VINYL ACETATE-ETHYLENE (VAE) DISPERSIONS PROVIDE HIGH PERFORMANCE VERSATILE BINDERS FOR A VARIETY OF COATINGS APPLICATIONS

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VAE dispersions continue to gain popularity across the global architectural coatings market. Due to their unique properties and characteristics, VAE based dispersions offer excellent cost/performance balance along with the development of formulations with a low environmental impact. This balance of high efficiency, quality, performance, and compliance with ever increasing environmental standards will continue to be a requirement in the future for the coatings industry.

Ethylene is the ideal internal plasticizer for vinyl acetate monomer due to the main chain plasticization effect which leads to polymers with very low minimum film formation temperatures (MFFT). The lower the MFFT, the easier it is for the latex to form a film without the use of coalescing aids, which allows for the reduction of VOCs in a formulated paint.

VAE dispersions, however, are more than just low VOC capable binders for interior wall paints. Utilization of various other main monomers as well as functional monomers allows for the development of versatile, high performance co- and ter-polymers which can be utilized in a variety of coatings applications from high pigment volume concentration (PVC) to exterior.

THE COMMON PERCEPTION OF VAE TECHNOLOGY/GOING BEYOND INTERIOR HOUSE PAINT

VAE copolymers have been used in the coatings industry for approximately 50 years, so the technology is not new. They have historically been categorized as binders with excellent scrub resistance and touch-up properties. And over the last 15-20 years as volatile organic compounds (VOCs) have been more strictly regulated and enforced in the coatings industry, they have gained prominence as “The” low VOC capable technology due to their inherently low solvent demand.

The most common VAEs for the coatings industry typically range from 0 to +12 ºC in glass transition temperature (Tg) and <5 ºC minimum film formation temperature (MFFT). They are either solely surfactant stabilized or co-stabilized with surfactant and protective colloid, and they usually have little, if any, functionality.

However, VAE technology, and more specifically ethylene based dispersions, goes well beyond those parameters as it is a chemistry that is used in many other markets and applications. Commercial ethylene based co- and ter-polymers range in Tg from -40 to +29 ºC with a variety of stabilization packages, particle size distributions, and functionalities. These polymers are used in markets such as adhesives, carpet, paper coatings, caulks, and non-wovens, and compete with a variety of binder technologies such as vinyl acrylcs, pure acrylcs, styrene acrylcs, and styrene butadiene latexes.

The history and experience of developing ethylene based dispersions for these other markets can be applied to the coatings industry to create binders that go beyond just interior low VOC house paint. Ethylene based dispersions can be developed for applications such as elastomeric coatings, high PVC coatings, flame retardant coatings, and more to name a few.
THREE LEVERS IN EMULSION POLYMERIZATION THAT CAN BE USED TO DIAL IN PERFORMANCE

In the world of polymer synthesis there are three levers which can be used to dial in the performance of the dispersion.

- **Main monomers** – primary monomers which contribute to the mechanical properties and hydrophobic nature of the dispersion
- **Stabilization** – materials used to stabilize the individual latex particles and determine the particle size distribution of the final dispersion
- **Functional monomers** – monomers used at low levels to provide specific performance properties

MAIN MONOMERS

In terms of VAE copolymers, the main monomers are obviously vinyl acetate and ethylene with vinyl acetate being the high T₉ component which brings cohesive strength, heat resistance, and a more hydrophilic nature, and ethylene being the low T₉ component which ultimately plasticizes the vinyl acetate reducing the overall polymer T₉ and changing the polymer properties. The balance of vinyl acetate and ethylene determines factors like adhesive versus cohesive strength, tensile strength, elongation, hydrophobic nature, and heat and water resistance.

With typical architectural coatings grade VAEs having a T₉ between 0 to +12 °C, vinyl acetate accounts for the majority of the monomer content by weight (vinyl acetate content is typically >85%). This is primarily because ethylene is such an efficient co-monomer in terms of plasticizing vinyl acetate, so <15% is all that is necessary to get the polymer T₉ into the proper range. Ethylene is such an effective plasticizer for vinyl acetate because of the combination of an extremely low T₉ (approx. -100 °C) and a similar reactivity ratio to vinyl acetate. This allows for a more random distribution of monomers during the polymerization process which leads to main chain plasticization.

In terms of vinyl acetate-ethylene copolymers, the amount of the individual monomers can be adjusted to create a range of polymer glass transition temperatures from approximately -30 °C to approximately +25 °C. At the low end of that range the polymers exhibit good adhesive strength, especially to plastics, have good flexibility, and are more hydrophobic. At the high end of that range the polymers exhibit good cohesive strength with excellent adhesion to cellulosic substrates, have excellent heat resistance, and are more hydrophilic. Since MFFT typically moves in relation to T₉, the harder the polymer gets (higher T₉), the higher the cosolvent demand would be when talking about a coatings application.

There are a number of other monomers that also have similar reactivity ratios to vinyl acetate and ethylene, the utilization of which can lead to co- and ter-polymers that have an even broader range of T₉ and more varied physical and performance properties. Several of these monomers are listed in Table 1.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Glass Transition Temp. (°C)</th>
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<tbody>
<tr>
<td>Vinyl chloride</td>
<td>+82</td>
</tr>
<tr>
<td>VeoVa® 9</td>
<td>+70</td>
</tr>
<tr>
<td>VeoVa® 10</td>
<td>-3</td>
</tr>
<tr>
<td>Vinyl laurate</td>
<td>-70</td>
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Table 1: Monomers with reactivity ratios similar to vinyl acetate and ethylene

All four of these monomers are hydrophobic, and the variety of T₉ brings a different balance of properties when polymerized with vinyl acetate and/or ethylene. There are a number of
commercial products already in existence (not necessarily for the coatings market) that use some combination of vinyl acetate, ethylene, and one or more of these various monomers. Because these monomers have similar reactivity ratios to vinyl acetate and ethylene, the polymerization process tends to be more ideal meaning shorter processing times and more random distribution of the monomers in the final polymer chain.

Focusing on vinyl chloride, this monomer provides performance comparable to that of styrene. With a relatively simple chemical structure (Figure 1), vinyl chloride provides hydrophobicity, chemical resistance, water resistance, vapor resistance, and durability. An additional inherent benefit of vinyl chloride is that it has strong flame retardant properties. Therefore, polymers made using vinyl chloride monomer can be used to make flame retardant coatings, typically without the use of any additional flame retardants in the formula. This can help simplify the formula and reduce the overall cost by eliminating the need for flame retardant pigments.

Figure 1: Chemical structure of Poly (vinyl chloride)

![Chemical structure of Poly (vinyl chloride)](image)

In its natural state, vinyl chloride is a toxic gas. However, when polymerized with other monomers via emulsion polymerization, the resulting dispersion is no more hazardous than any standard dispersion. When finished properly during the manufacturing process, the polymer will have extremely low residual vinyl chloride levels that are well below typical local or regional regulatory requirements.

It is possible to polymerize other monomers (e.g. acrylates) with vinyl acetate and ethylene as well. However, the reactivity ratios of these monomers are dissimilar enough that the polymerization process is not as ideal and the distribution of monomers is not as random. Utilization of acrylate monomers allows for the broadest range of T_g, especially on the low end where soft monomers like butyl acrylate (T_g of -56 ºC) and 2-ethylhexyl acrylate (T_g of -70 ºC) can be used to create polymers with a T_g of -40 ºC or lower.

Through the utilization of these various monomers (i.e. vinyl acetate, ethylene, vinyl chloride, VeoVa®, vinyl laurate, and acrylates), a broad spectrum of dispersions can be developed that vary significantly in T_g and performance properties. This broad spectrum of dispersions provides viable options for coatings applications beyond just interior house paint, including elastomeric, roof, fire retardant, and many more.

STABILIZATION
There are two primary types of stabilization in any waterborne dispersion: colloid and surfactant. The two can be used independently or in combination. The type of stabilization can impact a variety of properties including particle size distribution, rheology, water resistance, heat resistance, film clarity, and adhesive properties.

Colloid stabilization refers to water-soluble polymers that become chemically grafted to the polymer chain. They provide a bulky layer on the outside of the polymer particle and impart stability by steric hindrance of the particles. Typical protective colloids in emulsion polymerization are polyvinyl alcohol (PVOH) or hydroxyethyl cellulose (HEC). PVOH is very common as a stabilizer for dispersions used in adhesive applications, specifically those used for...
cellulosic substrates as PVOH has a strong affinity for cellulose. HEC is more common in coatings grade products, typically in combination with surfactants.

Protective colloids provide the dispersion with a larger average particle size and a much broader particle size distribution, leading to a more Newtonian rheology and better flow and machining characteristics. Colloid stabilized dispersions tend to have high heat resistance, poor water resistance, and good adhesion to wood and glass.

Surfactant stabilization refers to the use of surface active agents, or soaps, to provide stability to the dispersion. The surfactants adsorb onto the latex particle at the particle/water interface, thus providing stability to the dispersion.

Typical surfactant types used in emulsion polymerization are nonionic and anionic (Figure 2) and the two provide stabilization in completely different ways. Nonionic surfactants provide stability by steric hindrance, much like colloidal stabilization, due to their neutral charge and relative bulkiness depending upon the level of ethoxylation on the hydrophilic portion of the molecule. Similar to colloid stabilized latexes, the particle size tends to be a little larger, the particle size distribution tends to be broader, and mechanical properties tend to be better because of the steric stabilization. Anionic surfactants provide stability through electrostatic repulsion due to their negative charge. However, the negative charge can also lead to increased water sensitivity and reduced adhesion. Anionic stabilized latexes are typically smaller in average particle size due to the lack of ethoxylation relative to nonionic surfactants. Because of the differences that the types of surfactants provide, it is very common to use a combination of nonionic and anionic surfactants in the polymerization process. This controls particle size and distribution while maximizing performance properties.

Figure 2: Chemical structure of typical anionic and nonionic surfactants

<table>
<thead>
<tr>
<th>Anionic Surfactant</th>
<th>Nonionic Surfactant</th>
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</thead>
<tbody>
<tr>
<td>(sodium lauryl sulfate)</td>
<td>(ethoxylated nonylphenol)</td>
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Surfactant stabilized latexes typically have a smaller average particle size and a narrower particle size distribution than colloid stabilized latexes. Surfactant stabilized latexes are typically more water resistant, have better adhesion to plastic, and are more thixotropic in rheology.

**FUNCTIONAL MONOMERS**

Functional monomers are monomers that are added at low levels (typically <5% of total polymer weight) during the polymerization process for a very specific purpose or performance attribute. They could be added to increase adhesion, to increase pigment binding, to improve water resistance, to provide cross-linking, or to change a myriad of other performance properties.

While functional monomers may impact the mechanical properties of the polymer like the main monomers would, they are not as instrumental in developing the overall mechanical properties of the polymer because of the low usage level. The downside to functional monomers is they can negatively impact other performance properties, plus they add additional cost to the polymer along with potential manufacturing complexity.

Figure 3 is an example of how acrylic acid can be used as a functional monomer in the polymerization of VAE. The acrylic acid, added at low levels, incorporates itself into the backbone of the polymer providing carboxylation. The carboxylation can provide properties such as freeze/thaw resistance, adhesion to metal substrates, and increased pigment binding. Acrylic
Acid can also help stabilize the dispersion by adding extra ionic charge to the system and increasing the static repulsion of the latex particles. The downside to the addition of acrylic acid to a polymer intended for a coatings application is that it can lead to water sensitivity issues.

Figure 3: Acrylic acid as a functional monomer in the backbone of a VAE copolymer

CONCLUSION
While VAE copolymers are often classified as the technology of choice for low VOC interior flat-low sheen coatings, the possibilities for usage of ethylene containing polymers reach far beyond that application. Due to the availability and versatility of co-monomer types, stabilization methods, and functional monomer choices, the properties of ethylene containing polymers can be modified to develop high performing options for a variety of coatings applications. This includes but is not limited to roof coatings, exterior paints, elastomeric coatings, high PVC coatings, and flame retardant coatings.