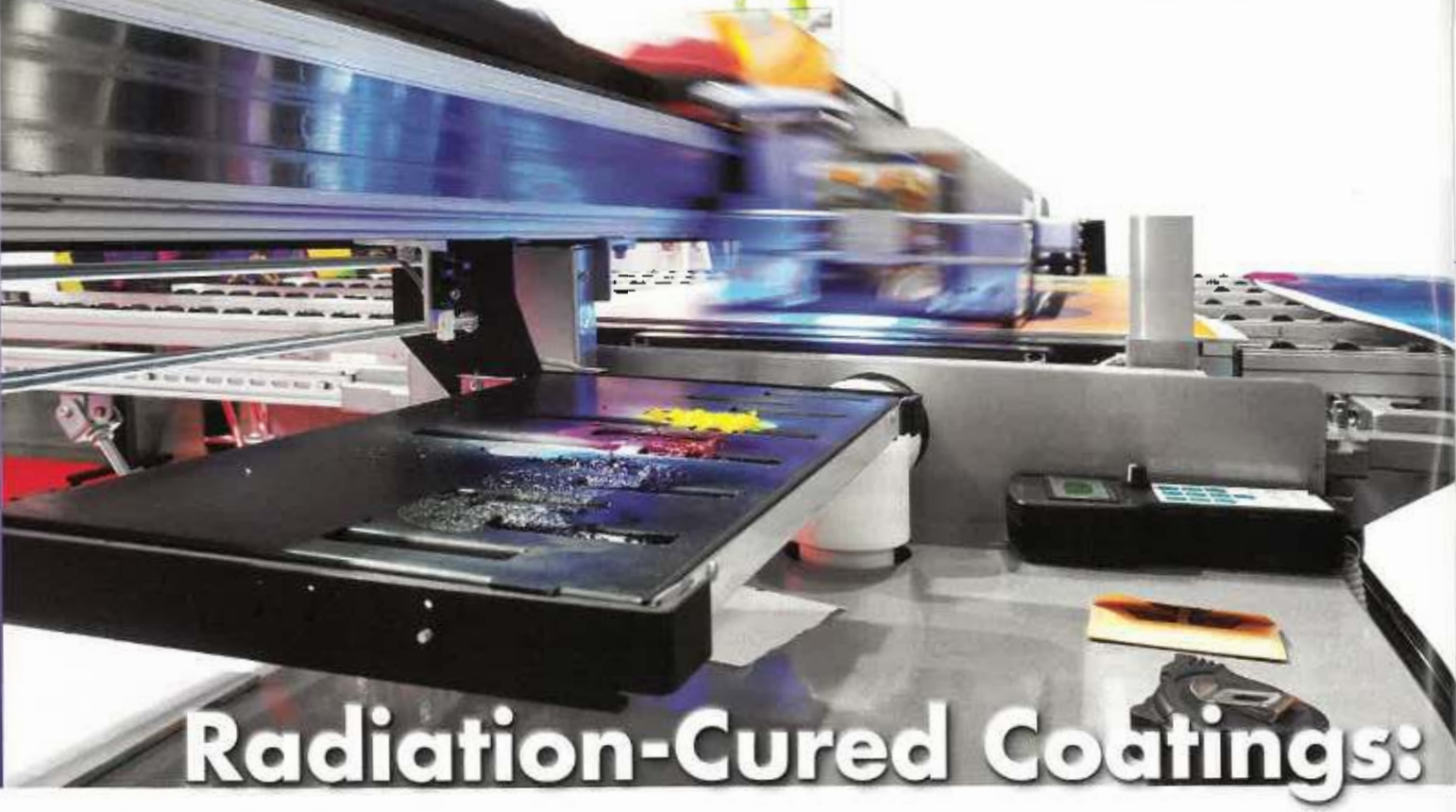

Radiation-Cured Coatings:

REGULATIONS + PERFORMANCE EXPECTATIONS DRIVE ADVANCES

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Developers of raw materials used in the formulation of radiation-cured coatings and manufacturers of UV-, EB-, and recently, LED-cured coatings are faced with numerous challenges that range from increasing regulatory requirements to growing expectations for more sustainable coatings. At the same time, there are significant cost pressures driving the introduction of products designed to provide maximum value in use. Collaboration across the supply chain is becoming increasingly critical for effective and efficient development of innovative technologies that address real customer and market needs.

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The global market for radiation-cured products in 2012, including coatings, inks, and adhesives, is estimated by market research firm Transparency Market Research to be $4.93 billion—and growing at a compound annual rate of 7%, to reach $7.93 billion in 2019. Radiation-cured coatings accounted for nearly 80% of the volume, according to the research firm, while on a regional basis, Asia Pacific accounted for approximately 40% of total value, followed by Europe and then North America. The firm also expects Asia Pacific to be the fastest-growing regional market in terms of both production and consumption. The value of the North American radiation-cured coatings market in 2013 is estimated by Michael D. Brown, president of consulting firm StrategyMark, Inc., to be approximately $700 million. The main end-use markets for radiation-cured coatings include graphics arts (~33% share), optical fiber (20%), general OEM metal and plastic products (20%), and wood furniture and flooring (20%), according to Brown.

DEMAND FOR SUSTAINABILITY

One of the drivers for continued growth of the radiation cured market is the rising interest of coating applicators and consumers for more sustainable products. Radiation-curing processes consume less energy and produce less waste. Often the coatings contain very low or zero volatile organic compounds (VOCs) and hazardous air pollutants (HAPs). Applicators also benefit from im-

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proved productivity due to faster line speeds, lower curing temperatures, and smaller footprints. Of added benefit for the consumer are the improved coating properties often seen with radiation-cured systems, including increased durability, scratch and corrosion resistance, and clarity. "The desire to be more sustainable is definitely a consistent trend that we are seeing, with particular emphasis on reducing waste," notes Dan Sweetwood, president and CEO of Allied PhotoChemical. Sartomer is also seeing growing demand for materials made from renewable/naturally sourced chemistries, according to Heather Rayle, senior business director with Sartomer Americas. In response to this trend, Sartomer has developed its Sarbio® biorenewable product line, which is certified by the U.S. Department of Agriculture for its biorenewable content. The company has also developed waterborne polyurethane dispersion (PUD) technology to meet customer demands for solvent-free systems.

Large corporate customers are also being proactive about their environmental practices. The choices that companies like Walmart are making with respect to packaging are directly affecting the radiation-cured coatings market, according to David Harbourne, president of Heraeus Fusion UV North America. "These companies are definitely influencing the use of radiation curing as a means to improve the sustainability of packaging. They are also driving the growing development of waterborne radiation-cured coating alternatives," he explains.

Food producers are also affecting the development of raw materials and coating formulations intended for use in food packaging. In this case, the issue is migration of the ingredients in the coating through the packaging and into the food. For example, a global food producer has established specific requirements for radiation-cured coatings, according to Syed T. Hasan, manager of new business development and idea management for transportation and industrial coatings and plastics and printing, packaging & adhesives in the dispersions & pigments division of BASF Corporation.

REGULATORY DRIVERS

Numerous regulations are also influencing the radiation-cured coatings market, and many overlap with the sustainability drivers previously outlined. As with all other segments of the coatings industry, reduction of VOCs is a key issue, and thus there is a need for those companies still using radiation-cured coatings formulated with solvent-based diluents to switch to those using reactive monomer diluents or waterborne systems. "Water based UV technology is becoming a more popular choice because, in addition to the minimal use of cosolvents, these formulations have low odor and the cured coatings are recyclable and reclaimable, so there is less hazardous waste to dispose of than for solvent-based technologies," notes Chuck Gambino, an associate scientist with Bayer MaterialScience. The company has developed a portfolio of UV waterborne PUDs to satisfy customer and market needs, and relies on collaboration with customers and other players in the value chain in order to develop products that offer the most value.

Legislation on the migration of packaging components into foods is also under development, with Switzerland already having passed an ordinance. Allnex, meanwhile, is closely monitoring the status of existing and emerging "chemicals of concern" legislation, including those related to migration, as well as potential regulations on specific chemicals such as tin, organotin compounds, and bisphenol A (BPA). Tin-based compounds are often used as drying agents for radiation-cured coatings. BPA is a building block for acrylated epoxy resins, which are the most widely used resins in black energy-cured flexo inks, general industrial energy-cured coatings, and overprint varnishes for consumer product packaging and graphic arts. Notes David Kent, technical customer service manager for coatings, EMEA with Grace, "Resin suppliers and coating manufacturers are challenged in equal measure to produce both alternative resins with the same high reactivity and relatively low cost, as well as to formulate coatings with equally fast-curing, high-film clarity, durability, and resistance properties."

An additional challenge, according to Audrey De Wulf, global marketing director for Radcure with Allnex, is that "while the regulatory status of identified chemicals of concern varies from country to country, many of the end products commercialized by Allnex are used in more than one global market segment and regulated county. In addition, many of our customers are either multinational in

markets served or global in reach, and thus it has become incumbent for Allnex to design products with the broadest regulatory acceptance possible." He also notes that at the moment there are no easy answers for many of these "chemicals of concern" issues. "The amount of time and effort required to vet the appropriateness of ink and coating systems via migration studies and tox analyses is enormous, and many companies can't afford to commit several years to a testing program and then find out that certain ingredients within their elected systems are no longer acceptable," he comments.

The company is trying to overcome these issues. In 2013, Allnex launched a line of non-intentionally added tin and organotin ("tin-free") energy-curable resins and aqueous dispersions that address existing and emerging regulations, norms, and specifications restricting the use of tin and organotin derivatives, including brand owner requirements and the European Union Decision 2009/425/EC, which restricts usage of Sn (IV) to a maximum of 0.1% by total weight in consumer products and packaging ingredients. Allnex's "tin-free" range includes aromatic and aliphatic urethane acrylates, polyester acrylates, and diluted polyester selections that are optimized to provide the same outstanding performance as conventional analogues. The company has also identified several new chemistries that are either currently commercially available or in development as resin system replacements for standard BPS epoxy acrylates, according to De Wulf.

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Along with concerns about tin compounds and BPA, Rayle notes that there are regulations affecting the use of perchloroethylene in airplane manufacturing, and California's new Safer Consumer Products law (also known as the California Green Chemistry Initiative) will impact the use of numerous chemicals in that state. In addition to the ingredients used in coating formulations, another major concern for users of UV-cured coatings is the upcoming European legislation on mercury, including the mercury in the UV lamps used for curing. The revised Restriction of Hazardous Substances (RoHS) directive does not apply to fixed installations through 2016, so a large part of coating operations will be exempt at least until then, according to Harbourne. He does note that small lamps for nail varnishing (e.g., nail polish curing), will be subject to the requirements of the directive. After 2016, the automatic exemption for fixed equipment will no longer be in effect, and companies will need to apply for exemptions.

In Asia, China is the leading user of radiation curing technology, and the industry is being affected by the government's determination to clean up smog and reduce VOC emissions from manufacturers. In September 2013, the State Council released the Air Pollution Prevention and Treatment Action Plan to guide air pollution treatment in the coming years. One of the 10 measures in this policy deals specifically with VOC regulations. "Local governments have already started to pursue local implementation, including the closure of coatings factories that do not meet standards. In response to these closures, the research and development teams of coatings companies are proactively researching UV and waterborne technologies with new vigor," notes Tara Strunk, Asia Pacific marketing manager for coatings & digital media with Grace.

Compliance with the Globally Harmonized System of Classification and Labeling Chemicals

(GHS) is also causing a lot of confusion, according to Sweetwood. "This regulation affects raw material suppliers, formulators, and customers. There are a large numbers of changes that need to be made, and nobody wants to make a mistake. In the end, it's not that different from what people have become used to with existing requirements, but a lot of time and energy is still being spent on compliance," he observes.

MEETING COST CONSTRAINTS

The global industry is also faced with continued pricing pressures, particularly in more mature markets, such as wood coatings. Customers are, as a result, looking for lower-cost options in materials, according to Rayle. In fact, De Wulf believes that as overall cost of ownership becomes an increasing constraint, the market is expecting the development of new products that meet but do not exceed new requirements. "In some cases, price is the main driver, and customers are accepting lower performance at lower price as long as the product is sufficiently fit for use," he states. For these customers, Allnex introduced a robust tin- and VOC-free radiation-curable polyurethane dispersion that offers a combination of versatility, stability, and cost-effective performance for formulators of water-based UV-curable wood coatings who are looking to differentiate and customize their products, according to De Wulf. Equipment purchases were also lower in 2013 after picking up during the initial recovery period following the recession, largely due to the current uncertainty in the markets, according to Harbourne. "Many buyers are putting off the purchase of new equipment because they are too unsure of the future," he notes. On the flip side, because coating manufacturers are holding on to existing radiation-cured coating equipment for longer periods, there has been an increase in demand for spare parts.

AREAS OF INNOVATION

Fortunately, despite these numerous challenges, the radiation-cured coatings market remains in modest growth mode. Sweetwood notes that some companies are bringing manufacturing lines back to the United States from abroad, and many of these firms are attracted to radiation curing because of the efficiency, productivity, and compliance benefits it provides. However, the need for innovation in radiation curing remains very high, according to Marc Roelands, a global business director with DSM. "Market and regulatory drivers, combined with increased industry awareness regarding safety and health concerns, continue to force the industry to develop innovative new solutions that can satisfy global market needs in terms of both product and environmental, health, and safety performance," he asserts.

The top areas of innovation include waterborne UV-cured coatings, LED (light emitting diode) curing, direct-to-metal applications, filmic substrates, field-applied coatings, improving adhesion to multiple substrates, increasing photoresponse times for faster line speeds, and the use of UV with thermal curing for composite substrates.

With respect to waterborne radiation-cured coatings, some coating manufacturers are concentrating on waterborne UV polyurethane dispersions to address market needs for applications in the industrial coatings marketplace. Resin suppliers such as Bayer MaterialScience are working with lamp manufacturers, coatings formulators, and end users to understand and harness the power of the technology for commercial applications, according to Raymond Stewart, a senior scientist with Bayer MaterialScience. "Water-based systems are seeing increasing use in a variety of applications, including direct-to-metal coatings and field-applied flooring coatings," he says.

Direct-to metal consumer product applications, in fact, comprise a growing end use segment for radiation-cured coatings. Demand appears to be at its highest in emerging markets, such as China and Brazil, and is driven by a desire to cut manufacturing costs, improve overall manufacturing process efficiencies, and lower VOCs in compliance with local air quality regulations, according to De Wulf. He notes that the challenges are adhesion and overall cost of ownership against existing organic solvent and waterborne coating technologies. Sartomer has been working with customers to develop radiation-curable products for metal substrates and anticipates that there will be significant future interest for this application, according to Rayle.

Meanwhile, although the initial euphoria about field-applied radiation-cured coatings has subsided,

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this market also holds great potential, according to Sweetwood. "Companies seem to have oversimplified this market because it seems straightforward, when in actuality field-applied coatings require precision, extensive process know-how, testing, etc. I do believe that it will eventually live up to its potential, though, most likely first in Europe, where the most progress has been made to date," he explains. De Wulf adds that Allnex continues to support efforts to make this technology mainstream through new product introductions, general market education, specific customer support, and co-supplier interactions. Two new products from Allnex use technology that indicates exposure to UV via a color change, thereby assisting the contractor in the accurate application and curing of the floor coating.

Another market segment within the packaging industry that is providing potential growth for radiation-cured coatings is flexible plastics, or filmic substrates. These materials are attractive because they allow for packaging in all types of shapes, are lighter in weight than rigid materials, and provide better protection if they are multi-walled, according to De Wulf. "Coatings are often applied to filmic substrates in order to homogenize the surface for better printability and can serve as barrier protection with a decorative function," he notes.

There are hurdles to the use of radiation-cured coatings for plastic packaging, however. De Wulf points out that as the demand for and usage of virgin and recycled plastics in consumer product packaging increases, the demand for low migration profile resins with robust adhesion to filmic and rigid substrates also increases. "Finding raw material building blocks and resin systems that promote adhesion to nonporous plastics while complying with regulatory requirements for indirect food contact is a constant challenge," he observes. Roelands adds that ensuring proper adhesion to a variety of substrates is also an issue and requires technological advancements, some of which have been achieved and are already driving the growing use of radiation-curable coatings on metals and plastics. Allnex recently launched several oligomeric systems that promote adhesion to plastic for flexo and litho applications with supporting toxicity and migration test data.

With UV-cured coatings for glass substrates, the use of radiation cured coatings to color glass beer bottles is increasing in popularity, according to Brown. "This approach enables beverage bottlers to produce colored bottles without having to incorporate any pigment in the glass, which makes it much easier to recycle the glass," he explains. Brown has also seen growing interest in more functional radiation-cured coatings. Roelands agrees that the ability to deliver radiation-cured coatings with differential "feel" (haptics) is of growing importance, as is the need to provide continuous improvements in curing speed to maximize productivity of industry coating lines.

Grace, meanwhile, is focused on developing additives that can be used to achieve deep matte effects (60° gloss below 5 units) in radiation-curing systems while maintaining optimum properties in the dry coating. "With current systems, low gloss levels can sometimes be reached, but this often requires high addition levels of the matting agent and frequently leads to fewer unwanted effects such as loss in film clarity, poor surface quality, low stain and chemical resistance." Kent says. "Technology advances to address these matting effects will almost certainly involve a step-out from current particulate product technologies and a move towards alternative mechanisms for creating the micro-roughness required for low-gloss surface coatings," he adds. In the meantime, Grace is constantly developing functional silica matting additives that are designed to perform with changing raw materials and formulations. "We help formulators to select the optimum grade for a new formulation and conduct practical trials, and generally the process is more complex for VOC-free radiation-cured coating systems and formulations

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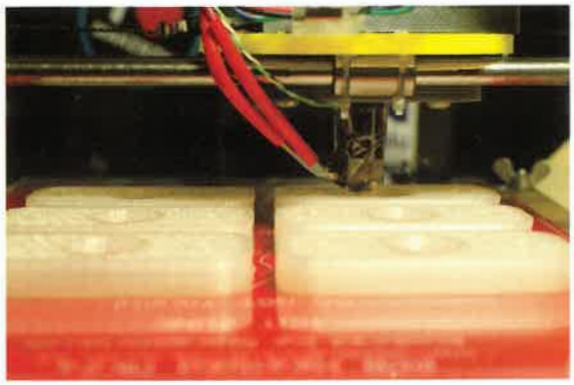
designed for roller coating application, where high concentrations of matting agents lead to high viscosities and problems with aeration and foam release. To address this challenge, new materials are currently under development with the goal of coupling high matting efficiency with low thickening and fast de-aeration properties," notes Kent.



One interesting application to note is the use of radiation curing in 3D printing applications. Many companies, and particularly start-up firms, have chosen to focus on the emerging 3D printing market, according to Sweetwood. "It's clearly an exciting space and there is no lack of media coverage. In a way, such exposure is good for traditional radiation-cured coatings formulators," he notes.

DEVELOPMENTS IN LED CURING

The area with the most active development efforts appears to be LED curing, however, and there are vigorous efforts to develop UV LED technology to replace Hg lamps, according to Hasan. UV LED lamps are becoming more popular due to lower operating costs, lack of ozone generation, and longer wavelength emission spectra versus standard mercury lamps. In addition, UV LED lamps are considered to be more environmentally friendly and can be used for curing UV-sensitive materials. They also result in less heat development in the substrate, so heat-sensitive materials can be coated using LED lamps. The longer lifetimes of LED bulbs and the fact that LED lamps do not contain mercury are further advantages of the technology, particularly considering the European RoHS Directive discussed previously. "We continue to see a growing interest in LED curing, particularly with customers that are new to radiation curing asking about this type of coating system, and the ink jet/graphics art market has widely adopted the technology," says Sweetwood. "It's fair to say that the LED companies are doing a terrific job of marketing LED curing, and we recently completed some in house testing that confirmed that the technology has continued to improve," he continues.

UV LED technology, according to Harbourne, has indeed moved from the introduction phase, through which it struggled over the last three to four years, into the adoption phase. "Our customers are looking to evaluate UV-LED systems now, so Heraeus Fusion UV has introduced a UV LED-curing platform in response to this market need," he says.

There are still issues to be addressed with LED curing, however. Both the LED lamps and formulations for LED curing are quite expensive, according to Hasan, although prices are coming down with time. There is also a lack of short wavelength emissions from LED lamps, which can result in oxygen inhibition that leads to reduced coating properties or uncured, tacky surfaces, according to De Wulf. "Developing short wave (UVC range) LED systems with enough power is therefore a key goal," Hasan notes. Allied also runs into challenges with 3D applications where it is not possible to get the LED lamp close enough to the part or to maintain the proper distance.

In addition, the transition to LED lamps is influencing coatings formulations. First, as long as LED lamps cannot achieve the short wavelengths required for good surface cure (lower energy transferred to the coating), using more reactive monomers (bifunctional as opposed to monofunctional) will be required, which generally translates to increased cost of the coating formula, according to Strunk. She also notes that the specific UV wavelengths emitted require careful selection of more expensive photoinitiators that are able to absorb at these wavelengths and thus ensure good cure. "For these reasons," adds Rayle, "suppliers need to understand and prepare for the trend toward LED curing." In 2014, Allnex is launching a unique co-resin for low-intensity UV-curing formulations that enable easy-to-formulate coatings that mitigate oxygen inhibition, according to De Wulf. "When used as a co-resin, this new resin transforms UV-curable formulations into UV LED-curable formulations that provide tack-free surfaces with performance similar to coatings cured with higher-intensity UV light. Based on new chemistries that maximize cure response, this UV LED transformer has low viscosity, low color, and good stability," he states.

INVESTING IN THE FUTURE OF RADIATION CURING

The complexity of radiation curing in general must continually be addressed, according to Harbourne. "This technology appears to be simple on the surface, but is in fact complicated, and a greater understanding of the curing process is needed in order to enable the development of

new solutions," he asserts. Achieving that goal will require collaboration across the value chain, says Roelands. "It is clear that resin and coating manufacturers alone cannot drive the required technology advances. Radiation-curing coating equipment and lamp manufacturers will also play a crucial role in responding to the key trends driving the market," he states. "DSM does believe that through such collaborations, the industry will be able to deliver the technological advances required to continue to widen the use of radiation-cured coatings and ensure strong global growth in the years to come," he continues. Sweetwood agrees: "We have always believed that choosing the right partners is a critical piece of our business, and includes raw material suppliers, equipment integrators, and even (sometimes) customers. We are so much better when we team with companies that allow us to stick to our strengths and at the same time by leveraging a partner's expertise. I think it's one of the keys to doing business in this era."

To extend its portfolio range and in response to various market trends, Allnex acquired the nonwaterborne Desmolux® (a Bayer trademark) radiation-curing resins business of Bayer MaterialScience in 2013 and moved its Americas headquarters to state-of-the-art facilities in Alpharetta, GA, with a significantly larger radcure applications lab and enhanced capability for joint customer and co-supplier development projects in 2014.

"DSM also has a clear commitment to strengthen the technology for radiation-curable coatings, because it is one of the key sustainable coating technologies, next to water- and powder-based technologies," according to Roelands. To this end, the company has invested in a new facility for the production of a variety of classes of radiation-curable resins and monomers that is operated under its DSM-AGI joint venture. DSM is also developing new easy-to-matte coatings, formulations that provide steel wool resistancy, those that are suitable for vacuum metallization, waterborne UV systems, and field-applied radiation-curable coatings.

Sartomer believes that the future is bright for radiation-cured coatings. "This technology is still in the early stages of adoption for advanced coatings, and we expect continued growth, especially for sustainable chemistries that provide more environmentally friendly solutions at a cost equal to or near that of traditional solutions," says Rayle. CT