VeoVa™ Monomers for Water Whitening Resistant Latex Films

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1 Background

In paints, whiteness is often desirable: white pigments and extenders improve coatings’ color and opacity. When it comes to latex, however, paint chemists prefer that the dried latex film does not turn white when in contact with water. Latices that turn white easily in the presence of moisture are believed to have inferior water resistance properties and poor durability.

Adding small quantities of VeoVa 10 vinyl ester, the most hydrophobic monomer in the market, can make designing acrylate latices for exterior applications easier by helping to prevent whitening. VeoVa 10 vinyl ester enhances the water whitening resistance of purely acrylic formulations. Either with conventional surfactant systems or with co-polymerizable types, water whitening resistance may be remarkably improved with VeoVa monomers.

Such latices, with their outstanding water resistance, would be perfect binders for exterior clear coat applications on granite or other stone finishes where the standard for non-whitening is extremely high. These latices can also improve the performance of exterior coatings, which have always been plagued with failure caused by moisture and water. Pigmented exterior systems often still suffer from rain marking, dirt streaking, alkali, discoloration from efflorescence, and rapid leach-out of dry film preservatives by torrential rains in the tropics. VeoCryl (VeoVa vinyl ester-modified pure acrylic) emulsions may provide the solution for all these paint failures caused by water, mainly because the VeoVa monomer’s bulky molecular structure acts as an umbrella.

2 Why does water turn dried latex film white?

Latex is a form of colloid wherein the dispersed solid phase (polymer particles) are suspended in the continuous phase (aqueous). In its wet state, latex looks whitish or translucent, due to light scattering as it travels through the multiple media.

Normally, when latex particles dry to form a continuous clear film, the liquid water evaporates while ionically-charged or water-soluble components such as surfactants, initiators, buffers and so on, remain trapped in interstitial areas of the film. Because they are more hydrophilic than the latex particles, however, these components tend to attract water and may become a driving force for the migration of water into interstitial areas. This migration results in “water whitening,” which looks exactly like the original colloidal latex.

This mechanism is how, in real stone applications, the film may become white after rainfall. Understanding the factors affecting the whitening phenomenon of dried latex films helps polymer chemists design better latices for exterior applications.

3 A more precise test to measure water whitening

A common laboratory method to test water whitening resistance is the visual observation of dried film on glass panels when immersed in water. There are two common ways to report the results upon visual examination. One is, after immersion for 2 hours, observe and report the degree of whitening based on a relative scale of 1 to 5; a second one is to observe and record the time it takes for the dried film to turn white. This test method has typically been used for laboratory screening but the reporting is subjective. For this paper we used an alternative method of measuring the degree of whitening—objectively, by reporting the Delta L (change in whiteness) using a spectrophotometer/colorimeter—described below.
4 Methodology

Mix the latex with the appropriate amount of coalescent agent required to form a film at the desired minimum film-forming temperature (MFFT) and stabilize at room temperature (at least overnight) before use.

1. Clean glass panels with ethanol to make sure there is no contamination
2. Apply a 150 μm wet latex film on the clean glass panel, preparing each sample in triplicate
3. Retain glass panel under curing conditions
4. Immerse glass panel in deionized water for a defined period of time
5. Remove glass panel from water and lightly dry the film and glass with soft paper making sure not to destroy the latex film. Immediately place the glass on a black plastic panel (Leneta scrub panel) and measure the L value with a spectrophotometer, e.g. with a BYK 6802* spectro-guide colorimeter.
6. Report water whitening resistance by calculating $\Delta L = L_n - L_0$, $L_n$ is the L value after immersion of latex film in water for a given length of time, and $L_0$ is the initial L value of the latex film
7. Calculate the average $\Delta L$ for the triplicate samples

5 Results

Below, the results are discussed along with factors that affect water whitening resistance.

1. Hydrophobic monomers improve water whitening resistance

Latex containing hydrophobic monomers, especially VeoVa 10 vinyl ester, significantly improves the whitening resistance of a latex film. This effect is clearly shown in Figures 1 and 2, in which the whitening of a pure acrylate is compared with that of a VeoCryl (a VeoVa vinyl ester-modified acrylic) emulsion.

Figure 1. Water whitening of pure acrylate compared with VeoCryl, after immersion in water, over time.
2. Higher hydrophobic monomer content increases water resistance

Increasing the VeoVa 10 vinyl ester content improves resistance to water whitening. In Figure 3, a typical pure acrylate (MMA/BA/AA) was modified with varying proportions of VeoVa 10 vinyl ester.
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3. Reactive or co-polymerizable surfactants provide better water whitening resistance than traditional surfactants

Resistance to water whitening can be further improved through selection of appropriate surfactants, as shown in Figure 4. However, as shown in Figure 5, VeoCryl outperforms pure acrylate regardless of whether a traditional or reactant surfactant is used.

Figure 3. Water whitening of the clear latex film after 3 days of immersion. Increasing percentages of VeoVa 10 vinyl ester are associated with perceptibly decreased whitening.

Figure 4. Whitening of a VeoCryl system (Acrylic/VeoVa 70%/30%) containing different surfactants.

Figure 5. With both reactive and traditional surfactants, VeoCryl emulsion performs better than pure acrylate.
4. When functional monomers are added, optimal levels must be determined

Silquest** A-174NT silane monomer increases water whitening resistance but exhibits an optimum, depending upon the formulation (Figure 6). Silquest** A-174NT silane is a methacryloxy functional trimethoxy silane.

Figure 6. Performance of VeoCryl (Acrylic/VeoVa 10, 70%/30%) with varying functional monomer contents. 1%wt Silquest** A-174NT based on total monomer delivers optimal performance in this latex formulation.

![Graph showing performance with varying functional monomer contents](image)

5. Cross-linking monomers such as HDDA (hexanediol diacrylate) functional monomer also show an optimum, depending upon the formulation

As with the Silquest** functional monomer above, optimal levels of cross-linking monomers must be determined, as shown in Figure 7.

Figure 7. With a latex formulation based on VeoCryl (Acrylic/VeoVa 10, 70%/30%), 1.5%wt HDDA based on total monomer is optimal.

![Graph showing performance with varying cross-linking monomer contents](image)
6. Curing conditions affect water whitening resistance

Higher curing temperatures and longer curing times exert a positive effect, as shown in Figure 8.

Figure 8. Water whitening of VeoCryl (Acrylic/VeoVa 10, 70%/30%) samples dried for various lengths of time, at various temperatures.

6 Conclusions

Hydrophobic monomers are key in achieving good water whitening resistance whilst keeping the latex stable and delivering on other performance criteria such as outdoor durability. VeoVa 10 vinyl ester (the most hydrophobic monomer) increases water resistance, even in all-acrylate systems. Although many acrylates exhibit good water resistance, modification with VeoVa 10 monomer further enhances hydrophobicity and water whitening, and hence, water resistance.

In designing effective water whitening resistant latex, other factors should also be considered. The important roles of co-polymerizable/reactive surfactants vs. traditional surfactants must be accounted for, and levels of silane monomers and functional monomers like hexanediol diacrylate (HDDA) must be optimized. Curing conditions, such as temperature, humidity and drying time, can also affect the water whitening resistance of a latex film and must be controlled. When these concepts are carefully applied to formulations with hydrophobic monomers, latices with superior water whitening resistance can be produced.
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