

DEVELOPMENTS IN **VINYL ACETATE-ETHYLENE (VAE)**COPOLYMERS FOR USE IN ARCHITECTURAL COATINGS

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S. Krieger, K. Gohr, H. Petri, T. Fichtner, and S. Rumrich, Celanese Emulsions GmbH Vinyl acetate-ethylene copolymers (VAEs) have steadily gained market acceptance and share in the last decade as binders in the coatings industry, predominantly in flat, interior, low-emission decorative paints. Although well-established in the market, they still show above average growth rates compared to the total market for water-based binders for paints and coatings in North America.* Today, as the world embraces "green technology" and consumers opt for products with a lower carbon footprint, new technology in the form of vinyl

*Kline Global Business Opportunities in Synthetic Latex Polymers, 2006-2017, Vol. III: North America acetate-ethylene acrylic inclusion emulsions will enable the paint manufacturer to formulate low-VOC exterior paints without sacrificing performance.

The case for VAE-based emulsions is strong. VAE emulsions exhibit good pigment binding and hiding power, two critical application properties for flat interior paints. They can also formulate well with many different pigmenting systems, giving broad latitude to the chemist. In deep tone paints, vinyl-based emulsions (including VAE) offer excellent color retention. However, traditional VAE emulsions could not compete with exterior paints because of deficiencies in dirt pickup behavior. The new inclusion technology addresses this issue.

This paper was presented at the 2011 Western Coatings Symposium, October 23-26, 2011 in Las Vegas, NV.

UNDERSTANDING VAE TECHNOLOGY

The ability of an emulsion-based paint to form a homogeneous, crack-free, and rigid film during drying is measured by its minimal film formation temperature (MFFT), which is determined by the binder and by the presence of solvents and plasticizers in the paint.

During drying, the emulsion transforms from a colloidal dispersion to a polymer film. This film formation process can only occur if the film is formed at temperatures at or above the MFFT. If the drying occurs at a temperature below the MFFT, no film formation will be possible and the result of the drying process will be a film with cracks and without mechanical stability.

The MFFT of the emulsion correlates directly to the glass transition temperature (T_g) of the polymer: the higher the T_g , the higher the MFFT. However, the level of correlation varies between the different polymer emulsions. For example, polymers like styrene-acrylics (S/A) that are commonly used in conventional waterborne decorative paints have nearly identical T_g s and MFFTs. On the other hand, systems such as VAE emulsions allow the formation of a film at a significantly lower temperature than their T_g . For interior decorative paints, the MFFT of the paint must be below $5\,^{\circ}$ C.

The addition of solvents or plasticizers to the paint leads to a temporary softening of the polymer binder and decreases the MFFT. Because of the high MFFT of the binders used for conventional waterborne interior paints, the addition of solvents or plasticizers is necessary to lower the MFFT of the paint and therefore allow the formation of the film. Low-emission paints, on the other hand, are formulated without solvents or plasticizers because they use binders like VAE emulsions that allow excellent film formation at low temperatures without the need for solvents or plasticizers.

NEW INCLUSION TECHNOLOGY FOR EXTERIOR PAINTS: EXPANDING THE APPLICATION FIELD OF VAE

Improving the weathering performance is the focus of this study. By introducing hard acrylic polymer domains into a VAE polymer, it is possible to combine the positive properties of VAE emulsions and hard acrylic emulsions into one binder system.

Through the introduction of small, hard domains into the VAE polymer matrix (*Figure* 1), and by utilizing "inclusion technology," the polymer properties are changed significantly.

The properties of polymer particles obtained by the inclusion technology are significantly different from either simple copolymerization or established heterogeneous emulsion polymerization techniques.

As can be seen in *Figure* 2, standard copolymerization of the hard acrylic monomers greatly increases the

MFFT while the new inclusion technology with the same hard acrylic monomer affects the MFFT very little. This low MFFT in the new inclusion technology will enable solvent-free formulations.

Heterogeneous polymerization or blending in hard polymer particles can also achieve a similar MFFT. However, this technique does not influence the mechanical strength as significantly as the new inclusion technology. *Figure* 3 shows the data of the tensile strength of the resulting polymer film.

Compared to blending, the smaller size domains achieved by the inclusion technology lead to a significantly

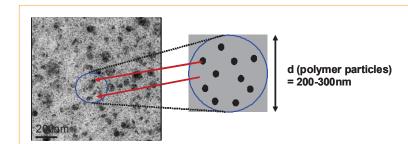


Figure 1—TEM picture: Polymer film showing evenly distributed domains of the hard polymer which are significantly smaller than the size of the emulsion particles.

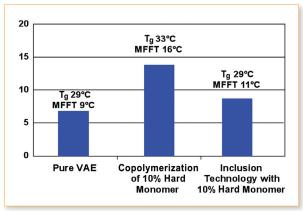


Figure 2—Effect of inclusion technology on MFFT of the emulsion.

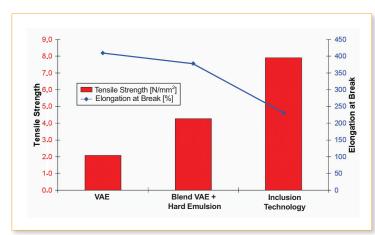


Figure 3—Mechanical properties of different polymers.

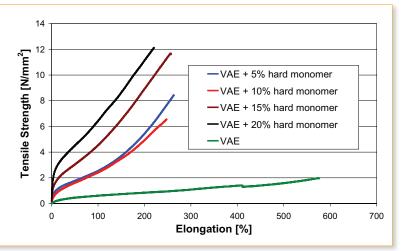


Figure 4—Inclusion polymers at different levels of incorporated hard monomer.

tougher polymer. There is also a loss in elasticity, but a significant elongation above 200% can still be preserved and is sufficient for emulsions utilized in exterior paints.

The amount of hard monomer included in the VAE also plays an important role in tensile strength. As shown in *Figure 4*, as the amount of hard monomer increases, the tensile strength is increased. However, it should be noted that our data demonstrates that the greatest effect is achieved with the incorporation of the first 5%.

The tensile strength of the polymer film is representative for the bulk material. Although this is a good indicator of the softness and also the tackiness of a film, there are other factors influencing the surface tack of a film. A more direct measure for surface tack is blocking, where the actual force which is needed to separate two polymer films (which were put together under a defined

pressure) is determined. Figure 5 demonstrates that with the inclusion of hard domains, not only does the bulk film become tougher, the surface tack is also significantly reduced.

With this mechanical data, it could be hypothesized that exterior paints based on VAE inclusion technology would have tough, low-blocking films and therefore would show less dirt pickup. The real experiments with a new optimized VAE emulsion based on the described inclusion technology showed that this assumption is correct. The new VAE inclusion copolymer with an optimized quantity of hard domains and with an MFFT of less than 5°C shows a significant improvement in outdoor weathering tests in comparison to a standard VAE emulsion as is demonstrated in Figure 6 for white exterior paints (24 months). A comparison is also made with a hard pure acrylic emulsion (MFFT 18°C) and hard styrene/acrylic emulsion (MFFT 20°C). The exterior paints with PVC 50 and 30% binder content (16% solid polymer) were exposed in Istanbul. Turkey close to a main street with heavy traffic in order to illustrate the impact of pollution on the paint surface.

The delta L-values (white color change) were measured for all systems (*Figure* 6) over time. The new VAE inclusion technology gives a visible improvement versus a standard VAE emulsion and hard styrene/acrylic emulsion and is roughly comparable to the performance of hard pure acrylic emulsions with MFFT of 18°C.

IMPORTANCE OF COLOR RETENTION IN EXTERIOR PAINTS

Deep tone paints were also tested because it is well known that there could be a significant difference in performance between white and deep shade systems. It

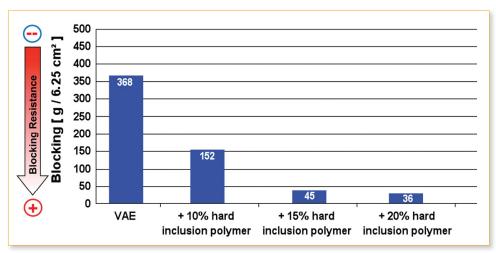


Figure 5—Blocking of polymer films.

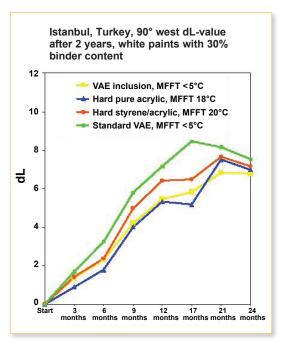


Figure 6—Exterior weathering results for an exterior paint formulation.

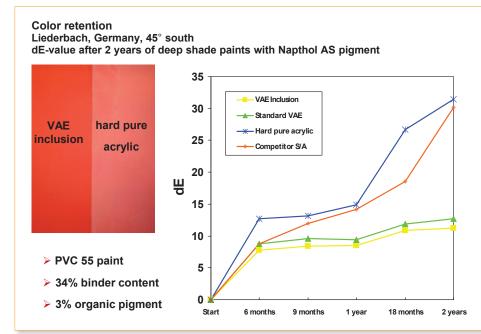


Figure 7—Color retention of deep tone paints formulated with Napthol AS pigment.

is already known that vinyl acetate copolymer emulsions like VAE-vinyl chloride emulsions show excellent color retention in deep shade paint formulations. For the outdoor exposure tests, 55-PVC deep shade paint with 34% binder content (18% solid polymer) was formulated by using ${\rm CaCO}_3$ as fillers. For the pigmentation, 1% of ${\rm TiO}_2$ and 3% of a very light sensitive red pigment (Naphthol AS) were used in order to rapidly see the impact of the binder polymer on the color retention. As shown in *Figure* 7, the VAE inclusion emulsion exhibits better color retention in comparison to both hard styrene acrylic and hard pure acrylic emulsions.

The outdoor weathering exposure results show that the new VAE inclusion emulsion performs well both in white and tinted formulations.

CONCLUSIONS

Today, VAE emulsions are binders utilized in the paint and coatings industry, especially for low-VOC interior paints where they also demonstrate good application properties such as wet scrub resistance and good blocking behavior. By using the new VAE inclusion technology, it is possible to synthesize an emulsion which combines the positive properties of vinyl-based emulsions and hard acrylic polymers (good weathering behavior). This results in significant improvement over standard VAE and hard styrene acrylic binders and is roughly comparable to pure hard acrylic emulsions in outdoor weathering performance in white paints. In addition, the new VAE inclusion technology shows superior results in color retention over hard styrene acrylic and hard pure acrylic systems in deep tone paints.

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