Sustainable Technology for Semitransparent Deck Stains

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With new types of decking being introduced and pressure to formulate using greener, sustainable technology, new binder approaches are needed for semitransparent deck stains. Many conventional acrylic waterborne semitransparent stains have poor adhesion to the new types of wood treatments such as copper azole, leading to early failures on exposure. Other alkyd-based waterborne stains can have slow dry and poor early water resistance on high tannin woods such as cedar and redwood. There is also a need for a highly UV-resistant coating which will help preserve the distinctive colors and appearance of exotic wood species such as Ipé and mahogany. At the same time that these substrates are being introduced, environmental initiatives have created a demand for a binder which is free of alkyl phenyl ethoxylate (APEO) surfactants, has low or zero volatile organic compounds (VOC), and which can be formulated without heavy metal driers. The development and testing of a new semitransparent stain binder which meets these environmental goals and also offers improved performance is presented.

MARKET TRENDS AND PERFORMANCE REQUIREMENTS

Many types of water-based binder chemistries are currently being used in semitransparent stains to meet the California Air Resources Board and Ozone Transport Commission regulations of less than 250 VOC. Alkyd acrylic hybrids, water reducible alkyds, oil in water or water in oil alkyd emulsions, modified linseed oil, acrylics, polyurethanes, and vinyl acrylics have all been recommended for this use. In order to comply with the California South Coast Air Quality Management District's 100 g/L VOC regulations for semitransparent stains, many companies are now evaluating binders designed for use at lower VOC levels. The 100 VOC stains usually have about four gallons less glycol or cosolvent than stains formulated at 250 VOC.

The lower glycol and cosolvent levels are a significant concern in semitransparent stains since removing the hydrophilic solvents may give a more

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hydrophobic film as the stain is drying and might reduce resolubility of the stain. Resolubility or lapping is important since painters often have to brush over a partially dried coat of the stain and the ability of the first coat to blend into the second will prevent the rebrushed area from having a different color or sheen. Most water-based technologies, even water-reducible alkyds, do not give as good lapping as oil-based stains because the water used as the solvent does not dissolve the drying, partially coalesced polymer.

There are many ways of increasing the water solubility of the polymers to improve this property but it is important that the polymer also have good early water resistance. Deck stains must have good water resistance after an overnight dry so that the colors from a damp deck (which might have been exposed to dew) are not tracked into the house. Since commercial deck cleaners based on sodium hypochlorite/ sodium hydroxide are frequently used, the stain should be insoluble in these solutions so that it is not removed when the deck is cleaned. On the other hand, the stain should be easily dissolved in aqueous deck strippers so that solvent-based paint strippers do not have to be used if the stain is to be removed. These conflicting solubility requirements make formulating a stain binder challenging.

Along with the proper solubility profile, the stain should be designed to meet possible future environmental regulations. Since there is concern about the bioactivity of degradation products of alkyl phenyl ethoxylate (APEO) surfactants,[1] many companies are requesting that polymers be supplied without this class of surfactant. Many of the older acrylic binders recommended for semitransparent stains do contain this class of surfactant. New stain binders should be made without these surfactants so that companies are not forced to reformulate if these surfactants are eventually regulated in the North American market.

There have also been concerns about the toxicity of cobalt salts and increasing regulatory scrutiny in Europe,[2] so stains which do not use this metal drier are desirable. The binders which require the metal driers can also have poor performance on some of the substrates used for decking. The activity of the metal driers can be inhibited on high tannin woods like cedar and redwood,[3,4] and water reducible oils or alkyds may have much slower dry on these substrates. The slower dry can result in stains which are tacky and water sensitive after an overnight dry.

Performance requirements of the semitransparent deck stains are demanding. UV light degrades the lignin in wood and, to some extent, the cellulose, and gives a weathered wood surface largely composed of loosely bound fibrils of partially degraded cellulose.[5] Semitransparent stains are frequently applied without adequate preparation of the substrate, so they need to be formulated at low viscosity and use binders designed to penetrate through the upper layer of loose fibers. The UV light can also degrade the stain binder as well as the substrate. Although hindered amine type UV light stabilizers can reduce UV-induced degradation of the different stain binders, a binder transparent to UV light should have the best long-term durability.

The stains also need to have good performance on new decking substrates. Some types of copper-based wood treatments which have replaced the CCA decking are reported[6,7] to give bonds with reduced adhesion with water-based stains or adhesives. New stain binders need to have good adhesion on these new copper-based wood treatments. Other types of exotic hardwoods such as Ipé and mahogany are also being used for high-end decks. These woods often have a very distinctive and beautiful color variation along the grain when new; however, they fade to gray as rapidly as other types of wood. A stain which slows the bleaching of these woods while still allowing the colors to show through would be desirable. Finally, many new decks are made of wood plastic composites. These composite decks come in many colors but most will fade to a gray on exposure to UV light and could be stained to restore the natural wood color. Since these composites do not allow penetration of the stain even when weathered, a film-forming semitransparent stain with good abrasion resistance is needed.

Many commercial stains are also often formulated to give water beading. Water beading is sometimes thought to be a good measure of water repellency;

however, the actual value of this property in extending coating or substrate life is debatable. While water beading shows resistance of the stain to penetration by liquid water, wood can also pick up water from moisture vapor. Water vapor at atmospheric conditions of high humidity moves freely through stain and paint films, even those with excellent water beading. In extended periods of high humidity, this water vapor can raise the moisture content of wood up to the fiber saturation point. Since wood undergoes dimensional changes below the fiber saturation point, the different interfaces in wood undergo the same dimensional stresses from absorption of liquid water and water vapor from humidity. Nevertheless, the protection of wood from liquid water may be of some value. Horne et al[8] found that the exposure of wood to UV light and water was worse than just exposure to UV light, and they proposed that the effect of the water was to leach the water-soluble UV degradation products of lignin from the wood. In that study, exposure of wood to water without UV light did not lead to significant degradation. Water repellency in a stain with good UV protection is thus probably desirable but not critical to the protection of a wood substrate. Aesthetically, water beading may be a problem, however. The water beads can remain on the surface of the deck for hours after rainfall and can leave rings of dirt when they dry. A stain which would sheet water from the surface would probably be more desirable as a mechanism to protect the wood from liquid water.

At the same time that the stain formulator is trying to meet these VOC and performance requirements, there are some market trends which are pushing the performance to higher levels. Several paint companies are beginning to put multi-year performance guarantees on the labels of semitransparent deck stains. At the same time that more durable stains are being marketed, there is also a trend toward more translucent wood toners. These lightly tinted stains and toners do not have as much UV blocking pigment as semitransparent stains but still need to give adequate UV protection of the wood substrate to prevent graying and degradation of the surface. Nearly transparent inorganic nano-sized UV blocking pigments[9] and new efficient, leach resistant encapsulated organic UV absorbers[10] are available and may be necessary for the more translucent stains and wood toners.

Acrylics are one class of water-based binder chemistry which is promising for semitransparent stains. Acrylics are quite transparent to UV light and therefore more durable on exterior exposure than alkyd-based binders, which absorb UV light and degrade relatively rapidly. These acrylic binders do present a set of challenges to the stain formulator, however. Because they are such durable films, the acrylics in semitransparent stains can sometimes flake and peel if the UV light causes the wood beneath it to degrade. An acrylic-based stain should have enough UV protection built into it to prevent the degradation of the substrate. Another challenge for formulators is that most acrylics do not have the resolubility necessary for good lapping properties. Finally, most acrylics are not removed by commercial aqueous deck strippers very well.

A new acrylic binder has been developed to meet these challenges. This APEO-free acrylic polymer incorporates a unique functionality which helps it adsorb onto the surface of iron oxide pigments. This adsorption helps separate and stabilize conventional and ultrafine iron oxide pigments against flocculation both in the wet stain and also as the film is drying. Since nonflocculated iron oxide pigments would be expected to be more effective at blocking UV light, the adsorbed polymer might have the effect of reducing the degradation of the underlying wood substrate and giving a longer service life than conventional acrylics.

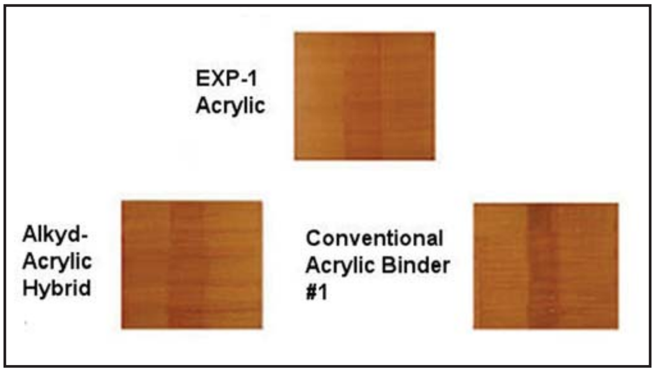
The new acrylic binder also incorporates a unique dual charge stabilization to give improved adhesion on wood and treated wood substrates. It is thought that the particle stabilization may keep the particles from flocculating and may slow the increase in viscosity as the water is wicked from the stain into the substrate. Since they are less flocculated and lower viscosity, the polymer particles may have better lapping and achieve some penetration into the open lumen of the fractured surface cells. This closer association with the irregularities on the surface of the wood might be expected to help form a better bond between the polymer particles and the wood.

Finally, the new acrylic polymer has carefully balanced hydrophilic functionality to give good resolubility and lapping at 100 VOC, but still have excellent water resistance after an overnight dry. The acrylic polymer also has excellent resistance to high pH sodium hydroxide/sodium hypochlorite commercial deck cleaners, so the surface can be cleaned without damaging the stain. On the other hand, it was also designed to be easily removed with commercial water-based deck strippers.

MATERIALS AND METHODS

An experimental acrylic polymer (designated EXP-1) was tested for stain performance and compared to two conventional acrylic stain binders, an alkyd acrylic hybrid stain binder and two commercial acrylic semitransparent stains which were made at 150 and 250 VOC. The experimental polymer was made to have good film formation at low temperatures (40°F) and required just 2% coalescent. Coalescent was added as needed to the conventional acrylic binders to give good low temperature film formation at 40°F. The

Figure 1—Ten-minute lapping of semitransparent stains on cedar. The darker area in the middle of the panels is where the fresh stain was brushed on top of a coat of stain which had dried for 10 min. Stains with worse resolubility and lapping have darker, more visible areas where the coats overlapped. The conventional acrylic stain has less resolubility and worse lapping than the EXP-1 stain.



commercial controls were purchased as untinted bases and the same level of universal colorant was added to each stain (1.5 oz. of universal colorant per gallon). The experimental stains were formulated at 20% volume solids and were made at 100 VOC with Texanol® and propylene glycol.

Laboratory tests for lapping were run on smooth cedar siding at 10 min dry time by brushing 15 strokes into a drying stain film with a new coat of stain. Lapped areas were evaluated for sheen and color differences where the second coat of stain was applied over the drying first coat.

The relative resolubility and early abrasion resistance were estimated using a Crockmeter rub test. A 3.5 wet mils drawdown was made on white Leneta Scrub charts and tested for resolubility in the wet stain at set time intervals (2.5, 5, and 7.5 hr). These tests used a James Heal motorized Crockme-ter with 1000-gm weight and a 5/8-in. diameter stylus covered with linen cloth. The cycles to cut through across a shim were recorded.

This test on a non-porous surface like the Leneta Scrub Chart might be expected to overestimate the effect of glycols on the resolubility of a stain. Hydrophilic glycols in water-based stains brushed on wood might be expected to leave the stain film by rapid wicking into the wood along with the water, but on a non-porous substrate, the glycols would leave the film only by slower evaporation after the water. In order to determine the effect of VOC on the lapping and Crockmeter rub test methods, a stain based on a conventional acrylic binder was made at 100 VOC (with 1 gal of propylene glycol) and at 250 VOC (with 5.5 gal of propylene glycol).

Overnight water resistance was evaluated for one and two coats on both treated pine and smooth cedar by drying the stained panel for 16 hr, then placing it into a fog box for 6 hr. The color rub off was evaluated by rubbing the surface lightly with a damp cheese cloth for 15 strokes and visually rating the color transfer onto the cheese cloth.

The Crockmeter rub resistance test was used to evaluate the development of overnight water and chemical resistance for the different binders. The overnight cure test was first run dry to estimate the abrasion resistance of the binders, and then the resolubility with water, 0.2 molar ammonium hydroxide (at pH 11), a commercial deck cleaner (aqueous solution of sodium hypochlorite/sodium hydroxide at pH 11.8), and a commercial water-based deck stripper (sodium hydroxide base) were tested.

Scanning Electron Micrographs (SEM) were collected for HEUR thickened mixtures of transoxide yellow oxide and either the EXP-1 binder or a conventional acrylic binder. The SEMs were taken on a JEOL 6700 Field Emission SEM at 15 keV and 2,000x magnification.

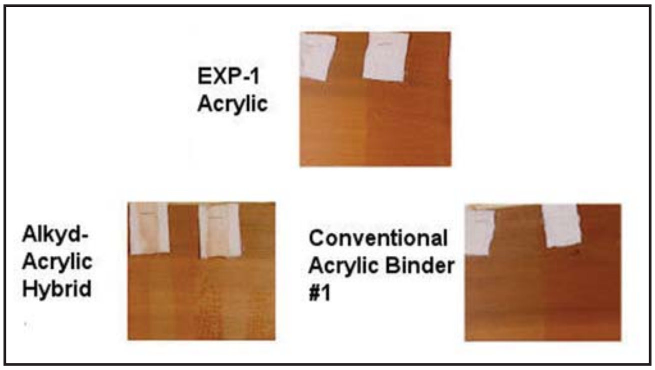
Results of the lab testing were compared to a one-year exposure for these stains. Horizontal up exposures with and without foot traffic on cedar, Trex, weathered CCA, copper azole treated pine, Ipé, and mahogany were evaluated.

Table 1—Lapping of Stains and Resolubility of Drying Films

		Crockmeter Rub Test on Drying Films Rub Resistance (Cycles to Cut Through)[2]		
	10 Min Lapping: Smooth Cedar Substrate[1]	2.5-Hr Dry	5-Hr Dry	7.5-Hr Dry
Exp–1 Acrylic Binder (100 VOC)	Good	21	63	55
Conventional Acrylic Binder #1 (100 VOC)	Poor	300+	300+	300+
Conventional Acrylic Binder #1 (250 VOC)	Fair	300+	300+	300+
Conventional Acrylic Binder #2 (100 VOC)	Poor	300+	300+	300+
Alkyd Acrylic Hybrid Binder (100 VOC)	Good	28	54	74
Aqueous Commercial Acrylic Stain #1 (150 VOC)	Fair	100	175	250
Aqueous Commercial Acrylic Stain #2 (250 VOC)	Fair	120	240	300+

(1) The lapping test was run on smooth cedar. A second coat was brushed with 15 strokes onto a first coat of the stain that had dried for 10 min. Lapping was rated visually from excellent (no visible sheen or color differences on the lapped area) to very poor (large color or sheen differences on the lapped area).
(2) Development of rub resistance during dry was run on 3.5 wet mils drawdown on white Leneta Scrub charts. At specified time intervals, the wet stain was applied to the drying film and the cycles to cut through across a shim were recorded. Low numbers (<60 cycles) in this test indicate good resolubility of the drying stain in fresh wet stain.

Figure 2—Overnight water resistance of semitransparent stains on cedar. Stains were applied one and two coats on smooth cedar panels. Panels were dried overnight and then placed in a fog box for 6 hr. The wet panels were rubbed with cheese cloth and the water resistance was rated by the amount of color transfer to the cheesecloth. The alkyd acrylic hybrid stain has severe color transfer and the film is being washed from the surface on the double coated area.



TEST RESULTS

Lapping and Resolubility During Dry

In the lapping tests on smooth cedar (*Figure* 1, *Table* 1), the experimental acrylic EXP-1 in a 100 VOC stain was significantly better than the stain based on the conventional acrylic binders, even when the conventional acrylics were formulated at 250 VOC. The EXP-1 stain was equal to the alkyd acrylic hybrid stain binder for lapping.

In Crockmeter resolubility tests (*Table* 1) of the different stains during dry, the EXP-1 binder and the alkyd acrylic hybrid were excellent with cut through at ~ 60 cycles and removal of the film along the path at up to 7.5 hr. The conventional acrylic binders at 100 VOC (or with additional glycol at 250 VOC) and two commercial stains based on acrylic binders had fair to poor resolubility at 2.5 hr.

Color Transfer and Solubility in Aqueous Solutions after Overnight Dry

All the binders had good overnight water resistance in a color rub off test on pine, however the alkyd acrylic hybrid had poor overnight water resistance on the cedar substrate (*Figure* 2, *Table* 2).

In the overnight dry Crockmeter rub test, all the stains based on acrylic binders and commercial acrylic stains had excellent water resistance and resistance to the commercial deck cleaner (no failure at 300 cycles). The commercial acrylics had poor resolubility in the aqueous commercial deck stripper and in a dilute ammonium hydroxide solution (0.2 Molar, pH 11), while the EXP-1 stain had good resolubility in those two solutions. The alkyd acrylic hybrid stain had poor dry abrasion resistance at one-day dry and was retested at one-week cure. At one week the alkyd acrylic hybrid binder had fair water resistance but poor resistance to the commercial deck cleaner.

SEM Images

SEM images (*Figure* 3) of the EXP-1 binder and one of the conventional acrylics in HEUR thickened stains containing ultrafine iron oxide pigments indicated that the experimental acrylic had fewer pigment particles exposed at the surface. The stain based on the EXP-1 binder also had smaller pigment particles and less pig-

Table 2—Resistance Properties of Stains After 16-Hr Dry

	16-Hr Dry Water Resistance Color Transfer[1]		16-Hr Dry Crockmeter Test Rub Resistance (Cycles to Cut Through)				
			(Higher Rub Resistance Desirable)			(Low Rub Desirable)	
	Pine Substrate	Cedar Substrate	Dry Abrasion[2]	Water[3]	Commercial Deck Cleaner[4]	Dilute Ammonium Hydroxide[5]	Aqueous Deck Stripper[6]
Exp–1 Acrylic Binder (100 VOC)	5	5	300+	300+	300+	45	55
Conventional Acrylic Binder #1 (100 VOC)	5	5	300+	300+	300+	300+	300+
Conventional Acrylic Binder #1 (250 VOC)	5	5	300+	300+	300+	300+	300+
Conventional Acrylic Binder #2 (100 VOC)	5	5	300+	300+	300+	300+	300+
Alkyd Acrylic Hybrid Binder (100 VOC)[7]	5	2	250	200	55	60	45
Aqueous Commercial Acrylic Stain #1 (150 VOC)	3	2	300+	200	250	200	300+
Aqueous Commercial Acrylic Stain #2 (250 VOC)	5	5	300+	300+	300+	300+	300+

(1) Color Transfer: 16-hr dry then place in high humidity cabinet for 6 hr. Rate color transfer onto cheesecloth after 15 strokes. Ratings: 1–5; 5: no transfer and excellent, 1: severe transfer and very poor.
(2-4) High Crockmeter numbers for dry abrasion, water, and the commercial deck cleaner (pH 11.8 aqueous solution of sodium hypochlorite/sodium hydroxide) indicate good early abrasion resistance, good early water resistance and good cleanability with aqueous commercial deck cleaners.
(5-6) Lower Crockmeter numbers for dilute ammonium hydroxide (pH 11; 0.2 molar solution) and the aqueous commercial deck stripper indicate good resolubility in those media.
(7) The alkyd acrylic hybrid Crockmeter tests were run after one-week dry since the dry abrasion was low for that binder after one-day dry.

ment flocculation than the stain with the conventional acrylic binder.

Exposure Results

Exposures of the stains were also evaluated. When exposed horizontal up on copper azole treated pine, stains based on two conventional acrylic binders were showing flaking and peeling on the latewood grain after just 6 months exposure (*Figures* 4 and 5).

In another footbridge exposure on treated yellow pine, the experimental stain binder had better durability than a commercial oil-based stain, a commercial water-based alkyd acrylic hybrid, and a commercial semitransparent stain based on an acrylic binder with alkyd modification (*Figure* 6).

In another horizontal up exposure at six months on dark woods like cedar, mahogany, and Ipé, a stain based on EXP-1 had better color retention than stains based on two conventional acrylic binders with the same levels of ultrafine iron oxide pigment and UV absorbers (*Figure* 7).

DISCUSSION

In the lapping tests the experimental acrylic EXP-1 was equal to the best of the water-reducible stain binders and better than the conventional acrylic binders. Interestingly, there was little change in the lapping as the glycol level in the conventional acrylic stain was increased from 100 to 250 VOC; however, it is possible that the hydrophobicity of the acrylic binder tested may have been too great to see small differences in lapping due to increased glycol levels. It is clear, however, that the EXP-1 binder was equal in lapping to the best of the water-based binders and stains tested.

From the drying studies using the Crockmeter on nonporous substrates, the stain based on the EXP-1 binder had much longer resolubility (more than 7.5 hr) in the wet stain than conventional acrylics (less than 2.5 hr), even when the conventional acrylics were formulated at 250 VOC with additional propylene glycol. The excellent resolubility of the EXP-1 stain probably contributed to the good lapping performance. The stain based on the EXP-1 acrylic binder was equal to the alkyd acrylic hybrid stain for resolubility.

After an overnight dry, all the stains showed good color rub-off resistance on treated pine decking; however, on cedar, the acrylics were much better than the alkyd acrylic hybrids for overnight water resistance. The difference between the substrates was thought to be caused by the higher tannin levels in the cedar slowing the drier catalyzed oxidative cure of the alkyd based stains. The slower dry could be a significant problem if

Figure 3—SEM images of semitransparent stains with ultrafine red iron oxide colorant. Smaller pigment particle size and less exposed pigment at the surface may indicate that the EXP-1 polymer is adsorbed onto the surface of the pigment and is preventing pigment flocculation.

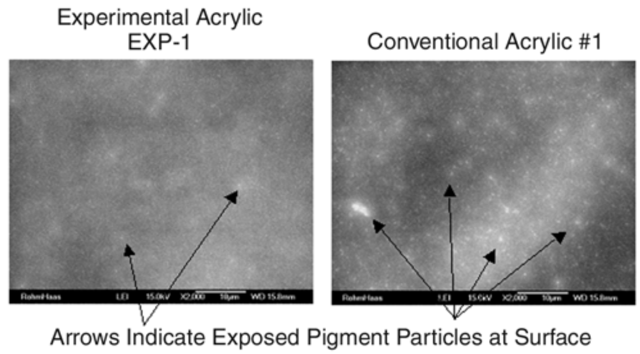


Figure 4—Adhesion to copper azole treated pine; six-months exposure at horizontal up. The conventional acrylics have severe flaking and poor adhesion on the latewood grain. On the same board, the EXP-1 acrylic has no flaking or loss of adhesion.

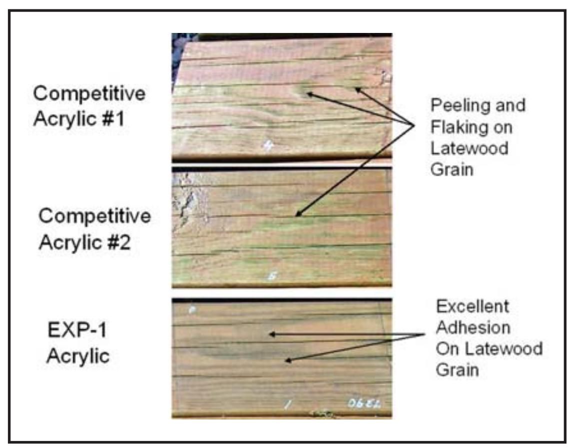


Figure 5—Flaking on exposure (copper azole treated pine decking exposed horizontal up). Flaking was rated from 1–10 (a rating of 10 is no flaking). The conventional acrylics have severe early flaking and loss of adhesion on copper azole treated pine. The EXP-1 stain has excellent adhesion.

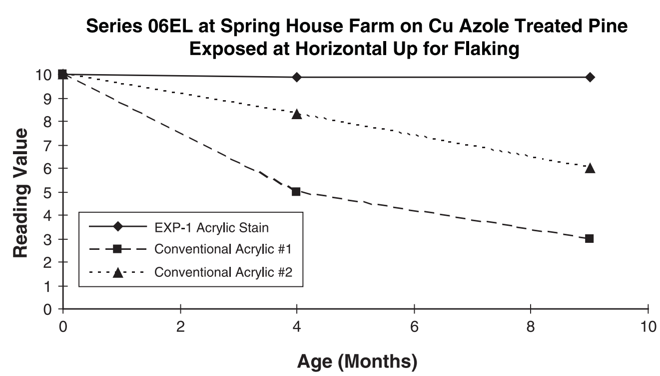
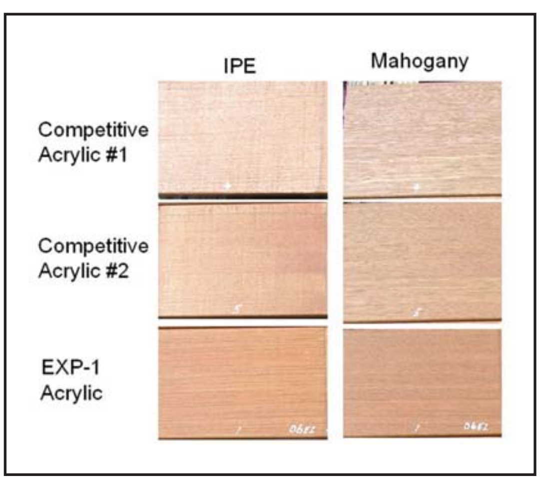


Figure 6—Thirty-month exterior durability of EXP-1 and commercial stains. After 30 months exposure at horizontal up, the EXP-1 stain has better durability (less flaking, erosion, and color fade) than the commercial semitransparent stains.

the alkyd acrylic hybrid stain remained tacky and water sensitive overnight.

In Crockmeter testing of films dried overnight, the EXP-1 stain was excellent when tested dry, which indicates good early abrasion resistance, and when tested with water, showed excellent early water resistance. It also had good resistance to commercial deck cleaner, indicating that the EXP-1 stain could be cleaned as necessary without damaging the film. The EXP-1 stain did redissolve moderately easily in dilute ammonium hydroxide and in commercial sodium hydroxide-based deck stripper, so it could be removed from the surface of the deck if necessary. Stains based on the conventional acrylic binders had excellent dry abrasion and resistance to deck cleaner and water, but they did not redissolve in the dilute ammonium hydroxide solution or the aqueous commercial deck stripper. The alkyd acrylic hybrid had poor abrasion resistance after an overnight dry so it was tested after a one-week dry. At one-week dry, it had fair water resistance but poor deck cleaner resistance and that sensitivity may mean that the films based on the alkyd acrylic hybrid would be damaged when the decks are cleaned.

Figure 7—Color retention of dark hardwoods at six-months exposure horizontal up. On Ipé and mahogany boards, the EXP-1 stain has less bleaching of the substrate than the stains based on the conventional acrylic binders.



The SEM micrograph shows fewer pigment particles exposed at the surface of the EXP-1 stain and fewer pigment agglomerates compared to a conventional acrylic. Since there were fewer pigment particles exposed at the surface, it seems likely that the better dispersion of the ultrafine iron oxides was due to polymer adsorption onto the surface of the pigment. The unflocculated ultrafine iron oxide pigments might be expected to give longer durability on exposure since the wood substrate is better protected from degradation by UV light.

One-year exposures of these stains also showed better color retention for the EXP-1 stain on the darker wood substrates. This improved color retention may indicate less UV degradation of the dark wood substrates for the EXP-1 stain. Superior adhesion of the EXP-1 binder compared to conventional acrylics on copper azole treated yellow pine was also seen in the exposures. Better long-term durability of the EXP-1 stain on treated pine can also be seen in the exposures where it was compared to commercial water-based and solvent-based semitransparent stains.

CONCLUSION

Using a combination of innovative technologies in an acrylic stain binder, a 100 VOC semitransparent stain was formulated. This new binder offers some key advantages over current aqueous stain binder technologies. The excellent resolubility of the stain gives it better lapping than conventional acrylic binders. The good overnight water resistance on high tannin woods is an improvement on alkyd acrylic hybrid or water reducible alkyd stains which need driers for cure. The durable acrylic binder, in combination with ultrafine iron oxide pigments, gave a longer stain life in exposure testing. The stain also had superior adhesion to difficult substrates like copper azole treated woods. Low-VOC, APEO-free, and metal drier-free semitransparent deck stains based on this combination of innovative acrylic technologies can give improved performance while meeting environmental and regulatory requirements.

ACKNOWLEDGMENTS

The author would like to thank Cathy Finegan, Wei Zhang, Al Maurice, Susan Gill, Bill Howell, Shelly Fox, Martha Wittek, Jocelyn White, Pete Eastman, and other

members of the analytical, research, synthesis, and marketing teams for their pioneering work in developing the EXP-1 stain binder. CT

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