Vinyl Acetate-Versatic Acid Vinyl Ester Copolymer for

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Vinyl acetate (VA)-vinyl versatate (VeoVa[™]) copolymer emulsions are widely used for interior and exterior architectural coatings. Polymer emulsions based on vinyl acetate monomer (VAM) have been manufactured and marketed for the paint industry since 1930. The performance of polyvinyl acetate as a paint binder was severely limited by the ease of hydrolysis and relatively high glass transition temperature (T_{d}) of the polyvinyl acetate resin (VA). To improve paint properties such as scrub resistance and alkali resistance, the vinyl acetate-based binders were copolymerized with softer comonomers. The use of softer monomers based on esters of acrylic acid and esters of maleic acid led to materials with lower T_{g} , but the resistance to acidic and alkaline pH remained low.¹

The alkaline hydrolysis problem of the vinyl acetate backbone was resolved

in the 1960s after the introduction of vinyl versatate (VeoVA-10 or VeoVa) from Shell Chemical Company. VeoVA 10 is a saturated monocarboxylic acid of highly branched structure containing 10 carbon atoms. This unique, highly-branched, carbon-rich structure provides the monomeric unit with a hydrophobic nature and a strong resistance to efflorescence (saponification). Since VeoVa has approximately the same reactivity ratio as VA, their resulting copolymers are more uniform than those of vinyl acrylic. When used in paint, this VA-VeoVa resin system exhibits better coating performance characteristics than vinyl acrylics or styrene acrylics. This article explores the impact of various monomer systems including VeoVa on the VA backbone and how the resulting copolymer influences various characteristics of interior coatings and exterior masonry coatings.

BACKGROUND

VeoVa has the same reactive group as vinyl acetate; its reactivity is close to that of vinyl acetate in free radical polymerization. This unique, comparable reactivity feature benefits synthesizing random copolymers of vinyl acetate, which is highly desirable to enhance the performance of interior and exterior coatings.

At room temperature, the water solubility of VA is 2.58% and VeoVa is 0.0001%⁻⁷. This inherent resistance to hydrolytic attack in addition to VeoVa's low water absorption are desirable properties for paints for masonry substrates.

Wu et al.² studied the mass transfer of vinyl versatate on VA-VeoVa in batch and semibatch emulsion polymerization. The researchers concluded that monomer feed rates determined the monomer polymerization rates and had little impact on copolymer composition. In addition, Unzue et al.³ studied optimal strategies for the emulsion polymerization of vinyl acetate and VeoVa-10 in order to maximize the polymer production rate and scrub resistance of latexes produced in reactors with a limited capacity to remove heat. The optimal strategies were implemented in lab-scale reactors. It was found that a 40% reduction in process time can be achieved while still maintaining product quality.

The alkaline hydrolysis of polymers is a subject of both practical and theoretical interest for cases where masonry coatings are to be applied to alkaline substrates and adequate resistance to hydrolysis is essential for satisfactory performance and durability.⁴ Several authors have sought to correlate the resistance of a polymer emulsion to hydrolysis by aqueous sodium hydroxide with resistance of a pigmented air-dried film to efflorescence (lime burn) and have concluded that resistance to hydrolysis is dependent on steric effects of the polymer.

Davies et al.⁴ studied the alkaline hydrolysis of aqueous polymer emulsions, particularly vinyl acetate copolymers (*Figure* 1). The rate of hydrolysis was reduced with increasing proportion of branched hydrophobic vinyl comonomers (VeoVa). It was concluded that the major factors influencing ease of hydrolysis are steric and other environmental impacts arising from copolymer microstructure. This is discussed in the next section.

The authors further observed that an ethylene comonomer on a vinyl acetate backbone exerted the same level of hydrolytic resistance on a weight basis as VeoVa. The authors concluded that it is possible that ethylene exerts some protection of vinyl acetate units by increasing the steric effects of the polymer backbone through more compact folding, thus leading to more effective shielding of the hydrolyzable units. Ethylene is a hydrocarbon and does not contain any hydrolyzable functional groups as compared to carbonyl ester-containing monomers such as vinyl ester, acrylate monomers. *Figure* 1 also shows that alkaline-hydrolysis resistance of vinyl acetate-ethylene (VAE) emulsions is much superior to vinyl acetate-butyl acrylate copolymer (commonly called vinyl acrylic). Alkaline hydrolysis requires the presence of ester linkages as discussed below.

SELECTION OF COMONOMERS FOR VAM

The most important technical criterion to select a comonomer for VA includes glass transition temperature (T_g) and kinetics. In *Figure* 2, the chemical structure and the T_g are indicated. It should be noted that the chemical structure of VeoVa represents only the main component as the commercially available product is usually a mixture of several isomers. As shown in *Figure* 2, all the comonomers give softer (lower T_g) homopolymers relative to VA. VA copolymers with a wide range of glass transition temperature could be produced by using the appropriate weight fraction of comonomers.









Monomer 1 (M1)	Monomer 2 (M2)	$r1 = \frac{k_{11}}{k_{12}}$	$r2 = \frac{k_{22}}{k_{21}}$
VA	BA	0.06	6.00
VA	2-EHA	0.10	9.20
VA	E	1.49	0.77
VA	VeoVa	0.99	0.93
K ₁₁ : Polyr	mer-M1* + M1 -	→ Polymer-	M1-M1*



Figure 3—Comparison of VA/comonomer emulsions at a ratio of 70/30.

Copolymerization of two or more monomers during free radical polymerization is an effective way of altering the properties of polymers.⁵ If the reacting species are monomer 1 and monomer 2, the composition of the resulting polymer is not a mixture of blends of homopolymers of monomer 1 and monomer 2, but a statistical copolymer of both monomers. The reactivity of the monomers varies with the type and concentration of the other species in the reactor feed. It is assumed that the reactivity of the growing polymer chain is determined by the last added monomer unit, independently of the chain length and composition. For two-component polymerization, r1 and r2 are known as monomer reactivity ratios, which are the ratios of the reaction rates of homopolymerization to cross-polymerization for individual radicals. If reacting monomers have similar reactivity ratios, the resulting copolymer structure would be random. In Table 1, the reactivity ratios of the commonly used comonomers for free-radical polymerization are shown. However, difference in reactivity ratios often leads to diversion in the copolymer composition versus starting materials. To investigate the extent of these deviations, copolymer emulsions of VA with butyl acrylate (BA), 2-ethyl hexyl acrylate (2-EHA), and VeoVa were prepared under emulsion polymerization conditions. Emulsions comprised of 70% VA and 30% various comonomers were studied in paints. The emulsion polymer comprised roughly 30–45% of the typical formula for latex paint.

COMPARISON OF COPOLYMER MORPHOLOGY

Vinyl acrylic is one of the most common polymers used in architectural paints and coatings. Vinyl acetate/butyl acrylate (VA-BA) is the primary industrial polymer used in North America for vinyl acrylic emulsions for architectural paint and coating applications. In Europe, vinyl acetate/2-ethyl hexyl acrylate (VA/2-EHA) is the primary monomer used for vinyl acrylic. In this work, we study both the hydrolysis resistance of the polymer and a characteristic of paint made with the polymer called wet scrub resistance. Wet scrub resistance is a test that literally rubs a brush over a prescribed film of paint until the paint "fails" and rubs off. It is measured in brush cycles. This test is actually a measure of the pigment binding power of the paint. Higher brush cycles indicate a more durable paint. The alkali resistance is a measure of the hydrolysis resistance of the polymer itself. This can also be called the saponification number of the emulsion. In this measurement, a lower number indicates that it is more suitable for use in paints for masonry surfaces, which tend to be very alkaline in nature.

Figure 3 shows the results of these tests. Due to the large difference in reactivity ratio of the acrylate (BA or EHA) with VA, it is to be expected that copolymers of these monomers may consist of blocks of acrylate and vinyl acetate.⁶ The differential scanning calorimeter was used to study the T_o of vinyl acetate copolymers. T_o-DSC curve for VA-VeoVa (70/30) and VA-BA (70/30) copolymers exhibited multiple transitions. On the other hand, VA-VeoVA copolymer exhibits only one glass transition. This clearly shows that the copolymerization of BA and 2-EHA with VA under identical emulsion polymerization conditions results in a non-uniform polymer. The acrylate monomers with vinyl acetate form block polymers that are not able to space the vinyl-acetate moieties. This is in agreement with previous studies on alkali resistance of various vinyl acetate-acrylic polymers.

In contrast to this, the VeoVa tends to form a random copolymer with VA since the reactivity ratios, r1 and r2 values, are near unity in each case. Besides providing the satisfactory resistance to hydrolytic attack under alkaline conditions, the regular spacing of VeoVA along the growing polymer chain is probably responsible for the excellent pigment-binding capacity of these systems. To substantiate this assumption, various experiments with the copolymers were performed.

Three copolymer emulsions with VA/VeoVA (65/35) were prepared under the same conditions except the monomer dosing was varied (Figure 4). In the case of homogeneous composition, the monomer was fed in the reaction over the entire time. In the case of heterogeneous composition 2, the addition of VA during the first half of polymerization time was followed by the feed of a VA and VeoVa mixture in the second half. Heterogeneous composition 1 was prepared in the opposite way, i.e., in the beginning; the VA-VeoVA was fed followed by the addition of pure VA. The two-stage process emulsions (heterogeneous 2 and heterogeneous 1) yielded much higher saponification numbers, indicating lower alkali resistance. In addition, these two emulsions produced paints with much lower wet scrub resistance than the paint based on the homogeneous. This clearly proves that a more random polymer, such as shown in the homogeneous, gives better coating properties than an irregular polymer microstructure. In connection with the heterogeneous way of making polymers, it can be argued that in order to compensate for differences in reactivity ratios of the acrylate with the VA, various monomer feed methods could be designed to force random copolymerization. Though this is possible, such process optimization would always be more complicated than a standard reaction of VA with VeoVa. This makes the vinyl esters, such as VeoVA, for any given free-radical process the monomer of choice for VA.

As would be expected, as the amount of VeoVa increases on the VA backbone, both T_g and MFFT decrease (*Figure* 5). It is interesting to observe that as the ratio of the VeoVa monomer increases, the delta between the T_g and MFFT decreases. This can be explained by plasticization of the films by water, which acts as plasticizer. In the case of T_g , the measurements are done on dried films of polymer, whereas the MFFT measurements are made on wet latex which contains residual water. Copolymers with higher amount of VA are more hydrophilic and, subsequently, the plasticization of polymer films by water is more efficient and the difference between T_g and MFFT is greater for emulsions with lower VeoVa levels.

The effect of the monomer ratio of VA/VeoVa on alkali resistance of the emulsion and on wet scrub resistance of the paint was also tested (*Figure* 6). These results clearly show that as the level of the VeoVa increases, the wet scrub resistance increases, indicating a more durable paint film. In



Figure 4—Impact of polymer synthesis on wet scrub resistance and hydrolysis resistance.



Figure 5—The effect of monomer ratio VA/VeoVa on MFFT and T_o.



Figure 6—Impact of monomer ratio of VA/VeoVa on wet scrub resistance and alkali resistance.

 Table 2—Physical properties of VA/VeoVA emulsions.

	Celvolit 2456	Celvolit 2383
% Solid	50	53
pН	6	4
Visc. (cps)	200	1500
Тg	19	29
MFFT	11	14
PS(nm)	175	200



Figure 7—Particle size of VA/VeoVa emulsions.

other words, the pigment binding power of the paint has increased. However, the effect seems strongest until about 25% VeoVa and then it begins to level off. In addition, at very low levels of VeoVa, very poor alkali resistance of the emulsion is indicated. Here, the VA is being hydrolyzed. As the VeoVa ratio is increased, the alkali resistance increases. Again, a plateau occurs around the 20–25% ratio. These results indicate that paint with a 15–25% VeoVa ratio could be used to create an interior paint with excellent scrub resistance and an exterior paint with excellent alkali resistance designed for masonry surfaces.

Effect of Physical Properties and Particle Size

The VA/VeoVa emulsions, Celvolit 2456 and Celvolit 2383 (Celanese Emulsions), were used in this study. Celvolit 2456 has a long history in the marketplace but Celvolit 2383 is a relatively new development from Europe. It has a higher viscosity



Figure 8—Weathering data of deep shade paints.

and different T_g and MFFT values. Physical properties are detailed in *Table* 2.

In addition, the particle size of the emulsions was measured by aerosol spectroscopy and the results are shown in *Figure* 7.

The particle size data indicates that both VA-VeoVa polymers have a small particle size and similar particle size distribution. The small particle size of the resin results in high pigment binding capacity in formulated paint. As discussed earlier, this would be exhibited in good wet scrub resistance of a resulting interior paint.

Exterior Durability

As mentioned previously, exterior coatings based on VA/VeoVa copolymers exhibit good alkali or efflorescence resistance, making them ideal for masonry paints. However, the impact of the monomer is greater. In *Figure* 8, the impact of VA/ VeoVa versus other monomers is shown in exterior paint exposure panels. The VA/VeoVa-based deep shade paints, including Celvolit 2456, exhibit better fade resistance versus the styrene acrylic paint. The VA/VeoVa paints also showed lower chalking and better resistance to dirt pick-up. The exterior paints based on Celvolit 2456 have superior pigment binding power, high efflorescence resistance, and very low water uptake and exhibit good compatibility with cement.

Resin-bound plasters are also commonly used on masonry dwellings. It is common to use styrene acrylic emulsions as masonry binders. Celvolit 2456 was also formulated into a resin-bound plas-

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Figure 9—Monomer comparison of weathering on resin-bound plasters.

ter to compare to this standard choice. The results of a series of panels exposed at 45°, facing south after two years of weathering are shown in *Figure* 9. The exterior performance, such as dirt pick-up and durability, of the VA/VeoVA-based plaster was found to be comparable to the styrene acrylic product.

CONCLUSION

Va/VeoVa is a very versatile copolymer emulsion for use in many paint and coating applications. VeoVa is a logical choice to pair with the VA backbone because of their very similar reactivity ratios and resulting single glass transition temperature. As the ratio of the VeoVa to the VA increases, the alkali resistance of the emulsion increases, making it a solid choice for use on alkaline masonry substrates. In addition, VeoVa is a monomer of choice for interior and exterior paints because it results in higher pigment binding power, giving paint superior wet scrub resistance. Both the wet scrub resistance and efflorescence resistance are optimal at a ratio of 15–25% VeoVa in the copolymer. Outdoor paints based on VA/VeoVa technology show less fading, less dirt pick-up, and less chalking than styrene acrylic resins. Resin-bound plasters based on VA/VeoVa emulsions exhibit similar weathering properties to styrene acrylate. In summary, Va/VeoVa emulsions are a natural choice for use on masonry substrates.

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