Going Beyond Low VOCs with Biobased Raw Materials

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The paint and coatings industry has made great strides in significantly reducing the content of volatile organic compounds (VOCs) in most formulated products sold today. However, in response to growing pressures from various end-user groups, all members of the coatings value chain are focused more than ever on sustainability and improvement of every aspect of environmental performance, from reducing water and energy consumption and lowering emissions from production processes, to using more environmentally friendly raw materials, eliminating toxicity, and increasing functionality. In the latter category, renewable feedstocks are receiving significant attention as an important mechanism for potentially achieving a better environmental profile while also maintaining or enhancing product performance. Questions must still be addressed, however, such as how to obtain reliable supplies of natural materials with consistent quality that result in a true and measurable reduction of environmental impacts—and do so at a cost that is competitive with that of existing materials. As growing numbers of both biobased versions of existing raw materials and alternative renewable feedstocks become commercially available, more suppliers of key ingredients for formulated paints and coatings manufacturers are developing new products and evaluating their potential.

Interest in biobased raw materials stems from several sources. Some users support their sustainability claims by employing coatings based on renewable raw materials in their products, according to Brad Fogg, market segment manager, industrial coatings for agriculture, construction, and earth moving (ACE) in BASF's dispersions and pigments business. For example, Timothy G. Staub, global vice president of business development with Green Biologics Ltd., notes that biobased ingredients are seen as providing lower carbon footprints and improved life cycle performance combined with higher purity, because they often lack the impurities intrinsic to petrochemicals. "We strongly believe that sustainable products with an improved carbon footprint as alternatives to standard products will be the preferred options," states Thomas Metz, head of global technical marketing for Clariant's coating business. "From this point of view, the development of products based on renewable raw materials is an important part of our focus for the future," he continues.

The coatings industry, in fact, is long familiar with biobased raw materials; many early coating systems were based on natural oils, rosins, waxes, gums, polysaccharides, and other materials, and many of these ingredients are still used today. This experience gives credence to the notion that biobased raw materials are suitable for use in high performance paints and coatings and can help companies reach sustainability goals. Initially, notes Eric Dumain, global business development manager for Arkema, these materials were used because they were widely available before the petrochemical industry was fully established. "Now we are coming full circle, returning to biobased materials as a major feedstock. Raw material suppliers recognize that oil and other extracted materials are finite resources. Long-term business survival dictates the need to find alternatives that can be produced indefinitely using finite land resources, hence the attractiveness of biobased or biorenewable materials," he observes.

Offering Increased Functionality

Although many biobased materials are produced as drop-in replacements for existing chemicals derived from petrochemical feedstocks, several novel materials are being developed or have already been introduced to the market that offer new functionality that can enhance desired performance properties, or even impart new properties to paints and coatings. These materials are of interest to coating formulators seeking to differentiate their products through increased performance, notes Célene DiFrancia, senior vice president of engineering polymers and coatings for Elevance Renewable Sciences. Also, the diversity of biomass around the world should provide access to a larger and more robust palette of new materials for greater innovation, according to Dumain. One such new material is octadecanedioic acid, which is now commercially produced by Elevance from natural oils via proprietary metathesis technology. The diacid is being explored as a biobased raw material for new additives and resin systems for paints and coatings with improved hydrophobicity, flexibility, and chemical resistance and as a zero/low-VOC coalescent for waterborne coatings.

Other examples of functional biobased additives include enzymes, antimicrobial peptides, metal binding proteins/peptides, antibodies, protein/lipid receptors, protein ion channels, and nucleic acids, which are the result of new stabilization technologies developed by companies like Reactive Surfaces. "These materials can now be incorporated into paints and coatings and impart dynamic functionality that has not been possible before," states Steve McDaniel, chief technology officer of Reactive Surfaces. The company has benefited from the expanding interest in biobased coatings with unique functionalities and now, following the recent startup of a new manufacturing facility, provides commercial quantities of enzyme-based additives for self-cleaning and self-decontaminating coatings, as well as antifingerprint and antichemical warfare coatings. Reactive Surfaces also launched its first functional coating in 2015, a self-cleaning thin film for plastic and glass screen protectors for electronic touch screens. These dynamically functional films contain the enzyme lipase, which continually breaks down grease, fats, and oils, such as those found in fingerprints, in order to keep such electronic surfaces smudge-free. McDaniel also expects that commercial quantities of its first antimicrobial peptide-based additives will be available by the end of 2015.

As with any other coating raw materials, however, biobased ingredients must offer a compelling value proposition against existing products on the market in order to experience strong demand. "Unless regulations specify the use of biobased, or more sustainable ingredients in general, the performance must match existing technologies," says Fogg. Adds Dumain: "As is the case with broadening the acceptance of other 'green' concepts, short-term competitive pressures drive expectations of equivalency in mission-critical supply chain parameters, including competitive pricing, performance, short lead time availability, secondary sourcing to avoid supply disruptions, and global material consistency (same properties regardless of sourcing region)." In the field of pigments, for example, Metz notes that the both the coloristic properties and durability of any biobased alternatives must meet performance expectations over the full life cycles of applied coatings.

Overcoming Misconceptions

Manufacturers are faced with misconceptions about biobased materials. "Some people still believe that biobased means higher cost and lower performance," says Scott Cooley, North American coatings technology director with Reichhold. The company's response has been to develop low-

VOC, vegetable oil-based waterborne alkyd latex, oil-modified urethane, and epoxy ester resins that meet current customer needs. Alberdingk Boley has also expanded its technology to include low-VOC, water-based polyurethane dispersions (PUDs) and solvent-free polyols for crosslinked urethane systems using biobased building blocks. Arkema offers two technically distinct water-based approaches: biobased alkyd emulsion resins for high gloss architectural and industrial applications that are compatible with most other coating resin chemistries and can be formulated to < 50 g/l, and a water-based acrylic modified alkyd dispersion that is produced using surfactant-free technology that provides improved corrosion resistance, according to Dumain.

Meanwhile, BASF offers a range of natural oil-based, solvent-free polyols designed for use in two-component PU coatings and adhesives that have low viscosity combined with good hydrophobicity and hydrolysis and chemical and UV resistance, according to Fogg. Croda, on the other hand, offers biobased building blocks to resin manufacturers for the synthesis and modification of coating binders. Use of its renewable dimer-based polyester polyols, dimer acids and diols, 36-carbon aliphatic primary diamines, azelaic acids, and fatty acid amides can lead to improved coating properties compared to conventional petrochemical-derived compounds, including moisture resistance, adhesion to low energy substrates, and flexibility in various resin systems, including but not limited to polyurethanes, epoxies, alkyds, and acrylics, according to Bryan Danek, Croda's sales director for North America.

Introducing Biobased Alternatives to the Marketplace

It can be challenging to get new biobased materials with unique functionality introduced to the market. Not only must companies invest in coating formulation development, but the adoption times can also be longer. In particular, it can be difficult to achieve any real market penetration for new biobased products being introduced to the market simply because they are not yet produced at commercial scale, according to Yasmin Sayed-Sweet, vice president of sales and marketing for Alberdingk Boley. Customer concerns about the ability of suppliers of biobased raw materials to align supply quantities with market adoption is also an issue, according to Rich Weber, global business leader for NatureWorks Performance Chemicals. Resistance to change, particularly if even the slightest alterations to an established process are required, also creates a barrier to the adoption of novel biobased materials, according to McDaniel. Reactive Surfaces has also had to overcome unfamiliarity with the use of materials like enzymes, peptides, and other functional biological molecules in paints and coatings and the misperception that biological substances are typically unstable and difficult to work with. "We appear to have crossed over a significant barrier with the commercial introduction of self-cleaning coatings in the electronics and automotive industries," he notes.

On the other hand, Weber notes that biobased raw materials that provide improved functionality, improved economics, and decreased negative impacts will ultimately be the most successful. "The three-way intersection of more stable pricing, improved functionality, and meeting the requirements for green chemistry are attracting strong interest from customers that need to provide more sustainable products as part of their brand definition," he adds.

Biobased drop-in replacements carry their own challenges, too, according to Alistair Reid, manager of innovation, partnerships, and biobased materials with AkzoNobel. It is necessary to confirm that these materials are fit for their purpose, and that different sources of the raw materials do not introduce different impurities and sources of variation. For biobased pigment development, the biggest challenge is the very limited availability of biobased aromatic compounds that are essential for the synthesis of many organic pigment types, such as azo compounds, according to Metz. "To have biobased building blocks available at a reasonable price and in a reliable quality will be the key challenge for the future development of biobased organic pigments," he asserts.

Reid also notes that work needs to be done to establish logistics systems for economically and sustainably moving the various types of biomass that have been proposed as feedstocks (agricultural and forestry byproducts, cover crops, food processing, municipal and water wastes, etc.), which are dispersed, low density, or otherwise difficult to obtain in quantity, where they need to be for processing. On the flip side, DiFrancia points out that biobased feedstocks have the advantage of being independent of volatile oil prices, a situation that reduces supply chain risk.

It is also important to remember that raw materials derived from renewable carbon-containing resources reduce the amount of new carbon released, thereby enabling better management of the carbon cycle, according to Cooley. He does note, however, that the benefit decreases when moving through the value chain to final formulated paints and coatings. In addition, to maximize the advantages of biobased raw materials, it is essential that all members in the paint and coatings value chain work to make sure all components of formulated products are more sustainable.

Equally important is the need to understand that biobased raw materials do not necessarily lead to more sustainable paints and coatings, according to Reid. "It is necessary to consider all of the inputs and consequences of land use throughout the life cycle of a biobased material, such as the fuel and fertilizer used to raise crops converted to renewable chemicals," he says. "It is also as important to consider each biobased raw material individually, and evaluate not only the inputs required to produce the renewable material (e.g. crops or otherwise), but also the impact of any downstream chemical processes and whether biodegradability is an option at the end of product life," adds Bret Chisholm, director of the Combinatorial Materials Research Laboratory at North Dakota State University's Center for Nanoscale Science and Engineering.

AkzoNobel uses life cycle analysis (LCA) to compare alternatives for all of its products, whether formulated with biobased materials or ingredients derived from petrochemicals, and only sources environmental impact vs. incumbent raw materials. Staub would like to see a standardized accounting procedure for calculating and reporting the benefits of biobased and other sustainable technologies, as well as a direct link between marketing claims and biobased product content, which can be determined using C-14 analysis procedures like those used for the BioPreferred program run by the U.S. Department of Agriculture.

Despite the many challenges that face the adoption of biobased raw materials in paints and coatings, the general consensus is that in the short term, products with assured availability and reasonable cost/performance ratios will penetrate the coating supply chain. Once these initial users are convinced that newer biobased materials are suitable for use in paints and coatings, additional market demand will be created, according to

Sayed-Sweet. The most successful products, according to DiFrancia, will be those that provide a complete package of desirable features, including performance improvement, regulatory compliance, an attractive environmental profile, and an acceptable cost.

In addition to Elevance's commercially available C18 diacid, biosuccinic acid is being offered in larger quantities by several companies, such as Myriant, BioAmber, Corbion/BASF, and Reverdia (a DSM/Roquette joint venture), as a raw material for coating resins. BioAmber and Ecoat are evaluating pentaerythritol alkyd resins containing BioAmber's biobased succinic acid and have found that SA can replace between 20 and 35% of the PA with retention of performance. Myriant reports that it has produced for a line of developmental 100% biobased polyester polyols for customer evaluation using its bio-SAs that it claims are comparable in performance to adipic acid polyols. Clariant, meanwhile, is the first pigment supplier, according to Metz, to manufacture quinacridone pigments based on renewable raw materials—in particular, biosuccinic acid, which it is using to produce its Hostaperm Pink E pigment. "Up to 35% of the molecular structure of this quinacridone pigment can now be derived from renewable materials," he says.

Companies that produce lactide-based polymers are also targeting paint and coatings applications. NatureWorks recently introduced a high purity, polymer-grade lactide rich in meso-lactide for the production of amorphous copolymers, adhesives, coatings, emulsions, printing toners, and surfactants. According to Weber, the product has a lower melting point and is more susceptible to ring-opening than racemic and pure L- and D-lactide for easier processing with lower energy consumption. Meso-lactide also enables CASE (coating, adhesive, sealant, and elastomer) customers to tune specific physical properties, such as melt viscosity and glass transition temperature (Tg), to their target applications. The company also recently expanded lactide production at its Blair, NE facility from 140,000 to 150,000 tonnes per year and is in the engineering stage for a second manufacturing facility in Southeast Asia.

In fact, several companies are working toward the production of biobased versions of key paint and coatings raw materials. Although BASF recently elected to exit its R&D collaboration with Novozymes and Cargill to develop a biobased process for 3-hydroxypropionic (3-HP) and acrylic acid, the latter two companies are proceeding with the project and hope to find a new commercialization partner. Global Bioenergies recently achieved the first milestone for its BioMA+ project for the production of renewable methacrylic acid, which is financed by the French "Investissements d'Avenir" state program. Myriant is also targeting acrylic acid, as well as lactic acid, muconic acid, and fumaric acid. Solvents are not escaping attention, either. Green Biologics produces 100% biobased n-butanol and acetone via microbial fermentation process that are drop-in replacement solvents requiring minimal reformulation. Staub notes, however, that they are higher purity with very low water content and low odor compared to traditional solvents on the market. In addition, the biobutanol can be used to produce esters (with acrylic or acetic acid) that are greater than 55% biobased. A range of 100% biobased butyl esters derived from its biobased n-butanol and other biobased reagents, such as di-butyl succinate and butyl lactate, is also under development.

Research for the Future

Significant research on biobased coating raw materials is also under way in numerous academic laboratories. For instance, Chisholm has been doing a lot of work with novel polymers derived from plant oil-based vinyl ethers. "The technology provides tremendous versatility with respect to tailoring polymer properties for a specific coating application," he notes. Most recently, his group generated plant oil-based polymers that cure rapidly by auto-oxidation, but have cured film properties that are more like two-component epoxy-amine resin systems than alkyd resins.

At the University of Southern Mississippi (USM), the Thames-Rawlins Research Group has formulated zero-VOC, waterborne architectural coatings and low-VOC, waterborne Navy Haze Gray (NHG) coatings with resins prepared from SoyAA-1, which is derived from soybean oil. USM is also working closely with Reactive Surfaces to develop that company's growing line of biobased functional additives, including biobased molecules that can repolymerize within a resin matrix after depolymerization has occurred. Antibacterial soybean-oil-based cationic polyurethane (PU) coatings with incorporated ammonium groups and coatings formulated with plant-based proteins, including biodegradable barrier coatings for food packaging and hay bales, have also been developed by researchers at Iowa State University (ISU).