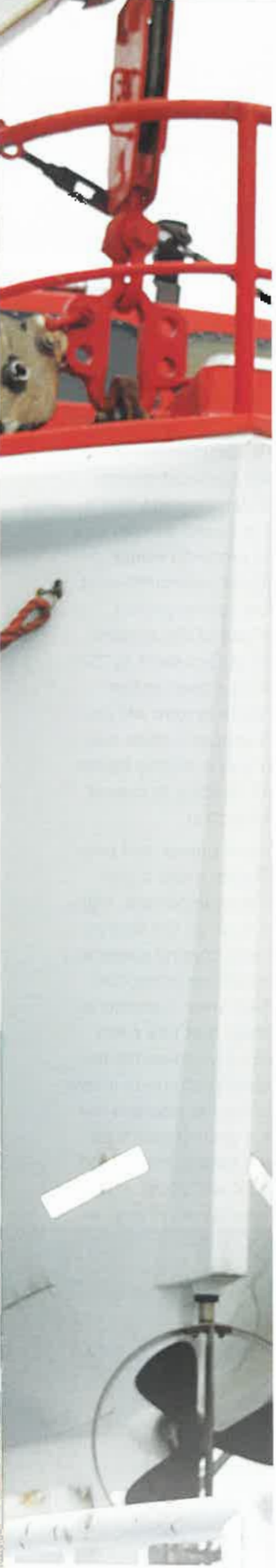

The 'Rebirth' of ALKYDS:

Improved Performance Energizes Market

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Alkyd coatings found widespread use in architectural, agricultural equipment, and light industrial applications until increasing regulatory restrictions on VOCs led to a dramatic decline in demand for these traditionally solventborne resins. Water-reducible alkyds, the first attempt by industry to develop lower-VOC, aqueous alternatives, met with only limited success, and it appeared that the market for alkyds would remain significantly diminished. Recent advances in hybrid and 100% alkyd latex technologies, however, have enabled the production of low- to zero-VOC alkyd resins that have performance characteristics similar to those obtained with solvent-based products. As consumer interest in "greener" products made from renewable resources continues to grow, the outlook for these new alkyds seems much brighter.

Conventional alkyds exhibit properties that cannot be matched with other resin technologies such as acrylic latexes. Very high gloss and durability are combined with application performance, including desirable open times and flow and leveling characteristics that lead to reduced brush marks and allow for easy touch up. Alkyds have also been appreciated for their excellent wood penetration and adhesion to metal, and consumers prefer their "non-chemical" smell. They have found wide use in architectural and industrial coatings, from sash and trim paints to deck coatings and stains and direct-to-metal formulations for corrosion resistance.

To meet initial VOC-reduction requirements, alkyd resin suppliers first developed high solids solventborne and water-reducible products. Water reducible alkyds are comprised of a high acid number alkyd resin in a polar solvent that is then dispersed in water along with the pigment, other additives, and a volatile amine, which serve to neutralize the acids. They not only have a limited shelf life, but have not met performance expectations. And, as with their high solids counterparts, they have VOC levels that are well beyond the allowable limits expected for the future.

A second strategy for alkyd resin suppliers was to develop hybrid products with other resin types – particularly acrylics in the early development stages. The goal with this approach was to help stabilize the alkyd portion of the resin and retain the desirable alkyd characteristics while enhancing other aspects of the coating with complementary properties of the second resin. Today, most resin manufacturers offer alkyd hybrids with many other resin types in addition to acrylics, including urethanes, epoxies, and phenolics. Generally, the hybrids are offered with varying ranges of modifier content to allow for adjustment of specific properties.

Advances in surfactant technology have played a critical role in leading to further developments in waterborne alkyd technology. Alkyd dispersions generally fall into one of two categories based on how the surfactant is incorporated into the resin system. In some cases, the surfactant is mixed into the water with the resin and provides external stabilization. In other cases, the surfactant is actually chemically bound with the resin. "Alkyds that rely on external surfactants tend to be higher solids systems than those where the surfactant is chemically bound, but we have observed that the latter type tend to perform better," remarks Mohamad D. Shalati, a senior research fellow with Nuplex Resins. In these cases, the surfactant is often an acrylic resin and thus these resins are considered hybrids.

Those systems where the surfactant provides external stabilization are in fact 100% alkyd dispersions, or alkyd latexes. Both new surfactant technology and specialized production processes have been developed and combined to lead to production of highly stable waterborne alkyds with performance characteristics similar to those of solvent-based resins, according to Carl J. Sullivan, vice president at Reichhold Coatings Resins.

Both hybrid alkyd dispersions and alkyd latexes can be formulated in very low- VOC (50 g/L or less) or zero VOC coatings for use in most applications where solventborne alkyds have been employed in the past, including light architectural/decorative (trim enamels, wood coatings, and stains), light industrial (direct-to-metal), and auto primer surface applications.

"New waterborne alkyd technology is attractive for many reasons," observes Terry Scoville, global marketing manager with Cytec Industries. "The fact that these resin systems are prepared largely from renewable resources is definitely a factor, as consumers, and thus paint formulators, are looking for more sustainable solutions. Today, coatings can be formulated with water-based alkyds that have the application properties and formulation stability of solventborne paints but still meet new, lower requirements for VOC content."

Adds Dennis Ryer, product manager for Liquid Resins with Cook Composites and Polymers (CCP): "There is a real push by major paint manufacturers to move from high solids formulations to waterborne coatings, so we expect there will be continued and increasing focus on efforts to adopt water-based technologies. This push is largely driven by VOC compliance needs, but consumers are definitely looking for alternatives to solventborne alkyds that still have the same performance characteristics. This interest may contribute to even greater growth potential."

"Now that performance and stability issues have been successfully addressed with waterborne alkyds, there is a lot of interest in them," agrees Tony Rende, senior executive with OPC Polymers.

OPC has introduced several zero-VOC modified alkyd dispersions using acrylic, urethane, and other modifier resins. "We offer a range of products with varying modifier type and content and also often develop customized products for our customers," says Rende. Current development efforts are focused on improving dry time and addressing yellowing issues, which has always been a concern with alkyd resins.

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The company is also working on 100% alkyd dispersions that do not incorporate any modifier resins in order to provide a comprehensive range of products.

In addition, OPC is going through its entire alkyd product line with the intention of offering waterborne alternative versions of all its solvent-based products. "In some cases, applying the new technology is relatively easy and in others it is more challenging and complex. But we ultimately expect to have our entire line be zero VOC."

Nuplex is also developing both hybrid and 100% types of waterborne alkyds. Its latest product, Setaqua 6030, is a zero-VOC acrylic/long alkyd hybrid dispersion targeted for porch and deck stain applications due to its excellent wood penetration ability and high gloss and durability. It is also recommended for architectural high gloss enamels and direct-to-metal formulations. The technology is based on dispersed polymeric particles that possess a core-shell morphology, in which the acrylic polymer is grafted onto the high molecular weight alkyd. The particles are formed via the copolymerization of a hydrophilic macromonomer (comb-like, segmented block, A-B type copolymers), a hydrophobic alkyd and bridging acrylic monomers that possess both ionic and nonionic groups. When neutralized and dispersed, the alkyd particle is thus stabilized by both non ionic (steric) and ionic interactions.

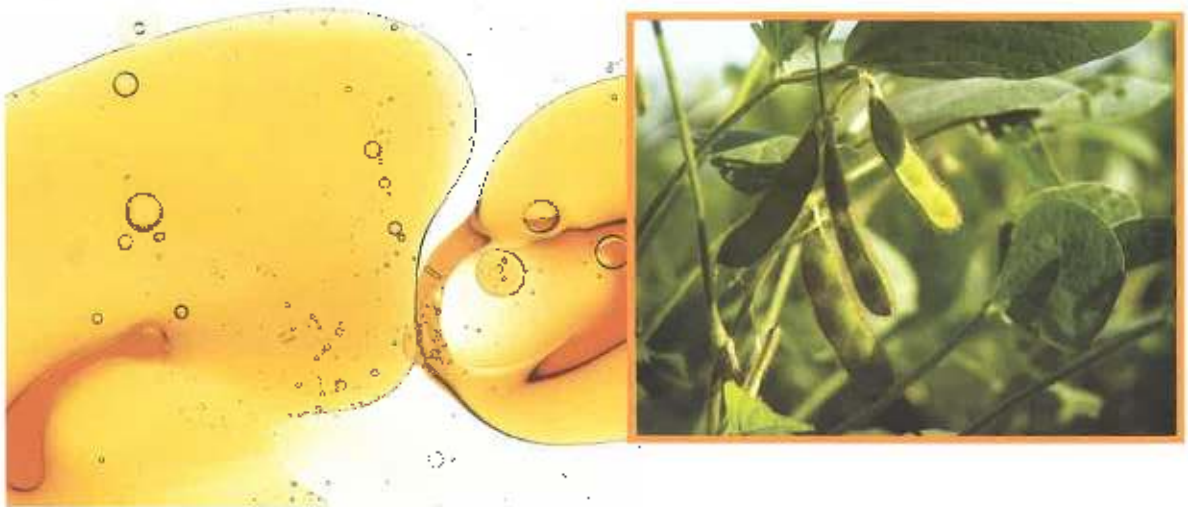
Another area Nuplex is working on is the development of waterborne alkyds that provide corrosion protection equal to that of solvent-based coatings, which is a challenge because water itself is corrosive. "The market also continues to demand higher solids in water based formulations for improved stability and durability," notes Philip L. Shuffett, R&D manager for Nuplex Resins. "Even so, waterborne alkyds today have achieved similar performance to solvent-based coatings, and these technology advances have propelled alkyd dispersions/emulsions to the forefront and have led to increased investments in R&D of these new resin systems," adds Shalati.

Cytec, too, offers both hybrid resins and 100% alkyd dispersions. In the latter case, the company uses proprietary polymer emulsification techniques rather than relying on traditional surfactants to provide a low viscosity, very stable alkyd dispersion. Scoville is seeing interest for these products largely in architectural applications. There is also interest in this sector for the company acrylic and urethane modified alkyds, while its epoxy hybrids are being used in light industrial applications because of their attractive adhesion and anti-corrosion properties.

Recently, Cytec launched a cationic alkyd/epoxy hybrid emulsion for stain-blocking applications, which has good adhesion and stain blocking ability without the need for added blocking pigments. Currently, Cytec is continuing to improve the performance of its water-based alkyds while minimizing VOC content. "We are looking to provide products that meet unmet needs in the market," states Scoville. "The high molecular weight resins in our dispersions mean that coatings retain the desirable properties of alkyds, and because of the nature of the chemistry of alkyds and dispersions in general, the performance of these products can even surpass that of solventborne resin systems."

Reichhold has most recently invested in the development of 100% alkyd latex technology and has launched several products that achieve alkyd-like performance in a waterborne media, with VOC content below 50 g/L, according to Sullivan. "In these new resin systems, special surfactants help stabilize the latex but account for no more than 5% of total solids, so they truly are waterborne alkyds. Hybrids, in contrast, can contain up to 40% or more of the modifier resin."

The company uses the typical range of renewable materials in these new alkyd latexes, including soybean, linseed, and tall oil fatty acids, for example. "The key to successful development of these waterborne systems has been the screening and development of surfactant technology that provides both shelf and process stability to alkyds, which otherwise would be hydrolyzed over time upon exposure to water," Sullivan comments.



As with solventborne alkyds, curing/crosslinking occurs when the coating is exposed to oxygen. Reichhold's products have a similar dry time to waterborne acrylics, but maintain the desired performance properties of solventborne alkyds, including brushability. They have, in fact, generated a lot of interest in the architectural market, as DIYers are looking for water-based products but have been disappointed with vinyl acrylics in applications such as gloss trim enamel and wood stains. "There is a slowly shifting realization in the marketplace that with alkyd dispersions it is possible to get performance features not possible with other aqueous technologies," Sullivan says. "There still lingers, however, the perception of poor performance for waterborne alkyds that is associated with water-reducible products, and resin suppliers are working hard to overcome that hurdle."

Reichhold is also working to develop a greater understanding of green certification programs such as Green Seal and Green Guard, and hopes to find ways to encourage formulators to use alkyd latexes in coatings they intend to submit for evaluation. "Consumers and contractors want green products, but they need to be available at a competitive price and provide the same performance as other alternatives. We believe that waterborne alkyds will enable coating manufacturers to develop products that meet these expectations," Sullivan states.

In its pursuit of greener, more environmentally friendly alkyd resins, CCP has turned to new technology based on Procter & Gamble's (P&G) Sefose® sucrose esters prepared from renewable feedstocks by esterifying sucrose with fatty acids in a solvent-free process. The two companies jointly developed Chempol® MPS alkyd resins by controlling the choice of natural oil feedstocks used for esterification in both the alkyd and the Sefose sucrose ester. "Typically, all eight hydroxyls on the sucrose molecule are esterified, resulting in low molecular weight, low viscosity, highly functional, hydrophobic compounds that co-react with the alkyd backbone to provide very desirable properties for coating applications," explains Ryer.

Like traditional alkyds, these new resin systems undergo auto-oxidative crosslinking in the presence of cobalt and manganese driers. While first-generation products were high solids formulations, CCP has advanced the technology so that it now also offers alkyd emulsions at

zero VOC. Together, CCP and P&G won the 2009 Presidential Green Chemistry Challenge Award in the "Designing Greener Chemicals" category. CCP is targeting typical applications where long oil alkyds are used, such as gloss topcoats, floor stains, porch and deck applications, and metal primers.

Dean Webster of the Department of Coatings and Polymeric Materials at North Dakota State University has also been studying the use of P&G's Sefose sucrose esters. His research group has emulsified the esters using surfactants along with cellulose thickeners to adjust the rheology and has been studying the stability and rheology of the dispersions as a function of composition. No coalescing agent is required to produce a quality film, which self-oxidizes using typical drying catalysts. In addition, Webster is studying the auto oxidation of coatings made with these new resins using confocal Raman spectroscopy.

Other academic groups are researching improved methods for preparing hybrid alkyd resins. F. Joseph Schork at the University of Maryland has, for example, employed mini-emulsion technology to polymerize acrylic monomers with fatty acids to prepare polymers with alkyd groups grafted onto the acrylic backbone. "The trick is to get the alkyd groups near the surface of the particle so that they can undergo oxidative curing/crosslinking," he says. Coatings prepared with these resins have desirable hardness and adhesion characteristics as seen with solventborne alkyds.

Meanwhile, Mark Soucek at the University of Akron has explored many different types of alkyd resins including acrylic hybrids and UV-curable alkyds. For waterborne resins, his group has used controlled free radical polymerization to prepare acrylic-alkyd-acrylic block copolymers. The free hydroxyl groups located on the chain ends of medium oil alkyd resins were esterified to prepare new macro-RAFT agents for constructing well-defined acrylic alkyd hybrids. Both acrylate-alkyd and acrylate-methacrylate-alkyd resins were synthesized. Films prepared with a modified alkyd were evaluated, and for co-acrylic alkyds, the order of the block was found to be important in determining film properties including cross-hatch adhesion, gloss, and solvent resistance. "This approach allows for great control in the construction of the acrylic-alkyd hybrid resin and thus provides the ability to select specific acrylates that will give the desired water dispersibility and coating performance characteristics," Soucek states.

Others, such as James Rawlins at the University of Southern Mississippi, have chosen to begin with an acrylic, vinyl acetate, or styrene backbone and build in alkyd functionality. "We reasoned that the high molecular weight on the backbone would make it possible to attain the desired properties more easily, as it wouldn't be necessary to build in the molecular weight, as is common with conventional alkyd systems," he explains. His group has developed a versatile platform of vegetable oil macromonomers (VOMMs) that combine various acrylate and alkyd functionalities and thus have both hydrophilic and hydrophobic characteristics. Latexes prepared via copolymerization of VOMMs such as SoyAA-1, which is derived from inexpensive soybean oil, and acrylate monomers are very similar to semi-drying or non-drying alkyds and do not require any drying agents. "Most importantly, we can tune the performance characteristics by changing the different functionalities. In this way, for example, we can produce resins that are both tacky and non tacky at room temperature," Rawlins notes.

While the technologies being developed by these various university research groups have yet to be commercialized, the different approaches have attracted interest from industry and many are being explored by resin and paint manufacturers. While finding new avenues for the sale of alkyd resins obviously benefits the resin suppliers, formulators have also recognized the potential value of the advances being made in low-VOC alternatives.

"In our quest to develop new waterborne technology platforms that delight our customers, AkzoNobel is keeping an open mind on the particular technologies that we need to use going forward," says an AkzoNobel spokesperson. "Alkyd technologies used in either high solids solventborne or waterborne products continue to be improved and be refined. Water-dispersible alkyds, either used alone or in combination with other technologies, probably have something to contribute, but are unlikely to form the entire answer. Therefore, we continue to maintain sufficient internal capability to keep our innovation options open for the future."

Clearly, while not yet making any strong commitments, even major players such as AkzoNobel show some interest in developing waterborne alkyd technologies. One of the most notable aspects about the renewed interest in alkyds, in fact, has to do with the level of that interest. "Within the paint and coatings industry, I haven't seen the heightened level of interest in any new technology in a long time like what we are experiencing with waterborne alkyds," asserts Rende. "Nearly all formulators are looking into the technology. And this activity is good not only for OPC and other alkyd suppliers, but for the industry as a whole. The more options available to the formulator, the better the products they will develop."