New chemistry for reactive emulsifiers

Benefits found in production and performance of aqueous alkyds

Charles F. Palmer, Jr.

The conversion of alkyds to waterborne form has a number of problems. Very high viscosities may occur during the invert emulsion process, while the surfactants used may impair the properties of the dried film. A new emulsifier that crosslinks during drying can improve final properties, while allowing emulsification to be completed before the solvent is stripped from the original alkyd.

While they are no longer the most widely used binders in coatings, alkyd resins are still of major importance since they remain the most commonly used resin or binder system in oil-based and solvent-based coatings. Alkyd coatings are relatively inexpensive and perform well, often with fewer film defects than other coatings.

They are used in many industrial and architectural applications. The hydrophobic nature of the alkyd polymer makes them good choices when water repellency is important. However, formulating alkyds into low VOC (volatile organic compound) waterborne coatings results in a number of problems, which can be minimised by the use of a new reactive emulsifier as described below.

The general nature of alkyds

Alkyd resins are polyesters generally prepared from a polyol, phthalic anhydride and unsaturated vegetable fatty acids such as linseed, soy, or tung oil (see Figure 1). The inclusion of the fatty acid confers a tendency to form a flexible coating. Alkyds are often categorised as long, medium or short oil, based on the amount of vegetable oil in the alkyd, thus, long oil alkyds have more fatty acid content than short oils.
Fatty acids known as drying oils have multiple double bonds which will air cure to give a hard coating. This curing reaction crosslinks the oligomeric alkyd chains to increase molecular weight and improve durability and other properties.

Alkyds are sometimes modified with other radical reactive monomers or polymers for a number of reasons. These are included (for example) to speed curing, improve water compatibility or solubility or reduce viscosity.

Solvents are employed in traditional alkyd manufacture to reduce the viscosity of the oligomeric polyester and often to help remove by-product water formed in the synthesis. These solvents include xylene or ketones.

### Role of alkyds in the shift to waterborne coatings

The legislation in many countries to reduce VOC content in coatings is limiting the usage of alkyds in many applications, since most traditional alkyds have a significant level of solvent. The solvent is necessary to reduce the viscosity of the alkyd resin and to allow easy application.

A number of new technologies have been developed recently to render solventborne alkyd coatings more environmentally acceptable by replacing some or all of the solvent with water. Alkyd resins are converted into useable waterborne products by one of two methods.

### Results at a glance

- Alkyd resins continue to be used in large volumes in solventborne coatings. However, the conversion of alkyds to waterborne form has a number of problems.

- Waterborne alkyds may be prepared either by grafting onto an emulsion polymer or directly by the invert emulsion process. The latter is more flexible, but the surfactants used lead to very high viscosities during production and may impair the physical properties of the dried film.

- A new type of emulsifier based on the styrenated phenol hydrophobe and containing allyl groups crosslinks during drying, thus improving final properties. It also allows emulsification to take place before the solvent is stripped from the original alkyd, reducing viscosity problems.

- The reactive emulsifier produced a more hydrophobic film which resisted water penetration better than a standard waterborne alkyd. Gloss and adhesion to metal also showed some improvement.

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### Table 1: Composition of emulsified alkyd

<table>
<thead>
<tr>
<th>Material</th>
<th>% by weight</th>
<th>Amount used</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Beckosol 6422-K3-75” (25% methyl n-propyl ketone solvent) short oil alkyd (Reichhold)</td>
<td>49.4%</td>
<td>741 g</td>
</tr>
<tr>
<td>Reactive A</td>
<td>4.0%</td>
<td>60 g</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>0.74%</td>
<td>11.1 g</td>
</tr>
<tr>
<td>Deionised water</td>
<td>45.86%</td>
<td>687.9 g</td>
</tr>
<tr>
<td>Solids content</td>
<td>41%</td>
<td></td>
</tr>
</tbody>
</table>

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Figure 1: Generic scheme of alkyd synthesis

One method is to graft an alkyd resin onto an emulsion polymer. This gives the coating some properties of both polymer types. The emulsion polymer and the surfactant additives that are used to manufacture the emulsion render the emulsion/alkyd polymer dispersible in water, while the grafted alkyd imparts alkyd-type properties such as toughness and resistance against various chemicals to the coating.

Additional processing steps are needed to make these hybrid products. The alkyd polymer needs to be of a particular type and structure in order to make a viable alkyd/emulsion coating. In some cases, the durability of these products is superior to those of emulsion polymeric coatings.

However, the alkyd resin chemistry must be altered to maximise the benefits from the grafting of alkyd resin onto the emulsion backbone. The additional processing steps increase costs. This process also employs additives such as coalescing solvents to improve properties such as the gloss and flexibility of the coating.

Figure 2: Generic chemical structures of styrenated phenol-based surfactants (‘Reactive A’)

Emulsification of the alkyd resin into water is the other method to remove some or all of the VOCs in the emulsified product. A key advantage of the emulsification process is that the alkyd resin used does not necessarily need to be altered to prepare the emulsion, so long as the proper surfactant and emulsification process is used to make the product.

The proper surfactant is one with the proper molecular weight, structure, and HLB (hydrophilic/lipophilic balance). Nonionic surfactants generally outperform anionic surfactants in making stabilising emulsions - as demonstrated by improved water sensitivity, better colloidal stability and lower foam profile when compared to an emulsion made with an anionic surfactant. However, in some cases, a small amount of anionic surfactant is used in conjunction with the nonionic surfactant to provide some charge stabilisation.

Limitations of the emulsification process

However, there are a number of technical difficulties and limitations with the emulsification process as described in the patent literature. Usually what is termed an invert emulsion process is preferred since it does not require high shear mixing and produces less foam.

In this process, the undiluted alkyd with little or no solvent is heated to a high enough temperature to reduce its viscosity to a manageable level. The solvent used to make the alkyd is usually removed prior to emulsion preparation and the alkyd is kept at elevated temperature to keep it from solidifying.

The surfactant package of choice is then added to the molten alkyd, followed by gradual addition of hot water. As the water is added, the mixture forms a water-in-oil emulsion. However, as the water content increases and the emulsion nears the inversion point (‘flipping’ from a water-in-oil emulsion to an oil-in-water emulsion) the viscosity often becomes unmanageably high.

The temperature is maintained as high as possible to reduce the viscosity, but one problem is that surfactants, especially nonionic surfactants, have lower water solubility at high temperatures. Once the inversion point is crossed, forming the final oil-in-water emulsion, the viscosity decreases.

These alkyd emulsions contain a few percent of surfactants that remain in the formulation and thus are present in the coating after application. There they can cause a number of problems. When surfactant-coated micelle spheres stack on a surface during the drying process and start to coalesce, the concentration of surfactant molecules at the intersection of micelles can become relatively high.

If the surfactant molecules remain unbound and free to migrate, when the dried coating is later exposed to water some of the surfactant molecules can dissolve. This reduces the surface tension of the water, improves its wetting of the coating surface and promotes its penetration through the coating. Damage to the substrate to be protected becomes much more likely. On metal substrates, this can lead to corrosion and loss of adhesion. In addition, extraction of the surfactant can lead to pitting and degrade the integrity
of the coating. Free surfactants can also plasticise the alkyd and prevent it from reaching maximum hardness upon curing.

**Solving the problems created by surfactants**

Many of the problems that are caused by extractable surfactants can be reduced if the surfactant can co-cure into the alkyd coating. This locks it into place so that it cannot be extracted by water. A number of patents claim reactive surfactants that can do this. They are usually based on fatty acid alkoxylates in which the fatty acid has a number of double bonds similar to the drying oil fatty acids. However, most of the known ones have some significant drawbacks. They are nonionic surfactants and so have lower solubility in hot water, which limits their ability to make inverse emulsions with manageable viscosity. Nonionics also cannot take advantage of charge stabilisation mechanisms to reduce particle size and improve emulsion stability.

Most nonionic surfactants used for alkyd emulsions have long ethoxylate chains to give them the high HLB value which is required to make a stable emulsion. These nonionics have a strong tendency to retard drying, probably due to complexation of metal ion drying agents. Long chain nonionics also have a tendency to plasticise alkyd coatings, reducing their hardness.

A new class of reactive surfactants has now been developed, based on the styrenated phenol hydrophobe and containing allyl groups, as shown in Figure 2. Instead of curing through fatty acid double bonds, these cure through the pendant allyl groups. Styrenated phenol is a polyaromatic hydrophobe, so these surfactants have good affinity for the aromatic groups in the alkyd. They are also inherently lower foaming than most linear surfactants. The alkoxylate chain is relatively short so that it has less affinity for chelating metal ions. Curing times have not been affected with the drier packages tested. The anionic character gives it charge-stabilisation ability. This surfactant chemistry is also available as a nonionic and as a phosphate ester.

**Emulsion preparation procedure outlined**

The materials used in alkyd emulsion preparation and their addition levels are shown in Table 1. The procedure used is as follows. Charge the solventborne short oil alkyd, ('Reactive A'), and ammonium hydroxide to a reactor flask equipped with nitrogen sparge, thermocouple, overhead mixing and condenser. Once the mixture is homogeneous, begin adding water at ambient temperature to the mixture in a slow stream so that the water is incorporated evenly into the mixture and does not pool on the surface.

As the water is added, the viscosity will rise until the inversion point is met, then the viscosity will begin to drop. When all the water is charged, allow the emulsion to mix for several minutes and then check the particle size. This emulsion was prepared at 41% solids.

After ensuring that the particle size is satisfactory, raise the temperature of the emulsion by heating to 70 °C with
Table 2: Comparisons between reactive and non-reactive surfactant based alkyd coatings

<table>
<thead>
<tr>
<th></th>
<th>Reactive surfactant formula</th>
<th>Non-reactive surfactant formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Beckosol 10-539” long oil alkyd</td>
<td>38.2</td>
<td>38.2</td>
</tr>
<tr>
<td>Reactive A</td>
<td>1.8</td>
<td>--</td>
</tr>
<tr>
<td>POE 20 DSP</td>
<td>--</td>
<td>1.8</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Water</td>
<td>58.8</td>
<td>58.8</td>
</tr>
<tr>
<td>Catalyst blend</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Drawdown properties after 2 weeks

<table>
<thead>
<tr>
<th></th>
<th>Reactive surfactant formula</th>
<th>Non-reactive surfactant formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross-cut adhesion</td>
<td>0B (100 % fail)</td>
<td>0B (100 % fail)</td>
</tr>
<tr>
<td>Pencil hardness</td>
<td>F</td>
<td>2B</td>
</tr>
<tr>
<td>60 ° gloss</td>
<td>117</td>
<td>113</td>
</tr>
<tr>
<td>Water contact angle</td>
<td>84.5 °</td>
<td>79.0 °</td>
</tr>
</tbody>
</table>

Figure 3: Alkyd emulsion particle size with solvent (left) and after solvent stripping (right)
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How different surfactants affect coating properties

Two more waterborne emulsions were prepared using the procedure as given above, but with a long oil solventborne alkyd. Identical amounts of reactants were used. The only difference was the emulsifier. Both emulsifiers (“RS-1618” referred to as ‘Reactive A’ and POE 20 DSP (poly(oxyethylene) with 20 POE units)) are distyrenated phenol based, have nearly the same ethoxylate chain length, and are both sulfates. The only significant difference between them is that Reactive A is reactive, while POE 20 DSP contains no reactive allyl groups.

After the emulsions were prepared, a cobalt-based drying catalyst package was added to the emulsion and drawdowns were made on steel “Q-panels”. After two weeks, the adhesion, pencil hardness, gloss, and water contact angle were checked. Results are shown in Table 2.

Review of the data in Table 2 shows that the alkyd coating with the reactive surfactant has a higher water contact angle. This indicates that the coating is more water repellent, evidence that the reactive surfactant is cured into the alkyd and not available to dissolve into the water and reduce its surface tension. The coating with the reactive surfactant is also significantly harder than the other. Presumably, this is due to the plasticisation of the coating by the unbound surfactant. The gloss of the coating is also higher with the reactive surfactant. This suggests that the surface has fewer defects. This might be due to a more homogeneous particle size distribution.

Adhesion to metal and rust protection are improved

Water drops were placed on each of these drawdown panels and allowed to stand covered so that they would not evaporate. The water drop on the alkyd coating with the non-reactive surfactant had significantly wet the coating and had spread out to cover a much larger area than the drop on the reactive surfactant coating. After two days, rust on the panel was clearly visible on the panel with non-reactive surfactant (see Figure 4). The coating with the reactive surfactant resisted the ingress of water and protected the steel much better than did the non-reactive one.

In another test of adhesion, drawdowns were made of an aqueous short oil alkyd emulsion prepared with the difunctional Reactive A surfactant according to the first example above and a commercially available waterborne short oil alkyd (assumed not to contain a reactive surfactant).

Both were catalysed with the same drier package. After 24 hours, a crosshatch pattern was scribed onto the alkyd surfaces. The attempt to scribe the crosshatch pattern on the commercial alkyd failed, while it was successful on the alkyd with reactive surfactant (see Figure 5). This failed the tape pull, however. The reactive surfactant emulsion thus had significantly better adhesion to the steel panel. It is not known what the mechanism for the improved adhesion is.

Benefits of reactive surfactants summarised

The reactive surfactants described here allow the viscosity problems found in the invert emulsion process to be reduced. They give a more hydrophobic coating (as measured by water contact angle) than structurally similar non-reactive surfactants. Similarly, they produce a more water-resistant coating (as measured by rust resistance) than structurally similar non-reactive surfactants. Both gloss and adhesion to metal can be improved by the use of reactive surfactants. Further work to develop and understand this technology is therefore under way.

Want to learn more about the new chemistry for reactive emulsifiers?

Tune in for the free web-based presentation of Dr Charles E. Palmer on 23 September 2014, 15.00 CET at www.european-coatings.com/live
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