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New Organic Coatings

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H.E. Ashton

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In selecting coatings for specific purposes, architects and other specifiers are confronted with a multiplicity of coating types. Although some manufacturers prefer users to rely upon the industry to supply the correct materials for each job, this is not entirely practical. There are so many terms derived from composition that are used for identifying, describing or classifying coatings that it is almost necessary for the user to have some knowledge of the components and their influence on the properties of coatings. Types of coatings and their general composition have been discussed in Digests 76 and 78. It is the purpose of this Digest to describe newer organic coatings and the advantages and disadvantages inherent in their composition.

The term "newer" is used here strictly in a relative sense. Some of the materials were introduced quite a few years ago and acquired immediate limited use, although they did not become commercially important for some years. Others are truly new in that their development and widespread use have transpired within the last decade, at least on this continent.

It should be noted in the discussions that the remarks apply only to the better coatings in each class. It is always possible to make cheaper products by reducing the quantities of costly ingredients, but such materials should not be expected to possess all the good properties of their respective groups. Labelling a product does not establish that the labelled ingredient is present in more than a minor proportion.

General
New coatings differ from older types chiefly in the binder, and terms such as acrylic, epoxy, and urethane, now commonly used in descriptions, relate to that portion of the coating (see Table I). As previously explained (CBD 76), the large molecules, or polymers, needed in the final dried film can be formed either completely or partially before application, or only after application. If a coating contains predominantly small molecules, the film requires a long time to cure; the resulting polymers are relatively small, as well, and it is not very resistant to weathering or chemical attack. Large polymers have more desirable properties, but if formed completely before application they require large quantities of solvent and can usually be redissolved by the same solvent.

Table I. Binders for various Liquid-Applied Coatings
<table>
<thead>
<tr>
<th>Coating</th>
<th>Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solvent Based</strong></td>
<td></td>
</tr>
<tr>
<td>Paint</td>
<td>Drying Oil</td>
</tr>
<tr>
<td>Varnish</td>
<td>Oleoresinous</td>
</tr>
<tr>
<td></td>
<td>Alkyd</td>
</tr>
<tr>
<td></td>
<td>Urethane</td>
</tr>
<tr>
<td>Enamel</td>
<td>Oleoresinous</td>
</tr>
<tr>
<td></td>
<td>Alkyd</td>
</tr>
<tr>
<td></td>
<td>Epoxy</td>
</tr>
<tr>
<td></td>
<td>Acrylic</td>
</tr>
<tr>
<td></td>
<td>Polyurethane</td>
</tr>
<tr>
<td></td>
<td>Poly Ester</td>
</tr>
<tr>
<td></td>
<td>Miscellaneous Synthetic</td>
</tr>
<tr>
<td>Lacquer</td>
<td>Natural Resins</td>
</tr>
<tr>
<td></td>
<td>Cellulose</td>
</tr>
<tr>
<td></td>
<td>Vinyl</td>
</tr>
<tr>
<td></td>
<td>Acrylic</td>
</tr>
<tr>
<td><strong>Water Based</strong></td>
<td></td>
</tr>
<tr>
<td>Solution or Soluble</td>
<td>Glue</td>
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<tr>
<td></td>
<td>Casein</td>
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</tbody>
</table>
In some of the newer developments the problem of low but permanent solubility of high polymers has been eliminated. More concentrated solutions of partial polymers are mixed with a second material shortly before application and the high polymers, which form during and after application, become insoluble because of chemical reaction. Such types are generally referred to as two-component or cold-curing coatings. Other new binders provide coatings that have better adhesion, better chemical or weather resistance, greater toughness or higher film thickness. The materials will be described in their approximate order of introduction as coatings.

**Alkyds**

The name, alkyd, is derived from the poly-functional alcohols and acids used in manufacture. Alkyds were invented in the 1920's but did not attain wide use until after World War II. Since that time they have become the most widely used resin in solvent-based coatings because of their versatility and good performance.

Alkyd manufacture, in contrast with that of oleoresinous varnishes, takes place in one kettle, and the resulting material is a very heavy syrup. The resins have a partially cross-linked molecular structure, the extent of the cross-linking being adjusted in the formulation to produce the product most suitable for a particular purpose. Alkyds that are to be air dried have a moderate oil content, and many of the cross-links form after application, just as oils dry. As the resin is not hard and brittle, less oil is required than in oleoresinous varnishes, and an oil content considered short for the latter is fairly long for an alkyd. Because there is a greater proportion of prepolymer in the molecule, there is less dependence upon air drying for final cure and it is possible to use slower drying oils, which have better colour retention than linseed. Alkyd films also change less on weathering than oils or oleoresinous films and have good adhesion, but they are subject to alkali attack.

Alkyds that are to be baked are formulated to contain a high proportion of cross-linking and consequently require strong solvents to dissolve them. Baking produces a more compact structure than air drying and is used where hardness is important. There is also less change upon aging because more of the oxidation-sensitive groups have been used. In baking alkyds, yellowing is further reduced by using oils different from those needed to produce air drying. In addition, many baking alkyds are modified with amino resins, which function as cross-linking agents, to increase hardness and colour retention. The combination of amino and alkyd resins is superior to either resin used alone.

**Vinyls**
Vinyl lacquers first achieved importance as coatings for ships and chemical plants. Resins composed of extremely large molecules that contain few points sensitive to chemical attack are needed to gain the required chemical resistance, but the resulting coatings are low in solids and have poor adhesion. Vinlys have to be applied over a special primer that reacts with a metal surface to provide adequate adhesion. If the substrate is not properly prepared, for example, the whole vinyl film may peel off in one sheet. It is necessary to use fast-evaporating solvents; in air-drying finishes because vinyl resins tend to retain some of the solvent. This, together with the resolubility of the resin, means that vinyls cannot easily be brush applied. Pigmented vinyls have shown outstanding weather resistance when applied under controlled conditions in factories to properly prepared surfaces. Their heat resistance, however, is rather poor.

**Acrylics**

Acrylic resins were introduced in the thirties, but became popular only in the last 10 years. Acrylic lacquers were developed from acrylic resins to improve the colour and colour retention of cellulose lacquers. The modification was ultimately carried to its logical conclusion with the use of acrylic resins alone. These resins are virtually colourless and do not darken or lose their gloss on outdoor exposure. For this reason they have been used extensively for the past few years on automobiles where their excellent stain resistance is valuable. Because of their manner of drying, acrylic lacquers are resoluble and have low solids content, although not so low as cellulose or vinyl lacquers.

Acrylic enamels, which are prepared from intermediate acrylic molecules and other resins and cured by heat, have recently been introduced to overcome the defects of the lacquers. In addition to providing greater film thickness, the enamels have better heat resistance and can generally be made as hard without being as brittle, thus improving toughness and mar resistance.

The excellent properties of the acrylic family extend to the latex field. The chief deterrent to greater use in exterior water-based coatings has been their high cost.

**Epoxies**

Epoxy resins can vary from low molecular weight liquids to high molecular weight brittle solids and are composed of chain-like alkali resistant molecules. They can be cured in two ways. If the resin is cooked with fatty acids from drying oils in the same way that an alkyd is made, an epoxy ester is formed. The film dries through the oil portion by reaction with oxygen as does an oil, oleoresin or alkyd. The three materials that contain partial prepolymers naturally dry faster than oil alone. The chief advantage of epoxy esters is that they are more alkali resistant. The only part of the molecular structure subject to alkali attack is the chemical bond with the drying oil. As with other resins, the properties of an epoxy ester depend upon the proportions of oil and resin.

Epoxy resins can also be cured by chemical cross-linking. If the finish can be baked, several different resins are possible, some of which yield coatings with excellent chemical resistance. In addition, coatings with properties approaching those of baked finishes can be obtained without heat by using certain compounds to cause cross-linking at room temperature. The type and amount of curing agent determines whether a flexible or a hard finish is produced. These coatings are properly called cold-curing epoxies. The term "catalyzed" epoxy is incorrect, because the curing agent enters into the reaction and becomes part of the cross-linked structure. Epoxy resins contain many molecular attraction groups not affected by alkali or water, so that their adhesion and chemical resistance are excellent, as evidenced by their use in high-strength adhesives.

Cold-cured epoxies can be produced in two forms: normal solution and high build. The solution type is made by dissolving solid resin in the required strong solvents, and contains about 50 per cent binder. The dry film thickness obtained from one coat is thus about the same as that from other enamels. Relatively thick films are produced from high-build epoxies, which
incorporate the liquid epoxy resins with little or no solvent. High-build epoxies have been used on dadoes in hospitals and similar applications where resistance to hard wear is required.

On exterior exposure epoxies tend to yellow and chalk excessively and they are used only where chemical resistance is more important than appearance. After mixing, many epoxies require a waiting period before application to allow sufficient cross-linking to occur for the desired film properties to be obtained. With high-build epoxies, there is a rather limited application period following the waiting time because with no solvent present the curing reaction is rapid. Strong solvents are necessary with the solution type and the odour is rather objectionable.

**Polyesters**

These materials are produced by dissolving a chain-like resin, which has reactive sites, in a solvent also having active sites. When a catalyst, usually called the initiator, and a promoter or accelerator are added, the resin and solvent cross-link to form a hard, glass-like solid containing almost 100 per cent of the original materials. Polyesters frequently have low impact resistance, although this can be improved by modifying the raw materials. They differ from epoxies by having both the components necessary for cross-linking present in the same can so that only the catalyst need be added to start the reaction that will turn the contents solid. Heat can also start the reaction, however, and if a polyester solution is stored in a warm place it gradually becomes viscous and finally gels. Some polyesters have a rather short pot-life, so that only small amounts should be prepared for use.

Polyesters have been used much more as structural plastics, where they are reinforced with glass fibres, than as surface coatings because it is difficult to cure normal polyesters in thin films. Applied as a film, the volatile solvent, which is a necessary part of the reaction, evaporates rapidly, with the result that only part of the polyester resin is cross-linked. In addition, the reaction started by the initiator is terminated by the oxygen in the air. Both processes result in incomplete cure at the surface and the film remains tacky. This defect has been overcome, in part, by incorporating paraffin wax in the solution. After application it floats to the top of the film and acts as a barrier to evaporation of solvent and entry of oxygen. If the extremely high gloss and film clarity that can be obtained from polyester is desired, however, it is necessary to remove the wax by sanding. (Some of the newer polyesters are reported to cure in the presence of air without using wax.) When recoating polyesters it is necessary to sand the surface well to obtain adhesion to the hard surface.

**Urethanes**

Polyurethanes have developed into a major product on this continent only since 1960, their main use being in the synthetic foam field. They are of great interest as coatings, however, because urethane films can provide greater hardness without brittleness than is possible with most other resins. Urethanes also have good chemical resistance, together with good adhesion, because the attractive groups in the molecules are not readily attacked chemically.

There are several ways to cure urethanes and they are grouped accordingly into two classes and five types, although one type is of interest only where the coating can be baked. The simplest urethanes to use are those supplied in one container. There are two in this class. The easiest method of cure, as with other resins, is to react a polyurethane with a drying oil. The product is variously described as oil-modified urethane, urethane-oil or uralkyd. Drying takes place through the usual oil mechanism but can be extremely fast. The second single-pack urethane reacts not with the oxygen in the air but with the water vapour, only a small amount being needed to cross-link the relatively large urethane molecules. Since humidity varies, the speed of moisture-cure also varies, with the lowest relative humidity for a reasonable rate reported to be 30 per cent, although slow curing will take place at 15 per cent.

Containers of moisture-cure urethanes have to be protected from water or the material will gel. Special techniques are required to pigment this type because most pigments, before dispersion,
absorb water from the air. With moisture-cure urethanes the properties of the two-component types can be obtained without the disadvantages of mixing on the job-site.

There are two types of urethane in the two-component class. The first is similar to the moisture-cure type, except that a small amount of chemical curing agent is used to cross-link the prepolymer. It too is difficult to pigment. The second and most commonly used reactive urethane is one where only a partial polymer is made. It is reacted, just before application, with castor oil or fairly large molecules of the correct chemical groups.

By varying the type of reactive component it is possible to obtain urethanes that range from rubber-like to glass-hard. This system has the advantage over the prepolymer urethanes, the polyesters, and many epoxies in that the two components are of equal volume. It is thus much simpler to prepare in small quantities than those systems where the curing agent or catalyst occupies a small volume in relation to the resin component. The partial polymer urethane is easily pigmented because the pigment can be dispersed in the second component. All reactive types have to be protected from water vapour to prevent gelation.

Urethanes have given outstanding performance, generally, on floors because of the tough film that can be produced. In the past urethanes subjected to exterior exposure have reacted in a manner similar to epoxies; i.e., they yellowed and chalked. New types with outstanding colour and gloss retention are now being introduced, although they are very expensive as yet.

**Conclusion**

Several of the new resins described in this Digest are used in two-component combinations, a procedure that provides excellent properties without baking. These systems, however, require mixing on the job, with an accompanying possibility of error, have a limited pot-life, and require frequent cleaning of application equipment. Some resins have been modified, usually by reaction with drying oils, to make them easier to use. Although such materials may result in marked improvements over older types of coatings, they should not be expected to have all the excellent properties of the unmodified resin.

Those responsible for specifying coatings can use a knowledge of composition to advantage. In general, properties and therefore the best use of any particular coating are determined by its composition.