A second strategy for alkyd resin suppliers was to develop hybrid products with other resin types—particularly acrylcs in the early development stages. The goal with this approach was to help stabilize the alkyd portion of the resin and refine 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 acrylcs, 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 Mamoud 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 Tony Scofield, 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.”

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The 'Rebirth' of Alkyds: Improved Performance Energizes Market

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 solventborn resins. Water-reducible alkyls, the first attempt by industry to develop low-VOC, aqueous alternatives, met with only limited success, and it appeared that the market for alkyls would remain significantly diminished. Recent advances in hybrid and 100% alkyl latex technologies, however, have enabled the production of low- to zero-VOC alkyl 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 alkyls seems much brighter.

Conventional alkyls 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. Alkylds 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 stairs and direct-to-metal formulations for corrosion resistance.

To meet initial VOC-reduction requirements, alkyl resin suppliers first developed high solids solventborn and water-reducible products. Water-reducible alkyls are comprised of a high acid number alkyl 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 above the allowable limits expected for the future.

A second strategy for alkyl 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 alkyl portion of the resin and refine the desirable alkyl characteristics while enhancing other aspects of the coating with complementary properties of the second resin. Today, most resin manufacturers offer alkyl 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 alkyl technology. Alkyld 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. "Alkylds 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 Mmamad 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% alkyl dispersions, or alkyl latexes. Both new surfactant technology and specialized production processes have been developed and combined to lead to production of highly stable waterborne alkyls with performance characteristics similar to those of solvent-based resins, according to Carl J. Sullivan, vice president at Reichhold Coatings Resins. Both hybrid alkyl dispersions and alkyl latexes can be formulated in very low-VOC (50 g/L or less) or zero-VOC coatings for use in most applications where solventborne alkyls 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.

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

In addition, OPC is going through its entire alkyl
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
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Nuplex is also developing both hybrid and
100% types of waterborne alkyls. Its latest prod-
uct, Setaqua 6030, is a zero-VOC acrylic/long
alkyl hybrid dispersion targeted for porch and
deck stain applications due to its excellent wood
penetration ability and high gloss and durabil-
ity. 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 alkyl. The particles are
formed via the copolymerization of a hydrophilic
macromonomer (combi-, segmented block, A-B
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Another area Nuplex is working on is the de-
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Itself is corrosive. “The market also continues to
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for improved stability and durability,” notes Philip
L. Shufflett, R&D manager for Nuplex Resins. “Even
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performance to solvent-based coatings, and these
technology advances have propelled alkyl disper-
sions/emulsions to the forefront and have led to
increased investments in R&D of these new resin
systems,” adds Shahi.

Cytec, too, offers both hybrid resins and 100% alkyl
dispersions. In the latter case, the company
uses proprietary polymer emulsification techniques
rather than relying on traditional surfactants to
provide a lower viscosity, volatile alkyl dispersion.
Scoville is seeking interest for these products largely
in architectural applications. There is also interest
in this sector for the company acrylic and urethane
modified alkyls, 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 alkyl/
epoxy hybrid emulsion for tin-blocking applica-
tions, which has good adhesion and tin-blocking ability
without the need for added blocking pig-
ments. Currently, Cytec is continuing to improve
the performance of its water-based alkyls while
minimizing VOC content. “We are looking to provide
products that meet unmet needs in the market,”
states Scoville. “The high molecular weight resin in
our dispersions mean that coatings retain the
desirable properties of alkyls, and because of the
nature of the chemistry of alkyls 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% alkyl latex technology and
has launched several products that achieve alkyl-
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 alkyls.
Hybrids, in contrast, can contain up to 40% or
more of the modifier resin.”

The company uses the typical range of renew-
able materials in these new alkyl latexes, includ-
ing soybean, linseed, and tall oil fatty acids, for
example. “The key to successful development of
these waterborne systems has been the screen-
ing and development of surfactant technology that
provides both shelf and process stability to alkyls,
which otherwise would be hydrolyzed over time
upon exposure to water,” Sullivan comments.

As with solventborne alkyls, curing/crosslink-
ing occurs when the coating is exposed to oxygen.
Reichhold’s products have a similar dry time to wa-
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interest in the architectural market, as DIYers are
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manence features not possible with other aqueous
technologies,” Sullivan says. “There still lingers,
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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 alkyl 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
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that meet these expectations,” Sullivan states.

In its pursuit of greener, more environmen-
tally-friendly alkyl resins, CCP has turned to new
technology based on Procter & Gamble’s (P&G)
Sefsol® sucrose esters prepared from renewable
feedstocks by esterifying sucrose with fatty acids in
a solvent free process. The two companies jointly
developed Chempol® MPS alkyl resins by control-
ling the choice of natural oil feedstocks used for
esterification in both the alkyl and the Sefsol
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 al-
ky backbone to provide very desirable properties for
coating applications,” explains Ryer.

Like traditional alkyls, these new resin sys-
tems undergo auto-oxidative crosslinking in the
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CCP can provide you with sustainable choices for your most demanding
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In its pursuit of greener, more environmentally friendly alkyl resins, CCP has turned to new technology based on Procter & Gamble's (P&G) Sefsol® sucrose esters prepared from renewable feedstocks by esterifying sucrose with fatty acids in a solvent-free process. The two companies jointly developed Chemrep® MPS alkyl resins by controlling the choice of natural oil feedstocks used for esterification in both the alkyl and the Sefsol® 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 alkyl backbone to provide very desirable properties for coating applications," explains Ryer.

Like traditional alkyls, 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 alkyl emulsions at lower solids levels. The company is also working on 100% alkyl 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 alkyl 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."

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Another area Nuplex is working on is the development of waterborne alkyls 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 alkyls today have achieved similar performance to solvent-based coatings, and these technology advances have propelled alkyl dispersions/emulsions to the forefront and have led to increased investments in R&D of these new resin systems," adds Shalati.

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The company uses the typical range of renewable materials in these new alkyl 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 alkyls, which otherwise would be hydrolyzed over time upon exposure to water," Sullivan comments.

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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 finishes, 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 Sefacol succrose 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 co-ocooxing 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 alkyl 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 alkyl groups grafted onto the acrylic backbone. "The trick is to get the alkyl 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 alkyls.

Meanwhile, Mark Soucek at the University of Akron has explored many different types of alkyl resins including acrylic hybrid and UV-curable alkyls. For waterborne resins, his group has used controlled free radical polymerization to prepare acrylic-alkyl-acrylic block copolymers. The free hydroxyl groups located on the chain ends of medium oil alkyl resins were esterified to prepare new macro-RAFT agents for constructing well-defined acrylic-alkyl hybrids. Both acrylate-alkyl and acrylic-methacrylate-alkyl resins were synthesized. Films prepared with a modified alkyl were evaluated, and for co-alkyls, 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-alkyl 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 alkyl 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 alkyl systems," he explains. His group has developed a versatile platform of vegetable oil macromonomers (VOMMs) that combine various acrylate and alkyl functionalities and thus both hydrophobic and hydrophilic characteristics. Lattices prepared via copolymerization of VOMMs such as SoyA-1, which is derived from inexpensive soybean oil, and acrylate monomers are very similar to semi-drying or non-drying alkyls 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 alkyl 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. "Alkyl technologies used in either high solids solventborne or waterborne products continue to be improved and be refined. Water-dispersible alkyls, 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 alkyl technologies. One of the most notable aspects about the renewed interest in alkyls, 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 alkyls," asserts Rendel. "Nearly all formulators are looking into the technology, and this activity is good not only for OPC and other alkyl suppliers, but for the industry as a whole. The more options available to the formulator, the better the products they will develop."