Coating Types and Common Failure Modes

Previous chapters in this volume have discussed some of the basic mechanisms by which coatings can fail, as well as the basic coating ingredients such as pigments, additives and solvents. However, the single most important ingredient in a coating is its binder or resin. The type of resin or polymer is so important that this is how coatings are named and marketed. One often hears of an ‘alkyd’ coating or an ‘epoxy’ coating. In contrast, one never hears of a ‘titanium dioxide’ coating or a ‘methyl ethyl ketone’ (MEK) coating.

This chapter will describe many of the common resins or polymers used in coatings as well as their particular strengths and weaknesses. It must be noted, however, that even in a single coating family, products of widely varying physical and chemical properties can exist. One of the intriguing characteristics of polymer science is its diversity. Slight changes in the chemistry of the monomeric building blocks of an acrylic, for instance, can result in a final polymer with dramatically different characteristics. Epoxies can be formulated hard and brittle, or relatively soft and almost flexible. While it is, to some degree, necessary to talk in generalities, one should always be aware of the existence of exceptions.

5.1 NATURAL RESINS AND OILS

Natural resins and oils have been used for centuries in the manufacture of decorative and protective coatings. They are derived from natural sources such as plants, animals and fossilized remains. Although oils such as linseed oil or fish oil are certainly ‘natural resins,’ they are usually considered separately in most discussions of the subject. This convention will be adhered to here.
5.1.1 Natural Resins

Many natural resins come from the tapping of trees and are exuded from the tree in order to protect it from cuts or wounds. Many of them have a carboxyl functionality and are acidic. The acidity of a resin is often expressed as its acid number, which is the number of milligrams of potassium hydroxide required to neutralize the acid in one gram of resin. The natural resins are often of relatively high molecular weight, and in the pure state are solids at room temperature. They are often used in the production of varnish, where they are heated together with varying amounts of vegetable oils. The natural resins impart hardness, gloss, moisture resistance and improved drying time, while the vegetable oil imparts flexibility and durability.

Examples of natural resins from trees, plants and fossilized materials include elemi, copal, dammar and rosin.

Elemi is a soft resin with a melting range of 176–248 °F (80–120 °C) and a low acid number (20–35). It is derived from a tree in the Philippines, is compatible with many resins and solvents, and imparts flexibility to lacquers and varnishes.

In contrast to elemi, copal is a hard, high-molecular-weight material with melting points as high as 300 °F (149 °C) and acid numbers ranging from 50, for the New Zealand variety, to as high as 140 for deposits in Central Africa. It consists of fossilized material from various tropical trees, and is of little use unless distilled under pressure and heat. Once treated, it can produce varnishes of excellent durability and weather resistance.

Manilla copal, obtained from the Philippines or the East Indies, is not fossilized but is rather obtained from the tapping of live trees. It is somewhat softer than fossilized copal and is soluble in alcohol. Harder, fossilized varieties are also available.

Dammar is a relatively soft resin with a melting range of 158–235 °F (70–113 °C) and a low acid number (20–30). It is obtained from certain trees in the East Indies and is soluble even in weak hydrocarbon solvents. It is used in varnishes, nitrocellulose lacquers and even as a modifier in certain alkyd coatings. It tends to improve gloss and colour retention.

Rosin, also known as colophony, is one of the most widely used natural resins. It has a melting point of approximately 176 °F (80 °C), is highly acidic (acid number of 150–180), and is soluble in alcohols and hydrocarbons. It is an exudate of pine trees and can be obtained domestically. Chemically, it consists of derivatives of phenanthrene (a polynuclear aromatic hydrocarbon), such as abietic acid (Figure 5.1).

Rosin usually has poor resistance to water and alkalis, tends to oxidize over time and is slightly tacky. Because of these deficiencies, rosin is often used as a precursor in the manufacture of other resin types. When reacted with glycerol or other polyhydric alcohols, rosin is converted to a product known as ester gum, a hard material used in varnish production. The reaction occurs between the car-
The primary use of most natural resins is in varnish manufacture. In the making of a varnish, the natural resin is ‘cooked’ together with a drying oil, such as linseed oil, to obtain a homogeneous solution, which is then thinned to obtain a workable viscosity. Such varnishes are referred to as oleoresinous varnishes. Although these varnishes are still in use for certain specific applications, they have been widely replaced by synthetic resins that offer improved performance and
which contain less environmentally regulated solvent. Although the term ‘varnish’ is still used to describe these transparent coatings, few of them are varnishes in the original sense of the word.

5.1.2 Oils

Vegetable oils, and to a much lesser extent, fish oils, are by far the most widely used class of natural resins, and have been used for centuries in the production of decorative and protective coatings. In the nineteenth and early twentieth centuries, they were by far the predominant paint binder. While coatings based solely on oil binders still exist, they basically constitute a niche market as wood preservatives and varnish-type films. However, large quantities of oils are still used in the production of more sophisticated coatings such as alkyds and epoxy esters.

Chemically, the naturally occurring oils are triglycerides. Triglycerides are the triesters of glycerol and a variety of fatty acids. Fatty acids are simply carboxylic acids that have a saturated or unsaturated aliphatic hydrocarbon group, usually from 15 to 17 carbon atoms in length, such as oleic acid (Figure 5.4). A typical oil (triglyceride) has a structure shown in Figure 5.5, where R can be derived from a variety of fatty acids.

The formulas of some of the more important fatty acids are as follows:

- Stearic acid: \( \text{CH}_3(\text{CH}_2)_{16}\text{COOH} \)
- Palmitic acid: \( \text{CH}_3(\text{CH}_2)_{14}\text{COOH} \)
- Oleic acid: \( \text{CH}_3(\text{CH}_2)_{7}\text{CH}==\text{CH}(\text{CH}_2)_{7}\text{COOH} \)
- Linoleic acid: \( \text{CH}_3(\text{CH}_2)_{4}\text{CH}==\text{CH}\text{CH}_2\text{CH}==\text{CH}(\text{CH}_2)_{7}\text{COOH} \)
- Linolenic acid: \( \text{CH}_3\text{CH}_2\text{CH}==\text{CH}\text{CH}_2\text{CH}==\text{CH}(\text{CH}_2)_{7}\text{COOH} \)
- Ricinoleic acid: \( \text{CH}_3(\text{CH}_2)_{5}\text{COH H CH}_2\text{CH CH CH}==\text{CH (CH}_2)_{7}\text{COOH} \)
- Eleosteric acid: \( \text{CH}_3(\text{CH}_2)_{3}\text{CH}==\text{CHCH}==\text{CHCH}==\text{CH(CH}_2)_{7}\text{COOH} \)

\[
\text{CH}_3(\text{CH}_2)_{7}\text{CH}==\text{CH(CH}_2)_{7}\text{COOH}
\]

**Figure 5.4** Structure of oleic acid, a typical fatty acid.

\[
\begin{align*}
\text{H}_2\text{C}=\text{O} & \text{C} & \text{R} \\
\text{HO} & | & \\
\text{H}_2\text{C}=\text{O} & \text{C} & \text{R} \\
\text{HO} & | & \\
\text{H}_2\text{C}=\text{O} & \text{C} & \text{R}
\end{align*}
\]

**Figure 5.5** General structure of a triglyceride, where the R groups can be any combination of fatty acids.
The natural oils do not consist of a single triglyceride made from glycerol and a single fatty acid, but rather consist of mixtures of triglycerides composed of a variety of different fatty acids. Table 5.1 gives the composition of some of the more commonly used oils [1].

The composition of a single oil type can vary significantly based on such factors as climate, soil and the particular strain of the actual plant.

The sources of the oils are rather obvious from their names, with the possible exceptions of linseed oil, which comes from flax, and tall oil, which is a by-product of the manufacture of Kraft paper from wood pulp.

Oils are classified as drying oils, semi-drying oils or non-drying oils. Drying oils form relatively hard, solid films upon exposure to air; semi-drying oils form tacky films, while non-drying oils essentially remain as viscous liquids. The category to which an oil belongs basically depends on the amount of carbon–carbon double bonds, or unsaturation, in the fatty acids making up the oil. The mechanism by which oil dries or cross-links is quite complex, involving oxidation at the double bonds, which is initiated by free radical formation. A free radical is a molecule that has an unshared electron. Peroxides and hydroperoxides (ROOH), which are naturally present in small amounts, are particularly prone to forming free radicals, as shown in Figure 5.6. These free radicals abstract hydrogen atoms on methylene (CH$_2$) groups adjacent to double bonds, thus producing a free radical on one or more of the fatty acid groups on the oil. Two free radicals formed on separate triglyceride molecules can combine to form a neutral species, and therefore a chain reaction of propagation and condensation (cross-linking) is initiated, resulting in a gradual increase in molecular weight and in the production of a relatively hard, solid film. The entire process is referred to as autoxidation.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Saturated$^b$</th>
<th>Oleic</th>
<th>Linoleic</th>
<th>Linolenic</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linseed</td>
<td>10</td>
<td>22</td>
<td>16</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Safflower</td>
<td>11</td>
<td>13</td>
<td>75</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Soybean</td>
<td>15</td>
<td>25</td>
<td>51</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Tung</td>
<td>5</td>
<td>8</td>
<td>4</td>
<td>3</td>
<td>80$^c$</td>
</tr>
<tr>
<td>Tall oil</td>
<td>8</td>
<td>46</td>
<td>$41^d$</td>
<td>3</td>
<td>2$^e$</td>
</tr>
<tr>
<td>Castor</td>
<td>3</td>
<td>7</td>
<td>3</td>
<td></td>
<td>87$^f$</td>
</tr>
<tr>
<td>Coconut</td>
<td>91</td>
<td>7</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Values expressed as %.

$^b$Mainly stearic and palmitic acids, although coconut oil contains several other saturated acids.

$^c$Eleosteric acid.

$^d$Linoleic and various isomers.

$^e$Rosin.

$^f$Ricinoleic acid.
The rate of the autoxidation reaction can be quite slow. In order to speed things up, catalysts are often used. These catalysts, or ‘driers’, are often metal salts of octanoic or napthenic acids. Some, such as cobalt and manganese salts, primarily catalyze cross-linking at the coating surface and are referred to as ‘surface driers’. Others, such as zirconium salts, catalyze cross-linking throughout the thickness of the coating and are known as ‘through driers’. Although properly formulated oil-based coatings can dry to the touch in a few hours, the process of oxidative cross-linking can continue for years. The free radical reaction can also result in the cleavage of bonds, thus resulting in low-molecular-weight by-products. Therefore, oil-based coatings based on drying oils can embrittle and discolour over a period of many years.

It is relatively rare to encounter coatings consisting of binders composed solely of natural oils. When used alone, oils form coatings which are relatively soft (but which can embrittle on ageing) and have poor impact, abrasion and chemical resistance. Oils are, however, extensively used in the next category of coatings to be discussed – alkyds and epoxy esters.

5.2 ALKYDS AND EPOXY ESTERS

5.2.1 Alkyds

Alkyds have been one of the mainstays of the coatings industry for much of the twentieth century. Despite the proliferation of more sophisticated, higher-performance coatings such as epoxies and urethanes, alkyds continue to be used in both the architectural and industrial maintenance markets. However, the regulatory drive towards lower and lower volatile organic contents (VOCs) may eventually result in a significant decline in their use.

Alkyds are basically oil-modified polyesters. They are prepared by reacting together polyols, dibasic acids and fatty acids (or oils composed of fatty acids).

Although several polyols can be used, two of the most common are glycerol (see Figure 5.3) and pentaerythritol (Figure 5.7). The most common dibasic acid is actually used in its anhydride form and consists of phthalic anhydride (Figure 5.8). Isophthalic acid (Figure 5.9) is also used fairly commonly.

There are two processes used to produce alkyds, namely, the monoglyceride process and the fatty acid process.

In the monoglyceride process, the oil (such as linseed oil) is first ‘cooked’ with a polyol (typically glycerol), which results in a transesterification reaction to form a monoglyceride (Figure 5.10). Once the monoglyceride has formed, the dibasic

\[
\text{ROOH} \rightarrow \text{RO}^- + \cdot\text{OH}
\]

Figure 5.6 Illustration of the formation of free radicals from a peroxide.
acid, such as phthalic anhydride, is added. The acid (or anhydride) groups of the phthalic anhydride can then react with the hydroxyl groups of the monoglyceride, thus forming the oil-modified polyester, or alkyd.

If it is desirable to use a polyol other than glycerol, the above process cannot be used. In this case, the fatty acid process is used whereby fatty acids are employed rather than oils (triglycerides), and the fatty acids, polyols and dibasic acids are heated together in the reactor in a single step.

There are two overlapping ways of classifying alkyds. They can be classified as drying or non-drying (sometimes referred to as oxidizing or non-oxidizing), or by a characteristic known as oil length.

Alkyds basically cure by the same autoxidation reaction previously described for the natural oils from which they are made. Therefore, alkyds based on drying
oils (oils whose fatty acids have conjugated carbon–carbon double bonds) such as linseed oil dry or oxidize to solid films and are therefore appropriate for use as coatings. In contrast, alkyds based on saturated, non-drying oils do not cure but basically remain as viscous liquids. They are not suitable for coatings, but are often used as plasticizers.

Oil length refers not to the length of the fatty acid chain (i.e., C<sub>16</sub> versus C<sub>18</sub>) but to the actual amount, in wt%, of oil (or fatty acid) used. Alkyds with an oil length greater than approximately 60 (60% oil by weight) are called long oil alkyds. Alkyds containing approximately 40–60% oil are considered to be medium oil alkyds, and those with less than 40% oil are known as short oil alkyds.

All other things being equal, long oil alkyds have lower surface tensions and hence better wetting properties than short oil alkyds. They are more tolerant of marginally prepared surfaces, and are better able to lift and displace small amounts of soluble organic contaminants such as oil or grease. They are also better able to penetrate and partially encapsulate minor amounts of rust or scale than are short oil alkyds. Initially, at least, they also result in softer, more flexible films than short oil alkyds. The latter are often used as ‘shop primers’, which dry rapidly such that steel can be shipped quickly to job sites for erection and subsequent topcoating.

However, since the oxidative curing process of an alkyd resin can continue for years, the final properties of the coating can be very much different from the initial ones. A long oil alkyd containing a large fraction of drying oils can, over many years, become as brittle, or even more so, than a short oil alkyd containing a relatively small fraction of drying oils. This is one example of why it can be dangerous to generalize too much about the properties of a specific class of coatings. Formulation variables can sometimes outweigh the so-called ‘distinctive characteristics’ often ascribed to a particular coating type.

Alkyds are good general-purpose coatings for a wide variety of applications. However, primarily because the backbone of the coating contains numerous relatively reactive ester linkages, they have poor resistance to alkaline environments. The reaction between an acid and an alcohol to form an ester is a reversible one, particularly so under moist, alkaline conditions. The reversible degradation of an ester to an alcohol and an acid is called hydrolysis, or saponification. Since the reaction occurs under alkaline conditions, the salt of the acid is formed rather than the free acid. The acid salt can usually be readily detected by analytical methods, thus making identification of saponification quite straightforward.

In addition to saponification, alkyds are also susceptible to chemical and sunlight-induced attack at the remaining double bonds. Certain chemicals, such as mineral acids, can add across double bonds. The unsaturation also provides sites for oxidation and free radical reaction.

Another failure occasionally encountered with alkyds is wrinkling. Wrinkling occurs when the surface of the alkyd dries considerably faster than the interior. The surface then contracts, and since the interior is still ‘mushy’, it is pulled along by the shrinkage of the surface, and a wrinkle results. This is usually a conse-
There are numerous ways to modify alkyds to improve certain properties. Common modifications include phenolic, styrene or vinyl toluene, and silicone resins.

Phenolic resins are made by reacting phenol (Figure 5.11) or substituted phenols with formaldehyde. They can be used in relatively small quantities to upgrade the adhesion, hardness and corrosion resistance of alkyds. Phenolic alkyds are sometimes termed ‘universal’ metal primers, since they may be recoated with a large variety of solvent-based coatings without the fear of lifting and wrinkling that can sometimes occur with the relatively solvent-sensitive unmodified alkyd coatings.

Alkyd resins can also be modified via an extra ‘cooking’ step where they are reacted with styrene (Figure 5.12) or vinyl toluene (Figure 5.13). This typically results in the formation of higher-molecular-weight resins, which translates to faster drying of the coating, along with a somewhat improved resistance to moisture and alkali. As might be expected of a ‘vinyl’-type modification, the resistance to solvents and aliphatic hydrocarbons such as grease and oils suffers.

Alkyds are also modified with silicone resins. The principal advantages are improved durability and heat resistance.
5.2.2 Epoxy Esters

Technically, epoxy esters could simply be considered as another type of modified alkyd. However, since they are usually referred to as ‘epoxy esters’ rather than ‘epoxy-modified alkyds’, it is felt that they deserve their own heading here.

Coatings based on epoxy resins constitute one of the most important classes of high-performance coatings. Epoxy esters, however, are not epoxy coatings and should not be confused with them. The coatings industry would probably be better off if indeed they were referred to as epoxy-modified alkyds.

Chemically, an epoxy-functional group (also called an oxirane group) is a three-membered ring consisting of two carbon atoms and an oxygen atom. Most epoxy resins are based on the diglycidyl ether of bisphenol A (DGEBA), which has the structure shown in Figure 5.14.

The commercially available epoxy resins are condensation products of DGEBA, with the structure shown in Figure 5.15, where $n$ is usually from 1 to 12.

The resins contain hydroxyl groups and oxirane groups, both of which can react with the carboxylic acid groups of the fatty acids present in an alkyd, thus resulting in the formation of the so-called epoxy ester. The epoxy resins can, to some extent, react with themselves (the secondary hydroxyl group of one molecule can react with the oxirane group on a second molecule), although this can be minimized by proper ‘cooking’ procedures.

The properties of epoxy esters can vary widely, depending to a large extent on the oil length of the alkyd. Long oil epoxy esters are more ‘alkyd-like’ and are soluble in aliphatic solvents such as mineral spirits. Short oil epoxy esters are more ‘epoxy-like’ and require stronger aromatic solvents such as xylene. However, even short oil epoxy esters are more like alkyds than epoxies.

![Figure 5.14](attachment:image1.png) Structure of the diglycidyl ether of bisphenol A (DGEBA).

![Figure 5.15](attachment:image2.png) General structure of typical commercially available epoxy resins ($n$ usually has values of 1–12).
Epoxy esters can be formulated with numerous advantages (and concomitant disadvantages) when compared to alkyds. They can dry faster and produce harder films with better adhesion and improved chemical resistance (although they are still susceptible to saponification). Although inferior to true epoxies in terms of most chemical and physical properties, they are easier to use and are more forgiving of minor surface contaminants. Unfortunately, like epoxies, they also tend to chalk badly when exposed to sunlight. Keeping in mind the various advantages and disadvantages of epoxy esters versus alkyds, the modes of coating failure are generally similar.

5.3 EPOXIES

When epoxy resins first became commercially available in the 1940s, they were used primarily in adhesives. They now constitute perhaps the single most important class of high-performance thermoset coatings. Epoxies can be formulated as two-component ambient-cured coatings, as high-temperature baking systems, as 100% solids fast-cure plural spray systems and even as powder coatings. Compared to the alkyds and epoxy esters previously described, they have superior adhesion, corrosion resistance, chemical resistance, and mechanical and physical properties.

The molecular weights of epoxy resins vary from approximately 400 (\(n = 1\) in Figure 5.15) to as high as approximately 4000 (\(n \approx 12\)). As the molecular weight increases, so too does the equivalent weight (the number of grams of resin containing 1 equivalent of epoxy groups). In some very high-molecular-weight epoxy resins (molecular weight of 15000–50000), there is so little epoxy (the oxirane groups simply make up the two ends of the long molecule) that the resin is really just a polyfunctional alcohol. Such resins are termed phenoxy resins and do not require curing agents. When used as single-pack primers, they have good chemical resistance and adhesion, and in some cases their impact and abrasion resistance is superior to two-component thermoset epoxies.

When \(n\) is 1 or less, the resins are viscous liquids. At \(n\) values of approximately 2, the resins are amorphous solids with epoxy equivalent weights of approximately 450–500 (molecular weights of approximately 900–1000), which ‘melt’ or soften at roughly 65–75 °C. They are usually sold as high-solids (70% or so) solutions in aromatic- or ketone-type solvents. These resins are used to produce the bulk of the conventional, two-component, ambient-cured epoxy coatings currently in use.

Since epoxy resins are of low molecular weight and are basically viscous liquids, they only produce useful coatings when they are cross-linked to form higher-molecular-weight material. Although some of these thermosetting reactions rely on the secondary hydroxyl groups on the epoxy resin backbone, most of them take advantage of the highly reactive terminal epoxy groups. These
groups are capable of reacting with almost any molecule which has an active hydrogen atom, including amines, carboxylic acids, phenolics, amino resins, anhydrides and isocyanates. The properties of the cured films depend to a large degree on the type of curing agent used.

5.3.1 Amine and Amide Curing Agents for Epoxy Resins

Amines and amine-functional amides are the most common curing agents for high-performance, ambient-cured industrial maintenance epoxy coatings. Aliphatic and cycloaliphatic primary amines react with epoxy resins via the mechanisms shown in Figure 5.16.

The secondary amine thus formed can now react, at a slower rate due to steric hindrance, with another molecule of epoxy resin.

Simple, unmodified aliphatic amines such as diethylene triamine (DETA) (Figure 5.17) are very reactive and result in coatings with short pot lives. Because DETA has two primary amine hydrogens and three secondary amine hydrogens for a total amine functionality of five, it forms very highly cross-linked coatings with excellent chemical and heat resistance and high cohesive strength. However, because of the high degree of cross-linking, flexibility and impact resistance tend to suffer.

Another disadvantage of amine cross-linking agents is their low equivalent weight, as well as significant toxicity problems. The equivalent weight of DETA, for example, is only 21. If used with a typical epoxy resin having an equivalent weight of 500, the stoichiometric mix ratio is 25:1 by weight. Such a large mismatch makes it difficult for a painting applicator to accurately mix the components in the correct ratio, thus increasing the possibility that the coating may not obtain its optimum chemical and physical characteristics. To complicate matters further, there is a very large difference in the viscosity of the epoxy resin component compared to the amine component. This difference in viscosity makes uniform mixing of the two components difficult, even if the proper amounts of each component are used.

\[
\begin{align*}
R\text{NH}_2 + H_2C\text{CH}CH_2\text{OR} &\rightarrow R\text{NH}CH_2\text{CH}CH_2\text{OR} \\
\end{align*}
\]

Figure 5.16 Illustration of the reaction between an amine and an epoxy resin.

\[
\begin{align*}
H_2\text{N}CH_2\text{NH}CH_2\text{NH}CH_2\text{NH}_2
\end{align*}
\]

Figure 5.17 Structure of diethylene triamine (DETA).
Another disadvantage of low-molecular-weight amine curing agents is the fact that they are usually somewhat water soluble, and also somewhat volatile. Particularly when exposed to high humidity or condensation shortly after application, they have a tendency to exude or ‘blush’ to the surface. In severe cases, this blush is visible to the unaided eye, but even in less severe cases it can sometimes interfere with the adhesion of subsequently applied coats of paint.

In the presence of moisture and carbon dioxide, the amine blush can be converted to a carbonate blush.

One common way to minimize blush formation is to allow the mixed coating to sit in the can for 15–45 minutes prior to applying it. This so-called induction or ‘sweat-in’ time allows the amine–epoxy reaction time to proceed, such that little or no free amine is available to blush. This procedure works reasonably well, but it does shorten an already short pot life.

This is a good time to point out another semantic flaw in the coatings industry. All too often, cross-linking agents such as amines are referred to as catalysts. This is a major error in nomenclature, since by definition a catalyst is an agent that speeds up a chemical reaction without actually taking part in it. Clearly, an amine is a cross-linking agent, or a co-reactant, and not a catalyst. True catalysts are, however, widely used in coatings.

One way to avoid some of the problems associated with amine curing agents is to use amine adducts instead. They are produced by reacting low-molecular-weight epoxy resins with an excess of an amine, such as DETA, to form an amine-terminated adduct.

The amine adducts have higher equivalent weights, higher viscosities, lower vapour pressures and reduced toxicities than their amine counterparts, and therefore avoid many of the problems associated with amine cross-linkers. Coatings produced from amine adducts generally have somewhat longer pot lives, and hence somewhat slower cure rates, than amine-cured epoxies. As a whole, their chemical resistance and solvent resistance, while still quite good, is somewhat less than that of amine-cured coatings. They generally have better flexibility and impact resistance. Blushing problems, while significantly reduced, are not necessarily eliminated through the use of amine adducts.

Other important alternatives to simple amine cross-linking agents are the so-called polyamides. These are prepared by reacting an amine, such as DETA, with dimer fatty acids to form amine-terminated polyamides. Dimer fatty acids are relatively high-molecular-weight carboxylic acids, obtained by reacting two C_{18} fatty acids. When these dimer acids are reacted with DETA or some other multi-functional amine, amine-functional polyamides are produced.

Although these cross-linking agents do have amide functional groups, it is somewhat confusing to refer to them as polyamide cross-linkers since the actual reactive groups are still the amine groups (especially the primary amine groups at the two ends of the molecule).

As is the case with amine adducts, there are a wide variety of polyamide cross-linkers on the market, all imparting somewhat different properties to the final
epoxy product. Since all of the polyamides are much larger molecules than the simple amine cross-linkers, and since there is a much greater distance between the highly reactive terminal primary amine groups, the cross-link density of a polyamide-epoxy coating is much less than that of an amine-cured epoxy. Reaction rates are slower; pot lives are longer; mix ratios are usually 1:1 or 2:1 by volume, and toxicity, blushing and mix ratio errors are reduced (but not eliminated).

In terms of the properties of the cured films, polyamide epoxies generally form less densely cross-linked, more flexible films than do amine-cured epoxies. Flexibility and impact resistance are improved, as is adhesion. However, chemical and solvent resistance suffer, although these properties are still good when compared to many other generic coating types. The combination of relative ease of use and good chemical and physical properties has made polyamide-epoxy coatings one of the workhorses in the area of general industrial maintenance coatings, as well as in several speciality coating applications such as food processing, marine and organic zinc-rich primers.

Cross-linking agents known as amido-amines are prepared by reacting monofunctional fatty acids, rather than dimeric fatty acids, with low-molecular-weight polyamines. Compared to the simple, unmodified amines, amido-amines have higher molecular weights and lower amine functionalities. The cross-linking reactions proceed mainly at the single primary amine group at the amine-terminated end of the molecule, with a much lower reaction rate associated with any secondary amines that may be present in the body of the molecule. The cross-link density is very low when compared to a simple amine-cured epoxy, and is even lower than that of a polyamide epoxy. Such coatings have very long pot lives, cure slowly, and have a better flexibility and impact resistance than even the polyamide epoxies. While their chemical resistance is comparable to the polyamide epoxies (and somewhat inferior to amine-cured epoxies), their solvent resistance is significantly poorer.

Ketimines are a rather specialized type of curing agent, where long pot lives and low application viscosities are especially important. Ketimines are considered to be ‘blocked’ curing agents, and are made by reacting a low-molecular-weight ketone such as MEK with an aliphatic primary amine. The structure of a typical ketimine formed from MEK is shown in Figure 5.18.

Since ketimines are tertiary amines, they have a very low reactivity towards epoxy groups. They decompose upon exposure to atmospheric moisture, forming

\[
\text{RN} = \text{C} - \text{CH}_2\text{CH}_3 \\
\text{CH}_3
\]

**Figure 5.18** Structure of a ketimine formed from a primary amine and methyl ethyl ketone (MEK).
the primary amine and, in the above example, MEK. The MEK volatilizes from the film, thus leaving the primary amine free to react with the epoxy resin.

The cycloaliphatic amines are a special class of aliphatic amines. Two examples of cycloaliphatic amines are diamine cyclohexane (Figure 5.19) and isophorone diamine (Figure 5.20). When cycloaliphatic amines are modified with organic acids as accelerators, satisfactory curing can be achieved at near-freezing temperatures. Although they are less volatile and hence less irritating than their non-cyclic counterparts, they are still often reacted with small amounts of very low-molecular-weight epoxy to further reduce volatility and blushing. In addition to low-temperature cure, they also have good adhesion to damp surfaces, along with the superior chemical, solvent, heat and moisture resistance associated with epoxies. They do, however, tend to be brittle.

The Mannich bases are another type of curing agent used to obtain low-temperature curing and adhesion to damp surfaces. Mannich bases are formed by the reaction between methyol phenol and a multifunctional primary amine. The phenolic hydroxyl is a powerful accelerator of epoxy ring opening reactions.

Powder coatings are a special class of epoxy coatings. These are solventless coatings provided in powder form, where the epoxy resin, pigments and curing agents are mixed, compounded by melting in extruders, cooled and then ground into a homogenous powder. The virgin powder has a high enough glass transition temperature \((T_g)\) such that it will not partially fuse during storage. The coatings are applied by specialized equipment either to hot substrates or to room-temperature articles that are then subsequently baked, in order to achieve both flow and cure and also to complete the cross-linking. A curing agent commonly used with epoxy powder coatings is dicyandiamide (Figure 5.21). Powder coatings are used in
numerous original equipment manufacture (OEM) applications such as electrical boxes and appliances, and in particular, for buried underground pipelines.

5.3.2 Epoxy Failure Modes

There are numerous types of epoxy resins that can be reacted with an even greater number of curing agents. There are also a large number of pigments, catalysts, additives and solvents to choose from. It is difficult, and sometimes risky, to generalize about epoxy coatings (or any class of coatings, for that matter). This author has often heard statements such as ‘that doesn’t appear normal for an epoxy’. Such observations are often difficult to support unless one has had previous experience with the particular product in question, or unless one has access to published data concerning the specific coating’s chemical and physical characteristics.

There are, however, some general, if sometimes tentative, conclusions that can be made about the performance of specific classes of epoxies and about their failure mechanisms.

Compared to thermoplastic coatings, as well as alkyds, epoxies have better adhesion properties, as well as a greatly improved resistance to chemicals, solvents, water and elevated temperatures. Abrasion resistance, flexibility and impact resistance can vary widely among the various classes of epoxies. In some cases, brittleness can be a major shortcoming. The corrosion resistance of properly formulated epoxies is generally quite good, and usually dramatically better than the thermoplastics and alkyds.

One of the major drawbacks of most, if not all, epoxies, is a poor resistance to sunlight. Because of the aromatic structure of epoxies, they absorb ultraviolet light. In addition to causing yellowing, the absorption of ultraviolet light results in a breakdown of the surface of the epoxy resin, resulting in a thin layer of loose, chalky material. The depth of this degradation is very thin and does not detract from the coatings chemical and physical properties. It can be objectionable if aesthetics are important, and can also cause serious problems with the adhesion of subsequently applied coats of paint if not removed. It is sometimes possible for an epoxy to chalk sufficiently in only a week of outdoor exposure such that certain types of coatings will not adhere well to them. In such instances, the degree of chalking is so slight that it is not readily observable.
In 1980, Croll [2] investigated the phenomenon that thick epoxy coatings appeared to cure faster than thin epoxy coatings. Croll confirmed that this was indeed the case by measuring the indentation hardness of coatings applied at varying thickness. By conducting his experiments under different atmospheric conditions, he was able to show that the effect was essentially non-existent when the coatings were cured under an inert atmosphere of dry nitrogen, but was quite pronounced when they were cured in moist air, and even more so when cured in a humid carbon dioxide-rich atmosphere. Croll concluded that the hardening of an epoxy coating is influenced by absorption of moisture, or moisture and carbon dioxide, from the atmosphere, and that thin coatings were affected the most because the water and gas can more completely diffuse through their entire thickness. He suggested that the cure of the coating was being disrupted by the reaction of the amine curing agent with carbon dioxide, likely catalyzed by moisture, to form a carbamate or an ammonium bicarbonate. This suggests another problem unique to epoxy coatings, that of ‘amine blush’.

Many of the lower-molecular-weight amine curing agents used in epoxies are somewhat water soluble. When exposed to high humidity or condensation shortly after coating application, or when the coating has been applied under relatively cool, damp conditions, the curing agents have a tendency to exude to the surface of the coating, resulting in what is usually termed an ‘amine blush’. The possibility of the formation of an amine blush on the surface of epoxy coatings has been widely recognized [3–5]. In many cases, the blush is visible to the naked eye, often as a thin, greasy or whitish layer. While it typically does not affect the properties or performance of the epoxy coating itself, it can sometimes cause significant adhesion problems with subsequently applied coats of paint.

Upon initial formation, the blush is, of course, the amine curing agent. However, as time goes by, this amine can react with carbon dioxide and/or water to form either an ammonium carbamate (sometimes referred to as an amine carbamate or as a carbamate salt) or an ammonium bicarbonate (sometimes referred to as an amine bicarbonate) [3–5]. These reactions are shown in Figures 5.22 and 5.23.

The problem of amine blush can be minimized by using higher-molecular-weight cross-linkers such as amine adducts and polyamides, or by observing

\[
R\text{--NH}_2 + H_2O + CO_2 \rightarrow R\text{--NH--C--OH} + H_2O
\]

**Carbamic acid**

\[
R\text{--NH--C--OH} + R\text{--NH}_2 \rightarrow R\text{--NH--C--O}^\delta \text{H}_3N\text{--R}
\]

**An ammonium carbamate**

Figure 5.22 Formation of an amine carbamate (a carbamate salt) via the reaction of an amine curing agent with water and carbon dioxide.
induction times. However, it is doubtful that it can be entirely eliminated. Often the problem can be mitigated by water washing of the coating prior to the application of succeeding coats of paint. If the coating is top-coated within a reasonable length of time with another coating that is compatible with the blush (such as another coat of epoxy), there may be no problems with adhesion. This is an inexact science, however, since this author has occasionally seen large amounts of blush successfully top-coated, while small amounts of blush can sometimes cause serious failure. As pointed out by Dinnissen [5], the problem of blush formation might be exacerbated during indoor applications during cold weather, when direct fired gasoline or kerosene heaters are being used, since they can considerably increase the carbon dioxide content of the air and can also produce significant amounts of water vapour.

Totally apart from problems with blushing and chalking, certain epoxies and other thermoset coatings can be difficult to top-coat simply because they are smooth and hard. The problem will be compounded if the topcoat has a relatively weak solvent system that cannot penetrate or soften the surface of the cured epoxy. Manufacturers often refer to a ‘re-coat window’, beyond which time the coating will be difficult to top-coat. Often it is recommended that the surface be lightly scarified by rough sanding or abrasive blasting. Occasionally, the applicator may be directed to rub the surface with a strong solvent, or to spray apply a solvent on the epoxy, in order to slightly soften it prior to topcoating.

Another problem relating to certain types of epoxies is that of stress. To one degree or another, all coatings have a tendency to shrink upon curing, and this is especially true with two-component thermoset coatings such as epoxies. If the coating, for whatever reason, is constrained from shrinking, it can develop considerable internal stress, and may be unable to resist the added stress imparted by the environment, and cracking or other types of failure may occur.

Commonly, however, the epoxy does shrink to relieve its internal stress. This can be a problem if it is applied to substrates (including certain coatings) which have poor cohesive strength, since the relaxation of internal stress in the epoxy results in the transfer of stress to the underlying coating or substrate. This so-called ‘shrinkage stress’ can sometimes result in massive cohesive failure (splitting) within the underlying layer. A classic example of this type of failure is the use of two-component solvent-based epoxies as topcoats over vinyl latex block fillers used on masonry walls. Not only does the highly filled (pigmented) block filler have poor cohesive strength, but it is also susceptible to the relatively strong solvents used in the epoxy.
Another problem encountered with the more densely cross-linked epoxies (or any densely cross-linked coating) is their inherent brittleness. There is usually no problem on thick, immobile substrates such as heavy structural steel, provided that there is no impact damage. However, if the substrate flexes in high wind, or is subject to expansion and contraction by thermal forces, the coating will be unable to flex with it. In this event, one of two things is likely to happen, depending on the degree of adhesion to the substrate.

If the coating has very good adhesion to the substrate, the stress may be relieved by cracking. Depending on the environment, this may lead to the ingress of water or other harmful materials to the substrate.

If the coating has marginal adhesion to the substrate, the stress may be relieved simply by detachment of the coating from the substrate. If the coating is thin, it may come off in small flakes. If it is thick (over about 5 mils), it may come off in large pieces. Neither of these options is desirable.

Another potential problem with epoxies, or with any coating that has a pot life of only a few hours or less, is the application of the coating near the end of, or slightly after, its pot life. It is important to remember that the reaction between the epoxy resin and the cross-linker begins immediately upon mixing the two components. The chemical composition of the paint in the can is continually varying, and the paint that is being applied 2 hours after mixing is, on a molecular level, not the same paint that was applied 2 minutes after mixing. The biggest differences between the ‘2-minute’ paint and the ‘2-hour’ paint are molecular weight and viscosity. These two interrelated factors can have significant consequences for both the flow and wetting of the coating. Although the incipient formation of a cross-linked, three-dimensional film will probably result in an increase in surface tension, if applied to a metallic substrate, the surface tension of the coating will still be lower than that of the substrate and wetting can still occur, at least theoretically. However, opposing the ability of the coating to wet the substrate will be the resistance to flow as a result of increased viscosity. It is entirely possible that localized areas of poor adhesion can occur simply because of the time at which a coating was applied after mixing.

The above discussion of failure modes assumes that there are no applicator errors. It is widely believed that applicator errors are responsible for the majority of coating failures, an opinion which is shared by this author. However, this opinion has been gleaned by piecemeal observations and individual experience, and any attempt to assign an actual percentage to the number of applicator-related failures would be pure guesswork. Based on the author’s experience, it is safe to say that more than half of all coating failures are applicator related.

Epoxies can fail by the same type of applicator errors that affect the performance of other types of coatings. Modern high-performance coatings are typically less forgiving of applicator error than simple coatings such as oil-based alkyls. Poor surface preparation, over-thinning, poor spray gun technique, contamination or painting when it is either too hot, too cold, or too damp can all contribute to the failure of an epoxy, as can applying the coating too thinly or
too thickly. In addition, there are certain applicator-related errors that are specific to two-component coatings.

One of the more common of these errors is ‘mis-mixing’ of the epoxy. This is more likely to happen with amine-cured epoxies where the mix ratio between the two components is disparate, such as 10 parts of component ‘A’ to 1 part of component ‘B’. The chances for mixing errors with coatings that have simple 1:1 or 2:1 ratios are not as great. Nevertheless, this author has seen more than one coating failure caused by the failure of the applicator to add any of the cross-linker (or converter) component.

When analyzing an epoxy coating for potential errors in mixing, two things should be pointed out. Firstly, since coatings are mixed at job sites and not in laboratories, small deviations from the ideal mix ratio should be expected. If the coating in question has to be mixed exactly at a ratio of 1.00 gal of component ‘A’ to 1.00 gal of component ‘B’, or else failure will occur, it is highly questionable as to whether or not it is a merchantable product.

The second factor to consider if mis-mixing is being investigated is whether or not the specific batch in question was produced properly at the factory. The finding that a coating contains less epoxy resin than expected does not necessarily mean that the applicator is at fault. The error could have occurred at the factory.

Other epoxy application errors include failure to observe induction times (which could cause blushing and possibly inter-coat adhesion failure), application of the coating at or beyond its pot life (which could cause adhesion failures) and topcoating beyond the re-coat window (possibly causing inter-coat adhesion failure).

5.4 MODIFIED EPOXIES

Epoxy chemistry is very versatile, and the types of curing agents and reaction pathways are too numerous to be adequately covered in this present text. However, a few important classes of modified epoxies will be included here, as the investigator of coating failures will likely encounter most of these at one time or another.

5.4.1 Acrylic Epoxies

The term acrylic epoxy may appear incongruous, as acrylics are often thought of as soft, water-based coatings and epoxies as hard, solvent-based coatings. As the three-membered epoxy ring is highly reactive towards functional groups containing active hydrogens, it is possible to react it with carboxylic acids.

If the carboxylic acid group is attached to an acrylic resin, one has formed an acrylic epoxy. The coatings usually require both a catalyst and a relatively high-
temperature bake to achieve full cure. Such coatings have properties which are intermediate between an acrylic and an epoxy. They tend to have better hardness, adhesion and chemical resistance than an acrylic, and better light stability and flexibility than an epoxy.

5.4.2 Coal Tar Epoxies

Coal tar epoxies are an important class of epoxy coatings. They are used extensively in the water and sewage industries due to their thick barrier properties, reasonably good chemical and moisture resistance, and relatively low cost.

Refined coal tar pitches are used in ratios of approximately two to three times the amount of epoxy/cross-linker. The coal tar and cross-linking agents are combined into one component, with the epoxy resin as the second component. Many of the curing agents discussed previously can be used. Higher levels of coal tar result in softer, more slowly curing coatings with reduced chemical and solvent resistance, while higher levels of epoxy result in harder, faster curing, more brittle coatings.

The characteristics imparted to non-modified epoxies by the various curing agents are also observable in the coal tar epoxies. Amines give faster curing coatings and harder, more abrasion-resistant films with better chemical resistance, while polyamide systems are generally more flexible and impart better wetting properties. In waste-water service, an additional advantage of amines is a better resistance to hydrogen sulfide and bacteria.

Coal tar epoxies generally come in one colour, that is, black. They have poor resistance to ultraviolet light and will tend to develop a bronze colour on the surface. They are also extremely difficult to re-coat, and therefore usually must be applied as a single thick coat.

5.4.3 Epoxy Phenolics

Phenolic resins are produced by reacting phenol (Figure 5.11), or a substituted phenol, with formaldehyde (Figure 5.24) to give the structure shown in Figure 5.25.

The phenolic hydroxyl group is relatively reactive, and when reacted with epichlorohydrin (Figure 5.26), one of the precursors of epoxy resins, epoxy functionality can be grafted onto the backbone of the phenolic resin. Coatings made

\[
\begin{align*}
\text{H} & \\
\text{H—C=O} &
\end{align*}
\]

*Figure 5.24* Structure of formaldehyde.
from these resins have excellent adhesion and chemical resistance and a high cross-link density.

In another type of epoxy phenolic coating, the phenolic resin may be considered a cross-linking agent and reacts via its phenolic hydroxy group (in the case of phenolic novolacs) with the epoxy ring on an epoxy resin. This type of coating is one of the most chemically resistant systems available, with excellent adhesion. It usually requires a bake in the 300–400 °F (149–204 °C) region to attain optimum properties, and is often used where extreme chemical exposure is required, such as in the lining of railroad tanker cars.

5.5 PHENOLICS

Phenolic resins are produced by reacting formaldehyde with phenol or substituted phenols. When the reaction is carried out under alkaline conditions, the resins are termed resole phenolics, and when carried out under acidic conditions, novolac phenolics are formed.

5.5.1 Resole Phenolics

The general structure of a resole phenolic prepared from cresol is shown in Figure 5.25.

Other commonly used substituted phenols include methyol phenol and \( p \)-tertiary butyl phenol. Depending on the reaction conditions, some of the phenolic monomers can be cross-linked by ether bridges (\( \text{CH}_2\text{O}\text{CH}_2\text{−} \)) rather than by methylene bridges.

Depending on the raw materials used and the extent of reaction, two different subcategories of resoles can be produced, namely, those that are soluble in oxy-
genated solvents (termed ‘alcohol-soluble phenolics’) and those that are soluble in hydrocarbon solvents (termed ‘oil-soluble phenolics’).

Alcohol-soluble resole phenolic resins require baking to achieve cure, usually in the presence of an acid catalyst. Under these conditions, the resins self-condense via the reaction between the phenolic hydroxyl groups, or between these hydroxyl groups and methyol groups. In this process, ether linkages are formed, and either water or formaldehyde is liberated.

Because all of the linkages in a baked resole phenolic coating are either of the methylene or ether variety, there is nothing to hydrolyze. Such coatings have excellent resistance to moisture and alkali. Because of the stability of these linkages combined with high cross-link density, the coatings have excellent chemical resistance and low permeability, which imparts superior corrosion resistance. Adhesion is also usually quite good. Such coatings are used in tank linings in severe chemical service, and also for can linings in the food and beverage industries. However, because of their high cross-link density, they tend to be brittle and often require plasticization. Because of their aromaticity, they can darken significantly, both on baking and on exposure to sunlight.

One of the main uses for oil-soluble resole phenolics is in the production of high-quality varnishes. The phenolic resin is cooked with linseed or tung oil, sometimes after first being modified with rosin.

5.5.2 Novolac Phenolics

Novolac phenolics have the general structure shown in Figure 5.25.

Novolac phenolic resins contain little or no methyol functionality, and will generally not self-condense. Such resins are thermoplastic. They are usually soluble in alcohol or other oxygenated solvents, but if prepared from \( p \)-tertiary butyl phenol, solubility in hydrocarbons can be achieved. Alone, they have little use as coatings. However, they are used to some extent in varnish production.

5.5.3 Phenolic Failure Modes

Two of the biggest problems with phenolics are their brittleness and baking-related problems.

The brittleness is a consequence of both their rigid aromatic structure and their high cross-link density. This can be ameliorated somewhat by external plasticization, or to a lesser extent by the use of larger hydrocarbon groups on the substituted phenolic monomer.

In a controlled factory environment, heat-related problems of thin-film can coatings are relatively rare. However, this can sometimes be a problem when higher-build coatings are applied to large storage vessels or railroad tank cars. Portable heat sources are often used in such situations, and constant, accurate
temperature control can sometimes be a problem. Since phenolics darken upon baking, the degree of colour change is often used to determine whether adequate cure has been achieved.

5.6 AMINO RESINS

The resins discussed in this current section, sometimes referred to as amino resins, do not have suitable physical properties with which to make coatings. However, they are widely used as cross-linkers with many other types of resins. Rather than discussing them piecemeal in later sections, they will be introduced as a group here.

Amino resins usually amount to perhaps 30% or less of the non-volatile vehicle content of various thermoset coatings. They are easily the major cross-linking agent for such coatings, and can be used with acrylics, polyesters, alkyds, epoxy esters and even epoxies. Unlike the thermoset epoxy coatings discussed in the previous section, thermoset coatings cross-linked with amino resins are almost always single-component, rather than two-component, coatings. This is possible because their reaction rates are extremely slow at low temperatures, and they must be baked to achieve cure.

The most commonly used amino resins are based on melamine, or 2, 4, 6-triamino-1, 3, 5-triazine (Figure 5.27).

The three primary amino groups on melamine make it a very versatile precursor. Pure melamine itself is not used as a cross-linking agent. It is reacted with formaldehyde and an alcohol. The first step, the reaction with formaldehyde, results in the formation of methylated melamine. The structure of fully methylolated melamine (hexamethyol melamine) is shown in Figure 5.28.

Depending on the stoichiometric ratio of melamine to formaldehyde, less than fully methylated melamine can be produced.

The next step in the production of melamine–formaldehyde (MF) resins is termed ‘etherification’ and involves reaction with a low-molecular-weight alcohol (usually methyl or butyl alcohol). Depending on the degree of methylolation of the initial melamine, the type of alcohol and the ratio of methylated melamine to alcohol, numerous types of useful MF cross-linking resins can be produced. One of the more common ones is hexamethoxymethylmelamine (HMMM) (Figure 5.29).

![Figure 5.27 Structure of melamine.](image-url)
In addition to the etherification reaction between the methylol groups and the alcohol (methanol, in the case of HMMM), it is also possible for limited self-condensation (self-etherification) between two methylol groups on adjacent molecules of methyl melamine. It is not unusual for a small amount of dimer to be formed during the production of HMMM or other MF resins.

Benzoguanime resins (Figure 5.30) are perhaps the next most widely used type of amino cross-linking agent. Like melamine, benzoguanime is also based on triazine.

Benzoguanime differs from melamine only in the replacement of one of the \(-\text{NH}_2\) groups with a phenyl group. It undergoes the same types of reactions with
formaldehyde and alcohols as melamine, resulting in similar cross-linking agents but with lower functionality.

Urea (Figure 5.31) can also be reacted with formaldehyde to form methylol derivatives. These derivatives, like its melamine and benzoguanamine counterparts, can be subsequently etherified with alcohol to make urea–formaldehyde cross-linking resins. Like melamine and benzoguanimine resin, some amount of self-condensation also occurs to produce dimers.

Yet another class of amino resins is based upon glycoluril (Figure 5.32). Glycoluril can react with formaldehyde to form tetramethylolglycoluril (TMGU). Depending on the pH of the reaction medium, lower methylolated analogues, as well as self-condensation products, can be formed.

The etherification reaction previously described between other methylolated amino resins and alcohols also occurs for TMGU, resulting in the formation of glycoluril–formaldehyde resins. Tetramethoxymethyl glycoluril is a solid used as a cross-linker for certain powder coatings. Mixed ether resins such as dimethoxy-methylidioxyethylmethyl glycouril are liquids, and are used in coil and can coatings to provide greater flexibility than many of the other amino resins [1].

5.7 ACRYLICS

The most accurate definition of an acrylic resin is any resin formed from derivatives of acrylic acid (CH$_2$=CH–COOH). This simple definition belies the variety and complexity of acrylic resins, which are used in such diverse applications as plastics, fabrics, caulks and sealants, latex house paint, and high-performance thermoset coatings.
Table 5.2 Structures of some common acrylic monomers.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acrylate</td>
<td>(CH_2\text{CHCOOCH}_2\text{CH}_3)</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>(\text{CH}_3) (\text{CH}_2\text{CCOOCH}_3)</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>(\text{CH}_2\text{CHCONH}_2)</td>
</tr>
<tr>
<td>Hydroxyethyl acrylate</td>
<td>(\text{CH}_2\text{CHCOOCH}_2\text{CH}_2\text{OH})</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>(\text{CH}_2\text{CHCOOH})</td>
</tr>
<tr>
<td>Styrene</td>
<td>(\text{CH}_2\text{CHC}_6\text{H}_5)</td>
</tr>
</tbody>
</table>

Table 5.2 shows the structures of some of the common acrylic monomers used in coatings. Although styrene may not be considered a derivative of acrylic acid, it is included because of its widespread use in many acrylics.

Acrylic resins are produced from acrylic monomers via a free radical addition reaction occurring at the carbon–carbon double bond site. An almost endless variety of polymers can be built depending on the monomers used, their ratios and the reaction conditions.

Acrylic coatings can be considered as belonging to one of three subgroups, namely, solution acrylics, acrylic latex coatings and thermosetting acrylics.

5.7.1 Solution Acrylics

Solution acrylics, also referred to as acrylic lacquers, constitute the earliest use of acrylic polymers as coatings. Since they are single-component, thermoplastic coatings that dry and cure only by solvent evaporation, they are also referred to as acrylic lacquers. They are used on furniture, and at one time huge quantities were used for automotive coatings. Their use in the automotive industry is now restricted primarily to the refinish market. They are also widely used in acrylic aerosols for consumer use.

Since solution acrylics do not cross-link, their chemical and physical properties must be ‘built in’ at the time of manufacture. They have relatively high molecular weights (usually 75,000 or higher), and consequently are rather low in solids content to achieve workable viscosities.

In addition to molecular weight, another fundamental property of a solution acrylic is its glass transition temperature \(T_g\).

The glass transition temperature has several different definitions, all of which are approximately equivalent. The most common definition in the coatings industry is that the \(T_g\) is that temperature below which a polymer is in a hard, glassy
state, and above which it is in a softer, rubbery state. Another useful definition
is that the $T_g$ is that temperature where there is a sudden, discontinuous increase
in the polymer free volume. The latter may be roughly described as the amount
of space available for polymer segments or chains to freely rotate, or to move
about, in.

A furniture coating provides a simple example of why the $T_g$ is an important
consideration for an acrylic lacquer. If the coating’s $T_g$ is too low (more than a
few degrees below room temperature), the coating will be flexible (a good thing)
and soft (a bad thing), and heavy objects such as bookends might actually stick
to the coating. Conversely, if the $T_g$ is too high, the coating will be hard (a good
thing) and brittle (a bad thing), and a heavy object (the bookend is a good
example) dropped on the coating might very well crack it. With a thermoplastic
coating such as an acrylic, the $T_g$ can be controlled to some extent by molecular
weight, but to a much greater extent by the choice of monomers. For instance,
the $T_g$ of a homopolymer of methyl acrylate is 10°C, while it is 105°C for a
homopolymer of methyl methacrylate [1]. Generally, the $T_g$ is roughly an additive
property characteristic of the relative proportions of the monomers used. Thus, a
polymer made up of a 50/50 blend of methyl acrylate and methyl methacrylate
would be expected to have a $T_g$ of roughly 58°C.

An examination of the structure of acrylic resins shows that they contain ester
groups. Such groups are subject to alkaline hydrolysis or saponification. However,
the ester groups do not constitute the backbone of acrylic coatings but are instead
pendant to it. Although saponification of an acrylic lacquer can occur, the con-
sequence is usually not as disastrous as saponification of an alkyd.

Some advantages of acrylic lacquers include a good resistance to ultraviolet
light, gloss retention, flexibility and a reasonably good resistance to alkali.
Disadvantages include difficulty in obtaining high-gloss pigmented coatings,
relatively poor adhesion, very poor solvent resistance and high VOC levels.
Acrylic lacquers are in much lower demand now than they were even 10 years
ago. VOC restrictions will likely end up outdating them entirely.

5.7.2 Acrylic Latex Coatings

Acrylic latexes are used in huge amounts in the coatings industry. They make up
the bulk of architectural coatings, and are now gaining a significant market share
in industrial maintenance areas as well. They have the notable advantage of being
very low in VOC (their principal solvent is water), without having to sacrifice
molecular weight.

A latex is basically a dispersion of polymer particles (the discontinuous phase)
in water (the continuous phase). The latex is usually made by a process called
emulsion polymerization. In this type of polymerization process, relatively high
levels of surfactants are mixed and agitated in hot water.

When the concentration of surfactants exceeds what is known as the ‘critical
micelle concentration’ (CMC), they will associate into discrete spheres or parti-
icles known as micelles. Their hydrophobic ends will be oriented inward, while their hydrophilic tails will be oriented outward. The inside of the sphere, then, is a localized hydrocarbon-rich environment conducive to the solubilization of organic molecules. When acrylic monomers are added to this blend of surfactants and water, they, along with polymerization initiators, will migrate into the interior of the micelles, and polymer formation will begin.

One of the advantages of this type of system is that its viscosity is, for the most part, dependent on the continuous (aqueous) phase. Very high-molecular-weight polymers (several hundred thousand) can be formed in micelles with little or no increase in the viscosity of the system. As was the case with solution acrylics, the properties of the final polymer can be controlled by judicious selection of monomers and reaction conditions.

How latex coatings form films is still the focus of considerable research. It is commonly believed that it is a multi-step process.

The first step is the evaporation of water, allowing the discrete latex particles to come into physical contact. The next step, which is assisted by the incorporation of small amounts of organic co-solvents, or ‘coalescing aids’, is a melting or fusion of latex particles into one another. The final step is the evaporation of the residual water and, over time, the evaporation of the co-solvents.

The coalescence of the latex particles is critical in achieving the desired properties of the coating. Two of the main factors governing this are humidity and the glass transition temperature \((T_g)\) of the acrylic emulsion.

For coalescence to occur, the latex particles must first come into close contact with one another, which will not happen until most of the water evaporates from the coating. The rate of evaporation of water will be much slower under humid conditions than under dry conditions.

Once the latex particles are in close proximity to one another, effective coalescence will still not occur if the \(T_g\) of the latex is significantly higher than the ambient temperature. In such a situation, the latex will be in a hard, glassy state, with little free volume and limited molecular motion. The films formed under such circumstances will have little cohesive strength and high permeability.

Paradoxically, it is generally desirable to have a final coating with a \(T_g\) several degrees higher than the expected ambient temperature. A \(T_g\) that is lower than ambient would cause the coating to be soft and sticky, and objectionably porous. Windows would stick to their window sills; house paint would pick up and retain dirt; and coatings for metals would allow moisture and possibly other deleterious materials easy ingress.

One way in which this conundrum can be solved is by the coalescing aid serving in the dual role of a volatile plasticizer. During film formation, the coalescing aid, or organic co-solvent, helps to solubilize and plasticize the coalescing latex particles, thus depressing their \(T_g\) to below ambient. Within a day or two after application, however, the co-solvent has largely evaporated, and the \(T_g\) of the dried film is now higher than the prevailing ambient temperatures.

Two monomers which are routinely used to elevate the \(T_g\) are methyl methacrylate \((T_g\) of the homopolymer is 105°C) and styrene \((T_g\) of the homopolymer is
100 °C). Methyl methacrylate imparts exterior durability, and the methyl group makes hydrolysis more difficult due to steric hindrance. Styrene also imparts good resistance to hydrolysis because it has no ester linkages to hydrolyze, although it can yellow and degrade when exposed to sunlight. It is often employed in primers to impart hardness, water resistance and lower permeability.

Acrylic latex coatings make up the bulk of the house paint and architectural coatings market. Two big advantages to the consumer are low odour and an easy clean-up with water. A big advantage in the regulatory arena is an extremely low VOC. When first introduced to the marketplace, latex coatings were greatly inferior to the tried-and-true oil-based paints, but rapid advancements in technology have quickly closed the gap. In addition to the application and VOC advantages of acrylic latexes, they also tend to be more ‘breathable’ than oil-based coatings. They allow the moisture inside a structure to more easily diffuse through the coating and therefore have less tendency to blister than do oil-based products.

In addition to breathability, acrylic latexes are also usually more flexible than oil-based paints, especially after the latter have oxidized and cured for a year or two. Acrylics will flake and ‘disbond’ less readily from wood that has undergone repeated expansion/contraction due to changes in humidity and temperature.

However, acrylic latex coatings do not penetrate as effectively into the pores of the wood as do oil-based coatings, somewhat compromising initial adhesion. Latex coatings often contain a plethora of additives required to ‘fine tune’ the rheological properties of the coating. Many of these are water soluble, thus imparting water sensitivity to the dried films. Some additives are cellulose based, therefore making the coating subject to microbial attack while in the can.

Because of tighter VOC requirements, acrylic latex coatings are beginning to be used more extensively on structural steel. Formulation with fewer water-sensitive additives is required. Because of their higher surface tension and poorer solubilizing ability, surface preparation for such coatings must be quite good.

Many of the failures encountered with acrylic latex coatings are related either to water sensitivity or incompatibility with existing or subsequent coatings.

Water sensitivity can be due to poor cure (coalescence), perhaps because of low temperatures or high humidity. Although the evaporation of water from the films is greatly retarded by high humidity, the evaporation of the co-solvent, or the coalescing aid, is not. When the humidity finally does go down and the water eventually evaporates, the co-solvent may not be around in sufficient quantities to promote good film formation. Water sensitivity can also be due to excessive or non-judicious use of additives.

Acrylic latex coatings have virtually no organic solvents in them, and usually have functional groups of low to medium polarity, with little ability to form covalent bonds. They also have little ability to soften or otherwise bond with hard, smooth coatings. They are generally not recommended for application over thermoset coatings (including aged alkyds). Likewise, solvent-rich, high-stress coatings such as epoxies could soften and lift an underlying coat of acrylic latex.
Related to the acrylic latex coatings are the water-reducible or so-called ‘water-soluble’ acrylics.

Water-reducible acrylics are made by incorporating a certain amount of carboxylic acid functionality into the pendant groups along the acrylic backbone. This is usually carried out by using a few percent of a monomer such as acrylic acid. By then using a volatile amine such as ammonia to react with the acid groups, salts are formed which allow the resins to be dispersed, or reduced in, water. The pH of such coatings is usually well over 8. Such resins are more often used as part of a baked thermosetting system, rather than as room-temperature lacquers.

5.7.3 Thermoset Acrylics

Another common use of acrylic resins is in baked, thermosetting systems for automotive, appliance and other OEM finishes. The acrylics used in these formulations have functional groups that allow them to react with other cross-linking resins. Since the molecular weight will increase dramatically during the baking process, the initial molecular weight of the acrylic resin can be low (roughly 10000–20000), resulting in a relatively high-solids product and a concomitantly low VOC. It is common to use monomers such as hydroxyethyl methacrylate to impart the desired amount of hydroxyl functionality to the acrylic. Most of the other monomers used in thermoset acrylic resins are the same as those used in thermoplastic acrylic lacquers. Such resins are usually cross-linked with MF or benzoguanamine–formaldehyde (BF) resins. Such resins were discussed above in Section 5.6.

Unlike several other types of thermoset coatings, an acrylic-MF or acrylic-BF coating consists of only a single component. The cross-linking reaction is so slow at room temperature that it does not become a factor. However, the reaction rate is not zero, so the choice of catalyst is important if shelf lives of more than 6 months are required. Normally, the applied coatings are baked at 250 °F (121 °C) or higher to achieve satisfactory cure.

The reaction between a hydroxyl-functional acrylic resin (R−OH) and an MF or BF resin occurs at both the hydroxyl and ether groups. The reactions are catalyzed by small amounts of strong acids such as \( p\)-toluene sulfonic acid (pTSA). As expected, acrylics with primary hydroxyl functionality react faster than those with secondary functionality. The rate of reaction with MF or BF resins will depend somewhat on the volatility of the alcohol formed. The more quickly this reaction product leaves the dried film, then the more the reaction will shift to the right.

Generally, an MF resin is used at levels of perhaps 20–30% of resin solids. Higher levels of MF resin will generally result in brittle coatings, perhaps as a result of excessive self-condensation.

The amount of acid catalyst can affect several properties of the cured film, as well as influence shelf stability. While higher levels of catalysts have the
beneficial effect of lowering cure temperature, in some cases they can compro-
mise the durability of the cured coatings. This is because, in addition to cross-
linking between hydroxyl groups and MF resins, cross-linking can also occur
between carboxylic acid groups on the acrylic and hydroxyl or ether groups on
the MF resin. This results in the formation of an ester linkage, which can subse-
quently degrade by hydrolysis. This hydrolytic degradation can be catalyzed by
the residual acid left in the film.

Thermoset acrylic/MF coatings can be formulated that have wide variations in
properties, since their final characteristics are derived not only from the specific
acrylic and MF resins, but from the type and amount of catalyst, pigmentation,
and even curing conditions. Properly formulated and cured coatings have excel-
lent adhesion and chemical resistance, along with superior weathering and ultra-
violet light resistance. It is not surprising that they are so widely used in automotive
topcoats. They are also used as appliance coatings and as coil coatings.

Potential problems with acrylic/MF coatings include poor application pro-
PERTIES if the coatings are near or beyond their storage lives, and potential sus-
ceptibility to hydrolysis if too much residual acid catalyst remains in the cured
films. Other problems are related to cure problems. Too low a cure can result in
unexpectedly soft coatings with low cross-link density and poor chemical and
physical properties. Too high a bake can result in brittle coatings and even
yellowing.

There are numerous, competing reactions occurring simultaneously when an
acrylic-MF coating is curing. The two most obvious competing reactions are that
of the acrylic-MF reaction and the self-condensation of the MF resin with itself.
Typically, the stoichiometry and catalyst package is optimized for a certain time
and temperature. If the actual curing conditions are different, the relative rates of
the reactions may change, thus resulting in coatings with less than optimum
properties.

BF resins are also commonly used to cross-link with acrylics. Because there
are only two $\textbf{$-$NH}_2$ groups per molecule versus three on an MF resin, their cross-
link density will be less. Coatings prepared with BF resins have better alkali and
detergent resistance than those prepared from MF resins. They are poorer,
however, in terms of their exterior durability. Acrylic resins can also be cross-
linked with isocyanates. Coatings produced in this fashion, however, are consid-
ered as urethanes, and their chemistry will be discussed below in Section 5.9.

5.8 POLYESTERS

Polyesters are polymers obtained by reacting multifunctional acids or anhydrides
with multifunctional alcohols (polyhydric alcohols) to form a polymeric back-
bone containing ester groups. In this sense, they are similar to alkyds, but without
the extra modification due to natural oils. This results in resins or polymers that
have a much simpler structure than that of an alkyd.
As a consequence of the lack of oil modification, polyesters do not contain the fatty acid characteristic of alkyds. The acids used in the manufacture of polyester resins do not contain conjugated double bonds. Since these double bonds are the sites for oxidative cross-linking (curing) of alkyd resins, it is apparent that polyester resins must rely on a different curing mechanism than an alkyd. The curing mechanism largely depends on whether or not the polyester resin is saturated or unsaturated. It is convenient to regard polyesters as falling into one of these two classes.

5.8.1 Saturated Polyesters

With the obvious difference that there is no oil modification, saturated polyesters are manufactured much like alkyds. They can be produced from a large number of di- and/or polyfunctional alcohols and acids. Some of the commonly used starting ingredients are shown in Tables 5.3 and 5.4.

Polyester resins equal, or perhaps even surpass, acrylic resins in their ability to be molecularly engineered. With such a large number of combinations of starting materials, polyesters can be produced with a wide range of chemical and physical properties. The characteristics of polyesters can be affected by the resin

<table>
<thead>
<tr>
<th>Polyol</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neopentyl glycol</td>
<td>CH$_3$HOCH$_2$C—CH$_2$OH</td>
</tr>
<tr>
<td></td>
<td>CH$_3$</td>
</tr>
<tr>
<td>Trimethylol propane</td>
<td>CH$_3$CH$_2$C—CH$_3$OH</td>
</tr>
<tr>
<td></td>
<td>CH$_2$OH</td>
</tr>
<tr>
<td>Pentaerythritol</td>
<td>CH$_2$OH</td>
</tr>
<tr>
<td></td>
<td>HOCH$_2$C—CH$_2$OH</td>
</tr>
<tr>
<td></td>
<td>CH$_2$OH</td>
</tr>
<tr>
<td>1,6-Hexanediol</td>
<td>HO—CH—CH—CH—CH—CH—OH</td>
</tr>
</tbody>
</table>
used to cross-link them. Therefore, one can see the danger in carelessly ‘lumping’ all polyesters together.

The type of alcohol, type of acid, stoichiometry and reaction conditions determine the properties of the polyester resin. Four of the most important characteristics are molecular weight, type of end groups, degree of branching and choice of monomers.

Like any other solution resin, viscosity is a function of molecular weight and, therefore, so is the VOC. Most polyester resins have relatively low molecular weights, typically in the 5000–10000 range.

Resins produced by reacting a diol, such as ethylene glycol, with a diacid, such as isophthalic acid, are linear. If a trifunctional (or higher) ingredient is used, branching will occur. Branched polymers are usually of higher viscosity than linear polymers of comparable molecular weight, and also ultimately result in cross-linked films of greater density and chemical resistance, and less flexibility and impact resistance. All other things being equal, a polyester containing a high level of pentaerythritol (hydroxyl functionality of 4) will result in a much harder, more chemically resistant coating than one based on 1,6-hexanediol. The latter will perform much better where flexibility and impact resistance are required.

The distance between the functional groups also has an effect on the final properties of the coating. Polyesters prepared from succinic acid, where the acid groups are separated by only two carbon atoms, will be less flexible than those prepared from azelaic acid, with five carbon atoms separating the acid groups.

Since polyesters contain ester groups in their backbone, they are susceptible to alkaline hydrolysis (saponification) in the same way as alkyds. However,
they have generally been found to be more resistant to hydrolysis than alkyds.

At least in some cases this increased resistance appears to be due to steric effects, which slow down the rate of the hydrolysis reaction [6]. For example, polyesters produced from neopentyl glycol would be expected to be more resistant to hydrolysis than those produced from 1, 6-hexanediol.

Saturated polyester resins have no mechanism to cure, and therefore coatings prepared from them utilize cross-linking resins such as MF resin, BF resin or epoxy resin. Polyesters designed to cross-link with MF or BF resins are made by starting with an excess of polyol, such that the terminal end groups have hydroxyl functionality, while those designed to cross-link with epoxies utilize an excess of acid to impart carboxylate functionality.

The cross-linking reaction of a hydroxyl-terminated polyester with an MF or BF resin is much the same as that of the hydroxyl-functional acrylics previously discussed. Acidic catalysts are usually used, and baking temperatures are typically in the 250–300°F (121–149°C) range. The characteristics imparted by the MF or BF resin are similar to those imparted to the acrylic resins discussed above in Section 5.7.3.

Polyesters produced with carboxylic acid end groups can cross-link at the oxirane (see Figure 1.1) site in epoxy resins. This reaction is somewhat more sluggish than the hydroxyl–MF reaction, and temperatures closer to 400°F (204°C) are needed.

Coatings produced from saturated polyesters find a wide range of uses, such as flexible coil stock, can coatings, automotive base coats, appliance coatings, metal furniture coatings and exterior metal siding. For many applications, except those where aesthetics are highly desirable, polyesters can be formulated and applied as powder coatings.

It is also possible to formulate water-based saturated polyester coatings. This is achieved by using carboxylic acid-terminated polyesters, which are neutralized with volatile amines to make them water dispersible. Again, they are cross-linked and baked with appropriate curing agents. Unsaturated polyesters can also be reacted with isocyanates to form urethanes.

Aside from any problems associated with inadequate cleaning or pretreating of the metallic substrates to which these coatings are applied, potential problems include misformulation and curing errors.

Actual misformulation, especially where the end use of the product is known, should be rare. There is always the chance that a batching error can occur. Sending a product out the door with only half of the amount of MF resin will result in a final product with poor durability and inferior chemical resistance.

With any product that requires baking, cure should be one of the first things considered when a coating failure occurs. It is not uncommon for manufacturers to use ovens whose temperatures are not well monitored, or where the equipment used to monitor the temperature are not regularly calibrated. Variations in line speed can also affect cure.
5.8.2 Unsaturated Polyesters

Unsaturated polyester resins may be prepared by using an unsaturated acid in place of some of the saturated acid. Typically, the acids used are maleic anhydride (Figure 5.33) or fumaric acid (Figure 5.34). When the maleic anhydride ring opens, such as upon reaction with water, maleic acid is formed, which is simply the \textit{cis}-isomer of fumaric acid.

In theory, numerous diacids and diols can be used to make unsaturated polyester resins. In practice, the predominant choices are isophthalic acid, maleic anhydride or fumaric acid, and propylene glycol. Polyesters made with fumaric acid tend to be harder than those made from maleic anhydride. More flexibility can be imparted by substituting an aliphatic acid such as adipic acid for some of the isophthalic acid. In some cases, resins are made using epoxy materials for part of the diol component.

Unsaturated polyesters cure by free radical polymerization at the double bond sites. It is common to use peroxides, such as benzoyl peroxide or MEK peroxide, along with a promoter such as cobalt naphthenate, to initiate and catalyze the free radical reaction. It is also common to use styrene as a reactive dilutant. Styrene is a good solvent for the polyester, and by virtue of its double bond is also a co-reactant with it. It enables coatings to be formulated at near-zero VOC levels.

Oxygen can inhibit free radical reactions by reacting with radicals and by essentially ‘capping’ the reaction. This ‘air inhibition’ occurs at the surface of the coating, thus leaving it tacky. One way to overcome this is by formulating a small amount of wax into the coating. The wax will migrate to the surface and partially seal it off from oxygen. Other additives can also be used to reduce air inhibition.

\[ \text{Figure 5.33} \quad \text{Structure of maleic anhydride.} \]

\[ \text{Figure 5.34} \quad \text{Structure of fumaric acid.} \]
Unsaturated polyesters are much more common in the fiberglass industry than in the coatings industry. As coatings, they are often used in radiation-cured systems, where ultraviolet lamps or electron beam sources replace peroxide as initiators of free radicals. They are also used as high-build linings in severe chemical exposures, such as the interior of chemical storage vessels. In such uses they are often applied by plural spray equipment because of their very short pot lives once catalyzed. Chopped fiberglass may also be one of the ingredients of such coatings. The fiberglass imparts added strength, reduces permeability and allows for high-build applications.

Related to the unsaturated polyesters are the vinyl esters, which could perhaps be more appropriately considered as acrylics. These are typically formed by reacting acrylic acid or methacrylic acid with an epoxy. A typical structure is shown in Figure 5.35.

The only ester groups on these resins are at the end, thus giving them better hydrolytic stability than the typical unsaturated polyester coatings. Like the unsaturated polyesters, they cure by free radical polymerization initiated by peroxide catalysts and also contain styrene as a reactive diluent.

The vinyl esters and unsaturated polyesters typically impart considerable shrinkage stress and are very stiff. Surface cleanliness and surface roughness are thus very important in achieving good adhesion.

5.9 POLYURETHANES

Polyurethanes are one of the most versatile of all coatings, ranging from relatively simple lacquer-type coatings through high-performance automotive coatings to high-build chemically resistant elastomeric linings. They are usually formed by reacting an alcohol (R—OH) with an isocyanate (R—NCO) to form the urethane, or carbamate, structure shown in Figure 5.36.
Like epoxies, they usually consist of two components which must be mixed together shortly before application. One component typically contains a polyol, while the other contains the isocyanate.

The isocyanate group is highly reactive, and di-or polyfunctional isocyanates can be used to cross-link any number of resins that have functional groups containing active hydrogens. Although hydroxyl-functional resins are the mainstay of the industry, isocyanates can also react with aliphatic and aromatic primary amines, phenolics, carboxylic acids, secondary amines, ureas and water. Not all of these reactions result in the formation of urethane linkages, and hence the coatings are technically not urethanes. The classic example of this confusing nomenclature is the so-called ‘moisture-cured urethane’, which is not a urethane at all but is actually a polyurea.

When a diol is reacted with a diisocyanate, a linear polymer results, based on a backbone of urethane linkages. If water is present, it can react with the isocyanate to form a carbamic acid (Figure 5.37). The carbamic acid is not stable and readily decomposes to form an amine and carbon dioxide. Since amines are very reactive towards isocyanate groups, they will react to form a disubstituted urea (Figure 5.38).

Although the reaction of an isocyanate with water is slower than the reaction of an isocyanate with a primary hydroxyl group, the rate of reaction of isocyanates with primary amines is faster than the corresponding isocyanate–primary hydroxyl reaction. However, the relative reaction rate can change with different concentrations, temperatures and catalysts, which makes the study of such coatings all the more complicated (and interesting).

Once the disubstituted urea is formed, it is possible for the diversity to continue, as urea can also react with isocyanates, to form biurets (Figure 5.39).

The above reactions all occur at room temperature, and can be accelerated by the use of catalysts such as tertiary amines and organotin compounds (specifically dibutyltindilaurate). Isocyanates can also react with carboxylic acids, but at elevated temperatures, to form amides.

\[
\begin{align*}
H_2N & \equiv C \equiv O \\
& \equiv O \\
\end{align*}
\]

**Figure 5.37** Structure of carbamic acid.

\[
\begin{align*}
\text{R} & \equiv \text{N} \equiv C \equiv \text{N} \equiv \text{R} \\
\equiv \text{N} \equiv C \equiv \text{N} \equiv \text{R} \\
\end{align*}
\]

**Figure 5.38** General structure of a disubstituted urea.
COATING TYPES AND COMMON FAILURE MODES

The isocyanates used in coatings are usually divided into two types, namely, aromatic and aliphatic. The most commonly used ones are shown in Table 5.5.

Two of the major disadvantages of isocyanates are their toxicity and their volatility. It is common practice to use higher-molecular-weight versions. Thus, both 2,4-toluene diisocyanate (TDI) and 1,6-hexamethylene diisocyanate (HDI) are commonly used as their trimers, which are called isocyanurates. Another way to minimize the problem is to use isocyanate ‘pre-polymers’, made by reacting excess isocyanate with a polyhydroxy compound. Depending on the polyl used, polyurethanes based on aromatic isocyanates such as TDI and MDI can be formulated to produce hard coatings with excellent chemical and heat resistance. Unfortunately, a weakness of polyurethanes based on aromatic isocyanates is their strong tendency to discolour and chalk upon exposure to sunlight.

Polyurethanes based on aliphatic isocyanates, such as HDI and isophorone diisocyanate (IPDI), are greatly superior to the aromatics in terms of weathering resistance, and also have excellent chemical resistance. They are somewhat slower to cure than the aromatics, however, and are more expensive.

5.9.1 Two-Component Polyisocyanate/Polyol Coatings

The most common type of urethane coatings are the two-component, solvent-borne variety, where one component consists of a polyisocyanate and the other a polyol. The pigmented component usually contains the polyol, where trace amounts of moisture coming from the pigments have no effect on shelf life. Both aliphatic and aromatic isocyanates are used, with the former imparting significantly better colour retention and weathering resistance. The most common types of polyols are hydroxyl-functional acrylics, polyesters and polyethers.

Hydroxyl functionality is typically imparted to acrylics by incorporating a certain amount of 2-hydroxyethyl methacrylate (HEMA) into the monomer blend. HEMA provides primary hydroxyl groups for rapid cross-linking with the isocyanate. Occasionally, 2-hydroxypropyl methacrylate is used. The secondary hydroxyl functionality has the disadvantage of a slower reaction rate with the isocyanate, but the concomitant advantage of longer pot life.

The molecular weight of the acrylic resins used in urethane coatings is usually fairly low, of the order of perhaps 25000. This is quite low when compared to a conventional single-pack acrylic lacquer, but the molecular weight of the final,
**Table 5.5** Structures of some common isocyanates used in the production of polyurethanes.

<table>
<thead>
<tr>
<th>Isocyanate</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-Toluene diisocyanate (TDI)</td>
<td><img src="image" alt="Structure of TDI" /></td>
</tr>
<tr>
<td>1,6-Hexamethylene diisocyanate (HDI)</td>
<td><img src="image" alt="Structure of HDI" /></td>
</tr>
<tr>
<td>Isophorone diisocyanate (IPDI)</td>
<td><img src="image" alt="Structure of IPDI" /></td>
</tr>
<tr>
<td>Diphenylmethane diisocyanate (MDI)</td>
<td><img src="image" alt="Structure of MDI" /></td>
</tr>
<tr>
<td>m-Tetramethylxylene diisocyanate (TMXDI)</td>
<td><img src="image" alt="Structure of TMXDI" /></td>
</tr>
<tr>
<td>Isocyanurate of toluene diisocyanate</td>
<td><img src="image" alt="Structure of TDI Isocyanurate" /></td>
</tr>
<tr>
<td>Isocyanurate of hexamethylene diisocyanate</td>
<td><img src="image" alt="Structure of HDI Isocyanurate" /></td>
</tr>
</tbody>
</table>
cross-linked film will be extremely high. The low molecular weight of the acrylic resin and of the isocyanate allows high-solids coatings of low to medium viscosity to be easily formulated.

As discussed above in Section 5.7, the variety of monomers allows for a wide latitude in the molecular engineering of acrylic resins. These same monomers are available for ‘tailor making’ acrylic–polyurethanes with various properties.

One critical factor, however, is the $T_g$ of the final coating. It is desirable to have the $T_g$ of the fully cured coating slightly below the curing temperature (which quite often is room temperature). The $T_g$ of the coating will increase as its degree of cure increases. When the $T_g$ of the partially cured coating becomes equal to or higher than the temperature at which the coating is curing, there will be a sharp decrease in the free volume. The polymer chains will have much less room in which to move, mobility will decrease and eventually cease, and it will not be possible for the reaction to reach completion. One way to avoid this is to cure the coating at an elevated temperature, but this is usually not possible for industrial maintenance coatings.

Hydroxyl-functional polyesters are also widely used in the manufacture of two-component polyurethanes. The chemistry and characteristics of hydroxyl-functional polyesters have already been discussed (see Section 5.8). As in the case of hydroxyl-functional acrylics, the polyesters used to make polyurethanes are of relatively low molecular weight. This allows for the formulation of high-solids, low VOC coatings. The same $T_g$ consideration applies to polyester–polyurethanes as for acrylic–polyurethanes. The polyester–polyurethanes tend to permit higher-solids coatings with somewhat better adhesion to metals compared with the acrylics. The acrylics are often of lower cost, have superior exterior durability and are more resistant to hydrolysis.

Hydroxyl-functional polyethers are also used to make two-component polyurethanes. Since ether linkages are much less restrictive towards molecular rotation than many other functional groups, and since they tend not to have bulky side groups, polyether–polyurethanes tend to be very flexible, with much greater impact resistance than the much harder acrylic and polyester–polyurethanes. Their softness can make them unsuitable for many applications. However, they make superb, high-build elastomeric coatings and linings, and can survive relatively harsh environments.

Although acrylics, polyesters and polyethers are the most commonly used hydroxyl-functional resins used in two-component urethanes, they are not the only ones. Since alkyd resins have unreacted hydroxyl groups, they can also cross-link with isocyanates, as can epoxy resins through their secondary hydroxyl groups.

The two-component, solvent-borne urethanes have become perhaps the premier coating system for applications demanding excellent gloss and colour retention and good chemical resistance. Based on the above discussion, it is apparent that with the wide selection of available polyols and polyisocyanates, it is possible for the polymer chemist to produce urethane coatings that span a broad range of
chemical and physical properties. Despite their diversity, there are certain common features among the various urethanes relating to their mode of failure. This is especially true regarding their behaviour with water.

Isocyanates are very reactive and can react with water to form a disubstituted urea. The by-product of this reaction is carbon dioxide, which is a gas at room temperature. Not only does the reaction with water interrupt the designed curing pathway of the coating, resulting in unanticipated and often undesirable physical and chemical properties, but the escaping CO$_2$ can result in numerous voids in the interior of the cured coating. This ‘Swiss cheese’ effect can have serious consequences for the permeability and mechanical strength of the coating.

Water can come from many sources, including rain shortly after application, painting during periods of high humidity, using non-urethane-grade solvents which have small amounts of moisture, water in the paint lines and failure to properly seal containers after opening. If the water is present on the substrate as a consequence of a dew point inversion, not only will voids result but likely poor adhesion as well. In order to help guard against the possibility of moisture damaging the curing coating, most urethanes are formulated with a slight excess of isocyanate. Ratios of isocyanate to hydroxyl of 1:1 to 1:0 are common.

It is not unheard of in the paint industry for a contractor to thin the coating with the wrong solvent. More often than not, this usually has only minor consequences. However, if a two-component urethane is thinned with a solvent containing an alcohol, the monofunctional alcohol will react with the isocyanate and stop the cross-linking process. The consequences will depend on how much alcohol was used, but could be disastrous.

As with any two-component coating, there is always the possibility of a mixing error. Because of the complexity of the various reactions that can occur in a curing urethane, it is not always possible to predict exactly how a certain mixing error will affect the properties of the coating. However, an excess of polyol will nearly always result in a softer coating. This is because there are no side reactions for the polyol to undergo, and it will act as a plasticizer.

In industrial maintenance applications, two-component urethanes are often used as finish coats over epoxy intermediate coats. While not a urethane problem per se, they (and other coatings) can be very sensitive towards even small quantities of chalked coating on the surface of the epoxy. In some cases, this extremely thin layer of chalked epoxy, which can sometimes form as quickly as a week or two, can cause peeling of the urethane topcoat from the epoxy.

5.9.2 Urealkyds

Urealkyds, also called urethane alkyls, should not be confused with the two-component urethanes formed by the reaction between an isocyanate and the hydroxyl groups on an alkyd resin. Rather, they are basically modified alkyls where some of the phthalic anhydride is replaced with an isocyanate such as TDI.
Urealkyds are single-component coatings that typically dry faster and harder than conventional alkyds. They also have improved abrasion resistance and resistance to hydrolysis. Unfortunately, they are more expensive and, because of the use of the aromatic TDI, have inferior colour retention. The latter can be improved through the use of aliphatic isocyanates, but at even greater cost. They cure by the same process as alkyd resins, and therefore must be formulated with the same types of driers used in alkyds.

Urealkyds are largely used as varnishes, although technically they are not true varnishes. They are often used as clear varnishes on wood, where hardness and abrasion resistance is important.

5.9.3 Moisture-Cured Polyurethanes

Oddly enough, although water is considered a contaminant with conventional two-component polyurethanes, it is the primary cross-linking agent, along with the isocyanate, in moisture-cured polyurethanes. The source of the water is atmospheric moisture, and the polymer obtained is not a polyurethane, but rather a polyurea.

In the case of a two-component acrylic or polyester urethane, the bulk of the final, cured film is made up of the acrylic or polyester starting material, which initially may have had a molecular weight of 15000–25000. However, the hydroxyl ‘analogue’ to the polyester or acrylic is simply water, with a molecular weight of only 18. Therefore, viable coatings cannot be made simply by reacting water with the same relatively low-molecular-weight isocyanates used in conventional two-pack coatings.

The isocyanates used in moisture-cured urethanes are resins which have two or more isocyanate groups per molecule. They are generally made from hydroxyl-terminated polyesters reacted with an excess of a ‘conventional’ isocyanate such as TDI or MDI, or with an aliphatic isocyanate if colour retention is important. It is unavoidable that there are also a certain number of urethane linkages formed.

The coatings are single-component products, and when applied cure by reacting with atmospheric moisture. The rate of cure is humidity dependent. Below approximately 30% relative humidity, the cure is rather sluggish, and above 80%, the rate of carbon dioxide evolution from the curing reaction is rapid enough to generate bubbling in the coating. Therefore, humidities in the 30–80% range are preferred.

One of the main advantages of moisture-cured urethanes is the fact that they are single-component products. This saves time for the contractor and eliminates ‘mis-mixing’ as a potential cause of failure.

Other advantages include the ability of these products to be applied over slightly damp surfaces, rapid cure and a final coating which is hard, tough, somewhat flexible, and which has good adhesion to metal and good chemical resistance. Their light stability is variable, depending to a large degree on the type of isocyanate used.
One of the obvious disadvantages of moisture-cured urethanes is their sensitivity to moisture. They are often packaged under a blanket of nitrogen, and once opened must be used within a few days to avoid gelation. Great care must also be taken in the selection and handling of pigments, since many pigments contain trace amounts of water which can be detrimental to storage stability.

Another potential disadvantage of moisture-cured urethanes is bubbling caused by rapid CO\textsubscript{2} generation under conditions of high humidity. This problem is exacerbated at higher film builds. If high film build is desired, it is sometimes necessary to apply several thin coats.

As was the case with conventional two-component urethanes, alcohols must not be introduced into the coating. If such thinner is used, the alcohol will react with the isocyanate groups and severely interfere with the curing reaction.

### 5.9.4 Polyurethane Lacquers and Dispersions

Single-component, solvent-based polyurethane lacquers and single-component polyurethane dispersions in water are also available. The lacquers are simply thermoplastic, high-molecular-weight linear polymers prepared by reacting diols with diisocyanates. They are low-solids coatings that dry by solvent evaporation, and are used on flexible substrates such as fabrics and leather.

The polyurethane dispersions are essentially urethane latexes, and various methods are employed in their manufacture. They cure by the same process of water evaporation and coalescence as typical acrylic latex.

### 5.9.5 Two-Component Water-Borne Polyurethanes

Because of increasingly stringent VOC regulations, two-component, water-borne polyurethanes have been recently introduced. The problems in making such a coating are obvious, since the solvent (water in this case) can react with the isocyanate component. Several approaches have been utilized. These include the use of a blocked isocyanate and the preparation of a polyurethane polyol which is either emulsified in water by using surfactants or is made water reducible by incorporating some carboxylic acid functionality into the polymer and subsequently forming salts via the addition of a volatile amine.

Prior to application, the water-borne polyol component is mixed with a compatible isocyanate, which is not water-borne. The isocyanate then diffuses into the polyol phase, where it is essentially emulsified by the polyol and subsequently cross-links it.

Although the isocyanate reacts faster with the polyol than with the bulk water phase, it is apparent that the water must consume at least some of it. Therefore, NCO:OH ratios approaching 2:1 are often used to make up for this. The relative
rate of the various reactions will be influenced by, among other things, the tem-
perature and relative humidity at the time of application. If the temperature is
high and the humidity is low, the polyol–isocyanate reaction will be greatly
favoured. If the temperature is low and the humidity relatively high, the water–
isocyanate reaction will proceed more readily. Obviously, it is possible for the
same coating used on the same job site to have substantially different properties
depending on the weather at the time of application or, if a baked system, to be
substantially influenced by oven conditions.

5.10 VINYLS

Strictly speaking, any coating comprised of a polymer produced by the addition
polymerization of a vinyl monomer, or a combination of vinyl monomers, could
be considered a vinyl. A vinyl monomer is any molecule having the following
structure:

\[ \text{CH}_2=\text{CR}_1\text{CR}_2 \]

Based on the above, one could argue that poly(methyl methacrylate) is, there-
fore, a vinyl. However, in the coatings industry, it is commonly accepted that the
term ‘vinyl’ applies to a relatively small group of monomers, consisting princi-
pally of vinyl acetate (VA), vinyl chloride (VC), vinylidene fluoride and vinyl
butyral.

5.10.1 Solution Vinlys

Solution vinlys are typically based on copolymers of VC and VA. The resulting
poly(vinyl chloride) (PVC)–polyvinyl acetate (PVA) copolymers, which contain
approximately 14% VA, have molecular weights of 70000 or higher, and dry by
simple solvent evaporation. As a consequence, coatings produced from them are
very low in solids, and are being used less and less as VOC regulations continue
to tighten.

Although their usage is declining, solution vinlys have several desirable prop-
erties, including good resistance to acids, bases and water, and good flexibility
and impact resistance. At one time, they were widely used in the water and waste-
water industry, in chemical and paper plants, and on submerged structures such
as locks and dams.

In addition to their very poor solvent resistance, solution vinlys have relatively
poor adhesion. In order to improve their adhesion to metals, a small amount of
maleic acid or vinyl alcohol is copolymerized with the VA/VC. The more polar
nature of this group greatly improves the adhesion.
5.10.2 Plastisols and Organosols

PVC by itself is not a suitable resin for coatings. It is brittle, difficult to dissolve and has poor adhesion. In the plastics industry, however, hot applied high-molecular-weight PVC particles dispersed in a plasticizer, known as ‘plastisols’, are used for a variety of applications. Although not a convenient route for a paint or coating, when such plastisols are diluted with solvent, the resulting ‘organosols’ find considerable use as coil coatings for roofing and siding applications. After application, the coatings are baked to fuse the individual polymer particles into a continuous film.

Cured organosols have many of the desirable properties that were discussed in the previous section on solution vinyls. They have, however, their own set of potential problems.

The most obvious problem is that of poor adhesion, since the resin system is still the very non-polar PVC. Therefore, it is common to use a primer as a ‘tie coat’ to improve the adhesion of the coating system to the metal, and/or to apply some type of conversion coating to the steel stock to improve the adhesion.

Another potential problem with organosols is the evaporation of plasticizer. Although this can be minimized or even eliminated through proper choice of materials, if the wrong plasticizer is used in a very hot southern environment, embrittlement of the coating can gradually occur over an extended time period.

A third potential problem of an organosol is the fact that PVC is subject to degradation as a result of exposure to heat and light. PVC can undergo dehydrochlorination, resulting in the evolution of hydrochloric acid and the production of conjugated double bonds in the vinyl backbone. Not only can the hydrochloric acid being released have detrimental effects on the pigments and plasticizers in the coating, but the extensive system of conjugation can result in dramatic discoloration of the coating. Furthermore, over time, this conjugated polymer can begin to cross-link via an auto-oxidation process similar to that at work in alkyds, thus resulting in a greater cross-link density and associated embrittlement. This problem can be greatly alleviated by the use of appropriate stabilizing agents.

5.10.3 Vinyl Fluorides

Coatings can also be made from vinyl fluoride polymers, the most important of which is poly(vinylidene fluoride) (PVDF). This polymer is not readily soluble in most common organic solvents and is therefore used as a plastisol-like dispersion in a solution of acrylic resin.

Coatings based on PVDF have an outstanding chemical resistance, solvent resistance, heat resistance and weathering resistance. They are also relatively flexible. Because of the high temperatures (450–500°F (204–260°C)) required to fuse the individual particles of PVDF into a cohesive, continuous coating, they are principally used as high-performance coatings on coil stock intended for
commercial buildings. Their flexibility allows them to be bent and formed without cracking. They are usually applied by reverse roll coating at thicknesses of 1.5 mil or less.

5.10.4 Poly(vinyl butyral)

Poly(vinyl butyral) is prepared by first partially hydrolyzing PVA to give what could essentially be considered as a copolymer of VA and vinyl alcohol. This ‘copolymer’ is subsequently reacted with butyaldehyde to form poly(vinyl butyral).

Other poly(vinyl acetal)s can be made by using aldehydes other than butyraldehyde. They are all high-molecular-weight, low-solids coatings, and are therefore used in much smaller quantities than they once were. Because they contain a certain number of secondary hydroxyl groups, they can be reacted with a number of other resins at elevated temperatures to modify their properties. For instance, when reacted with phenolics and epoxies for can linings, they improve formability.

In the maintenance coating industry, poly(vinyl butyral)s are best known as ‘wash primers’. These are two-package coatings containing an inhibitive chromate pigment, where one component contains a large amount of sulfuric acid. When used as pretreatments over metal surfaces, they actually form primary chemical bonds with the metal, and substantially improve the adhesion of certain subsequently applied coatings such as maleic acid-modified vinyls, alkyds and epoxies. The product is sensitive to formulation error, must be applied in a very thin film (0.1–0.3 mil) and topcoated within a day, or sometimes within only a few hours.

5.10.5 Vinyl Latexes

Perhaps the single greatest use of vinyl coatings is in vinyl latex-based house paints. The high molecular weight of the vinyl resin is not a problem, since the coating takes on the viscosity of the continuous phase, which is water in this case.

The glass transition temperature for pure PVA is too high to achieve good coalescence at room temperature. Although one way to solve this problem is with plasticizers, it is more common to copolymerize the VA monomer with some low-$T_g$ acrylic monomer, resulting in the commonly used ‘acrylic-modified vinyl latexes’.

Vinyls and acrylic-modified vinyls are distinctly inferior to the 100% acrylic latexes in terms of both weathering and hydrolysis. Therefore, they are primarily used as interior coatings. Most flat interior wall paints are vinyl latexes. They are also commonly used in latex block fillers, which are highly pigmented coatings,
essentially used as a primer to fill the imperfections in rough masonry walls prior to the application of a smoother, glossier topcoat.

Although vinyl latex coatings are inferior to acrylics for exterior application, this does not prevent them being used in this fashion. Furthermore, if used as interior block fillers, they can be subject to premature failure if there is penetration of water through an exterior wall or from a construction defect, or simply from being used in the wrong location, such as shower facilities. Failures are often encountered with such coatings when topcoated with solvent-borne, high-stress coatings such as two-component epoxies. The solvent in the epoxy softens the solvent-sensitive vinyl, and the shrinkage stress of the curing epoxy is adequate to cause a cohesive failure within the weakened vinyl. Such failures are exacerbated by excessive thickness of either the vinyl or the epoxy, and by low curing temperatures of the vinyl block filler, which can often occur on new construction.

5.11 BITUMINOUS COATINGS

The term ‘bituminous coating’ causes much confusion, primarily because of the poorly defined nature of the materials from which they are made. Basically, a bituminous coating has its origin in either asphalt or coal tar. Although the class also includes coumarone indene resins (obtained from coke ovens) and hydrocarbon resins based on low-molecular-weight unsaturated hydrocarbons obtained from gasoline production, by far the largest quantities of such coatings are the asphalts and coal tars. Both are black or dark brown, due principally to a suspension of fine, elemental carbon particles.

Asphalt can be obtained from both natural sources and as residues from the distillation of certain types of crude petroleum oils. It is basically a semi-solid mixture of numerous hydrocarbons, which for the most part are aliphatic in nature. When obtained from natural sources, they are associated with varying levels of minerals. Asphalt obtained from Trinidad is high in mineral content and is used mostly for road paving material. In contrast, gilsonite, which is obtained from deposits in North America, is a jet black, brittle solid of very low mineral content and is suitable for asphaltic coatings. It is soluble in hydrocarbon solvents and is compatible with many oils and resins. It is used to some extent in high-gloss asphaltic varnishes.

Certain types of crude oil, such as Wyoming sour crude, contain 40% or more asphalt. The asphalt is obtained from the residues of the distillation process. Asphalts obtained from crude oils are generally preferred as coatings since they are of more uniform composition and contain lesser amounts of mineral impurities.

Asphaltic coatings are relatively inert and have extremely good chemical and water resistance. They are also inexpensive. In addition to their well-known use as roofing materials, they are also used as coatings for buried steel and concrete
structures. Hot applied asphalt coatings often contain fibrous reinforcing materials, or sometimes even glass cloth, and are applied at thicknesses of 100 mil or more. They are used as barrier coatings on such structures as underground storage tanks and buried pipelines.

Coal tar is a complicated mixture of hydrocarbons, primarily of aromatic character, which constitutes the major part of the liquid condensate obtained from the distillation of coal to coke. As a consequence, the production of coal tar is closely related to the production of steel. Although steel production has steadily risen, the production of coal tar has not, because more efficient blast furnaces require lesser amounts of coke. Although naphthalene is the single most prevalent compound in coal tar, it is present at levels of only about 6–10%. It is estimated that coal tar contains from 5000 to 10,000 different compounds, a mere 300 of which have been identified [7]. The compounds range from low-molecular-weight materials to a high-molecular-weight component known as coal tar pitch.

Coal tar is used in thick, hot applied coatings for tanks and pipelines, and as room-temperature, somewhat lower-solids coatings for steel subjected to water immersion. It is often used in the waste-water industry. Like the asphalts, it has good chemical and excellent moisture resistance, is inexpensive and can be applied as thick barrier coatings.

Because of their simple hydrocarbon structure, asphaltic and coal tar coatings have very good chemical resistance and excellent water resistance. They also have some major disadvantages, not the least of which is their aesthetic appeal. In addition to basically coming in only one colour, the coal tar coatings in particular have poor light stability, which is perhaps a consequence of their much greater aromatic content.

Because of their relatively high amount of unsaturation, the upper surface of bituminous coatings tends to oxidize and embrittle, and hence can crack or wrinkle. In addition, because of their poor solvent resistance, there are certain applications where they cannot be used. Not only can solvents from an industrial environment damage them, but they can generally not be topcoated by ‘conventional’ solvent-borne coatings, since a black-coloured bleed-through may result.

Perhaps the most important class of bituminous coating is the coal tar epoxy. Unlike asphalt and coal tar coatings, these are two-component thermosetting materials. The epoxy and cross-linking chemistries are similar to that already discussed above in Section 5.3, but one or both components are modified with high levels of coal tar. Since there is some evidence that components of the coal tar can slowly react with epoxy resins, many formulations have the coal tar component in with the converter component. Coal tar is used rather than asphalt because of its better chemical and water resistance.

The coal tar undergoes little chemical reaction with the epoxy/ converter system, but upgrades the coating by virtue of its improved chemical and water resistance properties, as well as imparting high-build properties. In the same fashion that coal tar imparts its desirable properties to the epoxy, the epoxy
imparts properties of its own to the coal tar. This includes improved solvent resistance, high cohesive strength, hardness, abrasion and impact resistance. Although epoxies are not known for their resistance to sunlight, coal tar epoxies have better weathering ability than straight coal tars. They do, however, develop an objectionable surface appearance, aptly described as bronzing.

Coal tar epoxies make very strong, highly impermeable barrier coatings with excellent chemical resistance. As such, they are used extensively in marine application and in the water and sewage treatment industries.

In addition to the surface bronzing of coal tar epoxies, other disadvantages include difficulties in application and re-coating. They are two-component, often highly viscous materials, and as a consequence there is always the possibility of ‘mis-mixing’. With other two-component materials, application near the end of their pot life may result in wetting problems and the potential for reduced adhesion. Furthermore, the coatings cure quickly to a dense, hard, relatively smooth finish, which makes for a short (as brief as a day or two) re-coat window. It is often desirable to apply them in a single coat to avoid the possibility of inter-coat delamination.

5.12 INORGANIC AND SILICONE-MODIFIED COATINGS

5.12.1 Silicone Coatings

All of the coating types discussed so far have been based on organic (carbon-based) binders. However, inorganic resins based on silicones and silicates also play important roles in coating technology.

Silicones, which are also called polysiloxanes, have the general structure shown in Figure 5.40. The monomers used to prepare these resins are chlorosilanes, such as trimethylchlorosilane and diphenyldichlorosilane. Chlorosilanes react with water to form silanols, which then condense with the elimination of water to form the silicone (or polysiloxane) resin.

If dichlorosilanes are used, the polysiloxanes are linear. If some trichlorosilane is also used, a three-dimensional branched structure is formed. The incorporation of monochlorosilanes result in chain termination and the production of low-

![Figure 5.40](image)

**Figure 5.40** General structure of a silicone (polysiloxane) resin.
molecular-weight oligomeric materials. These oligomers are what are commonly referred to as silicone fluids or oils.

Silicone resins used for coatings are based principally on dichlorosilanes, but a certain amount of trifunctional monomer is required to achieve adequate chain branching and cross-linking. These resins are usually of low molecular weight, and once applied have to be baked to achieve full cure and hence the properties expected of them. This thermosetting reaction is not fast, and may take as long as an hour at 400–450°F (204–232°C). Certain catalysts can be used to lower either the time or temperature.

Most silicone resins are based on either methyl or phenyl chlorosilanes, or a combination thereof. All are characterized by excellent resistance to weathering and ultraviolet degradation, and display excellent gloss and colour retention. They are also extremely heat resistant. Chemical resistance is better than the alkyds, but not as good as some of the high-performance thermoset organic coatings.

As might be expected, silicones with a high methyl-to-phenyl ratio have greater gloss and colour stability than those containing more phenyl groups, and are more flexible. Those containing more phenyl groups relative to methyl have superior elevated temperature resistance. At very high temperatures, any organic substituents that are present will burn off, and the silicone can continue to cross-link to form high-molecular-weight silicon dioxide (essentially glass). Chimney paints pigmented with aluminium flake have been used for years based on this mechanism. So long as the brittle, glass-like coating is not disturbed, it can provide long-term protection at extreme temperatures.

Pure silicone coatings are primarily used in applications where their temperature resistance is paramount. Typical applications include stacks, mufflers, furnaces, cookware and engine equipment.

Silicone coatings are relatively expensive, and there are numerous applications where extreme temperature resistance is not required. In such cases, the performance of conventional organic coatings can be significantly upgraded by modifying them with a certain percentage of a silicone.

Perhaps the most common of such coatings is the silicone-modified alkyd. In many cases, this is simply a conventional alkyd that has been cold blended, or mixed, with a silicone. This is usually done to improve the exterior durability of the alkyd, although an increase in heat resistance is a beneficial side effect. Levels of 20 or 30% silicone are common. The properties of the coating can be further enhanced if a low-molecular-weight silicone intermediate is chemically reacted with the alkyd. The reaction usually occurs between hydroxyl groups on the alkyd and silanol groups on the silicone.

Silicones can also be used to modify polyesters. The resin is prepared by reacting a silicone with a hydroxy-functional polyester. The product thus obtained must be baked and further cross-linked after application, often with MF resins. These silicone-modified polyesters have an excellent combination of properties such as flexibility, hardness, adhesion, temperature resistance and weatherability.
They are used extensively on coil coated metal for wall panels, as well as on cookware and appliances.

Silicones can also be used to modify acrylics. Again, these are usually intended for the coil coating market, and are baked and cross-linked with a melamine resin. They produce excellent quality finishes.

5.12.2 Silicate Coatings

Binders based on tetraethylorthosilicate (Figure 5.41) are used extensively in the manufacture of one of the most important types of industrial maintenance primers, namely, the inorganic zinc-rich primer. Since occasionally constituents containing other than ethoxy groups are used, the coatings are sometimes referred to as alkyl or alkoxy silicates.

Ethyl silicate binders are prepared by starting with a solution of tetraethylorthosilicate dissolved in ethyl alcohol. When a small amount of water is added to this solution, partial hydrolysis occurs and a certain percentage of the ethoxy groups is replaced by hydroxyl groups, with the liberation of ethyl alcohol (C$_2$H$_5$OH). Some of the partially hydrolyzed tetraethylorthosilicate then condenses to form oligomeric pre-polymers, with a concomitant increase in viscosity.

The partially hydrolyzed binders are mixed prior to application with a large quantity of metallic zinc dust pigment (zinc loadings of over 80 wt% are common) to produce the zinc-rich primer. After application, the pre-polymers react with atmospheric moisture and subsequently condense, as shown in Figure 5.42. The chemical term for the binder being formed is polysilicic acid, and it is believed that this also partially reacts with small amounts of zinc salts which are naturally present at small levels in the metallic zinc dust pigment.

Zinc-rich primers have superb corrosion resistance. This is because they are formulated above the critical pigment volume concentration (CPVC) with a pigment (zinc dust) that is more reactive than iron. The zinc, which is in electrical contact with steel, will protect it galvanically. Furthermore, as some of the zinc begins to corrode, the oxidation products tend to fill in some of the porosity of...
the high-PVC coating, thus improving its barrier properties. Inorganic zinc-rich primers are also hard and abrasion resistant, and have excellent adhesion to properly blast-cleaned steel and very good resistance to water, solvents and heat. They are used extensively on structural steel for a variety of applications.

However, inorganic zinc-rich primers do have their drawbacks. As might be expected of any coating formulated over its CPVC, they are brittle and have poor cohesive strength and impact resistance. Since the curing reaction with atmospheric moisture starts at the surface and works its way down, coatings applied much thicker than 4 mil or so have a tendency to mud-crack. Although inorganic zinc-rich coatings have very good adhesion to steel, they have poor adhesion to themselves. It is generally not possible to apply a second coat if the first coat was too thin. Luckily, a 1.5- or 2.0-mil coat gives excellent corrosion protection, especially when coated with a compatible intermediate or topcoat.

An additional problem occasionally encountered with zinc-rich coatings is the failure to keep the dense zinc dust pigment properly suspended in the pot during spray application. If some arrangement to keep the coating agitated is not observed, a film with inconsistent ratios of pigment to binder will result.

Perhaps the most common problem or failure an investigator will encounter with such coatings is a cohesive splitting of the primer when it is subsequently coated with an epoxy intermediate coat (zinc–epoxy–urethane systems are common in industrial coating situations). Quite often this is because the zinc-rich primer was not adequately cured at the time of topcoating. Consequently, the relatively strong solvents of the epoxy soften and weaken an already cohesively

![Diagram of curing reaction of ethyl silicate binder used in inorganic zinc-rich primers.](image)
weak film, and the subsequent shrinkage stress of the curing epoxy is sufficient
to pull the primer apart. The curing time of inorganic zinc primers can be very
humidity dependent, a fact often not recognized on the coating manufacturers’
product data sheets.

5.12.3 Polysiloxane Coatings

A relatively new generic type of coating, with commercial development begin-
ing in the 1990s, is polysiloxane coating. These coatings are gaining acceptance
for use in a variety of industries, such as new construction, marine, heavy-duty
OEM and industrial maintenance.

As discussed in Section 5.12.1, compared to conventional organic resins and
polymers, silicone resins have excellent resistance to weathering and ultraviolet
degradation, and are also extremely heat resistant. Chemical resistance is also
usually very good. These properties have led to the development of the silicone-
modified alkyds and pure silicone coatings discussed in Section 5.12.1. However,
while the silicone alkyds certainly have advantages over normal alkyds, they still
have the basic limitations inherent with alkyd chemistry and are not a panacea
for the entire coatings industry. Likewise, essentially pure silicone coatings, such
as those used for very high-temperature applications such as heat stacks, have
limited use because of their brittleness. Polysiloxane coatings have been devel-
oped to circumvent these limitations, and are essentially hybrid coatings which
attempt to make use of the desirable properties of both silicone and organic
resins.

The nomenclature of silicone resins can sometimes be confusing. Silanes are
monomeric silicone compounds with four substituents attached to the silicon
atom and are the building blocks for higher-molecular-weight resins. These four
groups can be the same or different, and can be inorganic or organic. Inorganic
reactive silanes have alkoxy silane groups and can condense via hydrolysis reac-
tions, similar to the inorganic zinc-rich binder curing reactions shown in Figure
5.42. Although the alkoxy side groups are of course organic, these silanes are
considered inorganic because when they condense, the reaction product is entirely
inorganic. Organic reactive silanes can contain a variety of organic functional
groups, such as amine, epoxy and isocyanate, which enable them to undergo
curing reactions with other organic resins, similar to the curing reactions of their
conventional organic analogues.

A polysiloxane is any resin or polymer that contains repeating silicon–oxygen
groups in its backbone or side chains, such as shown in Figure 5.40. Silicones
are polysiloxanes which predominantly have two organic groups attached to the
silicon atoms (again, as shown in Figure 5.40). By blending organic resins with
polysiloxane resins, or by organically modifying the polysiloxane resin itself,
hybrid inorganic–organic coatings can be obtained which, ideally, have the ben-
eficial properties of both the inorganic and organic resins. The amount of organic
modification varies from one generic type to another, but typically falls in the wide range of about 20–60% based on resin solids.

One of the first steps in realizing the benefits of hybrid inorganic–organic coatings (usually referred to as polysiloxane coatings) was the development in the 1990s of epoxy–siloxane hybrid coatings. These coatings are advertised as having the corrosion resistance of a typical epoxy coating, along with greatly improved weathering resistance. Indeed, one manufacturer of such coatings reports gloss retention of 90% after 18 months of outdoor weathering in Florida, which is dramatically better than that of a conventional epoxy coating.

A typical curing reaction of an epoxy–siloxane hybrid coating is shown in Figure 5.43. It is based on the use of an amine-functional alkoxy silane (amino silane) with a conventional epoxy resin. Note that this curing reaction is essentially the same as the curing reaction of a conventional amine- or amide-cured epoxy (Figure 5.16) except that in this case, the curing agent is an aminosilane instead of a purely organic amine or polyamide. By the use of this aminosilane, the benefits of silicone resin chemistry are imparted to the hybrid coating.

Figure 5.43 is not the only curing mechanism possible with an epoxy–siloxane hybrid. The alkoxy (O-R) groups attached to the silicon atom are also reactive and under certain conditions (such as the presence of moisture) can react with themselves (self-condense, as shown in Figure 5.42), or react with a low-molecular-weight silanol or alkoxy-silicone intermediate formulated into the coating. These reactive intermediates are usually very low in viscosity, which enable high-solids coatings to be formulated at relatively low viscosity.

Not all polysiloxane hybrids are two-component coatings. Single-component acrylic polysiloxane hybrids exist which are based on pre-reacting acrylic resins that have reactive functional groups (such as hydroxyl functionality) with alkoxy or even isocyanate functional silanes. This results in an alkoxy-functional

![Cross-linking reaction of an epoxy–siloxane hybrid coating.](image-url)
silicon-modified acrylic resin which can subsequently cure via condensation in the presence of moisture.

5.13 POLYUREAS

Polyurea coatings have become increasingly popular over the last decade or so. They share some of the same intermediate materials with polyurethanes and are sometimes confused with them. However, their chemistry and properties can be much different than the conventional polyurethanes.

As previously discussed (Section 5.9), a polyurethane is formed by the reaction between an isocyanate and a hydroxyl-bearing resin (the ‘polyol’). In contrast, a polyurea is formed by the reaction between an isocyanate and an amine (−NH)-bearing resin or precursor. The basic reaction is shown in Figure 5.44. The reaction product is a substituted urea, as opposed to a urethane (Figure 5.36). There are also such things as hybrid polyurethane/polyurea coatings. As might be expected, hybrid coatings are made by reacting an isocyanate with a resin blend, where the resin blend is made up of both amine- and hydroxyl-terminated resins. Whereas urethanes can be formulated to range from thin, hard, glossy coatings, such as automotive topcoats all the way to thick, heavy-duty elastomeric liners, polyureas and hybrid polyurea/polyurethane coatings are principally used in the latter category.

One of the big advantages of polyurea coatings compared to polyurethane coatings is their very high solids content. Typically, these coatings are 100% solids, meaning that they are free of any regulations concerning VOC. A second advantage is that they cure extremely fast, even at low temperature. Whereas a conventional polyurethane elastomer may require an overnight cure, most polyurea coatings can be walked on in a few minutes. Furthermore, moisture is always a concern when applying conventional polyurethanes. The isocyanate can react with both the polyol and with the water, resulting in curing problems. However, because the reaction time between an amine and an isocyanate is very fast, polyurea coatings are more tolerant of humidity and moisture during application than are polyurethanes.

Just as polyurethanes come in both aromatic and aliphatic varieties, based on the type of isocyanates used, so too do polyureas. The aliphatic varieties have much better resistance to discolouration (yellowing) than the aromatic types, but are more expensive, particularly for high-build systems. Indeed, aromatic systems

![Figure 5.44](image)

Figure 5.44 The reaction of an isocyanate with an amine to form a substituted urea.
are much more common in the industry. The types of isocyanates used in polyurea technology are very similar to those used in polyurethane technology, such as diphenylmethane diisocyanate (MDI) for an aromatic coating and IPDI for an aliphatic coating [8]. It is through the use of di- or trifunctional polyetheramines such as polyoxypropylene amine in the resin blend that the coatings develop the typical toughness and elastomeric nature usually associated with them. These polyether resins have typical molecular weights of 500–5000. They can be used with a chain extender such as diethyltoluene diamine (DETDA) to achieve a variety of properties.

Ironically, some of the advantages associated with polyurea coatings can also work to their disadvantage. Because they cure so rapidly, they also have extremely short gel times, often only a few seconds. This means that they must be applied using very expensive heated plural spray apparatus, where the two individual components are heated to reduce viscosity and are forced into a mixing chamber (the spray gun) using some form of proportional pumping to achieve the specified mix ratio, which is typically 1:1 by volume. Some newer isocyanates which reportedly can increase gel times from the normal 2–4 seconds to as high as 7 seconds are available [9].

A second potential disadvantage associated with the extremely short pot life is the fact that the coating reaches a very high viscosity in an extremely short time. While this makes the job go faster, the coating is only liquid for perhaps a second or two, which does not give it much time to flow and wet the substrate. As previously discussed (Section 2.1.2), flow and wetting are very important factors in achieving good adhesion between a coating and the substrate. While polyureas can certainly achieve good adhesion, it is believed that several failures have resulted from their lack of flow and wetting.

5.13.1 Polyaspartic Polyurea Coatings

Since roughly 2000, a new type of polyurea has been developed based on the reaction between polyaspartic ester compounds with aliphatic isocyanates. A polyaspartic ester contains both ester groups and secondary amine groups, as shown in Figure 5.45. It is also possible to use the technology to produce polyurethane/polyurea hybrids.

The commonly available polyaspartic ester products have the structure shown in Figure 5.45. It is the group designated ‘X’, located between the two nitrogen atoms, which varies and results in a variety of physical and chemical properties of the cured coatings. An examination of the chemical structure of a polyaspartic resin shows that the environment about the secondary amine groups is very crowded. This ‘steric hindrance’, perhaps combined with electrical effects imparted by the ester portion of the structure, significantly slows down the cross-linking reaction with the isocyanate component of the coating. Indeed, whereas typical polyurea coatings have pot lives (perhaps more appropriately called gel
times) of 5 seconds or less, polyaspartic polyureas (often simply called polyaspartics) can be formulated to have gel times from about 1 to 40 minutes. Not only do the longer gel times provide a longer window of application for the applicator, but the improved flow and wetting of such coatings would be expected to result in improved adhesion compared to polyurea coatings which gel in a second or two. Some of the longer gel-time formulations can also be applied with less expensive conventional spray equipment, as opposed to the use of plural spray equipment.

Because polyaspartic coatings are typically based on aliphatic isocyanates and aliphatic polyaspartic resins, they have good weathering characteristics. While they typically do not cure as fast or build as heavy in one coat application as conventional polyurea coatings, they still cure faster than conventional polyurethane coatings and can go on as thick as 10 mils in one coat.

5.14 POWDER COATINGS

Powder coatings can span a variety of generic coating types. They consist of solventless coatings provided in powder form, where the resins, pigments, curing agents and any additives are mixed, compounded by melting in extruders, cooled and then ground into a homogeneous powder. The virgin powder must have a high enough glass transition temperature ($T_g$) such that it will not partially fuse during storage, but have a low enough $T_g$ such that it will fuse and level during baking. The coatings are applied by specialized equipment (Section 6.5) either to hot substrates or to room-temperature articles that are then subsequently baked in order to achieve both flow and cure. Powder coatings are used in numerous OEM applications, such as electrical boxes and appliances, and in particular, for buried underground pipelines. The great majority are of the thermoset variety, although some powder coatings are thermoplastic.

Epoxies are one of the most common generic types of powder coating. A curing agent commonly used with epoxy powder coatings is dicyandiamide (Figure 5.21), although modified dicyandiamides are also used. As might be expected,
Epoxy powder coatings have very good mechanical properties, adhesion and corrosion resistance, but exterior weathering resistance is poor, and they chalk and discolour rapidly. They find considerable use in pipe for underground application, rebar and electrical equipment. For even greater hardness and chemical resistance, novolac epoxy resins or blends of novolac and bis-phenol A epoxy resins are used.

A family of powder coatings referred to as hybrid powder coatings consists of epoxy resins cross-linked with carboxylic acid-terminated polyester resins. These have somewhat better colour and gloss retention upon outdoor weathering than pure epoxy powder coatings. They cross-link primarily by opening of the epoxy (oxirane) ring by the carboxylic acid groups of the polyester.

Polyester powder coatings are also commonly used and have much better outdoor weathering characteristics than both epoxy and hybrid powder coatings. Depending on the type of cross-linking agent, either carboxylic acid or hydroxyl-functional polyesters can be used. A common system consists of carboxylic acid-functional polyesters cross-linked with triglycidylisocyanurate (TGIC, Figure 5.46). Such binders typically consist of 4–10% TGIC and 90–96% polyester resin.

If the polyester resins are hydroxyl functional rather than carboxylic acid functional, they can be cross-linked with blocked aliphatic isocyanates. They have gloss and colour retention equal to or better than TGIC cross-linked polyesters, and excellent mechanical properties and abrasion resistance [10].

Acrylic powder coatings are used for applications such as appliances because of their very good detergent resistance. The acrylic resins can be either hydroxyl functional or carboxylic acid functional, and can be cross-linked with a variety of curing agents. Epoxy-functional acrylcs cross-linked with dicarboxylic acids, such as dodecanedioic acid, or with carboxlic acid-functional resins are also available [11, 12].

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**Figure 5.46** Triglycidylisocyanurate (TGIC).
As might be imagined, the big advantage of powder coatings is the fact that they are solvent free and hence have zero VOC. As VOC is being more and more strictly regulated, this is a big advantage. They can also be formulated to have very good chemical resistance, adhesion and mechanical properties. Flammability and toxicity hazards are reduced, and relatively thick films can often be achieved in a single application. They can also be applied more easily to complicated shapes than liquid-applied coatings. There are no mix ratio problems as there might be with two-component thermoset liquid-applied coatings. Overspray can also be collected and reused.

Powder coatings also have some disadvantages compared to conventional liquid-applied coatings. Very large substrates cannot be coated, because of baking difficulties, nor can heat sensitive substrates be coated. While some powder coatings flow well and provide good appearance, they generally cannot rival liquid-applied coatings for aesthetics. Also, there is a smaller range of raw materials for the formulator to choose from, meaning that powder coatings do not span as wide a gamut of final properties as do liquid-applied coatings.

REFERENCES