Breakthrough Waterborne Technology Brings Alkyd Back to the Road

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According to National Association of Clean Air Agencies (NACAA), pavement-marking or traffic paint is defined as a coating labeled and formulated for marking and striping streets, highways, or other traffic surfaces including, but not limited to, curbs, crosswalks, driveways, parking lots, sidewalks, and airport runways. These coatings are an essential safety feature of modern infrastructure. They provide visibility to pedestrians and drivers through specific colors and incorporation of retroreflective elements, such as glass beads. Key performance attributes are the ability to adhere to and retain the retroreflective elements to maintain good nighttime visibility, adhesion to the surface for sustained durability, and ease of application. Generally, this market is driven by low cost coupled with high performance, although there are a wide variety of pavement-marking systems available depending on budgetary needs and performance requirements.

Historically, solvent-based products, mainly alkyd paints, were heavily used in this industry due to their low cost and wide range of application conditions, especially their reasonable dry times in colder temperatures and high humidity. This is mainly attributed to the hydrophobic nature of solvent-based paints, in which the drying mechanism is mostly independent of water vapor in the air. However, as a result of stricter environmental regulations, technology changes have altered the distribution of traffic paint, favoring waterborne systems. Starting in the late 1980s, waterborne traffic paint use began to climb and now has the majority of the volume in this market. The latest acrylic waterborne technology utilizes a pH-triggered mechanism that provides a quick set of the binder through adjustment to high pH with a volatile base, such as ammonium hydroxide. The high volatility of the ammonia lowers the pH of the film quickly and allows the film to rapidly build and hold integrity. However, the paint is very odorous, and stability issues can arise if the pH of the paint falls below a certain level before application to the surface. There are other niche coatings used on the roadways which consist of high performance epoxy, modified epoxy, MMA (methyl methacrylate), and polyureas, but they are used at much lower volumes. *Figure* 1 shows the market allocation shift, by volume, of the traffic paint industry in 1985 versus 2011.

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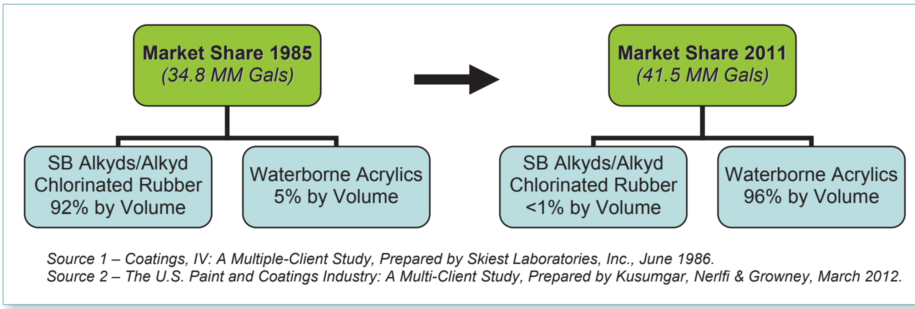


Figure 1—Traffic market transition of technologies over several years.

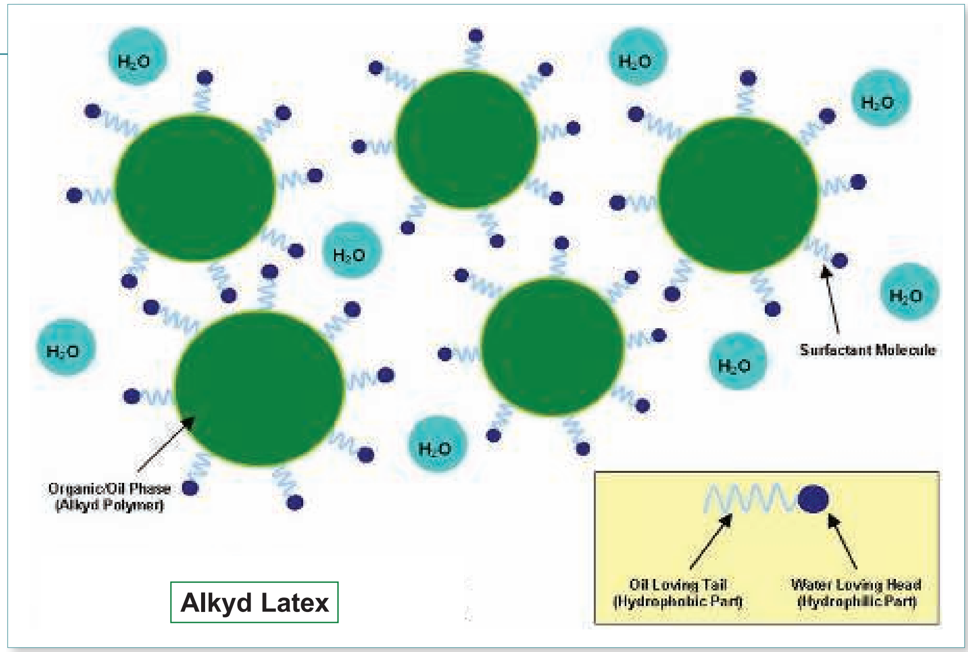
Because a large volume of traffic paint is purchased by government agencies or contractors of government agencies, the paint must meet certain specified performance requirements. Over time, traffic paint has been classified in federal and state specifications to reflect existing market needs. Traffic paint field performance is evaluated by its ability to provide visibility with the inclusion of reflective glass beads, long-term durability, and drying time, but is modeled after a series of laboratory evaluations that are outlined in the specifications. With the quick conversion to waterborne paints, all solvent-based traffic paint specifications previously referred to have been cancelled. These include TT-P-85E, TT-P-115F, and the most recent solvent-based paint specification, AA-2886B. Currently, the General Services Administration (GSA) has authorized the use of the up-to-date waterborne specification TT-P-1952E by all federal agencies. Exceptions are granted for the use of solvent-based paint that does not meet VOC regulations on a case by case basis. One of the disadvantages to having a single traffic paint specification is the chemical limitations associated with it. Presently, the waterborne traffic paint specification indicates that the binder must be a 100% acrylic copolymer. This creates very little competition in the market, as the larger companies continue to offer contractors the lowest prices of traffic paint because of the discount that they can pass along from large volume consumption. Until recently, there has been little motivation to challenge this specification to cover alternate binders. Competitive waterborne chemistries such as water-reducible alkyds, alkyd dispersions, polyurethane dispersions, and waterborne epoxies and epoxy-esters could not compete with acrylic latex technology for stability, price, solids content, or a combination of these factors. Although alternate waterborne chemistries will never satisfy the binder requirement of the TT-P-1952E, the performance characteristics defined in the specification could be replicated for industry acceptance.

According to the most recent definition of traffic paints, there are three different classes of waterborne products. Type I is classified as a regular-dry product for use under normal conditions (50% RH, moderate temps, slight breeze). The current upper limit for dry times for this type of paint is 10 min; however, this has not always been the case. The first generation of waterborne acrylic latex traffic paint dried to no-pickup in 45 min or less (TT-P-1952B). It was not until the "quick-dry" mechanism was put into practice that waterborne traffic paints were able to achieve this fast dry. Type II traffic paint is required to reach no-pickup in 10 min under normal conditions, but must also display this drying profile in adverse conditions. This class of paint is good for night striping, higher humidity (80%) environments, little to no air movement, and lower surface temps (down to 10°C). Type II paint is roughly 90% of the market, as it can be used under a wider climate range. There is a special humidity box test designed for laboratory testing as defined in the specification. All products must pass this test in order to be considered a Type II material. The final type, Type III, is for increased durability. These products are applied at higher film thicknesses and provide greater adhesion to glass beads.

Although these definitions are available and required for most DOT applications, it is common practice for traffic paint companies to classify their paints with reference to cancelled/previous versions of specification performance requirements for non-DOT applications to address all budgetary and performance needs of the industry.

Recent developments in alkyd latex synthesis have proven to offer a high performance alternative to current petrochemical-based products. Alkyd resins are formed by the step-growth polymerization of polyols and polyacids with the incorporation of pendant fatty acid chains. The fatty acid chains are introduced from integration of biorenewable oils, such as soybean and linseed oils, into the polymer structure. The resulting neat alkyds are then placed into an aqueous media by introducing surfactants and advanced processing techniques to construct a stable oil-in-water emulsion or alkyd latex with an average particle size of less than 1000 nm, but preferably lower than 350 nm. *Figure* 2 shows a schematic of an alkyd latex resin. Alkyd latex binders, when formulated into

Figure 2—Alkyd latex particle stabilization mechanism.



traditional coatings systems, show good flow and leveling characteristics, require minimal or no coalescing solvents, have nominal VOC, and develop good performance characteristics. The "go green" era has encouraged the increased usage of these biorenewable materials in traditional solventborne alkyd markets that are now dominated by waterborne technologies.

When considering the main performance features for a traffic paint resin, shear stability, high solids, competitive cost to current market offerings, and good early water resistance top the list. Most commercially available alkyd latexes do not exhibit this combination of properties, therefore limiting the use of current product lines in traffic paint. In the present study, experimental alkyd latex resins that target a balance of these properties were evaluated in a standard traffic paint formulation. A model resin was then selected from the initial assessment, followed by additive choice/level optimization to achieve optimum paint performance from this technology. This was coupled with a benchmarking study against commercially available paints. Comparison of lab performance in standard testing of the model alkyd latex versus a regular-dry commercial solventborne and regular-dry commercial waterborne paint was investigated.

MATERIALS AND TESTING

Synthesis

All alkyds used in this study were short oil soya-based. Alkyd polymers were synthesized using the monoglyceride process. During the alcoholysis or transesterification stage, the oil, polyol, and a suitable catalyst were added to the reactor and heated to reaction temperatures. Once top heat was reached, the temperature was maintained for one hour, and then checked for solubility in hot methanol (one part resin to three parts methanol). Following completion of the alcoholysis stage, the specialty monomer and polyacids were added below esterification reaction temperature. The reactor contents were then slowly heated to esterification temperature and held at constant temperature until a target acid value was obtained (ASTM D974) and a target molecular weight range was reached as measured by a solution viscosity. The main difference between the alkyds is the level of the specialty monomer that was incorporated for shear stability. Following alkyd synthesis, the alkyd resins were then dispersed into water using surfactants and advanced processing techniques. Each alkyd was emulsified using different levels of surfactant. Resultant alkyd latexes were characterized by measuring the average particle size, pH, solids content (30 min at 165°C), and viscosity. Shear stability of the materials was also evaluated. *Table* 1 summarizes the nine different alkyd latex systems and their resultant wet properties.

Instrumentation

The particle size and distribution was determined using a particle size analyzer, either a Microtrac or a Nanotrac 150. Samples were evaluated according to recommended procedures by the manufacturer. Viscosities were measured using a Brookfield Viscometer with a #3 spindle at 50 RPM.

Table 1—Experimental Short Oil Alkyd Latex Final Wet Properties

Alkyd Latex	Specialty Monomer Level	Surfactant Level	Viscosity, cps	NV, %	pH	Particle Size, nm
1	A	High	1030	56.9	6.2	211.0
2	A	Medium	46	49.1	6.0	298.2
3	A	Low	334	56.0	6.1	223.0
4	B	High	192	52.5	5.9	423.9
5	B	Medium	270	53.3	6.4	281.8
6	B	Low	164	52.2	6.2	342.4
7	C	High	1104	53.0	6.3	210.9
8	C	Medium	1760	52.6	6.3	440.1
9	C	Low	1358	52.6	6.2	766.1

Shear Stability

The shear stability of the alkyd latexes was measured with 150 grams of material in a commercial Waring blender (high speed) for 10 min. The particle size was measured before and after exposure to the high shear conditions. An increase of 100% or less of the initial particle size generally shows shear stability during pigment grinding.

Experimental Polymer Performance

Following emulsion formation, white traffic paint was made with each experimental resin using a standard traffic paint formulation. This screening formula was used to identify the optimum system for traffic paint applications. An example of the white traffic paint recipe is given in *Table* 2. Films were cast on glass panels and concrete blocks to evaluate no-pickup time and water resistance. A 20 mil gap film applicator was used for the initial screening. Films were allowed to air dry for appropriate times according to test procedures before evaluating. Water resistance testing was conducted according to TT-P-1952E. This test calls for films to be cast on concrete blocks at 15 wet mil and allowed to dry at room temperature for 72 hr. Films were then partially immersed into a water bath for 18 hr and allowed a two hour recovery period. If softening or blistering was still evident after the recovery period, the paint was considered a failure for this test. No-pickup time was evaluated according to ASTM D711. Conditions during evaluation of no-pickup times were 45% ± 3% RH and 75 ± 3°C.

Table 2—Alkyd Latex White Traffic Paint Experimental Polymer Screening Formula

Alkyd Latex Screening Formula[a]	
Raw Material	**#/100 gal**
Shear stable alkyd latex	460.03
Water	74.49
Pigment dispersant	6.69
Surfactant	2.56
Defoamer	1.00
Pigment	91.58
Extender pigment	759.62
Cobalt drier	2.53
Zirconium catalyst	3.16
Defoamer	2.00
Rheology modifier	1.04
Total	**1404.69**

Formulation Physicals	
Property	**Value**
P:B by weight	3.36
PVC, %	57.0
VOC, #/gal	0.07
VOC, g/l	7.87
NV, wt	0.79
NV, vol	0.65
WPG	14.05

(a) Generic formula for alkyd latex at 55% NV, add or subtract water accordingly for actual latex solids.

Traffic Paint Evaluation and Benchmarking Study

Based on initial water resistance and no-pickup testing, a single alkyd latex product was chosen to evaluate in complete traffic paint performance testing against current commercially available paints. Full testing on each system was conducted according to the current waterborne specification, TT-P-1952E, and the previous solventborne specification, TT-P-115F. *Table* 3 shows a summary of the tests that were conducted and the testing protocols that were utilized.

RESULTS/DISCUSSION

Because the traffic paint industry has undergone a huge transformation over the last few decades with a narrowed technology focus, the market has become less competitive due to fewer

Table 3—Summary of Performance Tests and Methods Conducted for Benchmarking Study

Test	Test Method
Accelerated package stability	ASTM D 1849
Flexibility	ASTM D 522
Water resistance	TT-P-1952E, Section 4.3.6
Freeze-thaw stability	ASTM D 2243
Color	ASTM D 2244
Directional reflectance	ASTM E 1347
Abrasion resistance	ASTM D 968
Accelerated weathering	ASTM G 154; TT-P-115F, Section 4.3.5[a]
Scrub resistance	ASTM D 2486
Consistency	ASTM D 562
Dry opacity	ASTM D 2805
Dry time (no-pickup)	ASTM D 711
Fineness of dispersion	ASTM D 1210
Bleeding ratio	ASTM D 969

(a) ASTM G 154 = Waterborne, TT-P-115F = Solventborne

Table 4—Shear Stability of Commercially Available Alkyd Latex Resins

Commercial Alkyd Latex Shear Stability			
Commercial Product	Particle Size, nm Before Shear	Particle Size, nm After Shear	Particle Size % Increase
Alkyd Latex 1	232.2	715.3	208.1
Alkyd Latex 2	334.1	1115	233.7
Acrylic Latex Control	164.7	187.9	14.1

resin options. This is primarily a result of the patent-protected acrylic technology and the tight performance standards in the federal waterborne specification that excludes competitive waterborne systems. Additionally, alternate waterborne resin chemistries have difficulty competing with the low-cost acrylic materials and achieving high volume solids in paint formulations. With acrylic shortages that occurred in 2010, there was a major traffic paint shortage that triggered special approval of solventborne alkyd paints in many areas in order to maintain safe driving conditions. Realization that this shortage is always a possibility and the impact it could have on the safety of U.S. infrastructure makes the prospect of an alternate waterborne binder for traffic paint an important option.

The main objective of the experimental polymer study was to obtain a high solids alkyd latex that possesses stability under high shear conditions. The reason for this is due to the high volume solids required for formulated traffic paint to conform to current specifications. To satisfy this criterion, it is imperative that grinding the high levels of pigment be done in the presence of the polymer binder. In previous screenings for alternate waterborne technologies for traffic paint, when attempting to grind pigment in commercially available alkyd latexes, the paint would gel after several minutes. A simple test method was developed to simulate this property by exposing the resins to high shear con-

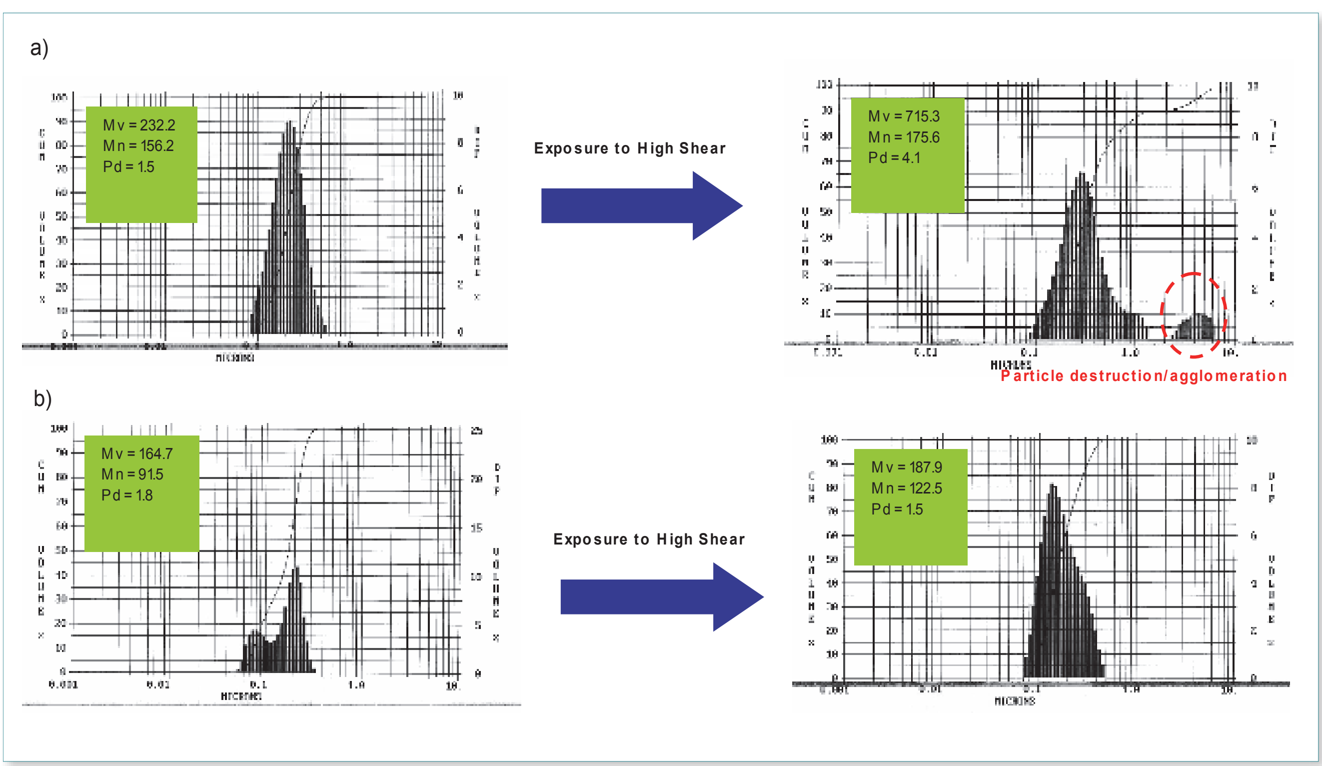


Figure 3—Particle size distributions before and after high shear exposure; (a)—commercial alkyd latex 1; (b)—acrylic latex control.

ditions in a commercial Waring blender. When the commercially available alkyd latex resins underwent this testing, a significant percentage of the particles were destroyed/altered, as is evident by the particle size distributions. *Table* 4 summarizes the change in average particle size of two commercially available alkyd latex resins and a commercial acrylic latex control before and after shear testing, while *Figure* 3 shows an example of the particle size distributions before and after testing commercial alkyd latex #1 and the acrylic control. It is known that commercial resin #1 does not contain the specialty monomer that was added to the nine experimental alkyd latex resins; however, the composition of commercial resin #2 is unknown. The distribution plots and the particle size increase show that a large portion of the commercial alkyd latex particles for both samples were damaged during high shear conditions, while the acrylic latex remained stable. The relatively unchanged distribution was targeted for alkyd latex development.

The specialty monomer that was incorporated into the polymer backbone was added at three different levels, A–C, ranging from lowest to highest, as shown in *Table* 1. Oil length and molecular weight targets were kept constant during neat alkyd synthesis. For emulsification, varying levels of surfactant were added to each alkyd base at high, medium, and low levels. The difference in surfactant was intended to balance stable particle size and water resistance. From previous work, it was known that a minimum level of specialty monomer is needed for shear stability of the emulsion, while more surfactant usually results in smaller particle size. The polymer design considered these factors. Shear stability testing was conducted on all experimental polymers.

Table 5—Average Particle Size of Experimental Alkyd Latex Resins Before/After Shear Testing

Experimental Alkyd Latex Shear Stability

	Particle Size, nm Before Shear	Particle Size, nm After Shear	Particle Size % Increase
1	210.5	324.4	54.1
2	298.2	326.9	9.6
3	223.0	262.9	17.9
4	423.9	392.0	-7.5
5	281.8	286.6	1.7
6	342.4	352.3	2.9
7	210.9	230.3	9.2
8	440.1	509.8	15.8
9	766.1	862.3	12.6
C-Acrylic Latex	164.7	187.9	14.1

The average particle size and percentage shift after testing is displayed in *Table* 5. All experimental alkyd latex resins possessed shear stability according to testing protocol, recalling that a 100% or less particle size increase typically results in a product that can withstand shear forces of the pigment grinding process. For alkyd latexes 1–3, initial particle size ranged roughly from 215–300 nm. There is no apparent trend relating surfactant levels to initial particle size in this series. However, the highest level of surfactant resulted in the largest increase in particle size, although it is still within the acceptable limits. Similar results were also found for alkyd latexes 4–6, which contained the mid-level of specialty monomer, but the intermediate surfactant load provided the lowest particle size in this series. The final series with the most specialty monomer in the backbone and lowest surfactant levels started to show an increase in particle size as surfactant amount was decreased. This appears to approach a minimum surfactant

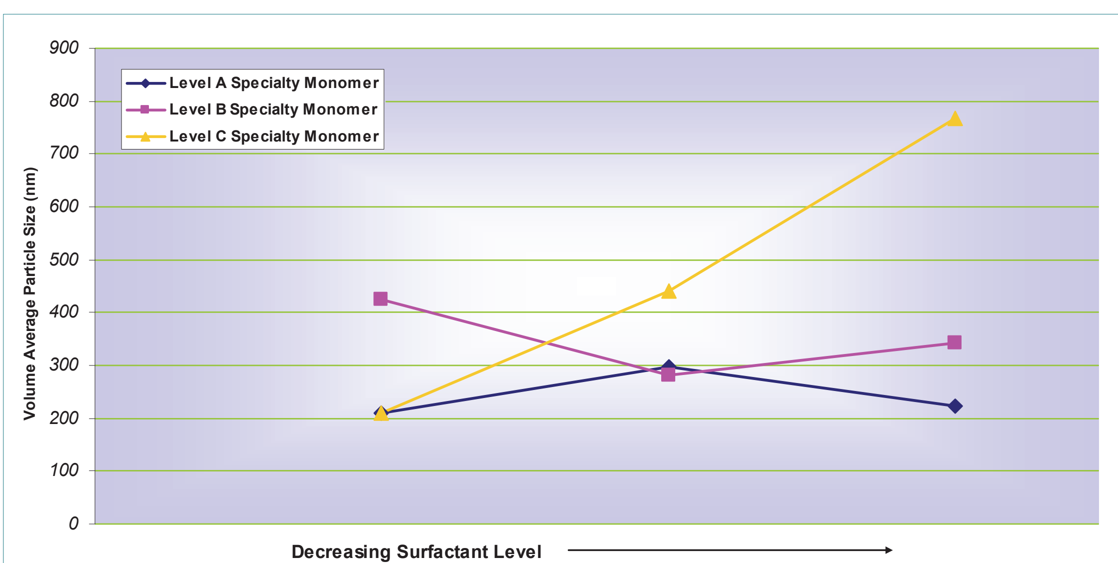


Figure 4—Particle size of alkyd latex resins with various levels of surfactant.

Table 6—Key Traffic Paint Performance Properties of Experimental Alkyd Latex Paints

	Stormer Viscosity (KU)	pH	No-pickup time (min)	Water Resistance (2-hr Recovery)
1	97	7.5	14	fail
2	93	7.3	14	fail
3	92	7.3	16	fail
4	101	7.4	10	fail
5	95	7.4	11	fail
6	101	7.3	10	pass
7	100	7.4	13	fail
8	115	7.4	14	fail
9	93	7.7	21	fail

Table 7—Optimized Alkyd Latex Traffic Paint Formulation for Traffic Paint Benchmark Comparison

Alkyd Latex Traffic Paint	
Raw Material	**#/100 gal**
Grind	
Alkyd latex # 6	431.00
Water	55.00
28% Ammonia	0.25
Pigment dispersant	12.50
Defoamer	3.00
Pigment	100.00
Extender pigment	733.00
Grind Total	1334.75
High speed disperse to 3+ Hegman grind	
Letdown	
Catalyst	4.30
Methanol	41.50
Defoamer	1.00
Rheology modifier solution	6.00
Associative thickener	1.70
Total	**1389.25**

Formulation Physicals	
Property	**Value**
P:B by Weight	3.79
PVC, %	60.4
VOC, g/l	75.0
NV, wt	0.77
NV, vol	0.60
WPG	13.89

level that is needed to obtain a particle size within the target range (<1000 nm, but preferably <350 nm). *Figure* 4 shows a graphic of the particle size variation with decreasing surfactant levels.

Since all experimental resins passed the shear screening test, each was evaluated in the paint formula shown in *Table* 2, with water content adjusted to allow for solids difference in alkyd latex resins to balance individual formulations. The assessment of these paints included water resistance testing on concrete panels according to TT-P-1952E and no-pickup time at standard conditions (45% RH±5%; 75°F±3°F). *Table* 6 gives a summary of all nine experimental paint properties. There are several trends that are evident. Paints 1–3 showed roughly the same no-pickup time and all failed the water resistance test. The next series of alkyd latex paints all had lower no-pickup times than the first series, and two-thirds failed the water resistance test. The last series of paints had increased no-pickup times and all failed the water resistance test. Results indicate that too high of a surfactant level and too much specialty monomer in the polymer backbone result in deficient water resistance in the film and increased no-pickup times.

The best candidate for a traffic paint resin was alkyd latex #6 with midlevel specialty monomer and midlevel surfactant. This polymer was evaluated in the benchmarking study. Particle size measurements of the latex before and after exposure to shear were also a factor in prototype selection, as prior experiments have shown that <350 nm provides the desired stability for the resin and the finished product.

When remaining traffic paint evaluation tests were done with paint #6, it was found that this particular formula did not pass oven stability testing. Additionally, the paint had a significant

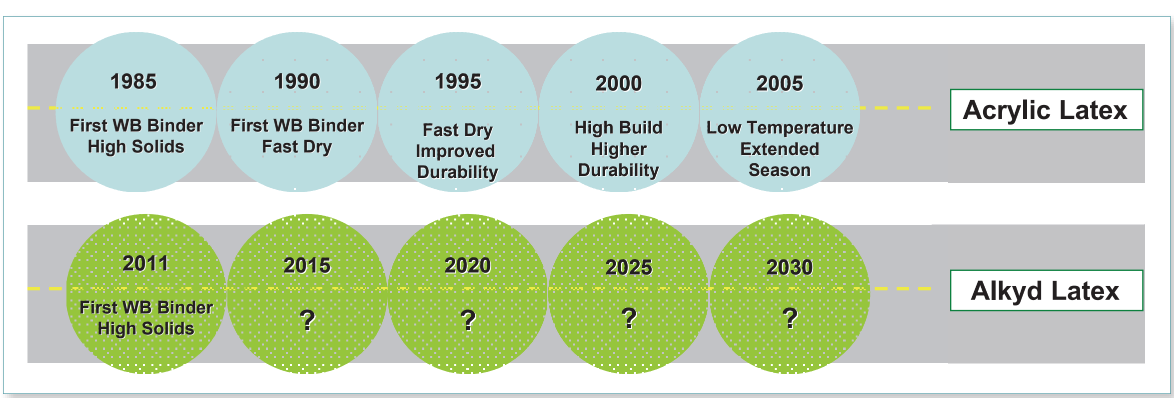


Figure 5—Progression of waterborne acrylic latex over 20 years and growth possibility for alkyd latex technology for traffic paint applications.

amount of residual foam. The formulation was optimized at 60% pigment by weight, reduced to 60% volume solids from 64%, and used a cellulosic/associative rheological package for stability. The formula used for the benchmarking study for complete evaluation of alkyd latex 6 is shown in *Table* 7. The alkyd latex was tested alongside a commercial regular-dry acrylic paint and a commercial fast-dry alkyd paint. All coatings evaluations were carried out according to the waterborne specification unless otherwise noted. *Table* 8 provides a summary of the complete evaluation. The data shows that the alkyd latex prototype resin meets the performance requirements of the current waterborne specification with the exception of allowed dry time. Also, it is important to point out that the flexibility was tested according to the cure schedule of TT-P-115F, as the cure schedule in the waterborne spec is overly aggressive for an alkyd latex system and would not give representative results.

Even though this first generation of alkyd latex for traffic paint does not exhibit the "quick-dry" mechanism of the acrylic latex, it *does* meet the remainder of the performance requirements. As with any new technology development, all performance aspects are not typically met in the first attempt. It took nearly 20 years for waterborne acrylic traffic paint to achieve the performance that it has today, with each successive generation (roughly every five years) providing an improvement over the prior invention. Most importantly, there are several applications that do not require this fast dry—for example, parking lots, new construction, smaller towns and municipalities, national parks, and some airport striping. Coning off sections of the roads/striping area is still perfectly acceptable in many end-use markets. A 20-min dry time is adequate for these striping needs, giving the contractor an additional low-VOC option. *Figure* 5 summarizes the development of acrylic latex waterborne paint with respect to time and shows the possibilities for the expansion of this latest technology for waterborne traffic paint.

Aside from the high performance and competitive cost of alkyd latex for traffic paint, the partially biobased material offers additional advantages to the market. As the trend for greener products continues, the soy-based material can help to reduce dependence on petrochemicals and lower the VOC emissions by reducing the need for a coalescing solvent. For example, one gallon of alkyd latex formulated traffic paint uses oil from roughly 12,000 soybeans. If the entire market, which uses close to 40MM gallons of paint every year, were to convert to alkyd latex paint, it would result in a 3MM bushel increase in soybean production per year and reduce the amount of petrochemical feedstock needed to produce the equivalent acrylic material by close to 4MM gallons. Additionally, as formulated, it saves approximately 9MM gallons of VOC released into the atmosphere per year, with the potential to save even more by using a lower-VOC alternative to alcohol to provide the formulation

Table 8—White Traffic Paint Performance Data of Alkyd Latex Prototype and Commercial Controls

White Traffic Paint Benchmarking Data

Test	Requirements	Alkyd Latex Prototype*	Commercial Acrylic	Commercial Alkyd
Abrasion resistance (Falling sand)	TT-P-115F/ 35 liters TT-P-1952E/ 150 liters	150	150+	110
Bleed ratio	0.90 min	1.00	1.00	0.88
Dry-No-pickup[a]	TT-P-115F Type 1 / 30 min TT-P-1952E / 10 min	25	30	13
Dry opacity	0.92 min @ 5 wet mil	0.98	0.98	0.98
Flexibility[b]	¼ in. Mandrel	Pass	Pass	Pass
Freeze-thaw resistance	TT-P-1952E / 3 cycles	Pass	Pass	NA
Scrub resistance	TT-P-1952E / 500 cycles	1500	1500+	NA
Water resistance	Full recovery after 2 hr	Pass	Pass	Pass
Viscosity	TT-P-1952E / 80-90 KU	85 KU	90 KU	77 KU
Volatile organic compounds	TT-P-115F / 100 g/L max TT-P-1952E / 150 g/L max	75	<250	<450
Fineness of dispersion, Hegman	TT-P-115F / 2 Hegman, min TT-P-1952E / 3 Hegman, min	5 1/2	6	4
Directional reflectance, Y	85 min	84.85	82.17	83.67

(a) Drying time is temperature, humidity, air flow, and film thickness dependent
(b) Cancelled specification test was used because cure schedule for the acrylic is too aggressive for an alkyd polymer
* This polymer and formulation have not been tested for performance on road tests with live traffic

with freeze/thaw stability in the future. Lastly, there is no strong ammonia odor with the biobased material that is commonly associated with waterborne traffic paint.

SUMMARY

The design of an alkyd latex targeted for traffic paint involved several different stages. Careful monomer selection was required to balance cost versus performance. Incorporation of a specialty monomer into the alkyd backbone was crucial for shear stability of the final alkyd latex. Following alkyd synthesis, a balance of surfactant level was done to optimize performance and stability and result in a high-solids, shear-stable material. White regular-dry traffic paint was successfully formulated using the selected alkyd prototype resin to produce a high performance, biobased alternative to acrylic latex paint. Lab evaluation of the new waterborne paint against two commercially available traffic paint products shows comparable performance to other traffic paint technologies, providing a viable option for end users. Ongoing research to maximize performance of alkyd latex for the traffic paint industry will provide an opportunity for the future growth of this technology.

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