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High Performance Polymers Derived from Biobased Resources

*By Jeffrey Danneman, Reichhold LLC 2, USA and
Jennifer Chu, Amec Foster Wheeler, USA*

Government agencies have fostered the change from fossil fuel-based coatings to those with a reduced environmental footprint. Foremost among these are AIM VOC limits that necessitate the use of water in place of hydrocarbon solvents. While a current coatings formulator will certainly consider these aspects in formulating new coatings, they will not be allowed to compromise performance. Using a combination of creative chemistry and advanced process technologies, vegetable oils have been incorporated into self-crosslinking polymers supplied in an aqueous continuous phase that allows the formulator to design the requisite dry film performance into coatings for multiple markets. Oil-modified polyurethane dispersions produce films with the exceptional abrasion and chemical resistance needed for gymnasium floor coatings.

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Alkyd latex polymers achieve a rich wet-look appearance on concrete/stone pavers and extended corrosion resistance over metal—all in shelf-stable formulations. Data comparing these technologies to their non-biobased counterparts are presented. Additionally, the status of these coatings through the U.S. Department of Agriculture's BioPreferred® Program is considered.

U.S. DEPARTMENT OF AGRICULTURE BIOPREFERRED® PROGRAM

The United States Congress established the foundation for the BioPreferred Program ("Program") in Title IX section 9002 of the Farm Security and Rural Investment Act of 2002, commonly known as the 2002 Farm Bill.^{1,2} The legislative history of section 9002 suggested that Congress had three main objectives: improve the demand for biobased products, spur rural economic development, and enhance the energy security of the United States by reducing its dependency on fossil fuels.³ Moreover, Congress expressed that its intent for including section 9002 was "to stimulate the production of new biobased products and to energize emerging markets for those products."⁴ Thus, Congress introduced the Program's two major initiatives: (1) procurement of biobased products by Federal agencies and their contractors and (2) the voluntary labeling of biobased products, now referred to as mandatory Federal purchasing and voluntary labeling, respectively.¹ Under the mandatory Federal purchasing initiative, Federal purchasers and contractors are required to buy biobased products that meet the criteria for certain product categories such as Interior Paints and Coatings—Latex and Waterborne Alkyd; Interior Paints and Coatings—Oil-based and Solvent-borne Alkyd; Multipurpose Lubricants; Roof Coatings; and Disposable Tableware. The Program was reauthorized and expanded by the Food, Conservation, and Energy Act of 2008 (2008 Farm Bill) and the Agricultural Act of 2014 (2014 Farm Bill).^{5,6}

The U.S. Department of Agriculture (USDA), the manager of the Program, oversees the Program's *Guidelines for Designating Biobased Products for Federal Procurement* as directed by law. Currently, the Program has identified 97 product categories for mandatory Federal purchasing, each with its own minimum biobased content requirement, and has awarded certifications for over 2,500 biobased products to display the USDA Certified Biobased Product label through the voluntary labeling initiative. Biobased products are derived from plants and other renewable agricultural, marine, and forestry materials and typically provide an alternative to conventional petroleum-derived products.² For the purposes of the Program, biobased products exclude food, animal feed, and motor vehicle fuels. Products that meet the requirements for one or both initiatives are shown in the BioPreferred Catalog, available on the Program's website (www.biopREFERRED.gov). Although users may not directly purchase products from the Catalog, sourcing information such as product details and the manufacturer or vendor's website is provided. To participate, manufacturers and vendors may visit the Program's website and select "How To Participate" in the left-hand navigation panel for instructions.

Mandatory Federal Purchasing

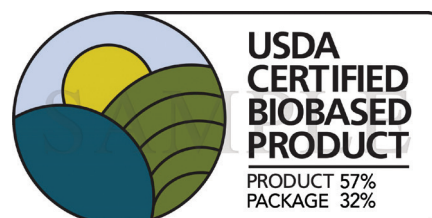
If a product's biobased content meets or exceeds the minimum biobased content requirement for one or more of the 97 product categories that have been identified for mandatory Federal purchasing, it is considered a "qualified biobased product."² Federal agencies and their contractors are required to purchase this product instead of the traditional, non-biobased alternative. To identify a product category for mandatory Federal purchasing, manufacturers and vendors provide the USDA with technical information for the products that comprise it. The USDA reviews this information to determine if the product category is appropriate to add to the Program's *Guidelines*. The USDA expects to identify product categories for intermediate

ingredients and feedstocks and complex assemblies in 2016.

Voluntary Labeling

While the mandatory Federal purchasing initiative focuses on Federal acquisition and support of biobased products, the voluntary labeling initiative aims to "promote the purchase of biobased products by commercial entities and the general public" through a customer-facing certification mark, the USDA Certified Biobased Product label.⁷ Manufacturers and vendors may apply for certification to display the label, which ensures consumers that the product or the product's packaging has been third-party tested and verified for biobased content through *ASTM D6866 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis*.² If, after testing through this method, a product meets or exceeds the minimum percent biobased content requirement for its particular product category, the product is considered a USDA Certified Biobased Product. If a product falls under a category that is not among one of the identified 97 product categories for mandatory Federal purchasing, the minimum percent biobased content requirement for that product is 25% by default. An example of the label is shown in *Figure 1*; the graphic is meant to represent the sun, soil and farm, and aquatic environments. In this example, the product is 57% biobased, its packaging is 32% biobased, and the "FP" indicates that it qualifies for mandatory Federal purchasing. All USDA Certified Biobased Products are subject to the USDA's periodic auditing activities.

FIGURE 1—Example of the USDA Certified Biobased Product label.



Using a combination of creative chemistry and advanced process technologies, vegetable oils have been incorporated into self-crosslinking polymers supplied in an aqueous continuous phase that allows the formulator to design the requisite dry film performance into coatings for multiple markets.

Achievements

After the Program was authorized by law, it received backing and attention from other branches of the U.S. Government. In particular, the Federal Acquisition Regulation, which directs all Federal purchasing, was updated in April 2012 to implement Farm Bill requirements for the procurement of biobased products.⁸ Additionally, on March 19, 2015, President Obama issued Executive Order (EO) 13693, "Planning for Federal Sustainability in the Next Decade."⁹ The EO establishes an annual target for the number of contracts to be awarded with BioPreferred and biobased criteria and the dollar value of these products to be delivered and reported under those contracts in the following fiscal year. Federal agencies are to ensure contractors submit timely annual reports of their BioPreferred and biobased purchases as well.

In June 2015, the Program submitted to Congress an in-depth economic impact study on the biobased products industry in the United States, *An Economic Impact Analysis of the U.S. Biobased Products Industry*.¹⁰ As mandated by the 2014 Farm Bill, this report was the first federally sponsored economic report of its kind for the biobased products industry. The report's key findings are that, in 2013, the U.S. biobased products industry contributed four million jobs, \$369 billion value added to the U.S. economy, and, for every one biobased products job, 1.64 more jobs were created in the United States.

Prior to the release of the June 2015 study, the Program also released *Why Biobased?*, a report that fuses the recent literature exploring the "opportunities in the emerging bioeconomy"¹¹ in October 2014. *Why Biobased?* also examines how "government policies and industry business-to-business sustainability programs are driving the biobased economy." The report states that "the biobased economy is, in fact, growing" and that it "offers great potential for increased job creation in numerous sectors across the U.S."¹²

Summary

The USDA BioPreferred Program plays an important role in expanding market opportunities for biobased products such as biobased paints and coatings, and the intermediates ingredients that are used to make them. Through the implementation of congressionally mandated purchasing requirements that harness the purchasing power of the U.S. Government and its voluntary, consumer-facing USDA Certified Biobased Product label, the Program continues to reduce our nation's reliance on petroleum, create new jobs, and increase the innovative use of renewable agricultural resources.

BIOBASED POLYMERS

In this article, the term "biobased" refers to products derived from biologic sources, mainly plants, and as such may be described as biorenewable. Today's polymer scientist has a number of biobased raw materials to utilize as new coating resins are conceived and developed. A recent notable addition to this list is succinic acid, augmenting age-old glycerin in polyester synthesis. Seed-stock derived fatty acids are now being modified to serve as pigment dispersants and surfactants, taking a lead from the historic use of soya lecithin for these purposes. Oil-seed products are among the oldest film-formers known, having been in use in forms similar to those available today since around the year 1400.¹³ That some of these have survived for many millennia is testament to the durability of these film-formers. For the past century, alkyds have taken advantage of the ambient cure capability of those seed oils containing sufficient quantities of unsaturated fatty acids to provide an autoxidizing crosslinked film and remain perhaps the most used biobased product in the coatings industry.

Regulations limiting the VOC of organic coatings have been implemented by various government entities over the last two decades and continue their trend to ever-lower numbers. For example, witness the recent changes in VOC limits for the Ozone Transport Commission (OTC) as well as several

Air Quality Management Districts in California and Utah.¹⁴ To enjoy the benefits of both biobased resources and self-crosslinking polymers, these regulations necessitated the development of water-dispersed polymers that satisfy the shelf-life requirements of the architectural and industrial maintenance markets. It is the performance of this class of polymers as compared to their fossil fuel-based (e.g., crude oil and natural gas, non-crosslinked counterparts) that is described in this article. The performance advantages are found across a multitude of coatings applications.

POLYURETHANE POLYMERS

Very few coatings are subject to the daily abuse of floor coatings. These coatings must withstand foot traffic, often with shoe soles embedded with sand, sliding chairs, endless spills of food and household chemicals, and the movement of the wood substrate due to changes in humidity. The toughness imparted to the film by inter-molecular hydrogen bonding between the urethane amine proton and carbonyl oxygen atom makes polyurethane chemistry ideally suited for this application.¹⁵

To obtain suitable performance in a water-dispersed form requires very specific chemical structures and processing of which a generic description is offered. First, a low molecular weight hydroxyl-terminated polymer, chosen from the class polyether, polyester, or polycarbonate, is mixed with dimethylol propionic acid (DMPA). A stoichiometric addition of an isocyanate (usually aliphatic) is then made to synthesize an isocyanate terminated "pre-polymer" that preserves the acid functionality of the DMPA. Processing is carried out in an aprotic, water-soluble solvent like methyl ethyl ketone (MEK) or n-methyl pyrrolidinone (NMP). This isocyanate terminated pre-polymer is added to a reaction mixture of water, a di-amine, and a tertiary amine. The di-amine will chain-extend the pre-polymer, reacting preferentially with the isocyanate groups; this reaction is an order of magnitude faster than the isocyanate-

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water reaction. It is the competing reaction with water that favors the use of aliphatic over aromatic isocyanates. Simultaneously, the tertiary amine will de-protonate the carboxylic acid on the DMPA, thus generating negative charges along the length of the newly chain-extended polymer. These negative charges provide the requisite polarity for dispersion in water; this class of polymers is commonly called polyurethane dispersion, or PUD. To reduce the VOC of the formulated coating made with this PUD to below 275 g/L as mandated by the South Coast Air Quality Management District (SCAQMD), the process solvent must be removed from some products via vacuum, which will add cost to the final product.

Incorporation of oxidizable fatty acids into this water-dispersed polymer utilizes an intermediate product. An oil such as soya or linseed is reacted with a polyhydric alcohol such as pentaerythritol via trans-esterification. Careful control of stoichiometry and process conditions yields a reaction mixture that is largely di-esters with two hydroxyl groups. This is introduced into the urethane synthesis with the hydroxyl end-capped polymer, DMPA and di-isocyanate where it is reacted into the backbone via the urethane reaction. The unsaturation on the fatty acid chains is nonreactive in this process and thus is preserved for oxidative cure in the applied film. These polymers are referred to as waterborne oil-modified urethanes (WBOMU). The lower solution viscosity, T_g , and film formation characteristics of this class allow for manufacture in reduced levels of solvent that produce formulated varnishes well below 275 g/L—thus precluding the need for the added expense of vacuum stripping.

For both classes of polymer, PUD and WBOMU, the molecular weight is significantly higher than the traditional aromatic isocyanate-based solventborne oil-modified urethane (OMU). As a result, the viscosity is much higher; thus, these products are offered to the market at solids ranging from 30–40% by weight so as to provide a reasonable viscosity. The composition is considerably higher in isocyanate content than traditional

TABLE 1—Performance of Biobased Polyurethanes for Flooring

POLYMER	WBOMU	PUD	PUD ACRYLIC	PUD ACRYLIC
BIOBASED CONTENT	50%	0%	0%	0%
COMPONENTS	1	1	2	1
MAR RESISTANCE	EXCELLENT	FAIR	EXCELLENT	POOR
STAIN, TOTAL	38	40	42	29
TABER ABRASION, MG LOST	71	24	105	112

solventborne OMU and, as noted, is largely based on aliphatic isocyanate. This results in a much higher cost. Consequently, many of the floor-coating products utilizing PUD technology are mixtures of PUD and (styrene) acrylic latex polymers. The (styrene) acrylic serves to reduce cost at the expense of performance. A number of these hybrid PUD/styrene-acrylic (PUD Acrylic) blended products are supplied as a two-component material; an aziridine is added on-site to enhance the performance, particularly the stain resistance, which was sacrificed for lower cost. To their detriment, aziridine chemistries often contain hazardous components. As demonstrated in *Table 1*, the self-crosslink of the WBOMU enjoys the ease and reduced toxicity of being one component and does not suffer performance deficiencies.

Three key performance attributes of floor coatings are mar resistance, stain resistance, and abrasion resistance. Mar resistance was assessed using several in-house methods and is reported subjectively. Measurement of stain resistance is a requirement set forth by the Maple Flooring Manufacturers Association (MFMA), and their protocol was used in this study.¹⁶ A total of nine reagents were used: water, 1% Spic and Span[®], Wesson[®] Oil, 50% ethanol, 70% isopropanol, Parson's Sudsy Ammonia[®], yellow mustard, Windex[®], and Formula 409[®]. Stain resistance for each reagent was scored on a 1 to 5 basis; with 5 equaling no effect and 1 equaling total film destruction. A maximum summed value of 45 is possible. Relative abrasion resistance is assessed with a Taber Abraser per ASTM D4060. The reader will understand that considerable variation is seen in data generated

by this instrument; to minimize testing variation, the results presented here were run side-by-side. Note that while the data presented are for in-house products, we recorded similar performance by category for commercial floor finishes.

The self-crosslink of the WBOMU provides excellent mar and stain resistance in a single component finish. Its wear properties are superior to standard solventborne OMU, which will typically lose 100+ mg of film in this test. While pure PUD has excellent abrasion resistance, the mar is not acceptable unless the film is cured with an aziridine (data not shown). The deleterious effects of adding an acrylic to the coating are obvious in the mar, stain, and wear resistance properties. A two-component composition compensates for stain and mar resistance but does little for wear.

ALKYD POLYMERS

Alkyds based on drying oils have been popular as architectural and industrial coatings vehicles for well over a century. Henry Reichhold was the first merchant supplier of this technology starting in 1927. In today's regulatory environment, the use of solvent-cut alkyds in architectural finishes is limited. Creative process engineering and sophisticated surfactant combinations have allowed these chemistries to be supplied as an emulsion at very low to zero VOC in a composition that resists hydrolysis for years.¹⁷ Products based on classic polyester (alkyd) chemistry ranging from 34–68% biobased content are commercially available.

A key aspect of alkyds based on drying oils relative to their fossil fuel-based acrylic counterparts is the fact that the

TABLE 2—Performance of Wet-Look Coatings on Porous Cementitious and Stone Substrates

POLYMER	ALKYD LATEX	SOLVENT ACRYLIC	ACRYLIC LATEX
BIOBASED CONTENT	59%	0%	0%
VOC, g/L	9	726	100
Δ L, RED PAVER	-2.30	-2.50	-0.57
Δ L, GRAY PAVER	-2.68	-1.93	-0.20
Δ L, SLATE	-11.42	-11.05	-4.30
CHEMICAL RESISTANCE			
GASOLINE	NO EFFECT	NO EFFECT	NO EFFECT
MOTOR OIL	SLIGHT STAIN	DARK STAIN	NO EFFECT
BLEACH	NO EFFECT	SLIGHT STAIN	NO EFFECT
SALT WATER, 5% SOLUTION	NO EFFECT	NO EFFECT	NO EFFECT
BRAKE FLUID	NO EFFECT	SLIGHT STAIN	NO EFFECT

alkyd is a liquid polymer which, as an applied film, will react with molecular oxygen and increase in glass transition temperature and molecular weight. The very low initial T_g precludes the need for coalescing solvents. Polymers based on acrylate monomers are essentially solid at room temperature. This can limit flow into porous substrates with a consequent lack of aesthetics in some applications. The higher T_g of acrylic polymers may also necessitate the use of VOC solvents for proper film formation.

This differential in substrate penetration is perhaps best demonstrated in a “wet-look” coating applied to porous concrete paver stones. This application dictates that the substrate appears dark without building a high gloss finish and is accomplished in part by the polymer penetrating deeply into the very small voids in the substrate. Quantifying this optical change is effectively done with a colorimeter by comparing the “L” values (CIE L.a.b color space) of the coated and uncoated substrate. As the substrate becomes darker from coating application, the “L” value will decrease. Thus, a greatly enhanced wet-look appearance will be reported as a large negative Δ L.

This coating application was long-held by solvent acrylic lacquers at well over 500 g/L VOC. With the advent of VOC limits, this market transitioned to acrylic latex with the subsequent loss of the desired appearance. Introduction of alkyd latex polymers provided a vehicle that would both meet VOC limits and provide the desired deep, rich, wet-look.¹⁸

Table 2 provides data for an alkyd latex, a commercial solvent acrylic, and commercial acrylic latex applied to several popular cementitious and stone surfaces. Note that no chemical analysis of these commercial products was undertaken; the descriptions provided here are taken from the product labels.

The fluid nature of the alkyd polymer allows the penetration necessary to alter the direction of reflected incident radiation and thus provide an enhanced “wet-look.” Post-application oxidation builds molecular weight and crosslink density that function to provide the improved chemical resistance relative to the high VOC acrylic lacquer. The exceptionally high molecular weight of the acrylic latex precludes penetration and development of the desired “wet-look” but does provide chemical resistance.

Air quality regulators monitor the usage of AIM coatings by category and use the associated tons of emitted solvent(s) to guide their changes in VOC limits. Such is the case with the new asphalt driveway sealer category added by SCAQMD¹⁹ and OTC¹⁴ member states. The 50 g/L limit imposed by these agencies limits this coating category to emulsion polymers. A comparison of emulsions based on alkyd, acrylic, and asphaltic binders was performed in the Reichhold laboratories.²⁰ In this work, we used commercial paint based on acrylic and asphaltic binders (label analysis), and formulated an in-house alkyd latex polymer in a similar fashion based on label and SDS analysis of the

commercial paints. An alkyd latex with 50% biobased content was utilized. This polymer has an acrylic modification to impart some lacquer dry character. Weathering is a function of both pigmentation and binder selection; one formulation using the alkyd latex was tailored for improved durability by utilizing a pigment combination well outside those seen in commercial products.

Commercial asphalt sealers are supplied in two basic formulations that we have designated as unfilled and filled. In this vernacular, filled coatings contain a significant volume fraction of large-particle silica sand in conjunction with a traditional paint extender. Typically, this silica is 270 mesh (50 microns) in top particle size and may provide some anti-slip properties to the applied coating. Other extender pigments noted in commercial products include Nepheline Syenite, Kaolin, calcium carbonate, and, while not a traditional coating extender, ground tire rubber. For comparison purposes, we have tested alkyd emulsions in both filled and unfilled pigmentations.

Filled and unfilled formulations along with the pertinent physical properties are presented in Table 3. Note that $\lambda = \text{PVC}/\text{CPVC}$, where PVC is the pigment volume concentration and CPVC is the critical pigment volume concentration calculated from oil absorption. Filled formulations maintain the same relative carbon black loading as the unfilled formulation. The weight ratio of silica sand to Nepheline Syenite was maintained as the PVC varied. The unfilled formulation is, as noted previously, designed for improved weathering and for stir-in production; the treated pyrogenic silica does not require aggressive high speed dispersion. Weights have been rounded to the nearest decimal place.

Weathering data is presented here for alkyd latex formulations using both pyrogenic silica and Nepheline Syenite due to its durability under both acid and alkaline conditions. Calcium carbonate weathered well in a QUV exposure at slightly alkaline pH but frosted in exposure to the slightly acid conditions required in cyclic prohesion. Also included is a formulation utilizing treated pyrogenic silica, chosen for durability, as the extender.

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TABLE 3—Asphalt Sealer Formulations, Pounds/100 Gallons

FORMULATION	UNFILLED	FILLED, LOW PVC	FILLED, HIGH PVC
WATER	0.0	170.0	165.0
CELLULOSIC THICKENER	0.0	4.0	4.0
AMMONIA	0.0	1.0	1.0
DISPERSANT	0.0	1.9	2.9
DEFOAMER	0.0	2.6	2.5
50 MICRON SILICA SAND	0.0	37.0	57.0
NEPHELINE SYENITE	0.0	81.0	128.0
CLAY THICKENER	0.0	5.2	5.0
		HIGH SPEED DISPERSE	HIGH SPEED DISPERSE
ALKYD LATEX	450.0	217.0	210.0
WATER	116.0	332.0	321.0
METAL DRIER ^a	7.0	1.0	1.0
DEFOAMER	2.2	2.5	2.5
SILANE TREATED PYROGENIC SILICA	28.0	0.0	0.0
PROPYLENE GLYCOL	10.3	0.0	0.0
BLACK DISPERSION, 38% PIGMENT ^b	0.0	17.5	19.9
BLACK DISPERSION, 12.5% PIGMENT ^b	37.2	0.0	0.0
ASSOCIATIVE THICKENER	20.0	5.2	5.0
WATER	202.0	41.0	40.0
FORMULATION PHYSICALS			
NONVOLATILE, WEIGHT	36.5	35.4	35.0
NONVOLATILE, VOLUME	33.2	24.9	25.0
PVC %, TOTAL	5.8	29.0	39.0
P:B, CARBON BLACK	0.05:1	0.05:1	0.05:1
Λ	39	50	65
VOC, g/L	50.0	4.1	3.6

(a) Total pounds used; the metal catalyst used in the filled formulas was selected for lower VOC.

(b) Carbon black dispersion, product in filled formula selected for lower VOC.

These coatings were exposed to accelerated weathering in both a QUV and a Xenon Arc Weather-Ometer. Trends were similar for both instruments; only the QUV data are presented (see Table 4). Coating degradation results in visible whitening of the film, which is evidenced by a large change in the L (light-dark) value. Accordingly, presenting color change as ΔL is adequately descriptive. Exposure hours are rounded to the nearest 100, ΔL is rounded to the nearest tenth. For the reported QUV exposure, the instrument settings used were:

UV lamps: UVA 340

UV cycle: 8 h at 60°C

Humidity cycle: 4 h at 50°C

The pyrogenic silica used in the unfilled coatings is among the most hydrophobic extenders available to the coatings chemist. With an oil absorption of 290, a very low PVC is required to reach a sufficient λ to provide the desired matte finish. This combination develops a film surface that is quite resistant to moisture ingress and subsequent hydrolysis. The UV absorption of the carbon black pigment further limits film degradation and this alkyd latex survives well over 4000 h of exposure before a significant color change is noted.

The filled formulations use larger particle size and much more hydrophilic pigmentation. The resultant ingress of water during exposure results in a more rapid surface degradation and the consequential whitening of the film. At 500 h of exposure, the color change is visible and becomes quite a bit more so at 1200 h. Note that in the early periods of exposure, the higher filler loading shows less color change. This is reversed beyond 4000 h and continued through 9000 h of exposure. Exposure to accelerated weathering of the commercial products resulted in color change similar to the filled alkyd latex formulation. Note that our accelerated weathering evaluations of these and other commercial products (all data not presented) did not necessarily show a correlation between warranty period and performance.

Table 5 shows the chemical resistance for a number of test films. This

TABLE 4—QUV Exposure of Alkyd Latex Asphalt Sealers with Variable Pigmentation

COATING	UNFILLED	FILLED, LOW PVC	FILLED, HIGH PVC
EXTENDER PIGMENT	SILANE TREATED PYROGENIC SILICA	SILICA SAND AND NEPHELINE SYENITE	SILICA SAND AND NEPHELINE SYENITE
PVC	5.8	29.0	39.0
Λ	39	50	65
Δ L AFTER 500 H	0.9	3.2	1.4
1200 H	1.0	3.5	2.0
2500 H	-0.5	3.8	2.6
4000 H	-0.5	2.6	3.1
5000 H	-2.8	4.5	7.0

testing was done as covered spot tests using a 24-h duration unless otherwise noted. The industry has not established a standard set of chemicals to be used in evaluating this class of coatings, and the full gamut of products tested is more extensive than reported here. The data is limited to the more pertinent and common reagents. Ratings are on a subjective 0–5 scale, with 5 being no noticeable effect and 0 being film destruction.

The data offers several interesting points. First, all commercial products are not created equally. Acrylic 1 is clearly inferior in chemical resistance, failing badly upon short-term exposure to brake fluid, in this case in a much less severe uncovered spot test. Second, as seen in previous data, the crosslinking of oil-based polymers imparts improved chemical resistance; the alkyd latex in both pigmentations is superior to non-crosslinked commercial acrylic products. Third, that the alkyd is liquid allows for excellent pigment binding and performance over a wide range of pigment volume concentrations. Finally, note that the filled alkyd latex formulation is under 5 g/L VOC and the unfilled formulation, minus the propylene glycol that is not needed for film formation, would be 15 g/L VOC. Fatty acids grafted to the polymer backbone reduce T_g thus often preclude the need for coalescing solvents.

The performance benefit of the self-crosslinking of biobased alkyd latex polymers formulated as blacktop sealers relative to their non-renewable counterparts is further demonstrated via ASTM D 5402 Resistance to Color Tracking and ASTM D 1308 Resistance to Re-emulsification. Resistance to color tracking was tested at one-day and seven-day dry times with 50 double rubs using water-wet cheesecloth. Re-emulsification is done with the same dry times and uses a one-hour water spot followed by 100 double rubs with a water-wet cheesecloth. A commercial asphalt emulsion offered as a seven-year product and a commercial product labeled as an acrylic were included in these tests. As part of our testing of

pigmentation the extender pigment used in the filled alkyd latex is calcium carbonate rather than Nepheline Syenite. The data are presented in *Table 6*. Pictures of the Re-emulsification test are included.

We see that with overnight dry, the alkyd latex consistently resists the transfer of coating to a wet cloth. Lacquer dry polymers lack a cross-link mechanism and do not appear to develop the requisite toughness to pass this testing regimen after a week's cure. That the more heavily filled alkyd latex was slightly inferior to the unfilled formulation may suggest that a difference

in formulation relative to the non-film-forming products is also a factor in their reduced performance.

The efficient pigment binding of alkyd polymers noted when testing asphalt sealer formulations was also demonstrated in the development of a 34% biobased content alkyd latex (Alkyd Latex 2) designed for metal primer applications. The rapid method of Asbeck²¹ uses a salt water spot test to identify coatings above critical PVC. Utilizing this method in evaluating this alkyd latex primer vehicle proved insightful. In *Table 7*, data are presented showing PVC and lambda (λ) for this alkyd latex

TABLE 5—Chemical Resistance of Several Asphalt Sealer Formulations

COATING	ALKYD LATEX 1	ALKYD LATEX 1	COMMERCIAL ACRYLIC 1 ^a	COMMERCIAL ACRYLIC 2
PIGMENTATION	UNFILLED	FILLED	FILLED	FILLED
BIOBASED CONTENT	50%	50%	0%	0%
MOTOR OIL	5	5	4	4.5
ANTI-FREEZE	5	5	5	4.5
BRAKE FLUID, DOT 3	4.5	5	0	4.5
GASOLINE	5	5	4	4.5
WATER	5	5	4.5	5

(a) 4-h uncovered spot test

TABLE 6—Asphalt Sealer Resistance to Color Tracking and Re-emulsification: Color Transfer

COATING	ALKYD LATEX 1	ALKYD LATEX 1	COMMERCIAL ACRYLIC 2	COMMERCIAL ASPHALT EMULSION
PIGMENTATION	UNFILLED	FILLED	FILLED	FILLED
BIOBASED CONTENT	50%	50%	0%	0%
COLOR TRACKING, 1 DAY	NONE	SLIGHT	MODERATE	HEAVY
COLOR TRACKING, 7 DAY	NONE	SLIGHT	MODERATE	HEAVY
RE-EMULSIFICATION, 1 DAY	NONE	MODERATE	HEAVY	VERY HEAVY
RE-EMULSIFICATION, 7 DAY	NONE	MODERATE	HEAVY	VERY HEAVY



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and Styrene Acrylic Latex 1, which was developed for use in metal coatings. Pigmentation is a fixed loading of red iron oxide and anticorrosive pigment. Calcium carbonate was used to adjust λ (PVC). Permeability was determined by the wet cup method and is reported simply as mg of water transmitted per hour at steady-state conditions.

Alkyd Latex Polymer 2 was successfully formulated into a red oxide metal primer that passed 500 h of salt fog and humidity testing at 1.5 mils DFT. The formulations are below 15 g/L VOC as no coalescing solvent was needed in this 34% biobased polymer. Efficient pigment binding allowed performance at λ values as high as 0.82.¹⁷ Stability of alkyd latex formulations is of paramount importance and is particularly difficult to achieve in formulations containing reactive anti-corrosive pigments. To demonstrate the remarkable stability of this red oxide primer, heat-aged studies of the latex and the formulated paint made from that heat-aged latex were undertaken. In addition to measuring the tested products for viscosity and pH change, aged materials were coated on cold-rolled steel and subjected to salt fog (ASTM B117) and humidity (ASTM D2247) testing. Data presented in Table 8 show minimal changes in viscosity or performance through this vigorous test regimen. Pictures of the panels after 336 h of salt fog are included.

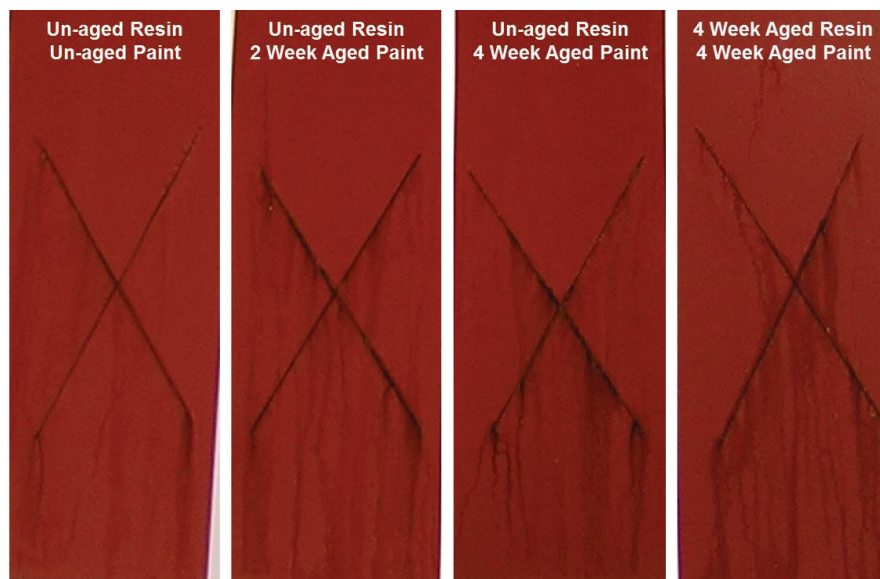
As a final demonstration, the performance of a low-VOC alkyd latex polymer with measured biobased content of 40% was evaluated via the National Transportation Product Evaluation Program (NTPEP). In annual tests alternating between roadways in the southern and northern area of the United States, coatings and the associated retro-reflective glass beads are applied transverse to roadbeds with typically 15,000 average daily traffic counts. The applied stripe is monitored for durability (wear resistance, amount of substrate showing) on a 0–10 scale and for retro-reflectivity. Retro-reflectivity is measured in milli-candelas (mcd) and is a function of the retention of the glass beads used to top-dress the applied coating; these beads are intended to (retro-) reflect a car's headlight back to the driver. Much of the

TABLE 7—Pigment Binding of Metal Primers

POLYMER	ALKYD LATEX 2	ALKYD LATEX 2	STYRENE ACRYLIC 1	STYRENE ACRYLIC 1
PVC	53	60	33	48
λ	85	95	50	60
SALT WATER SPOT TEST	PASS	FAIL	PASS	FAIL
PERMS, MG/H	2.3	5.4	2.8	4.8

TABLE 8—Heat Aged Stability of Alkyd Latex and Formulated Metal Primers

ALKYD LATEX STORAGE	UN-AGED	UN-AGED	UN-AGED	4 WEEKS 50°C
PAINT STORAGE	UN-AGED	2 WEEKS 50°C	4 WEEKS 50°C	4 WEEKS 50°C
FINAL VISCOSITY, KU	83	82	94	100
336-H SALT FOG SCRIBE CREEP, MM	3	2.5	4.75	3
336-H SALT FOG FACE BLISTERS	FEW #8	FEW #8	VERY FEW #8	FEW #8
336-H HUMIDITY BLISTERS	VERY FEW #8	VERY FEW #8	VERY FEW #8	FEW #8



road-marking market has been captured by the so-called “quick dry” acrylic latex polymers meeting Federal Specification TT-P-1952F, Type II. Alkyd latex with 40% biobased content using essentially identical pigmentation to this acrylic was applied to NTPEP test decks in Florida in 2012 and Pennsylvania in 2014. Alkyd latex had a durability of 10 (perfect), after

24 months on the test deck in Florida. Test decks on northern roadways are typically more severe due to the salt, sand, and snow plows used to maintain safe travel. Typically, the test results on concrete, a nonflexible surface, are more severe than testing on the thermoplastic asphalt. Durability and retro-reflectivity data for several white products as recorded for

TABLE 9—Durability and Retro-reflectivity of Several Traffic Coatings

COATING	ALKYD LATEX	COMMERCIAL ACRYLIC 1	COMMERCIAL ACRYLIC 2	COMMERCIAL ACRYLIC 3	COMMERCIAL ACRYLIC 4	COMMERCIAL ACRYLIC 5
BIOBASED CONTENT	40%	0%	0%	0%	0%	0%
VOC, g/L	100	150	150	150	150	150
WET FILM, MILS	20	20	15	15	16	25
POUNDS OF GLASS/ GAL OF PAINT	12	12	8	6	6	8
12-MONTH DURABILITY	9	9	9	9	9	9
12-MONTH RETRO- REFLECTIVITY, MCD	152	178	70	155	206	178

the skip-line section on the Pennsylvania concrete deck from 2014 are presented in Table 9. Polymers based on biobased materials require fewer VOC grams and are comparable in performance to their fossil fuel-based counterparts.

CONCLUSIONS

Incorporating significant biobased content into coating binders is best accomplished via vegetable oil-modified polyester or polyurethane polymers. This allows a biobased content of 34–68% for current commercially available products designed for various end uses. Providing these polymers as a latex or dispersion in water allows for formulations at VOC content well below the lowest established AIM limits worldwide. That these unsaturated oils crosslink to form thermoset films provides a level of performance that easily competes with thermoplastic fossil fuel-based binders. In addition to the low VOC and desirable performance, these polymers can be used in coatings that are favored in government purchases through the USDA BioPreferred® Program. They enjoy the marketing advantage of displaying the USDA Certified Biobased Product label.

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JEFFREY DANNEMAN, Reichhold LLC 2, USA, P.O. Box 13582, Research Triangle Park, NC 27709, jeff.danneman@reichhold.com, and **JENNIFER CHU**, Amec Foster Wheeler, Environment & Infrastructure Americas, 4021 Stirrup Creek Dr., Suite 100, Durham, NC 27703, jennifer.chu@amecfw.com.