The Natural Approach to Coatings

by Cynthia Challener
JCT CoatingsTech
Contributing Writer

Consumers in recent years have begun to demand more "natural" products. Store shelves have exploded with foods, dietary supplements, nutraceuticals, and personal care products containing natural ingredients. In the auto industry, cars painted in more natural, earthy tones are expected to take a greater share of the market in the next few years. Demand for natural shades in home decorating is increasing as well. Not surprisingly, there is also a growing interest in paint products manufactured with natural raw materials.

Of course, the first paints developed by the modern coatings industry were based on the natural raw material linseed oil and its derivatives. Waterborne coatings containing synthetic resins began gaining in popularity some decades ago and continue to receive attention as they are more "environmentally friendly" than the alternative, solventborne coatings. However, they are not as "green" as possible. To be sure, some specialty furniture coatings today are based on tung oil, and shellac is a natural material that continues to see use, but using a natural material or materials does not necessarily make a product green or environmentally friendly if oil and solvents are still used in the formulation process.

"The green movement is gaining significant momentum right now in the United States," asserts R. Scott Dautel, global new product leader for Coatings Additives with the Aqualon Division of Hercules Incorporated. "Of course, the natural product movement is an offshoot of broader environmental concern. Consumers want products that are perceived to be more environmentally friendly." Organizations like Green Seal, the Green Building Council (both in the U.S. and Canada), the Master Painters Institute, and the Greenguard Environmental Institute are helping to create that momentum by establishing standards for green building practices.

Green Seal began certifying a wide range of products and services after establishing science-based environmental leadership standards. There are three standards for paints and coatings -for anticorrosive paints, general paints, and recycled paints—that set levels for volatile organic compounds (VOCs), aromatic compounds, and other toxic substances. Currently, the organization is revising and combining the first two standards.

The Leadership in Energy and Environmental Design (LEED®) Green Building Rating System™ was developed by the U.S. Green Building Council (USGBC) as a "national consensus-based, market-driven building rating system designed to accelerate the development and implementation of green building practices," according to the organization. Points are achieved through the use of qualified products including paints and coatings (generally those that are Green Seal approved).

The MPI Green Performance Standard and "green" Approved Products List from the Master Painters Institute (MPI) consider both environmental issues (largely VOCs) and performance. The Greenguard Environmental Institute has an independent scientific board that certifies materials for interior use based on standards set for VOCs, formaldehyde, and other ingredients. Credit for the LEED rating can also be obtained for Greenguard certified materials.

The U.S. government and local officials, too, have taken several actions. The most notable, of course, are the continued reductions in allowable VOC levels passed by regional, state, and local agencies such as California's South Coast Air Quality Management District (SCAQMD). The U.S. House of Representatives also passed the Green Chemistry Research and Development Act of 2005 (H.R. 1215), which calls for various agencies to work together to enhance funding and coordination of green chemistry R&D, education, and training. The bill still awaits a vote by the U.S. Senate.

The Environmental Protection Agency's (EPA) Green Chemistry Program supports fundamental research in the areas of environmentally benign chemistry as well as a variety of educational initiatives, international activities, conferences and meetings, and development tools through voluntary partnerships with academia, industry, and other governmental and non-governmental agencies and organizations. Its Presidential Green Chemistry Challenge Awards recognize green products that have been successfully commercialized by industry.

Indoor air quality is another area of concern. "Wherever possible, architects, homebuilders, applicators, and consumers are preparing their indoor spaces by thinking about the source of materials and how those materials will affect the health of the people who will be using the space," says Gregory Hebert, business manager for Vermont Natural Coatings. Because coatings are a first-line element that people come in contact with, they too need to be as functional and healthy as any other material. "As the marketplace learns more about the benefits of natural coatings, demand grows."

Many natural coatings such as milk paints have no VOCs and do not outgas; therefore there is no odor issue and no potential for causing severe health reactions in people with sensitivities, according to Anne Thibeau, president and general manager of The Old Fashioned Milk Paint Co., Inc.

From the coating manufacturer's perspective, resins and additives derived from natural raw materials can help make it possible for their products to comply with the increasingly restrictive regulatory requirements for VOCs and low odor as well as meet the green building standards of the various organizations mentioned.

There is another, significant driver for the use of natural raw materials that does not, however, relate to consumer demand for green or environmentally friendly products. This driver relates to the basic market need to manufacture products with high performance at the lowest possible cost.

As crude oil prices continue to rise, the cost of naturally derived alternative raw materials has become competitive with petrochemical-based feedstocks. "Economics is now becoming a driver for switching to natural raw materials," notes Michael Hoppe, NAFTA market manager for Cognis Corporation. "Performance of course is always a key issue, and the cost/performance benefit must be right." Until recently, even though natural raw materials were recognized as offering some performance advantages, the price for these ingredients was prohibitive.

The use of natural products such as soy oil reduces the formulator's dependence upon petrochemical-based raw materials, according to Lee Orr, commercialization manager for the United Soybean Board. "In addition, soy and other natural materials have an established history of a more stable price structure because they are bio-renewable products," he adds. Soy oils are environmentally friendly and often reduce the level of VOCs in coatings and inks.

The fact that these natural raw materials are derived from renewable resources has become an important issue. "There is a growing awareness of the limited nature of our supply of petrochemical-based materials," explains Hoppe. Global warming and other political issues come in to play as well. "With natural raw materials, the CO_2 balance is zero," comments Cardolite Corporation's global marketing manager, Jean-Luc Dallons.

Novel chemistry is an added benefit as well. "Energy based on oil can be replaced by wind, sun, tide, or nuclear energies. That is not the case for organic chemicals that need carbon structures. Oil can only be re-

placed by natural renewable organic raw materials, and natural raw materials can have a structure that is very difficult, even impossible, to synthesize by man," says Dallons. The result is access to novel compounds that can have interesting and different properties compared to known synthetic materials. The potential is therefore limitless for development of new products. "We believe that natural coatings have tremendous opportunities in nearly any application. What is thought to be impossible today will become commonplace just years ahead," states Kevin L. Palmer, chief executive officer of Palmer International, Inc.

NATURAL COMPONENTS

Milk paints are one of the oldest types of paints used in the world and as such are based on all natural materials. Casein, the main protein in the milk of mammals, serves as the binder in milk paints. According to Robert E. Ball, product manager of the Protein Polymer Group at American Casein Company (AMCO), Cro-Magnon people mixed casein with wood ash to create the paints used in cave art found across Europe. Ancient Hebrews whitewashed their houses with paint based on casein. Woodworkers from ancient times through the Middle Ages used casein-based binder systems.

"Today, casein continues to be used in many industrial applications including label adhesives, paint, paper coating and sizing, latex emulsion, cement and lime mortars and grouts, and other applications requiring protective colloids or binders," he states. AMCO has been supplying casein protein polymers for technical applications since 1956 and specializes in casein protein polymers and their unique functional properties.

Casein is made up of many different amino acids. It contains cationic, anionic, nonionic, and nonpolar groups and is acidic yet possesses a high buffering capacity. It forms soluble salts with alkalies and chelates with various metals that impart water resistance to a formula. Casein protein polymers are also very reactive with various organic reagents such as formaldehyde, acid anhydrides, acyl chlorides, and carbon disulfide.

Photo courtesy of the Old Fashioned Milk Paint Co.

With these characteristics, protein polymers used in coating applications tend to afford better workability as well as color refraction improvements. "Cross bridging" of the ingredients of a coating offers emulsification and stabilization advantages as well, according to Ball. Synergies can also be obtained with other natural ingredients such as natural earth pigments.

"The molecular weight and size of the proteins as well as their amphoteric nature make them naturals for dispersions and emulsions. Color enhancement (snap) seems to improve with protein as the binder," Ball says. "Improvements in workability ("butteryness"), especially in high-solids coatings formulations, have been well received. Low-solids (grout, paint, spray) applicators also appreciate the flow and heal properties these proteins bring to the formulation. Crosslinking and water resistance are also advantages due to the characteristics of the large polymer."

Applications for AMCO polymers include use for interior and exterior "green" coatings used for straw bale houses, and in stucco, lime paint, milk paint, plus natural hydraulic lime and cementitious wall and ceiling coatings. "High pH materials such as lime and cement are the perfect environments for the protein polymer to function in."

AMCO got involved in the coatings industry when working with developers of paints based on older technologies. "Since then, we have migrated to a variety of uses in the construction trades. We focus on flexibility with regard to product development and technical assistance with the purpose of strengthening our position in this growing market," Ball explains.

AMCO has achieved the best success in growing its sales through the use of physical demonstrations of the performance of coatings containing casein. "We have found that mere verbiage cannot compare with field demonstrations and work shops," Ball states. One challenge the company continues to face is competition from the dairy industry for milk, and price fluctuations associated with the world milk situation.

Despite these difficulties, AMCO is committed to expanding the use of casein in numerous markets. The company opened a new technical facility in Burlington, NJ in February 2007. "This facility is dedicated exclusively to the manufacture of protein polymers used in industrial applications and confirms our commitment to the business," says Ball.

The Old Fashioned Milk Paint Co. has been painting historic homes and antique furniture, preserving original items, and producing replicas of early furniture with milk paint coatings for many years. The company's formulations, according to Thibeau, are based

on casein, lime, earth pigments, and clays. "Our coatings provide deep, rich colors and a velvety appearance as well as afford an 'old world' look," she says. They are suitable for applications wherever synthetic paints can be used.

"Milk paints have been used since antiquity. The desire of consumers for more natural products that contain no harmful ingredients that can harm the health of those using the products or adversely affect the environment has led to a growing interest in these formulations beyond our initial uses in restoration and preservation, to include in more 'regular' painting applications," notes Thibeau.

Milk paints are biodegradable. Because they contain all-natural ingredients, they are ideally suited for users that are hypersensitive to commercial coatings. As a result, they are not only appropriate for residential applications, but are also useful for painting sensitive environments such as hospitals, nurseries, and nursing homes.

The challenge for the Old Fashioned Milk Paint Company is getting the word out about its products. "It is hard for us to compete against the large paint manufacturers and their well-funded marketing organizations. They introduce 'greener' products that still are not wholly natural coatings, and from our perspective do not really address the issues. However, because they have such extensive reach in the market, we find it difficult to be heard," says Thibeau.

Vermont Natural Coatings, established only in 2004, is working hard to get the message out about its new PolyWhey natural wood finishes. The binder in these formulations is whey protein, which is a by-product of cheese making.

The company currently offers two products, one for floors and one for furniture. The PolyWhey furniture finish is available in gloss, semi-gloss, and satin. Its floor finish is available in semi-gloss and satin.

The technology was initially developed by Dr. Ming Ruo Guo, an associate professor in the Department of Nutrition and Food Sciences at the University of Vermont. The water-based finishes have excellent scratch, chemical, and water resistance, dry quickly, and do not yellow. Compared to traditional finishes, the PolyWhey products offer increased density and viscosity, lower VOC content, a harder and more scratch resistant film, better water resistance, lower toxicity, and much lower production costs, states the company. Their flowability also makes them easy to apply with a brush, spray gun, or lambs wool.

For Hebert, being able to run a successful business that improves air quality was the primary driver behind starting Vermont Natural Coatings. The second driver was to contribute to the development of the local economy in Vermont and help build infrastructure. "Cheese making is a cornerstone of Vermont's agriculture and its economy, and placing a business that needs a by-product of this industry in Vermont's agricultural center made good business and environmental sense. We also believe that we have created a healthy alternative to oil-based wood finish," he emphasizes. Because the wood finishes will fit right into the state's clean-and-green image, they should help sell Vermont wood products, Guo says.

The challenge right now for Vermont Natural Coatings is to create confidence with professionals and build name awareness. "Each of the potential professional users of our coatings has established themselves based on their expertise with known tools and products. We want them to sample our product so they can see its performance and know that it is safer for them and their customer. To do that, we have to break through their loyalties to familiar products—no small challenge," states Hebert.

The company has used its initial capital to invest in a state-of-the-art production line and research and development activities. "Our goal is to produce premium products that leverage natural, renewable components. We strongly believe that the marketplace can demand great quality and be environmentally responsible."

In addition to milk-based products, plant-based oils and other plant products can serve as raw materials for several different components of paint and coating formulations. Soy-based products; cashew nutshell liquid; vegetable oils such as linseed oil, sunflower oil, palm kernel oil, coconut oil, and olive oil; and cellulose have all been used to produce resins, curing agents, surfactants, defoamers, and other key ingredients for the paint and coating industry.

Soy is used in water and alkyd-based stains and sealers, as well as alkyd paints and new water-based paints for architectural and industrial coatings. In construction products, soy is used in roof coatings, adhesives, and caulks. Soy methyl esters are used as an additive in paint removers, degreasers, graffiti removers, and as a low-VOC vehicle-binder in coatings.

Photo courtesy of Vermont Natural Coatings.

Many different types of soy are available for producing these various products. The type of soy oil to be used depends upon the requirements of the specific formulation. Unmodified soy oil is the most cost effective form, says Orr. "However, if you require a soy oil to be linked with a synthetic

SOYBEAN PLANTS

chemical such as an acrylate, an oxidized or epoxidized soy oil may be more suitable," he notes.

Cashew nutshell liquid (CNSL) is another plant-based raw material that can be used for producing raw materials for coatings. Cardolite and Palmer International are two leading players in this area.

According to Dallons, Cardolite became involved in the production of this interesting raw material because it is a unique molecule that provides several advantages compared to conventional oil-based products. The decision has been a good one for the company, which recently constructed a new plant in China.

Palmer International has been active in the business for more than 50 years, and is currently expanding its production capacity in Pennsylvania, with project completion expected in the first quarter of 2008. The company has also increased its R&D staff by 30%.

Cardolite has been manufacturing phenalkamine curing agents based on cardanol (3 n-pentadecadienyl phenol), which is derived from CNSL, for many years. Due to the mixed aliphatic/aromatic structure of this compound, CNSL based products are compatible with a wide variety of organic solvents and resins, according to Dallons.

Palmer International has developed new phenalkamine hardeners that are currently being tested by several potential customers. "CNSL offers the best of both worlds: the strength and resistance of an aromatic compound with the flexibility of an aliphatic compound," explains Palmer.

Hardeners for epoxy resins based on CNSL, which are replacements for polyamide or polyamide adducted curing agents, are fast curing at low temperatures. They provide outstanding chemical and water resistance and anticorrosion properties and are available for use with high-solids formulations. Extensive surface preparation is not required.

Palmer International also produces a proprietary line of resins based on CNSL that it markets under the trade name Cashewthane™. These "super" alkyds provide the best characteristics of alkyd chemistry combined with the best characteristics of polyurethane chemistry, according to Palmer. "We do not think of ourselves as competing with these technologies, but rather as complementing and enhancing them. Cashewthane is a universal choice in formulating high solids systems, allowing developers to reduce VOCs, improve adhesion to a myriad of substrates, and bolster water and chemical resistance," he notes.

As with other producers of natural raw materials for coatings, the challenge is to attract initial interest in the technology. There is more awareness about epoxy curing agents, which have been available for some time. For Palmer International, Cashewthane is a brand new technology, and so convincing companies to even test the product takes considerable effort. "We have found, though, that once companies do test our resins they tend to become customers," Palmer asserts.

Two companies that have focused on developing additives based on natural raw materials from plants include Cognis Corporation and Aqualon, a Business Unit of Hercules Incorporated.

At Cognis, vegetable oils are key raw materials for many different types of additives designed for the paint and coatings industry. Surfactants are derived from palm kernel and coconut oils via the production of fatty alcohols. Epoxy curing agents (polyamides) are the condensation product of polyamines with dimer fatty acids that are prepared from tall oil fatty acids or other vegetable oil fatty acids. Bio-based polyols for polyurethane production are polyfunctional alcohols based on, for example, castor oil, soybean oil, palm kernel oil, etc.

"When it comes to additives, performance is the basic criteria, and it applies to products made from natural or synthetic materials," says Hoppe. "Wherever possible, Cognis uses natural raw materials. Our broader picture, though, is to produce sustainable products. In many cases, the performance of natural materials is excellent, and we find that our products are incorporated into a broad spectrum of paint and coating formulations," he continues.

He notes that there is even a growing interest in natural raw materials from industrial coating producers, who are beginning to feel more regulatory pressures with regard to VOCs at the same time that prices for petrochemical-based ingredients are climbing steadily.

As a result, they are looking for alternatives that are environmentally friendly and cost effective.

Key existing products from Cognis include its Disponil® AFX series of surfactants that are readily biodegradable and represent a high performance alternative to the environmentally problematic alkylphenol ethoxylates (APEO) used in many industrial processes, according to Hoppe. The Federation of German Industries (BDI) has given Cognis' Disponil AFX range of surfactants its prestigious "BDI Umweltschutzpreis" environmental award in the "environmentally friendly products" category for making a significant contribution to the sustainable development of the European chemical industry and in recognition of the innovative design of the product.

Bio-based polyols marketed under the trade name Sovermol by Cognis are used in two-component urethane formulations in various coating applications such as flooring and where protection is critical. The natural oil-based polyols used in solvent-free coatings, according to Hoppe, offer improved hydrophobicity, low viscosity, high chemical stability, and a broad adhesion spectrum.

The company also has, or will soon be introducing, several new products based on renewable resources. Cognis Europe launched Foamaster 350, a mineral oil-free defoamer designed for coatings and adhesives applications that is VOC-free, fogging-free, and low odor. The triglycerides used to produce the product come from rice bran, soybean, rapeseed, or sunflower oils. Currently, Cognis NAFTA is screening this defoamer and other newly developed mineral oil-free products for potential introduction to the region. "We need to first ensure that they meet our regional requirements from a performance and cost target standpoint before going to the market place," Hoppe explains.

Cognis is also in the process of launching Loxanol EFC 200, an emission-free coalescent developed for low VOC coatings formulations that is produced from renewable raw materials. This second generation coalescent contains 1% VOC and a lighter color compared to the first generation product, Edenol EFC-100. "Optimization in raw material selection and processing is allowing us to provide Loxanol EFC 200 at a lower cost to the market place than Edenol EFC 100," Hoppe comments. In addition, when compared to traditional coalescents, the product provides low odor, gloss enhancement, improved scrub resistance, and rheology modifier efficiency. Loxanol EFC 200 should be introduced to the marketplace in the third quarter of 2007.

In response to the growing interest in its natural-based additives, Cognis has expanded surfactant capacity in Kankakee, IL, and ethoxylation capacity in Mauldin, SC. Research and development efforts are focusing on the potential for the use of esters derived from vegetable oils in paints and coatings, particularly as solvent replacements and in similar applications. In preparation for growing demand, the company is also expanding its capacity to handle these types of products as well.

Aqualon for many years has offered an extensive line of cellulose ethers to the paint and coating industry for use as rheology modifiers/thickeners. In general, these additives are used in architectural paints at a ~0.5–1% level in the formulation, according to Dautel. While synthetic products are also used, these natural materials dominate the market because of their consistent performance. Cellulosic ethers provide a preferred feel when the paint is stirred, and provide excellent color compatibility.

In addition to rheology modifiers, Aqualon also manufactures defoamers for the industry. Recently, the company extended this product line with its new Advantage™ AV Defoamer based on vegetable oil. The non-mineral oil-based product is designed to minimize foam-related problems while reducing environmental impact. "Advantage AV Defoamer reduces or eliminates both entrained and surface foam that can cause quality, production, and application issues," says Dautel, "and it can be added at varying stages of the process to achieve the desired result."

No matter what the specific materials are, or whether the formulations are based on ancient techniques or completely new technology, interest is growing in paints and coatings that contain natural ingredients. "It's an exciting time to be in the green product business," says Vermont Natural Coatings' Hebert. "Many more manufacturers, builders, designers, and consumers are learning about and choosing products that respect the environment."