urea and the fully reacted hexa-methylol melamine is possible in a good state of purity.

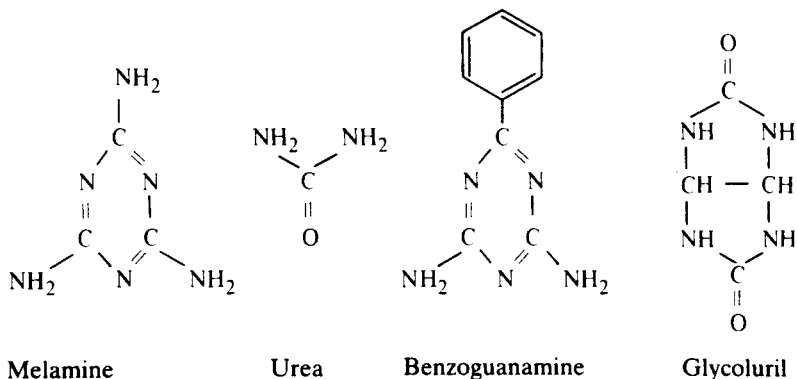
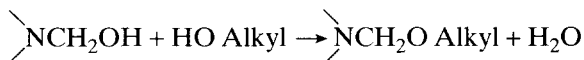


Fig. 2.20 — Typical amino compounds used in formaldehyde condensate resins.

The simple formaldehyde adducts that are water soluble, though finding applications in other industries, have no use in surface coatings. For coatings these adducts will be at least partly alkylated with lower alcohols, and this confers compatibility with other resins and allows solubility in organic solvents. The alcohols mainly used are propanol, normal or isobutanols, and, only in the case of melamine, methanol; the etherification reaction may be represented by:



The preparation of alkylated amino resins is normally three-stage, and pH adjustment may be carried out for each of the reaction stages. It is essential to have solvent process plant available to recycle and distil off solvent and to remove water of reaction, with the use of vacuum also necessary for some products. The detailed process will depend on the form of formaldehyde used which may be in either aqueous or alcoholic solution or as paraformaldehyde. Efficient removal of water (which is made more difficult by the presence of alcohol) is necessary to progress the esterification stage since the reaction is essentially an equilibrium. Good cooling of the condensate is necessary to allow effective separation of water from the solvent fraction. Employing a fractionating column can be advantageous, to aid the separation.

The first stage of reaction is the formaldehyde addition, which, if pH is favourable, will commence during heat-up. The melamine or urea will be dissolved in alcohol, and formaldehyde and some aromatic solvent may be present to modify the reflux temperature. This stage can be completed under total reflux. The second stage is the etherification stage during which water is removed. The third stage is the solvent distillation stage that may be completed using vacuum and is necessary to concentrate the product. With higher alcohols the resin is normally left in an alcohol-rich solvent blend in order to retain storage stability. Nevertheless storage life, especially in warmer conditions, may always be limited. Butylated MFs can be made with solids content of around 80%; above this reactivity loss is unacceptable for standard applications.

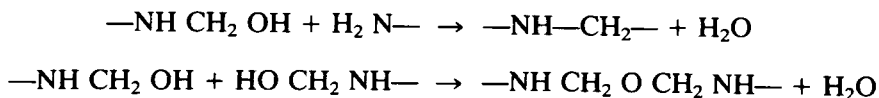


Fig. 2.21 — Reactions leading to polymerization in the preparation of formaldehyde condensation polymers.

The simple reaction scheme above is complicated in practice by a possible range of side reactions leading to a degree of polymerization (Fig. 2.21). Because of these and the impossibility generally of any meaningful in-process testing to control any particular stage, the key to successful nitrogen resin manufacture is strict control of pH, time and temperature regimes, distillation rates, and distillate quantities.

The degree of polymerization when it occurs is not high, though gelation in preparation is possible if a resin is misformulated. It should be noted that in polymerization reactions the secondary NH groups remaining after first additions onto primary amine groups are themselves reactive; with urea, for example, a mean functionality of three may be observed as the overall reactivity.

The effect of variation of the rates and extent of different reactions may show in a number of ways. For example, when excessive alkylation occurs at the expense of polymerization more water is formed, the tolerance of the final resin for mineral spirits will increase, the solids content will be high, and the viscosity will be decreased.

2.10.1 Characterization

Mineral spirits or petroleum ether tolerance, which indicates the degree of alkylation and the compatibility with other resins, is expressed as the volume compatibility to a given weight of resin, determined as the threshold at which haze develops in the blend. Solids are normally measured at a longer time and lower temperature than for other resins to obtain more reproducible and meaningful results; more than with any other resin, though, the figure obtained is not a true figure since a degree of decomposition and crosslinking is unavoidable during solids determination. Water contents are normally measured as an assurance of correct processing, and pH is characterized since this may affect storage stability.

2.10.2 Formulating

The condensation reactions involved, particularly the main formaldehyde addition and etherification reactions, are reversible, and so excess formaldehyde and alcohol concentrations are necessary to push equilibria towards the desired products. When formulating resins the ratio of formaldehyde to melamine or urea determines the degree of methylolation. With urea charging 2.4 mol of formaldehyde to attain the normally required 2 mol addition may be necessary; with melamine resins, where reactivities up to 6 are both possible and useful, a wide range of ratios may be used. The quantity of alcohol included, along with the processing conditions, then determines the degree of alkylation and polymerization, and the characteristics of the final resin. Again, a considerable excess of alcohol is normally required to be present, though its presence in the final resin helps storage stability. Reactivity of

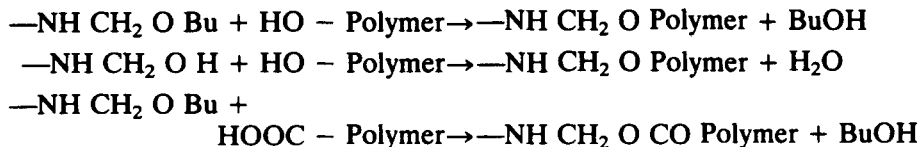


Fig. 2.22 — Crosslinking reactions possible between formaldehyde condensate resins and other polymers.

butylated melamine resins, for example, increases with decreasing formaldehyde to melamine ratio, and with decreasing degree of etherification.

Unlike other resins, specifying with accuracy the ratio of reactants actually incorporated into the resin is not possible; rather, specifying the ratio of reactants charged initially may be more meaningful.

2.10.3 Curing

Amino resins react on heating both with themselves, and with any other resin present containing functional groups, which will normally be hydroxy but equally possibly amino or carboxyl. The reactions are similar to those shown for formation, involving condensation and elimination reactions, where water, alcohol, or formaldehyde may be the products evolved (Fig. 2.22); the reactions leading to polymerization in preparation also occur.

The factors affecting reactivity are complex [122, 123]. As with formation, the curing rate and the relative importance of the above reactions are affected strongly by pH as altered by the presence of (typically) acid catalysts [124–126].

2.10.4 Uses

Melamine formaldehyde resins, because of their greater functionality, have significantly different properties from urea formaldehyde resins, having better chemical resistance, better colour retention at elevated temperatures, better exterior durability, and shorter baking schedules when in combination with hydroxy resins. It should be noted that their reactivity may be less than that expected for steric reasons. They are also more expensive. UF resins are very satisfactory, however, for general-purpose industrial finishes, and are extensively used in acid-catalysed room temperature cured wood finishes. Benzoguanamine resins find use for container coatings.

While strong acid catalysis of blends containing UF resin proceeds satisfactorily, with MF resins it may lead to self-reaction rather than co-reaction. Consequently for low bake or room temperature curing with MF resin blends, where high acid catalyst levels may be imperative with alkyd resins, for example, it is sometimes advantageous to prepare a precondensate with the MF resin.

Alkylated melamine resins will be chosen by their reactivity where high reactivity may mean high viscosity and rapid curing, but low mineral spirit tolerance and so poorer compatibility with alkyd resins. While the generally used resins are butylated, other alcohols are used. Secondary and tertiary alcohol-modified resins are generally slower curing but may result in harder films.

Special mention must be made of hexamethoxymethyl melamine (HMMM) resins that have secured their own place in coating compositions. Though available as the pure material as a waxy solid, they are most widely used in slightly modified or condensed form when they are more easily handled viscous liquids. They are soluble in water and in all common organic solvents except aliphatic hydrocarbons, and are compatible with practically all resin media. They are usually available at 100% solids. Unlike other alkylated MFs they are considerably more stable. As with other alkylated MF their preparation requires a high alcohol excess during reaction to ensure complete reaction; the problems of preparation include the removal of methanol containing distillate.

The superior adhesion and flexibility obtainable may be attributed to the lower tendency to self-condense and to a more satisfactory film structure [122, 123]. There is, however, a sharper optimum to the amount of HMMM required in any composition for the best properties. The resin finds particular use in high solids and water-borne compositions. It should be noted that HMMM is also more effective in that there is only an 18% loss of solids on stoving compared with 29% with a butylated equivalent.

HMMM has the disadvantage of increasing surface tension in the paint, resulting in application and film defects, and mixed methyl/butyl ether resins overcome these defects. Adequate water miscibility is retained if the methyl/butyl balance is correct, while hydrolytic stability and water resistance are improved. These mixed ether resins are finding increasing application.

2.11 Phenol formaldehyde resins

In the early years of the coatings industry, only naturally occurring resins were available to enhance the properties of natural oils. Early in this century, the availability of the hard oil-soluble phenolic formaldehyde (PF) resin allowed a more scientific approach to varnish making. The development of heat-reactive, soluble phenolic resins in turn enabled the development of baking finishes with excellent solvent and corrosion resistance; these resins still find application alone or in blends with alkyd or epoxy resins for can coatings, and tank and drum linings [127]. However, they have in turn been supplanted as crosslinking resins by amino resins because of the latter's far superior colour for most applications.

Unmodified phenolics may be oil-insoluble or soluble and may be heat-reactive or non-reactive. The initial reaction with formaldehyde and the subsequent reaction under acid conditions are shown in Fig. 2.23. The dimer shown can lose additional water to form a resin. This kind of resin is a *Novolac*, and in simple form, made with unsubstituted phenol alone, finds little use in coatings.

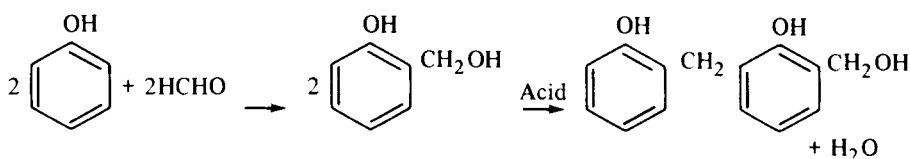


Fig. 2.23 — Novolac type phenolic resin formation.

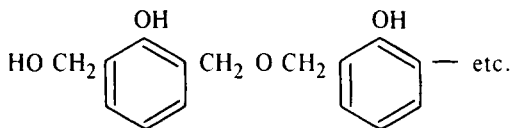


Fig. 2.24 — Resole type phenolic resin structure.

Alkali-catalysed phenolic resins are most common for coatings since these condense by ether formation and hence provide softer resins with some residual methylol groups for further reaction (Fig. 2.24). This class of phenolic resin is known as a *Resole*, and when made with phenol is only alcohol-soluble, but is thermohardening, unlike a Novolac. It can form a crosslinked structure without any additional curing agent.

Other phenols may be used including cresol, 2,4-xyleneol, and the *para*-substituted phenols such as *p*-phenyl phenol, *p*-*tert* butyl phenol, and diphenylol propane.

The more useful PF resins of both classes are made with *p*-substituted phenols. Oil-soluble and oil-reactive resins are obtained with *p*-*t*-butyl and *p*-phenyl phenols, where acid-catalysed Novolacs are non-reactive, and alkaline-catalysed Resoles are oil-reactive. It is also possible to etherify methylol groups with alcohols such as butanol, so improving oil solubility.

Rosin-modified phenolics have found considerable application for oleoresinous vehicles, and are prepared by heating a Resole-type PF with rosin when combination of unsaturated double bonds in the rosin and hydroxyl groups of the Resole occurs. The product is then esterified with a polyhydric alcohol such as glycerol or pentaerythritol to reduce the acid value. This type of resin can be either dissolved or cooked into oil for varnish preparation.

2.12 Epoxy resins

The epoxide or oxirane group has many reactions useful in resin chemistry, in particular those with carboxyl, hydroxyl, phenol, and amine (Fig. 2.25).

These reactions, which do not require high temperatures, are exothermic (70–80 kJ/epoxy equivalent) and are often readily catalysed. They can be exploited in the assembly of polymers and in curing reactions; in certain circumstances novel multistage reaction routes can be devised. The amine–epoxide reaction is particularly used in the cure of epoxy resins (see Section 2.12.2). The reaction with dicarboxylic anhydrides, as well as occurring in the manufacture of alkyds containing Cardura E10 (Shell Chemicals), is also used for curing powder coatings; in this reaction, requiring both initiation and catalysis, polyesters are produced both rapidly and exothermically without any water of reaction being evolved [128]. Since hydroxyl groups may always be present when epoxy resins are being cured, even when other reactive groups predominate, it should be noted that conditions of temperature and catalysis may enhance or suppress the possible etherification reaction with hydroxyls in relation to the other epoxy group reactions taking place [129]. For example, in the acid–epoxy reaction, base catalysis suppresses the etherification reactions that would otherwise occur.

The compound glycidyl methacrylate that has both vinyl unsaturation and an epoxy group is particularly useful as a bridge between condensation and addition

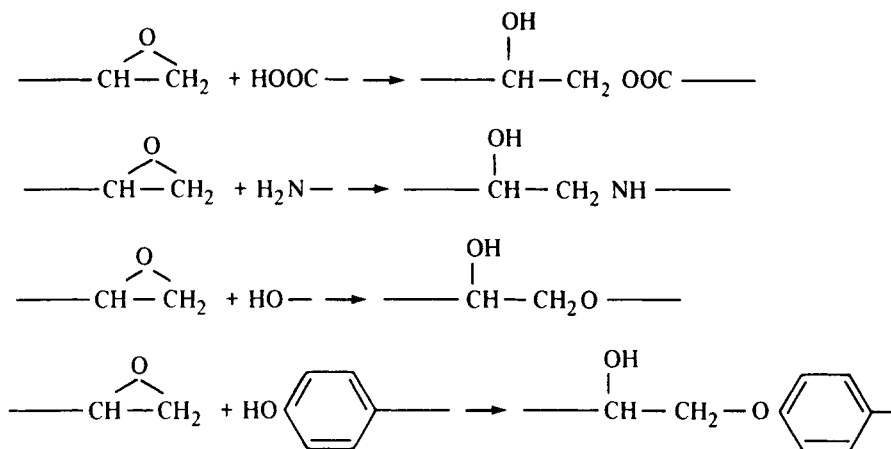


Fig. 2.25 — Typical reactions of the epoxide group.

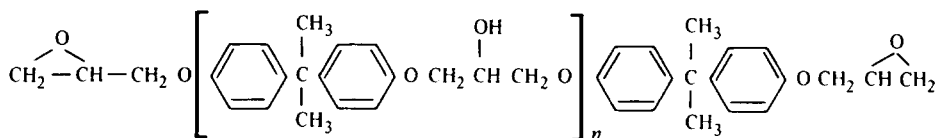


Fig. 2.26 — Generalized structure of bisphenol epoxide resins.

stages in polymerizations. Possibilities occur to react either group initially, the second then reacting in a subsequent stage.

The best-known epoxide containing materials are the range of preformed epoxy resins based on the reaction between diphenylol propane (bisphenol A) and epichlorhydrin [130]; their general structure is shown in Fig. 2.26.

Where n approaches 0, the resin approximates to the diglycidyl ether of diphenylol propane, and the product is liquid. As n increases from 2 up to about 13, solid forms with increasing melting points are encountered (Table 2.8). The lower-melting grades are often modified by pre-reaction before use in coatings, though the higher melting grades can be used in unmodified form for can or drum lining applications.

Because of problems including handling toxic epichlorhydrin, it is normal for coatings manufacturers to purchase epoxy resins of this type; it is, however, now common practice to 'chain-extend' liquid grades to higher molecular weight by reaction with diphenylol propane [131, 132]. Precatalysed liquid epoxy resin is available for use with this technique, which can reduce stocking of a range of grades and can provide access to intermediate solid grades; cost savings are also possible.

The formula above would indicate that all epoxy resins possess two terminal epoxide groups and all, except where $n = 0$, possess in-chain hydroxy groups. Higher molecular weight epoxy resins frequently depart from this linear structure owing to the incidence of side reactions in their preparation.

Considerable care is now taken in epoxy resin manufacture to eliminate free epichlorhydrin from the product because of its carcinogenic nature. Low molecular weight di-epoxides may also be carcinogenic, and consequently the available range

Table 2.8 — Typical grades of bisphenol epoxide resins and properties

Number of repeat units (<i>n</i>)	Melting point (°C)	Epoxy equivalent
0.5	Viscous liquid	225–290
2	64–76	450–525
4	95–105	850–950
9	125–132	1650–2050
12	140–155	2400–4000

of low molecular weight epoxies is now limited, with certain low molecular weight aliphatic di-epoxides now no longer available.

The outstanding properties of cured epoxy resins may be explained by their structure. The very stable carbon–carbon and ether links in the backbone contribute to chemical resistance, while a factor in their toughness is the wide spacing between the reactive epoxide groups and in turn the hydroxyl groups. The polar hydroxy groups, some of which may always remain, also help adhesion by hydrogen bonding. The aromatic ring structure enhances thermal stability and rigidity. Though these properties are attractive, aromatic epoxy resins yellow, and for this reason their major application is in primer and undercoat compositions where adhesion and corrosion resistance are particularly valuable. They are also used in can coatings for their good one-coat performance.

Epoxy resins may be formulated from phenols other than bisphenol A, for example diphenylol methane (bisphenol F). Epoxy-type materials may also be glycidyl ethers of other resins such as PF novolacs [133].

Epoxy compounds are characterized by melting point and by their epoxide group content or epoxy equivalent which may be expressed in a number of ways.

2.12.1 Epoxy esters

Both the terminal epoxide groups, and the secondary hydroxy groups of solid epoxy resins, can be reacted with fatty acids to produce the so-called epoxy ester. In esterification reactions each epoxide group is equivalent to two hydroxy groups. Epoxy esters are prepared by heating the fatty acid and epoxy resin in an inert atmosphere, preferably under azeotropic conditions to remove water of reaction, with temperatures of between 240 and 260°C normally being used. The reaction may optionally be accelerated by the addition of, for example, calcium or zinc soaps at 0.1 or 0.2% weight on total charge.

Typically the epoxy resin where $n = 4$ is used, and fatty acid content chosen to esterify between 40 and 80% of the available groups including hydroxyl. Medium (50 ~ 70% modified) and long (over 70%) oil epoxy esters of drying oil fatty acids are used in air-drying brushing finishes. Short (30–50%) oil-drying or non-drying fatty acid esters are used in industrial stoving primers and finishes. Stoved epoxy resin ester films, especially when cured with MF resin, are harder and of superior adhesion, flexibility, and chemical resistance than similar alkyd/MF formulations. Increased fatty acid content, as would be expected, imparts better aliphatic solubility, better exterior durability, and decreased hardness, gloss, and chemical resistance. Linseed, tall, and DCO esters are most usual, though all fatty acids and rosin can be used.

2.12.2 Other epoxy applications

Epoxy resins may be cooked into alkyd formulations, replacing part of the polyol. They also find a place unmodified as a third component in alkyd/MF compositions to upgrade the resistance properties of the films.

Epoxy resins react with PF resins to form insoluble coatings, and well-formulated high molecular weight epoxy/PF coatings meet the highest standards of chemical resistance. These products are suitable for the linings of food cans and collapsible tubes, coatings for steel and aluminium containers, and wire enamels. Curing probably involves the formation of polyether links between the hydroxyl groups of the epoxy, and methylol groups present in PF resins of the resole type; the epoxy also reacts with phenolic hydroxyl groups on the PF. With some PF resins, compatibility problems on cold blending may be solved by pre-condensation, involving refluxing the epoxy and PF resins together in solution, when some reactive groups combine, leaving the remainder free to react in the curing process.

Urea/formaldehyde resins or melamine/formaldehyde resins may be used to cure epoxy resins, giving stoved films of paler colour, but with a reduced level of chemical resistance compared with phenol/formaldehyde resins. Again, the higher molecular weight epoxy resins are preferred.

Two-pack epoxy/isocyanate finishes require separate solutions of high molecular weight epoxy resin and polyisocyanate adduct as the two components; the epoxy resin must be in alcohol-free solvent since the curing reaction is predominantly with in-chain hydroxyl groups on the epoxy resin. One-pack finishes can be formulated with blocked isocyanates.

Epoxy resins may also be used in two-pack compositions with polyamines or polyamides [134]. The films obtained possess outstanding chemical resistance, hardness, abrasion resistance, flexibility, and adhesion. Low molecular weight solid epoxy resins are used most. Though primary or secondary amines such as triethylenetetramine may be used, in order to avoid the toxic hazards involved in handling amines, amine adducts with low molecular weight solid epoxy resin will nowadays be used as hardeners. These adducts are prepared by the reaction of excess of an amine such as diethylene triamine with an epoxy resin to produce fully amine-terminated adduct. Reactive polyamide resins formed from dimerized fatty acids with diamine are also used.

Reactive coal tar pitches may be incorporated into an epoxy resin base for curing with amine, amine adduct, or with a polyamide resin. The derived coatings have excellent chemical resistance and are not brittle; they hence find use as pipeline, tank and marine coatings.

Epoxy resin modification with a silicone resin is possible to enhance water resistance; epoxy/silicone combinations are used in blends with other polymers with the cure mechanisms mentioned above.

2.13 Isocyanates

The isocyanate group (Table 2.9) is highly reactive with itself, and a number of other groups, and may be catalysed in its reactions. It reacts exothermically (40 kJ/mol) with many groups with active hydrogen atoms, in particular alcohols, amines, phenols, and water at room or moderately elevated temperatures [135]. Amine groups are most reactive, so that hydroxy groups are the most common reactive

Table 2.9 — Typical reactions and reaction conditions for isocyanates

Reaction	Temperature (°C)	Catalysts
$\text{RNCO} + \text{Alkyl OH} \rightarrow \text{RNHCOO Alkyl}$	25–50	Varied
$\text{RNCO} + \text{Alkyl NH}_2 \rightarrow \text{RNHCONH Alkyl}$	10–35	Not required
$\text{RNCO} + \text{Aryl OH} \rightarrow \text{RNHCONH Aryl}$	50–75	Tertiary amine

groups on resins cured by isocyanates. However amine groups are used with, for example, cathodic electrocoat resins cured with blocked isocyanates. Secondary alcohols and secondary amines react in a similarly way to primary but with less vigour. Both aromatic and aliphatic polyisocyanates are available, with the former generally more reactive than the latter.

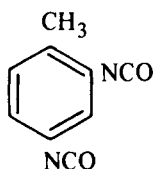
Water reacts with the isocyanate group at similar rates to secondary alcohols; the initial product is an unstable carbamic acid (RNHCOOH) which decomposes to a primary amine and carbon dioxide, and this amine group is of course then available to react with additional isocyanate. This reaction is normally to be avoided in coating formulations, though it is exploited in the production of solid and flexible foams. For this reason, systems to be reacted with isocyanates should be dehydrated, and low moisture content urethane grade solvents used.

Isocyanates also react with themselves under certain conditions and in the presence of certain catalysts [135]; these reactions are generally undesirable. Tin compounds are strong catalysts for isocyanate reactions and are also generally 'clean' in not promoting side reactions. It will be evident that all reaction products of isocyanates contain active hydrogen groups attached to the nitrogen atom of the urethane or substituted urea reaction product; hence, steric factors permitting, reaction can continue with these products if additional isocyanate is present, to give allophanates and biurets. All of the groups mentioned above may be present on simple molecules or attached to polymer molecules.

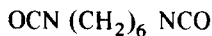
Low molecular weight diisocyanates are used in coatings manufacture in preparing urethane alkyds and blocked isocyanate crosslinkers. Toluene diisocyanate (TDI) is the main diisocyanate used for urethane alkyds (normally the mixed 2,4 and 2,6 isomers). Products derived from aromatic isocyanates such as TDI and diphenyl methane diisocyanate (MDI) tend to yellow; hence aliphatic isocyanates such as hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) now find higher usage (Fig. 2.27). Trimethyl hexamethylene diisocyanate (TMDI) and hydrogenated diphenyl methane diisocyanate (H_{12}MDI), not illustrated, also find application. Great care is necessary in the handling of all volatile isocyanates since their vapours are irritant and they are sensitizers at extremely low concentrations.

2.13.1 Isocyanate adducts and blocked isocyanates

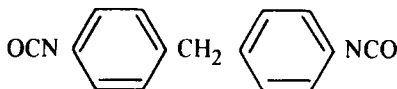
Owing to the toxicity of low molecular weight (volatile) isocyanates, polyfunctional (3+) isocyanate adducts of higher molecular weight are invariably used in two-pack applications of isocyanates. Three different adduct types have been used, namely the triol adduct, the biuret and the isocyanurate. An example of the first is the reaction product of 3 mol of TDI with 1 mol of trimethylol propane. The biuret is



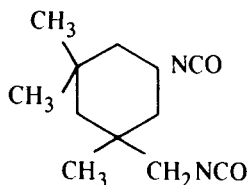
2, 4TDI



HDI



MDI



IPDI

Fig. 2.27 — Typical diisocyanates used in coatings resins.

prepared by reaction of 3 mol of diisocyanate with 1 mol of water, and the isocyanurate is the trimer formed by the reaction together of three isocyanate groups. Isocyanurates from HDI and IPDI are those most frequently used in 2K refinish paints. Isocyanurates may also be mixed with uretdione (isocyanate dimer). The structures of the HDI biuret, uretdione, and isocyanurate are illustrated in Fig. 2.28.

The reaction of the isocyanate group with low molecular weight alcohols, phenols, and certain other compounds such as lactams, may be considered reversible. If an isocyanate that has been 'blocked' or masked in this way is heated with a polymer with reactive groups, the low molecular weight blocking material is released. The urethane or substituted urea bond is then remade with the reactive group on the polymer. Whether free isocyanate groups are fully released in the reaction with a polymer is a matter of conjecture. Blocked isocyanate curing agents are used in automotive and various other solvent applied finishes, and powder coatings. Depending on the blocking agent, curing temperatures may be between 100 and 175°C [136–138] Automotive cathodic electrocoat formulations cure using blocked isocyanate; for powder coatings caprolactam blocked IPDI based crosslinker is used.

2.13.2 Polyurethane coatings

Two-pack (2K) finishes based on hydroxy functional resins and isocyanate adducts find application for tough high solvent-resistant coatings curing at atmospheric temperature or under moderate stoving conditions. Resins that may be used are alkyd, polyester, polyether, epoxy, and acrylic. Alkyds used are frequently castor oil-based. Two-pack alkyd finishes are used for wood finishing. Two-pack polyester finishes find application for high-durability transport finishes including marine and aircraft and by automotive manufacturers for painting plastic parts fitted after the main metal body has been painted and stoved at high temperature.

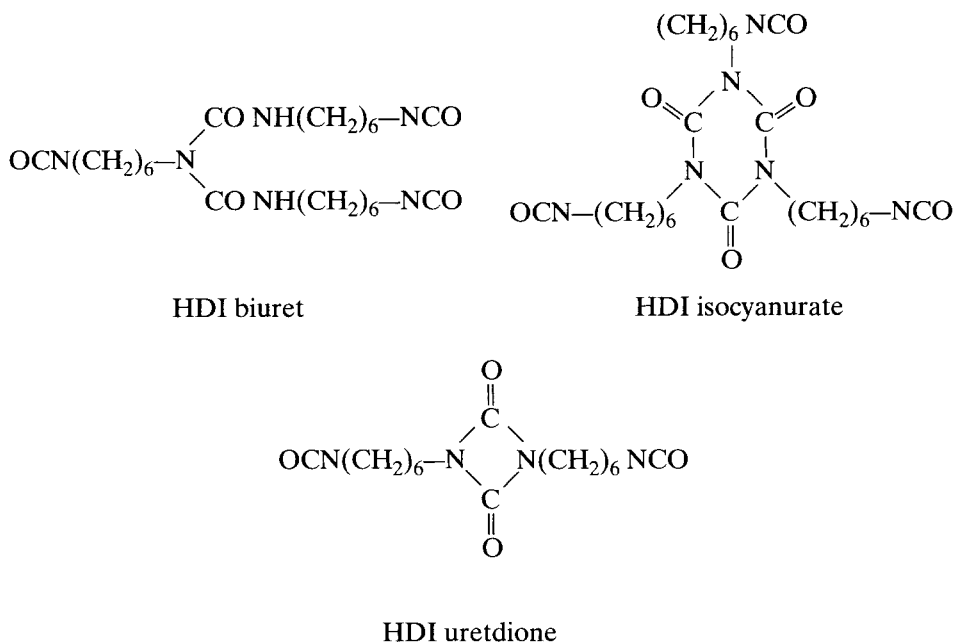


Fig. 2.28 — HDI biuret HDI isocyanurate HDI uretdione.

Two-pack systems with hydroxy functional acrylic and polyester resins (2K) have high usage in car refinishing, and in most European countries this type of finish now predominates. However, because of the toxicity of isocyanates and the danger of inhaling droplets while spraying, producers have in the past striven to develop systems avoiding the use of isocyanate, but with similar properties. For these, the isocyanate component could be replaced by a crosslinker such as a melamine/formaldehyde resin. Masked isocyanate polyurethane (PU) curing systems, sometimes mixed curing with MF, dominate in automotive OEM primers, and both solvent and water-borne systems are in use [139].

Two-pack systems such as the hydroxy polymer/isocyanate one may be difficult to formulate because of 'pot-life' difficulties, where conflict occurs between the need to accelerate curing but to retard bulk solidification to protect the application equipment. A development has been to accelerate curing of this type of system after application, by exposure to an atmosphere containing volatile amine catalyst (vapour phase curing) [135, 140].

Moisture-curing products may also be used, based on stable isocyanate terminated polymers obtained from the reaction of excess low molecular weight di- or polyisocyanate with a polyfunctional hydroxyl-terminated polyether. The pigmentation of moisture-curing finishes is difficult, though dehydrating agents are available to assist; the most frequent use of this type of product is for clear wood varnishes.

A special class of PU block copolymers incorporating both hydrophobic and hydrophilic segments is used in aqueous systems as one of the group of additives known as associative thickeners. HEUR (hydrophobically modified ethylene oxide urethane) associative thickeners consist of polyethylene glycol blocks linked via urethane segments. The end blocks are hydrophobic long aliphatic chains.

2.13.3 Polyurethane dispersions

Fully reacted, aqueous polyurethane dispersions have long been available, mainly used in applications other than traditional coatings, but their use in coatings is now increasing. They are typically prepared from DMPA (see Section 2.5.7), polyester-polyol and an excess of aliphatic isocyanate. These are chain extended with short chain diamines and solubilised with t-amine. [141, 142]. Crosslinking is possible with added aziridine or carbodiimide crosslinkers, autoxidatively by fatty acid modification or even by radiation curing via attachment of acrylate.

A recent development is of 2K reactive PU systems, where HDI adduct is homogenized into a pre-prepared aqueous millbase, and the hydroxy functional co-reactants can function as emulsifier for the isocyanate component. These protect the isocyanate groups from reacting with water, and while some reaction with hydroxyls does commence in the droplets, pot life extends to several hours.

2.14 Silicone resins

Silicone-oxygen and silicon-carbon bonds are particularly stable, and this has a beneficial influence on the behaviour of the semi-organic silicone resins, so that they are exceptionally resistant to thermal decomposition and oxidation.

For the surface coatings formulator, a range of reactive silicone resins is available for use in the preparation of silicone-modified polymers, and these may be either hydroxy or methoxy functional. Typical structures are shown in Fig. 2.29.

R may be phenyl or methyl, and both alkyl and aryl organo-silicones are currently available for resin modification. Reaction into a resin structure occurs through its available hydroxyl groups, when either water or methanol will be eliminated (Fig. 2.30); catalysis of these reactions is possible but not essential.

Polymers that may be modified include alkyd, polyester, acrylic, and epoxy. Silicone modification may typically be from 15% to 40%, though higher levels of modification of alkyds, for example, are possible for special heat-resistant applica-

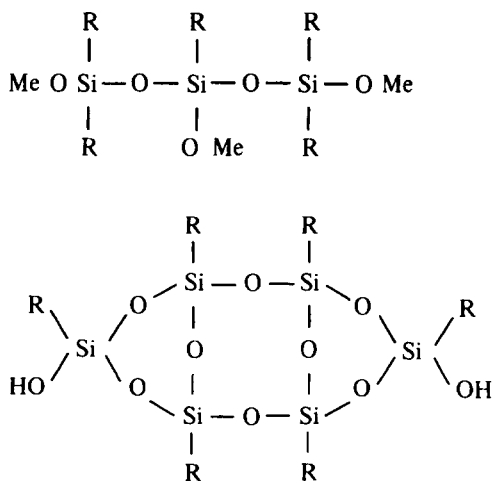


Fig. 2.29 — Typical silicone resins for polymer modification.

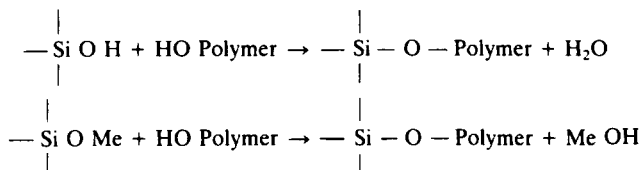
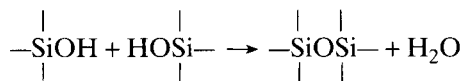


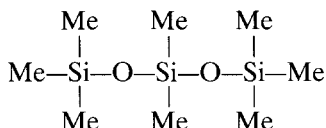
Fig. 2.30 — Silicone resin reactions with hydroxy polymer.

tions. The single largest use of silicone-modified resins is for coated steel coil for building structure facing. Silicone modification always considerably enhances durability (see Sections 2.5.8, 2.6.3, and 2.16).

Pure silicone surface coatings are available for special application where very high heat resistance properties are required. These resins cure by the same mechanisms as for modification, but here will be catalysed:



Alkoxy-silyl functional acrylic resins and emulsions were mentioned in Sections 2.7.5 and 2.8 respectively. These are moisture curing resins. Non-reactive linear silicones, e.g. poly dimethyl siloxanes of low viscosity, find frequent use in very low concentrations as flow control or mar aids in paint formulations:



These particular silicones are generally used in solvent based coatings. For water based systems, a range of block copolymers of poly dimethyl siloxane with polyalkylene oxides are available. Both poly ethylene oxide and poly ethylene oxide/propylene oxide di-block copolymers are used.

2.15 Vinyl resins

The term 'vinyl resin' commonly refers to polymers and copolymers of vinyl chloride, though the term has more general meaning. Vinyl chloride is a cheap monomer whose polymers possess good colour, flexibility, and chemical resistance. Vinyl chloride is, however, gaseous and a recognized carcinogen; hence, though it is readily polymerized by emulsion or suspension polymerization techniques in an autoclave, the polymer will be purchased by most surface-coatings manufacturers. For this reason polymer preparation is not further discussed. The polymers are nevertheless quite widely used in coatings.

Both homopolymers, and copolymers usually with vinyl acetate, are used; small amounts of an acidic monomer may also be present. A serious problem with vinyl chloride-containing polymers, if heated, is dehydrochlorination, and stabilization is often necessary with, for example, organo-tin compounds or group 2 metal carboxylates.

A major advantage of PVC connected with its polar nature is its ability to accept plasticizer. Plastisols and organosols are dispersions of dried PVC particles in either plasticizer or mixed solvent/diluent. The basis of both types of coating composition is that the particulate dispersion is stable until applied and heated, when the plasticizer or solvent swells the particles, softening them and allowing coalescence; this is resisted at room temperature because of the crystalline nature of the PVC particles. With plastisols, plasticizer is retained in the coating after coalescence; with organosols the solvent and diluent are lost through evaporation.

The formulation of an organosol requires much care and a fine balance between diluent and solvent. If the mixture is too rich in diluent, the particles flocculate and give a high-viscosity dispersion; if too rich in solvent the viscosity is too high, this time owing to solvent swelling of the particles.

Polyvinyl acetate/vinyl chloride copolymers are soluble in ketones or ketone/aromatic solvent blends, and this allows their use in lacquer formulations.

Vinyl resins are used in coatings for strip for Venetian blinds and for bottle tops where extreme flexibility and extrusion properties are required. They are also used in heavy-duty and marine coatings where properties of toughness, elasticity, and water resistance are paramount, and have application as thick coatings on coil-coated strip for building facings. Polyvinylidene fluoride dispersion is now used in the highest durability coil coating finishes in blends with acrylic resin containing up to 80% vinyl polymer. Compositions containing lower concentrations, for example 30–50% of vinyl polymer, may also be used where the acrylic resin will be a thermosetting resin of, for example, the self-reacting acrylamide-containing type.

PVC copolymer emulsions are used in emulsion paint compositions, and brief mention of formulations for this application has been made under emulsion polymerization.

Other resins find use; chlorinated rubber paints are formulated using chlorinated paraffins as plasticizing component. Chlorinated rubber may also be used as an additive with resins such as alkyds and acrylics. Polyvinyl acetals (formal and butyral) are also used, the latter particularly in resistive or active primers.

2.16 Water-borne systems

The four main technologies providing solvent reduction or elimination as so-called compliant coatings are waterborne, high solids, radiation-curing and powder coatings. The replacement of solvent in a coating by water also improves safety in application from the point of view of flammability and toxicity. Though water-borne systems have always found some application, legislation has accelerated the switch to waterborne systems. Electrodepositable coatings are a special class of waterborne system.

Water is however very different to organic solvents (Table 2.10), in ways which create many problems for the formulator. To reformulate a resin system to replace organic solvent by water (Table 2.10), requires an increase in the polarity of the whole polymer system either by the incorporation of some water soluble groups, or by the inclusion of surfactants, or both [142]. The polymer may finally be either in solution or in dispersed form. Unless very carefully formulated so that hydrophilic groups are destroyed or deactivated in curing, water sensitivity may be a problem in the final coating.

Table 2.10 — Comparison of the Properties of Water and Xylene

	Water	Xylene
Molecular weight	18	106
Melting point, boiling point (°C)	0, 100	-25, 139
Vapour pressure (mm) 20°C	23	8
Latent heat of vaporisation (J/g)	2259	395
Surface tension (mN/m) 25°C	72	27.5
Solubility parameter δ_D	15.5	20.1
δ_P	16	1.8
δ_H	42.3	2.5

The high surface tension creates problems with flow and wetting, and the increased likelihood of surface defects. Replacement of solvent by water need not affect the time to dry, though a consequence of the higher heat of vaporization could be increased energy requirements for stoving. However air-flows in ovens can generally be appreciably lower. Difficulties with control of rheology can be a reason to retain some solvent in an otherwise waterborne composition [143].

Polymers fully water-soluble without the addition of salt-forming additives exist; examples are polyethylene oxide or glycol, polyvinyl pyrrolidone, polyacrylamide, and copolymers containing a high proportion of these materials. Polyethylene glycol, typically having one or two terminal hydroxyl groups, has a major use as a reactant to make alkyds water-soluble or dispersible; polyethylene oxide occurs as the water-soluble portion of many surfactants.

Other water-soluble polymers, including polyvinyl alcohol, acrylic polymers with a very high acid content, and modified celluloses, find application as colloid in emulsion polymerisations. Some formaldehyde condensate resins, including hexamethoxymethyl melamine and certain phenolics, are water soluble, and therefore are used in preference to other resins as crosslinking resins in water-borne systems [144].

It will be recognized that polymers not containing soluble groups may be emulsified by added surfactant; this is not, however, common practice. Special cases of water-borne products prepared solely using surfactants were discussed in the section on emulsion polymerization (Section 2.8), and alkyd emulsions were also covered earlier. There are cases where resins are blended and one resin acts as emulsifier for other polymer species present; this is the case, for example, where the final cure requires the presence of an insoluble curing agent. The following is concerned with systems solubilized or dispersed with the aid of hydrophilic groups on the polymer backbone. Here the polymer will normally be prepared in the absence of water, and only when at its terminal MW is it transferred into water.

The major route to water solubility/dispersibility, is by the preparation of polymers with acid or amine groups on their backbone, which may be solubilized by salt formation by the addition of an alkali/amine or acid respectively. When the resins dissolve in water, these salt groups ionize, the counter-ions being carried in the bulk solution. There is a particular advantage in using volatile amine or acid in that water sensitivity in the final film is reduced, owing to the loss of the salt-forming agent; this sensitivity can be further reduced or eliminated if the crosslinking reaction can

then take place with these groups. As a general point it should be noted that many successful formulations are dispersions (colloidal or micellar), not solutions, simply because this can realize the highest solids and lowest viscosity. Resins may be prepared with a higher acid or amine content than necessary, the 'degree of neutralization' with salt-forming acid or amine then being about 60% to 85%. This may be fine tuned to give the optimum viscosity, stability, freedom from settlement, and application properties.

Early water-borne vehicles were alkali neutralized maleic adducts, the simplest being maleinized oils. Maleinized fatty acids reacted with polymer backbones still play a role in water-borne systems. Epoxy resins esterified with maleinized linseed oil fatty acids alone or in combination with other fatty acids followed by neutralization, can provide vehicles for both normal spray or dip and for electrodeposited application. Polybutadiene may be maleinized and can then similarly form the basis of water-borne systems. Both oil and polybutadiene-based systems may be cured by oxidation, usually stoved without the addition of further crosslinker. Water-borne alkyd and polyester systems have already been mentioned (Sections 2.5.7 and 2.6.1), specially formulated with a high acid value to give water solubility or to be water dispersible. Acidic acrylic systems are also preparable where, for example, maleic anhydride or acrylic acid are copolymerized with the other unsaturated monomers, and such thermosetting systems have already been described. Epoxy systems may be given acidic functionality by the ring-opening half ester reaction with a dicarboxylic anhydride, or trimellitic anhydride as described for alkyds and polyesters [145].

Water-borne resins may be self-crosslinking (alkyds, thermosetting acrylics) or may be crosslinked by added soluble or co-emulsified water-insoluble crosslinking resins. Fully soluble crosslinking resins may be blended into the system at any stage, and these include MF, UF, and phenolic resins, reacting as previously described for solvent-borne systems.

Carboxyl groups of waterborne anionic polymers can participate in reactions with a number of added crosslinkers. β hydroxyalkylamides were originally proposed for waterborne systems [146], though they now find use in the cure of powder coatings (see Section 2.20). Two other specialized crosslinkers are polycarbodiimides and aziridines, where use is practically restricted to curing polyurethane dispersions (see Section 2.13.3). The structure of these is shown in Fig. 2.31.

Epoxy resins can be formulated to be amine functional by reaction with secondary amines that will then be solubilized with, for example, acetic acid (Fig. 2.32).

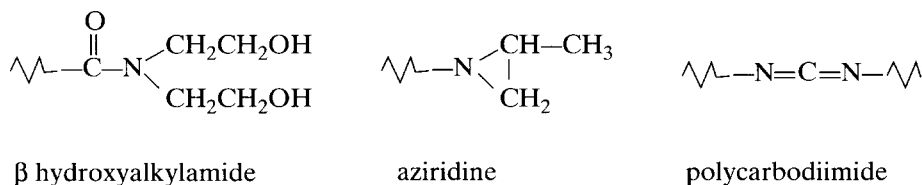


Fig. 2.31 — Functional group of β hydroxyalkylamide, aziridine and polycarbodiimide crosslinkers.

with air-drying alkyds, by neutralizing amine retarding oxidative crosslinking [150]. The presence of amines can also adversely affect colour retention.

Most water-soluble compositions contain a proportion of water-miscible co-solvent [151] which may have been a necessary component in the resin preparation state prior to water addition. However, its presence may also allow the paint formulator greater latitude to control properties such as stability, drying and particularly rheology [152], and still meet any required VOC levels required by pollution legislation. Disperse compositions may need to contain organic solvent to aid coalescence. The presence of water-miscible solvents may also aid emulsification in disperse systems as with the techniques to prepare so-called 'microemulsions'.

2.17 Resins for electrodeposition

Electrodepositable resins are a special class of water-borne resin [153, 154]. The polymer is carried in an aqueous medium and, on application of current via suitable electrodes, polymer in the vicinity of one of the electrodes is destabilized and deposited on the electrode. The deposited polymer builds up to form an insulating layer that ultimately limits further deposition. The electrodeposition process has been called electrophoretic deposition, though it is now recognized that electrophoresis plays little part in the process.

In anodic electrodeposition negatively charged polymer is deposited on the anode, and in cathodic electrodeposition positively charged polymer is deposited on the cathode. Compared with conventional painting, very uniform coverage of external surfaces can be obtained, and deposition of paint inside partially closed areas can be achieved ('throwing'). Paint utilization is high, and almost complete automation of the process is possible. These advantages are not achieved with simpler dipping processes. Since the films can only be built up on metal surfaces and to a limiting thickness, electropaints are either primers or for some industrial applications, one-coat finishes. Unpigmented clear systems are in use for coating metallic brightwork. Both anodic and cathodic commercial processes exist [155, 156]. Cathodic systems have now supplanted anodic systems particularly for automotive applications. Electrocoating is important in the application of can lacquers.

Almost all polymer types described in the previous section under water-borne coatings can be adapted to electrodeposition. In most cases, to be suitable for the electrodeposition process, the resin will be held in stable particulate or micellar dispersion, but not complete solution, by the action of hydrophilic ionic groups, which will provide the necessary colloidal stabilization. Non-ionically sterically stabilized dispersions, however, may also be electrodeposited [157, 158].

The system should be designed such that the deposited film has high electrical resistance so that shielded areas can receive adequate coverage. The system may contain organic solvent to aid the dispersion process and dispersion stability, and act as a flow promoter during coating and curing. The role of the neutralizing acid or base is fundamental both to stability of the dispersion and to the electrocoating process. In practice, for anionic systems either alkali or amines may be used, and for cathodic systems lactic and acetic acids are usual choices for the neutralizing agent.

The earliest anodic electrodeposition vehicles were based on maleinized oils and oil derivatives, and the chemistry of these developed through vinylated and alkyd type condensates to the use of epoxy esters based on maleinized fatty acids. Since epoxy resin-based systems exhibit such good performance as metal primers, solubilized epoxy vehicles play a major role in both anodic and cathodic systems, especially for automotive applications.

Alkyd and acrylic systems have been developed for electrodepositing and have found application in industrial systems. Anodic alkyd systems are based on high acid value resins, particularly those that are trimellitic anhydride-derived, and may be drying oil-modified. They may therefore be autooxidative/stoving, or if non-drying oil-containing or oil-free, cured by co-emulsified or soluble melamine/formaldehyde resin. Acrylic systems have been proposed for both anodic and cathodic formulations, in the former case by inclusion of higher than normal concentrations, of, for example, acrylic acid [104, 159]. In the latter case, they have been formed by the inclusion of a copolymerized amino monomer, such as dimethylaminoethyl methacrylate [160] or by including a glycidyl monomer that can be subsequently reacted with an amine [161].

Cathodic epoxy systems may be either primary or secondary amino functional, reacting epoxy resins with amines or quaternary amine salts can be used to give adducts with terminal secondary, tertiary, or quaternary amines or their salts. The relatively weak nature of these amines can result in poor dispersibility of these systems, and it is more desirable to incorporate primary amine groups. This can be difficult to achieve. However, useful methods have been developed; these include reacting an excess of a di-primary amine with an epoxy resin [162], or blocking primary amine groups on molecules with ketones, before reaction with epoxides through other functionalities [163]. These are illustrated in Fig. 2.34 and 2.35.

Because of their extremely high film alkalinity these systems crosslink sluggishly with melamine and phenolic crosslinkers. They can be effectively crosslinked with blocked isocyanates, which are designed to be stable at bath temperatures but

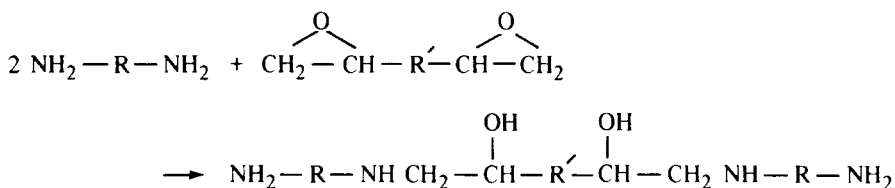


Fig. 2.34 — Reaction of epoxy resin with excess diamine.

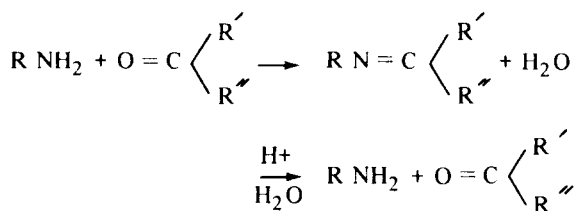


Fig. 2.35 — Ketimine formation and hydrolysis.

unblock at reasonable stoving temperatures [164]. Acrylic cationic systems may also be cured with these curing agents for one-coat systems where good colour requirements are more important than corrosion resistance.

2.18 High solids coatings

Changing one's paint formulation to higher solids is the simplest means available to reduce actual organic solvent content to achieve lower VOC. Current expectation will be for high solids spray paint to be applied at >75% solids, and for a brush-applied paint to be >85% solids. The trend to higher solids and hence lower solvent content is seen in all areas of paint application.

A number of approaches to achieving higher solids are possible. Powder coatings are of course a 100% solids system. 100% solids can be achieved where reactive diluents (e.g. unsaturated monomers) are used in place of solvent, as is the practice with unsaturated polyesters, and with radiation-curing polymers. The use of a reactive diluents as a partial replacement for solvent is possible with most systems. With epoxy systems, low molecular weight or monofunctional epoxides can be used. With PU systems, oxazolidines and low molecular weight polyols can be used. As described earlier (Section 2.3.2), with autoxidatively drying alkyds, some solvent may be replaced by diluent which is a vinyl monomer, which copolymerizes into the structure through the free radical nature of the autoxidative drying process [19]. Allyl ether-based oligomers have been examined as components of high solids alkyd systems [165] (though formation of acrolein limits their use) and specially formulated unsaturated melamine resins have also been used.

On the face of it, with all high solids systems, savings should be made in that less solvent is needed, and less energy used in the evaporation of solvent; however, the approach generally requires special formulating techniques and invariably the use of more expensive ingredients.

It is possible to obtain small gains in application solids with any paint by applying at higher viscosity or by heating the paint as a means of reducing viscosity. However, to achieve a significant increase in solids and to retain good application characteristics, it is necessary to redesign the overall system using polymer of lower molecular weight than before; the result of lower molecular weight is that less diluent is required to achieve application viscosity. However, lower molecular weight polymer always requires more crosslinking reaction in order to achieve final film properties, and lowered molecular weight has the consequence that special care is necessary with the concentration of reactive functional groups and their distribution.

Polymers for high solids systems are often referred to as 'oligomeric'. This term is used for low molecular weight polymers whose molecular weight is in that part of the molecular weight spectrum where polymer properties are only just starting to become apparent; this is in particular below the molecular weight where chain entanglement is significantly affecting viscosity. An oligomer may be of molecular weight 1000–5000, where the molecular weight for an older conventional thermosetting polymer might be 10 000–40 000, and a thermoplastic polymer not requiring crosslinking 80 000–100 000 [166, 167]. Telechelic refers to linear or branched polymer molecules possessing terminal functional groups; the design of these for high solids systems has been described [168].

To achieve low viscosity/high solids, good understanding is necessary of the relationship between molecular weight and viscosity for the resin, and for the interaction between all the components (oligomer, crosslinker, solvent, and pigment) [169]. Molecular weight and molecular weight distribution both require careful control. Narrowing of the molecular weight distribution is desirable; for alkyd systems narrower molecular weight for high solids systems has been achieved using iso-phthalic acid rather than *o*-phthalic anhydride.

In conventional coatings relatively few functional groups need react to yield crosslinked films. In high solids systems, a substantially larger number of groups must react to reach the same final crosslinked structure. This increase in functional group content does, however, tend to increase viscosity since these groups are generally polar; this in part offsets the viscosity decrease achieved through molecular weight reduction. The formulator must nevertheless try and ensure that each oligomer molecule has at least two functional groups attached.

Polyester formulation for high solids is relatively simple, using similar ingredients as for higher molecular weight polyester. Polyesters are usually certain to have two terminal functional groups, more if branched. For alkyds, higher functionality in reactants may be required. Thus high solids alkyds may be formulated using six functional dipentaerythritol and trifunctional trimellitic anhydride or tetrafunctional pyromellitic anhydride [170]. Higher solids alkyds will be of very long oil length in order to ensure a high overall content of oxidisable groupings and a sufficient number on each individual alkyd polymer molecule.

In the case of acrylic resins additional problems are experienced in preparation over normal formulations. High concentrations of expensive initiator may be required to reduce molecular weight; alternatively, high chain transfer agent concentrations will be required, leading to residual odour problems, difficult to tolerate for some applications. The use of high solids in preparation, which may be essential, results in higher degrees of chain transfer to polymer, leading to broadening of molecular weight distribution and consequent adverse effects on rheology. Unlike polyesters, in acrylics functional group content from a functional monomer tends to be random (see Section 20.6.1); it can hence be beneficial to include functional transfer agents such as mercaptoethanol to ensure that as many polymer molecules as possible carry at least one terminal reactive group.

Also in acrylics, the use of such bulky monomers as isobornyl methacrylate and cyclohexyl methacrylate has been found to give lower viscosity at comparable molecular weights [171, 172]. Higher molecular density is also achieved through branching of the polymer, so that a hyperbranched polymer has a substantially lower viscosity at comparable molecular weight or solution concentration, compared to linear polymer. Formulating practice has developed techniques to provide branched, hyperbranched, star and dendritic structures. Acrylic resins can be made more highly branched using ethylene glycol dimethacrylate [173] or using multifunctional transfer agents [174]. Techniques aiming for star or dendritic structures have been applied to obtaining both high solids alkyds and acrylics [172, 173, 175].

High solids acrylic and polyester resins are normally hydroxy functional, and hexamethoxymethyl melamine resins have found application as crosslinkers in high solids thermosetting finishes. The reasons for their suitability have been discussed [176]. With corresponding higher concentrations of functional groups in the oligomer part of the formulation, an amino resin may constitute as much as 50% or

more of the composition, compared with 10–40% in more conventional finishes. Blocked isocyanate are also used.

High solids 2K finishes with isocyanate adducts use the same acrylic and polyester resins described above.

2.19 Radiation-curing polymers

Radiation that can assist or control curing includes electron beam cure (EBC), ultraviolet (UV), and infrared (IR), and all these methods are practised commercially. Reduced energy consumption, improved environment protection, and, in particular, suitability for wood, paper, and plastic substrates have contributed to recent growth. For UV cure, photoinitiators are required, and for IR cure thermal initiators, in both cases normally to initiate chain addition polymerization. For EBC no added initiator is required, the electron beam producing radicals in the polymerizing layer through its own high energy. The systems employed are normally high solids, and typically the resin system is a blend of prepolymer and reactive diluent. Unsaturated polyesters are typical prepolymers and are used in combination with suitable vinyl or acrylic monomer diluents. The systems and mechanisms for UV, IR, and EBC have been reviewed [177]. Owing to the opacity of most pigments to UV radiation, the majority of UV curing finishes are clearcoats.

In addition to the unsaturated polyesters described earlier in this chapter, for UV cure, epoxy and polyurethane resins are also used. Epoxy acrylates are prepared by the reaction of bisphenol epoxy resins with acrylic acid. Polyurethane resins for photocuring are obtained by the complete reaction of di-functional isocyanates or polyfunctional isocyanate adducts with hydroxy ethyl acrylate. Rather than unsaturated polyesters with fumarate unsaturation, for UV curing, polyester acrylates are preferred, prepared by the esterification of hydroxy functional polyether or polyester with acrylic acid. In the preparation of all acrylate resins careful control of inhibitor levels is necessary to prevent polymerization, and final dilution with monomer may be necessary to retain fluidity. A major advantage of this type of prepolymer is low viscosity.

Monomers are necessary as reactive diluents especially for viscosity control, and apart from their viscosity and solvating ability other factors needing consideration include their volatility and photo-response. Crosslinking mechanisms are complex, and for any resin/monomer system there may be an optimum resin/monomer ratio for a given dosage of radiation to attain the required film characteristics. Acrylates give the fastest cure speed, and polyfunctionality is normally necessary; hence such monomers as hexanediol diacrylate and trimethylol propane triacrylate find considerable application. A broad range of such multifunctional monomers is now available commercially. The order of reactivity for unsaturated groups in radiation curing systems is acrylate > methacrylate > allyl = vinyl. UV/visible photo-initiators for unsaturated systems will be free radical generators, for example aromatic ketone; ketone/amine combinations are also used [178, 179]. Curing reactions are those described earlier for acrylic polymerization.

The cationic curing of epoxy resins using photo-initiators which release Brønsted acids on irradiation is a development in this field; systems using this method are based mainly on cycloaliphatic epoxy resins and aliphatic diepoxides; bisphenol epoxides degrade the curing efficiency of this system.

The most recent developments are in UV curing of water-borne finishes and of powder coatings. For the latter, heating is still necessary to fuse the coating, but further raising of temperature to effect cure is not.

2.20 Powder-coating compositions

Powder coatings possess advantages over conventional coatings in that no polluting solvent loss occurs on application, and owing to the use of electrostatic spray, little material is lost. Electrostatic spraying is also employed with solvent-borne coatings and is a method particularly suited to automation. Powders have three distinct temperature regimes to consider and this imposes special constraints on their formulation [180, 181]. The ingredients, and particularly the final composition, have to be solid and glassy at room temperature in order to be ground to size and for the powder to stay free-flowing on storage, and this requires that the blend must not soften or sinter below 40°C. Most powders are produced by comminuting an extruded melt which means that the final curing composition has to withstand this melting process. (Pigmentation is also achieved in the course of the extrusion.) Finally good flowout and then cure must occur at higher temperatures still after application. In formulation and production, additional factors such as particle size control, melt flow characteristics and resistivity need careful attention.

Epoxy compositions are widely used and are based on bisphenol resins cured with amines (dicyandiamide derivatives in particular) or phenolic crosslinkers. Optionally in so-called hybrid systems, saturated polyester may be mixed with the epoxy. Dimerized fatty acid modification may also be carried out to improve film levelling and adhesion, and epoxy resins containing branched species derived from epoxidized novolacs may be introduced to increase hardness. Dicarboxylic acid anhydrides and acidic polyesters are also used to cure epoxy powders, and these compositions have better performance than amine cured epoxies, being non-yellowing.

Polyester powder coatings may be hydroxy functional, and use melamine/formaldehyde or masked isocyanate curing agents [136], or may be formulated from acidic polyesters cured with added epoxy resin or triglycidyl isocyanurate (TGIC); the latter offers excellent durability and colour stability. Caprolactam is used as a blocking agent for masked isocyanates for curing powders, though release of this

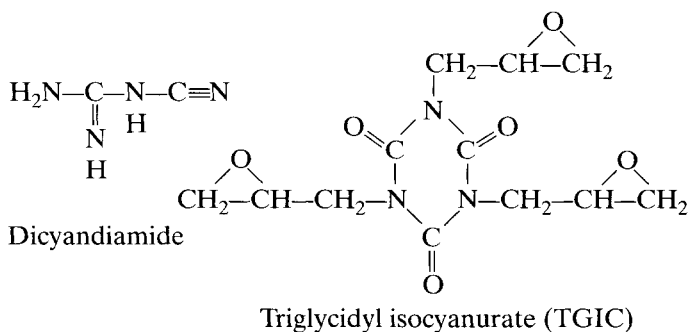


Fig. 2.36 — Typical curing agents for powder coatings.

agent from the curing film may be troublesome. Typical curing agents for powder coatings are shown in Fig. 2.36. The use of TGIC is now under threat on toxicity grounds, but β -hydroxyalkylamides (Fig. 2.31) are finding some use as a replacement [182].

Acrylic systems are available but to date have found limited application; possible use in automotive clearcoats may increase use dramatically.

Thermoplastic powders are also used containing, for example, nylon 11 or nylon 12, polyvinyl chloride, cellulose acetate and butyrate, or polyethylene. These are used as thicker coatings. Redispersed powders may be applied from water as the so-called slurry coatings or aqueous powder suspensions, and may also be electrodeposited (electropowder coatings).

2.21 Resin manufacture

In the preceding sections of this chapter, the manufacturing methods normally used for each resin type have been indicated. This brief section summarizes these, highlights certain general points, and indicates future trends. Plant design and operations require advanced engineering considerations and interested readers should consult elsewhere [183].

Resin processes divide mainly between high temperature (over 180°C) and low temperature processes where the latter are generally more fiercely exothermic. For exothermic processes, heat balance and safety, including considering the prevention of reaction runaway, are important in scale-up. Resins may be made in the melt or in solution, but will always finally be used in liquid form, either as solution or emulsified to a liquid dispersion form. Otherwise, resins will be produced in dispersed form by emulsion or dispersion polymerization.

Resin manufacturing plant has now moved a long way from the simple portable stirred and heated pot, satisfactory only for oleoresinous vehicles and step growth polymers such as alkyds, to the almost universal use of fixed plant. The reactor of this plant will have efficient agitation, be fitted with means of heating and cooling with sophisticated control, be equipped with vapour-condensing systems capable of azeotropic distillation, and will normally be attached to a thinning and cooling vessel. The plant may be multipurpose, but it is more usual to segregate high temperature, low temperature, and aqueous emulsion resins to different plants. One reason is the need of the latter two types of product for feed vessels for both monomers and initiator. Emulsion reactors, because of the inherent sensitivity of emulsions to shear, often need more carefully designed agitation systems and require other special facilities such as aqueous preparation vessels.

Computers now find extensive application in controlling larger scale resin and paint plant. The advantages of computerized control of resin plant are claimed to include stricter timing and control of process phases and improved accuracy [46].

Resin manufacturing processes for paint application are almost exclusively batch processes, and only few examples of large-scale continuous processes exist [107]. Most resin processes are carried out at atmospheric pressure, although examples of acrylic resin processes exist where reaction is carried out in sealed pressurized reactors [75]. Autoclaves capable of containing very high pressures are used in the manufacture of vinyl chloride and ethylene containing aqueous emulsions (see Section 2.8). Resin reactors may frequently have vacuum facilities attached, both for fume

control and for use in vacuum distillation. Automation of testing remains an ultimate goal, and to date only a few working examples exist [184].

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