NOVEL ACRYLIC POLYMER FOR Architectural Exterior

Architectural exterior coatings are subject to very harsh environmental elements. Extreme conditions like cold and hot temperatures, low and high humidity, and rain and snow test the ability of coatings to withstand cracking, limit water absorption, prevent leaching of materials from the surface, and adhere to multiple substrates. Another detrimental source of damage are UV rays, which induce polymer chain degradation leading to chalking and erosion of the coatings layer. Surface coatings are also subject to dirt and mildew growth resulting in a dirty appearance. When designing a polymer for exterior coatings, inventors must carefully consider the above destructive forces.

Professional and do-it-yourself (DIY) painters increasingly care

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Paint and Primer in One

COATINGS APPLICATION

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about efficiency—reducing the time and labor involved in painting surfaces. Paints with paint and primer in one capabilities help reduce the time and labor of painting jobs, so developing a polymer that provides both primer and topcoat properties is necessary, but also challenging. This objective further raises the performance requirement for the exterior polymer.

This study focuses on developing a polymer that addresses key needs for paint and primer in one exterior coatings, such as dirt pick-up resistance (DPUR), leaching resistance, early rain resistance, gloss retention, grain crack resistance, adhesion, efflorescence resistance, and tannin blocking. The outcome of the study is a polymer that is designed to withstand the exterior elements in formulations featuring <25 g/l volatile organic compounds (VOC).

FACTORS IMPACTING CRITICAL PERFORMANCE FEATURES

Dirt Pick-Up Resistance (DPUR)

Dirt pick-up is a surface phenomenon and is mainly influenced by hardness of the coating, surface energy, surface porosity, and the nature of the dirt. Softer coating surfaces hold on to dirt better than harder surfaces; therefore, a harder polymer is required to improve DPUR. Both highly hydrophobic and highly hydrophilic surfaces can provide better DPUR. However, hydrophobic surfaces are preferred because hydrophilic surfaces reduce water resistance of the coating.

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FIGURE 1—Film formation in emulsion polymers.[1,2]

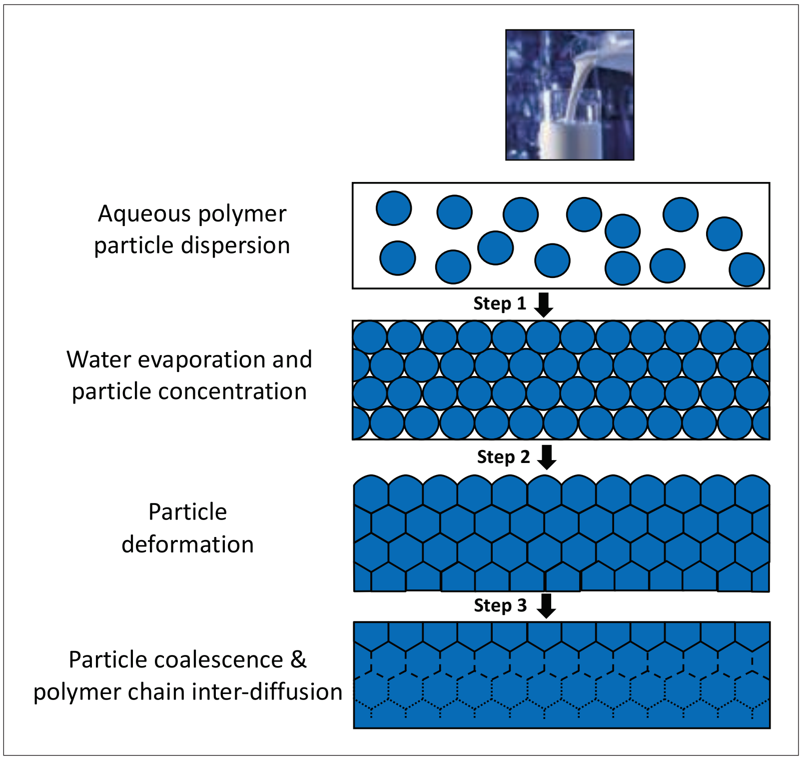
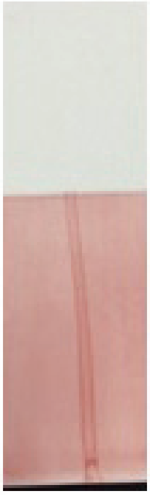


FIGURE 2—Leaching in exterior wall.

FIGURE 3—More dirt in leached trail.



Hydrophobicity can be measured in terms of water contact angle—the higher the contact angle, the better the hydrophobicity and the higher DPUR. Rough and porous surfaces tend to retain dirt better and consequently reduce DPUR.

Conflicting Demands: Film Formation at Low VOC and DPUR

A schematic of the film formation process[1,2] of emulsion polymer dispersions is depicted in three steps (*Figure 1*). The steps are 1) water evaporation and particle concentration, 2) particle deformation, and 3) particle coalescence and polymer chain inter-diffusion. The degree of particle deformation and polymer chain inter-diffusion depends on the minimum film forming temperature (MFFT) of the particles. Good film formation at low VOC requires soft polymers or hard polymers with permanent coalescing agents. Permanent coalescing agents remain in the film forever and reduce the hardness of the coating. Both soft polymers and hard polymers with permanent coalescing agents lead to reduced DPUR. Thus, low VOC and better DPUR are conflicting demands and a tough problem to solve.

Leaching Resistance

Rain and dew can leach water-soluble materials from the coatings surface and create a less than desirable appearance (*Figure 2*). Leaching resistance of coatings can be improved by reducing water-soluble materials, tailoring film formation kinetics, improving early water resistance, and incorporating crosslinking chemistry. Leaching of materials from the surface will ultimately create a porous surface, which can reduce the DPUR of the coatings. In *Figure 3*, more red iron oxide adheres to the leached surface, which appears as a darker red trail.

Tannin Blocking and Efflorescence Resistance

Polyphenols (tannin) found in wood and salts in concrete/masonry substrates migrate into coatings and negatively impact their appearance (*Figures 4* and *5*). Some of the factors that control these migration phenomena are film formation

FIGURE 4—Tannin migration from Redwood to coatings. Superior performing polymers (green box) block tannin migration, as compared to one coat of an inferior paint (red box) where the brown color of the tannin migrates through.

FIGURE 5—Efflorescence on concrete surface.

kinetics, hydrophobic–hydrophilic balance of the coating, water-soluble materials, functional groups in the polymer matrix, encapsulation of migrating materials, and adhesion of the coating to the substrate.

Grain Crack Resistance

Film hardness and elasticity play a critical role in controlling the crack resistance. These two properties need to be balanced to achieve crack resistance. Another factor that influences crack resistance is emulsion polymer particle coalescence and film formation. Particle deformation followed by polymer chain inter-diffusion along particle boundary (*Figure 1*) provide mechanical integrity to the paint film that is essential for grain crack resistance. An example where a poorly formulated paint did not provide grain crack resistance in a southern yellow pine board (red box) is shown in *Figure 6*. Other paints on the same board provide excellent grain crack resistance.

NOVEL POLYMER

A novel acrylic polymer was synthesized using the following design principles: particle morphology, low water-soluble polymers, and hydrophobic–hydrophilic balance. *Table 1* shows the physical properties of the novel polymer (Acronal® EDGE 4247). This polymer is free of alkyl phenol ethoxylate surfactants and can be used to formulate <25 g/l VOC coatings.

The performance of this novel polymer was tested along with four competitive polymers (competitive latex A through competitive latex D) in an architectural white flat coatings formulation. The formulation and its physical characteristics are given in *Tables 2* and *3*, respectively. These paints were tested for topcoat and primer properties, and the results are discussed in the following section.

FIGURE 6—Coatings on southern yellow pine boards showing both poor (red box) and excellent grain crack resistance.

TABLE 1—Novel Polymer Physical Properties

PROPERTY	VALUE
WEIGHT % SOLIDS	52 TO 54
PH	7.5 TO 8.5
VISCOSITY, CP	<1000
PARTICLE SIZE (VOLUME AVERAGE, NM)	100 TO 130
MFFT (°C)	6 TO 7

TABLE 3—White Flat Formulation Physical Characteristics

EXTERIOR FLAT FORMULATION	
VOC (g/L)	0[a] OR 20[b]
VOLUME % SOLIDS	41
WEIGHT % SOLIDS	57
PVC	46

(a) Zero VOC coalescing agent.
(b) VOC coalescing agent.

TABLE 2—White Flat Formulation

RAW MATERIAL	LB	GAL
WATER	50.0	6.0
TITANIUM DIOXIDE SLURRY	294.0	15.02
PIGMENT DISPERSANT	8.0	0.78
DEFOAMER	2.0	0.28
WETTING AGENT	3.0	0.35
BIOCIDE	3.0	0.33
INORGANIC FILLER/EXTENDER	230.0	10.57
MINERAL THIXOTROPIC THICKENER	4.0	0.20
GRIND FOR 20 MIN, THEN ADD:		
WATER	155.0	18.61
FUNGICIDE AND AN ALGAECIDE	10.0	1.03
NEUTRALIZING AGENT	1.40	0.19
DEFOAMER	2.0	0.28
NOVEL POLYMER (53% WEIGHT SOLIDS)	365.0	41.25
POLYMER PARTICLE COALESCING AGENT[a]	6.0	0.75
RHEOLOGY MODIFIER (HIGH SHEAR)	35.0	4.07
RHEOLOGY MODIFIER (LOW SHEAR)	2.50	0.29
TOTAL	**1170.9**	**100**

(a) Zero VOC or VOC coalescing agent.

EXPERIMENTAL

Dirt Pick-up Resistance

Paints were drawn down on a Lenetta black scrub chart using a 250 μ gap bar. The drawn down paints were cured for 24 h at 72°F and 50% humidity. The cured paints were exposed to UV-A radiation for 24 h in a UV chamber. Then, either red iron oxide or carbon black dispersion was applied to half of the cured paint. After 4 h, the paints were gently washed with a sponge and running tap water. The washed paints were dried for 24 h and the Y reflectance of the soiled and unsoiled areas was measured to calculate ΔY reflectance.

Surfactant Leaching

Tinted paints (2% Phthalo blue) were drawn down on a Lenetta black scrub chart using a 250 μ gap bar. Tests were done at cure times of 4 h and 24 h. At each cure time, three drops of water were deposited at the top of the drawn down paints. At 10 min, the chart was tilted to run the water off the panel. After 24 h, the appearance of the water trails was rated on a 0 to 10 scale with 10 being no change and 0 being severe change.

Efflorescence Resistance

Tiles prepared from plaster of Paris were coated with a specified amount of paint leaving one inch unpainted at one end. The paints were cured for 24 h at 72°F and 50% humidity. The uncoated ends of the tiles were placed in a sand bed soaked with 1% sodium sulfate solution for two weeks. Then, the appearance of the painted end of the tiles was recorded.

Early Rain Resistance

Paints were drawn down on aluminum Q-panels using a 250 μ gap bar and dried at 72°F and 50% humidity for 25 min. Then, the panels were placed under a 12-in. square shower head and showered for 10 min at constant water flow. The appearance of the test paints was compared to the appearance of a control paint.

Tannin Blocking

Tannin blocking was tested according to ASTM 6686-1 test method. Y reflectance and yellowness index were measured, not L* and b*.

Corrosion Resistance

Corrosion resistance was tested using cold rolled steel panels according to ASTM G85-11-A5 dilute electrolyte salt fog test method.

RESULTS AND DISCUSSION

Table 4 provides viscosity, film formation rating at 4°C, gloss, contrast ratio, tint strength, and scrub resistance of the coatings. The novel polymer excels in scrub resistance with 1915 scrub cycles at a PVC of 46. This high scrub resistance indicates excellent film formation and potential for the use of this polymer for even higher PVC coatings. Tint strength provides indirect evidence for the degree

FIGURE 7—Dirt pick-up resistance.

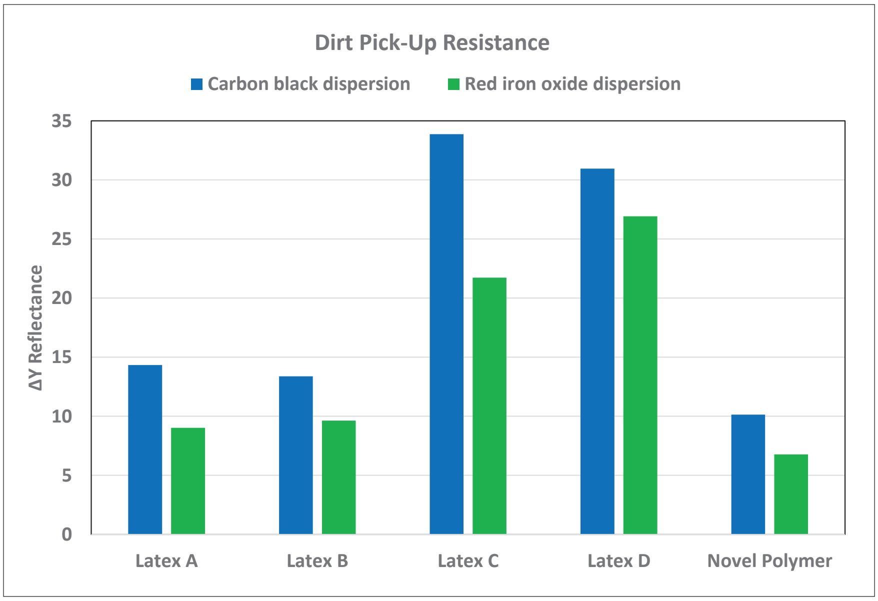
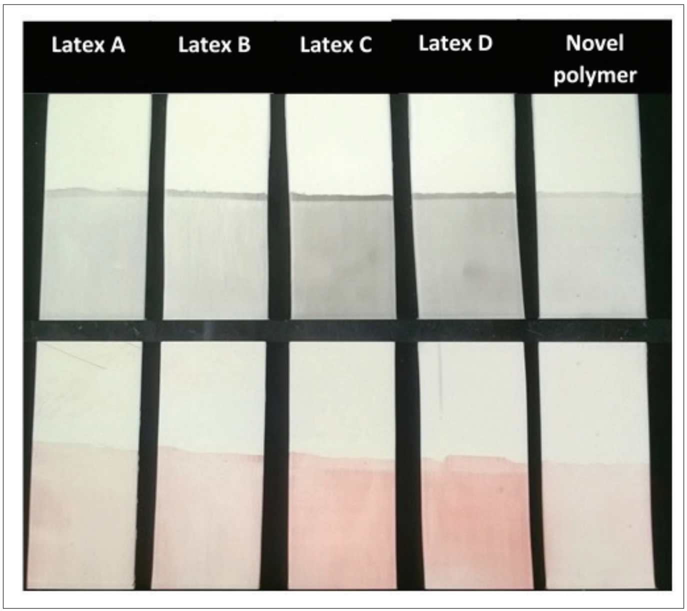


FIGURE 8—DPUR (carbon black and red iron oxide dispersions).



of TiO_2 distribution in the coatings matrix. The novel polymer provides the highest tint strength, while the competitive latices, except competitive latex B, provide significantly lower tint strength. Higher tint strength indicates lower TiO_2 demand to achieve the same degree of whiteness, resulting in cost savings.

Dirt Pick-Up Resistance

Two different type of dirt—aqueous iron oxide slurry and aqueous carbon black slurry—were used to test DPUR performance. The results are shown in *Figures 7* and 8. *Figure 7* shows ΔY reflectance for soiled and unsoiled paint surfaces. The novel polymer has the lowest ΔY reflectance for both type of dirt, indicating the best DPUR performance. *Figure* 8 shows the actual test panels. The novel polymer shows the best performance from visual examination.

Surfactant Leaching Resistance

Leaching test results after dry times of 4 h and 24 h are shown in *Figure 9*. The novel polymer and competitive latex A show similar performance at both dry times, but the other latices show inferior performance.

Early Rain Resistance

Early rain resistance was tested by a shower head water flow test method. The performance at 25 min dry time of the novel polymer is compared to a leading 50 g/l VOC commercial paint.

As shown in *Figure 10*, while the novel polymer does not exhibit any defect, the commercial paint does show defect.

Tannin Blocking

Tannin blocking of the coating is tested using Redwood and the results are shown in *Figure 11*. *Figure 11* shows the performance in terms of ΔY reflectance and Δ yellowness of the two-coat surface. The novel polymer has the lowest ΔY reflectance and Δyellowness indicating the lowest amount of tannin migration to the coating. *Figure 12* shows a Redwood board with one and two coats of paint (paint and primer in one application). The novel polymer with the second coat of the paint has the whitest appearance.

TABLE 4—Paint Properties

PROPERTY		LATEX A	LATEX B	NOVEL POLYMER	LATEX C	LATEX D
VISCOSITY	KU	108.2	113.8	106.8	105.2	98.9
	ICI	1.6	1.9	1.4	1.8	1.6
FILM FORMATION @ 4°C[a]		10	10	10	10	10
GLOSS	20°	1.5	1.5	1.5	1.5	1.5
	60°	4.2	4.1	4.1	4.3	4.1
	85°	3.2	3.1	3.0	3.7	4.0
CONTRAST RATIO		97.5	97.4	97.4	97.0	96.8
ALKYD DRY/WET ADHESION, 24 H		5B/5B	5B/5B	5B/5B	0/0	5B/5B
SCRUB RESISTANCE (CYCLES)[b]		1655	472	1915	1017	353
TINT STRENGTH[c]		93.4	99.8	100	93.8	92.9

(a) 1 to 10 rating scale with 10 being perfect and 1 being worst.
(b) ASTM D 2486 test method.
(c) 2% Phthalo blue tint.

FIGURE 9—Leaching resistance rating.

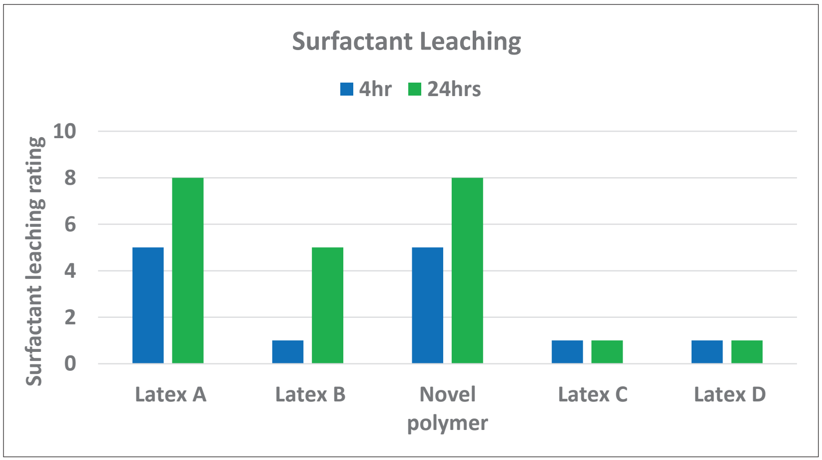


FIGURE 10—Early rain resistance.

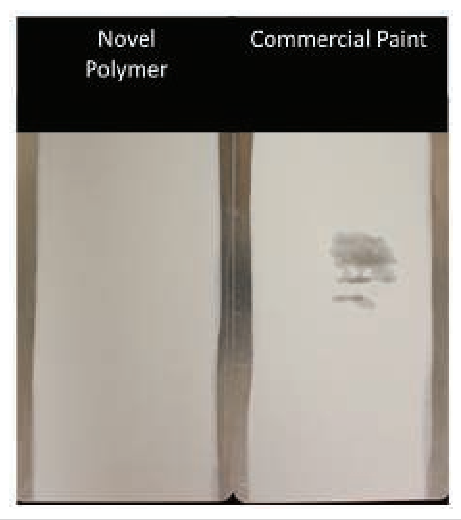


FIGURE 11—Redwood tannin blocking.

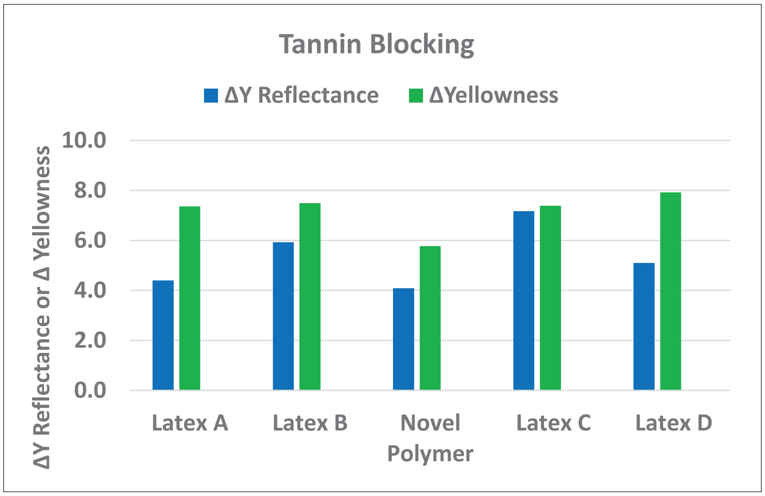


FIGURE 12—Redwood tannin blocking.

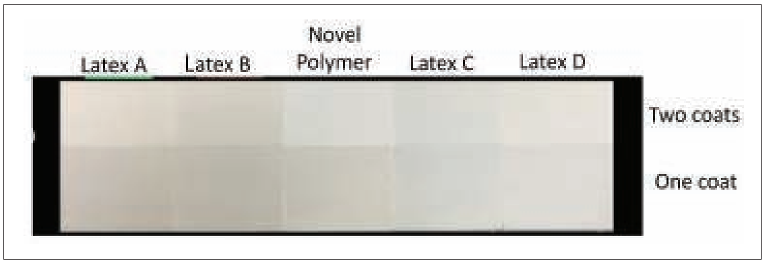


FIGURE 13—Efflorescence resistance.

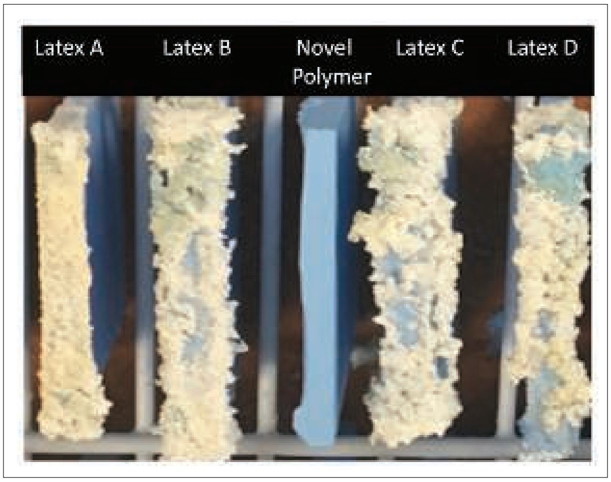
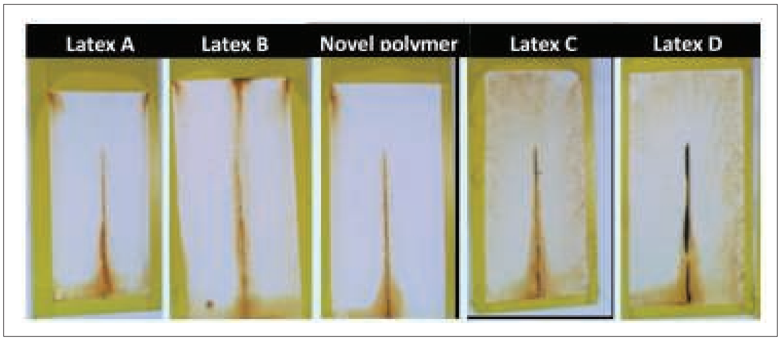


FIGURE 14—Corrosion resistance of cold rolled steel.



Efflorescence Resistance

The results are shown in *Figure 13*. The tile coated with the novel polymer-based coating does not show any salt or defect on the surface, indicating outstanding efflorescence resistance. All other paints show copious amounts of salt on the surface of the tile due to salt migrating through the coatings layer.

Corrosion Resistance

The novel polymer shows superior corrosion resistance along the scribe and on the surface at 250 h of testing (*Figure 14*).

Paint Film Mechanical Properties

Tensile stress and elongation play a critical role in controlling grain crack resistance. The paint film mechanical properties for the novel polymer, competitive latex B, and a leading commercial paint are provided in *Table 5*. The novel polymer has a much higher elongation without significantly compromising tensile stress. The % elongation is an important feature for withstanding harsh exterior elements, including hot and cold weather and freeze-thaw cycles.

TABLE 5—Mechanical Properties of White Flat Paints

PAINT FILM	PEAK TENSILE STRESS (PSI)	% ELONGATION
NOVEL POLYMER	442	185
COMPETITIVE LATEX B	584	69
COMMERCIAL PAINT	745	19

TABLE 6—Color Change ΔE in Accelerated Weathering Study (UV-A Radiation)

HOURS	NOVEL POLYMER	COMMERCIAL PAINT
250	0.3	0.4
500	0.9	0.9
1000	1.4	1.2
1500	1.3	1.3

Accelerated Weathering

A semi-gloss paint formulated with novel polymer and a leading commercial paint were tested for accelerated weathering according to the ASTM D4587-11 test method using UV-A radiation without condensation cycle. The results are given in *Figure 15* and *Table 6*. The novel polymer shows excellent gloss retention and minimal color change.

Natural Weathering

To study the natural weathering of the novel polymer, southern yellow pine and cedar wood boards were coated with flat paint formulated with the novel polymer, competitive latex 1, competitive latex 2, and a commercial paint. They were exposed to natural weathering at a 45°angle facing south, in Charlotte, NC. The results at 36 months of exposure are given in *Table 7.* The novel polymer is performing very well at 36 months of testing.

TABLE 7—Natural Weathering Results at 36 Months of Testing

PAINT	GRAIN CRACKING	CHECKING	FLAKING	CHALKING[a]	DIRT[a]	MILDEW[a]
COMMERCIAL PAINT	NONE	NONE	NONE	9	8	8
NOVEL POLYMER	NONE	NONE	NONE	9	8	8
LATEX 1	NONE	NONE	NONE	9	8	8
LATEX 2	NONE	NONE	NONE	9	8	8

(a) 1 to 10 rating scale with 10 being perfect and 1 being worst.

FIGURE 15—Gloss change in accelerated weathering study (UV-A radiation).

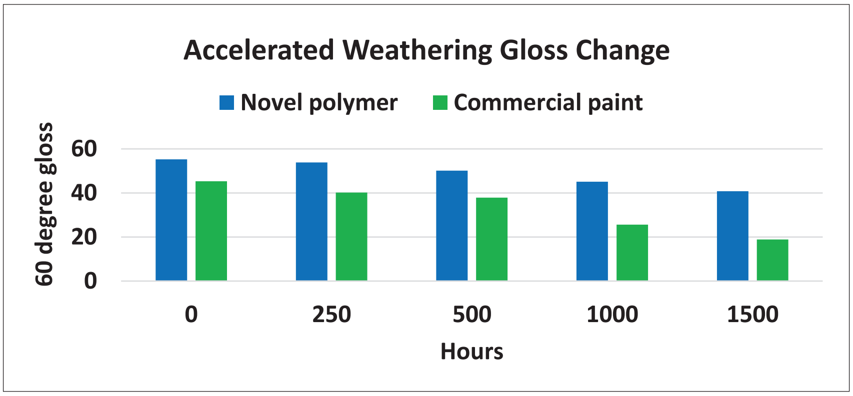
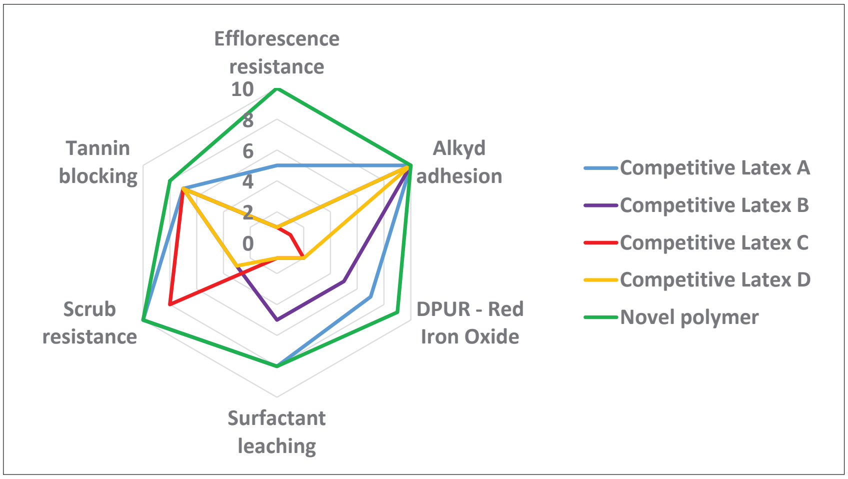


FIGURE 16—Spider diagram comparing performance of the coatings.



SUMMARY

Architectural exterior coatings are subject to the harsh elements of the environment. Careful consideration must be paid to these harsh conditions to overcome deleterious effects of these elements. The novel polymer developed using innovative polymer engineering has outstanding performance for paint and primer in one exterior coatings application. This polymer can be used to formulate <25 g/l VOC coatings. A benchmark study involving market leading competitive binders shows (*Figure 16*) that the novel polymer outperforms in DPUR, leaching resistance, tannin blocking, efflorescence resistance, scrub resistance, corrosion resistance, gloss retention, and tint strength. Natural weathering shows excellent results at 36 months of testing.

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References

1. Yoo, J.N., Sperling, L.H., Glinka, C.J., and Klein, A., *Macromolecules*, 23, 3962 (1990).
2. Taylor, J.W. and Winnik, M.A., "Functional Latex and Thermoset Latex Films," *JCT Research,* (1) 3 163-190 (2004).

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