VAE DISPERSIONS FOR A VARIETY OF COATINGS APPLICATIONS
Ethylene-based dispersions have grown in popularity as high performance versatile binders in efficient formulations with low VOCs, as Kevin Merlo, Wacker Chemical Corporation, discusses.

### VAE-dispersions for a variety of coatings applications

Vinyl acetate-ethylene copolymer dispersions continue to gain popularity across the global architectural coatings market, as they enable highly efficient formulations with low emissions and an excellent cost-performance balance. Yet, VAE dispersions are more than just low volatile organic compounds (VOC) binders: Their properties can be modified to develop high-performing options for a variety of innovative coatings applications.

The paints and coatings of the future must offer high efficiency, quality and performance, while simultaneously complying with ever stricter environmental and safety standards. That’s why the choice of binders plays a key role in high-quality coatings applications. Consequently, dispersions, based on vinyl acetate-ethylene copolymers (VAE), have become more and more popular in the paints and coatings industry: Ethylene is the ideal internal plasticiser for vinyl acetate monomer due to the main chain plasticisation effect, which leads to polymers with very low minimum film formation temperatures (MFFT). And the lower the MFFT, the easier it is for the latex to form a film without coalescing aids, which allows for reduced VOCs in the formulated paint.

VAE dispersions, however, are more than just low-VOC capable binders for interior paints. Utilisation of various other main monomers, as well as functional monomers, allows for the development of versatile, high performance co- and terpolymers for a variety of coatings from high pigment volume concentration (PVC) to exterior paints.

#### GOING BEYOND INTERIOR HOUSE PAINTS

VAE dispersions are not a new technology and have long been recognised for benefits, such as excellent scrub resistance and touch-up properties or their inherently low solvent demand. The most common VAEs for the coatings industry typically range from 0 to +12°C in glass transition temperature (T_g) and <5°C MFFT. They are either solely surfactant-stabilised or co-stabilised with surfactant and protective colloid, and usually have little, if any, functionality.

However, ethylene-based dispersions go well beyond those parameters and are, thus, used in many other markets and applications. Ranging in T_g from -40 to +29°C with a variety of stabilisation packages, particle size distributions and functionalities, they are used in sectors, such as adhesives, carpet, paper, caulks and non-wovens, and compete with a variety of binder technologies, such as vinyl acrylics, pure acrylics, styrene acrylics and styrene butadiene latexes.

The experiences gained from developing ethylene-based dispersions for other markets can be used to create binders that enable innovative applications beyond interior low-VOC paints. Three main levers influence the performance of the dispersion: Main monomers, stabilisation and functional monomers.

#### MAIN MONOMERS

The main monomers of VAE dispersions are vinyl acetate (VA) and ethylene (E), with vinyl acetate being the high T_g component bringing cohesive strength, heat resistance and a more hydrophilic nature. The low T_g component ethylene ultimately plasticises the vinyl acetate reducing the overall T_g and changing the polymer properties. The balance of the monomers 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 T_g between 0 to +12°C, vinyl acetate accounts for the majority of the monomer content by weight (VA content is typically >85%). Usually, less than 15% of ethylene is necessary to get the polymer T_g into the proper range, simply because ethylene is such an effective plasticiser for vinyl acetate due to the combination of an extremely low T_g (approximately -100°C) and a similar reactivity ratio to vinyl acetate. This allows for a more random distribution of monomers during the polymerisation process, which leads to main chain plasticisation.

### Table 1. Monomers with reactivity ratios similar to vinyl acetate and ethylene

<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>
</tr>
</tbody>
</table>
The amount of individual monomers can be adjusted to create a $T_g$ range from approximately -30ºC to approximately +25ºC. At the low end of that range, the polymers exhibit good adhesive strength, especially to plastics, good flexibility and more hydrophobicity. At the high end, the polymers show good cohesive strength with excellent adhesion to cellulosic substrates, outstanding heat resistance and more hydrophilicity. Since MFFT typically moves in relation to $T_g$, the harder the polymer gets (higher $T_g$), the higher the cosolvent demand is in coatings.

There are a number of other monomers with similar reactivity ratios to vinyl acetate and ethylene, the utilisation of which can lead to co- and terpolymers that have an even broader range of $T_g$ and more varied physical and performance properties (see Table 1).

All four of these monomers are hydrophobic and the variety of $T_g$ brings a different balance of properties when polymerised with vinyl acetate and/ or ethylene. Because they have similar reactivity ratios to vinyl acetate and ethylene, the polymerisation process tends to be more ideal meaning shorter processing times and more random distribution of the monomers in the final polymer chain.

Vinyl chloride, for instance, provides performance comparable to that of styrene. With a relatively simple chemical structure (figure 1), the monomer provides hydrophobicity, chemical resistance, water and vapour resistance, and durability. An additional inherent benefit is its strong flame-retardancy. Therefore, polymers including vinyl chloride monomer can be used for fire-resistant coatings without the use of any additional flame-retardant pigments in the formula – which can simplify the formulation and, thus, reduce the overall cost.

It is possible to polymerise other monomers (eg acrylates) with vinyl acetate and ethylene, although their reactivity ratios are dissimilar enough that the polymerisation process is not as ideal and the distribution of monomers is not as random. Utilisation of acrylate monomers allows for the broadest range of $T_g$, especially on the low end so that polymers with a $T_g$ of -40ºC or lower can be created. Altogether, through the utilisation of various monomers, a broad spectrum of dispersions can be developed that vary significantly in $T_g$ and performance properties, thus providing viable options for many coatings applications.

Lab test of flame retardant properties: Paints and plasters formulated with a vinyl chloride component, like the dispersion VINNAPAS CEZ 3031 (left), are less combustible and burn more slowly compared to styrene-acrylate-based alternatives (right) (photo: Wacker Chemie AG)

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**STABILISATION**

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

Colloid-stabilisation refers to watersoluble 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 polymerisation are polyvinyl alcohol (PVOH) or hydroxyethyl cellulose (HEC). PVOH is a very common stabiliser for adhesive applications, specifically for cellulosic substrates. 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-stabilised dispersions tend to have high heat resistance, poor water resistance and good adhesion to wood and glass.

Surfactant-stabilisation refers to the use of surface active agents or soaps,
to provide stability to the dispersion. The surfactants adsorb on to the latex particle at the particle/water interface, thus providing stability to the dispersion. Typical surfactant types in emulsion polymerisation are nonionic and anionic (figure 2), which provide stabilisation in completely different ways. Nonionic surfactants provide stability by steric hindrance, much like colloidal-stabilisation, due to their neutral charge and relative bulkiness depending upon the level of ethoxylation on the hydrophilic portion of the molecule. 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 stabilisation. Anionic surfactants provide stability through electrostatic repulsion due to their negative charge. However, the latter can also lead to increased water sensitivity and reduced adhesion. Anionic-stabilised latexes are typically smaller in average particle size and relative bulkiness depending upon the level of ethoxylation relative to nonionic surfactants. Because of these differences, it is very common to combine nonionic and anionic surfactants in the polymerisation process. This controls particle size and distribution, while maximising performance properties. Compared to colloid-stabilised latexes, surfactant-stabilised latexes typically have a smaller average particle size and a narrower particle size distribution. They are usually more water resistant, have better adhesion to plastic and are more thixotropic in rheology.

**FUNCTIONAL MONOMERS**

Functional monomers are added at low levels (<5% of total polymer weight) during the polymerisation process for a specific purpose or performance attribute. They could increase adhesion or pigment binding, improve water resistance, provide cross-linking or 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 for 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 backbone of a VAE dispersion. Acrylic acid can also help stabilise the dispersion by adding extra ionic charge to the system and increasing the static repulsion of the latex particles. The downside is that it can lead to water sensitivity issues.

**CONCLUSION**

While VAE dispersions are often classified as the technology of choice for low VOC interior flat or low sheen coatings, the possibilities for ethylene-containing dispersions reach far beyond that. Due to the availability and versatility of comonomer types, stabilisation methods and functional monomer choices, the properties of ethylene-containing dispersions 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.

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Wacker is the world-market and technology leader for aqueous co- and terpolymer dispersions based on vinyl acetate and ethylene marketed globally under the VINNAPAS® brand.

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