ABSTRACT

Vinyl neodecanoate is the vinyl ester of a highly branched tertiary monocarboxylic acid containing ten carbon atoms. This monomer is generally copolymerized with vinyl acetate to produce high performance latices which are mainly used in decorative emulsion paints, yet it can also be copolymerized with acrylic and methacrylic monomers. Coatings based on these vinyl neodecanoate/acrylic emulsion polymers show very high alkali and UV resistance, along with excellent durability, adhesion and water repellence characteristics. These properties make these copolymers suitable for a wide range of highly demanding applications. Additionally, vinyl neodecanoate modification of acrylic systems allows for the incorporation of low cost vinyl acetate without a loss in performance attributes, thus providing both enhanced performance and competitive economics compared to 100% acrylic systems.

INTRODUCTION

In the 1950’s, Dr. Herbert Koch, from the Max Plank Institute in Mülheim, Germany, found that olefins may react with carbon monoxide and water under the influence of strong acids to form tertiary branched neocarboxylic acids (Figure 1). Before the intermediate carbocation reacts with carbon monoxide, isomerization reactions are observed and, therefore, the resulting acid is composed of a number of isomers\(^1,2\).

![Figure 1. Koch reaction for the production of neo-acids](image)

The neocarboxylic acid can be converted into its vinyl ester monomer by reaction with acetylene. Today, these monomers are marketed under the trade name VeoVa™ vinyl ester and are also widely referred to in industry as vinyl versatate monomers, neo-esters or VV monomers.
VeoVa™ vinyl esters are very hydrophobic monomers with a highly branched tertiary substituted α-carbon structure. Their principal use is as hydrophobic co-monomers in vinyl and acrylic polymerization. Their alkyl neocarboxylic group is very resistant to degradation in alkaline conditions as there is no hydrogen on the α-carbon atom. The branched tertiary structure with bulky and hydrophobic hydrocarbon groups provides the neo-ester monomers (Figure 2) with a highly hydrophobic nature and low surface tension. Furthermore, they possess a strong resistance to hydrolysis and do not degrade under the influence of UV light.

\[
\text{CH}_2=\text{CH}\quad \text{CH}_3
\]

R¹ and R² = alkyl groups

**Figure 2. Chemical structure of VeoVa™ monomers**

VeoVa™ vinyl ester monomers easily copolymerize with various other monomers through the vinyl ester group. In this way the specific properties of the monomer can be imparted to its copolymers. VeoVa™ monomer enhances the performance of vinyl acetate and acrylic based latices, significantly upgrading key properties such as water and alkali resistance in both types of polymer systems.

Polymers based on VeoVa™ vinyl ester exhibit the required polymer hardness and flexibility balance, hydrophobicity and chemical resistance for the formulation of a wide range of latex coatings. The resulting paints are characterized by a very good water, UV and alkali resistance and therefore exhibit very good outdoor durability. VeoVa™ monomers have already been successfully used to manufacture VeoVa™/vinyl acetate copolymer latices. Used as binders for architectural paints, these latices provide improved scrub resistance and exterior durability. The hydrophobicity and resistance to hydrolysis and UV degradation imparted by VeoVa™ monomers make them particularly suitable for producing high-performance latices, especially when they are copolymerized with acrylic and methacrylic monomers. Acrylic emulsions modified with VeoVa™ vinyl ester can be formulated in protective coatings such as anti-corrosion paints, water repellent systems, wood coatings, elastomeric roof coatings and adhesive applications such as PSAs.

**GLASS TRANSITION TEMPERATURE**

The various VeoVa™ monomers mainly differ in the degree of branching and the length of the hydrocarbon chains. This leads to differences in the glass transition temperature (\(T_g\)) of their homopolymers and consequently to different copolymer properties. The broad range of \(T_g\)’s available within the portfolio of VeoVa™ monomers gives the polymer chemist a means to develop very hydrophobic polymers with a wide latitude of possible \(T_g\)’s.

VeoVa™ 9 monomer is the vinyl ester of neononanoic acid (nine carbon atoms) and is a harder monomer imparting a \(T_g\) of +70°C. Scholten and Van Westrenen illustrated the effect of chain branching by measuring the \(T_g\) of a series of polymers prepared from VeoVa™ 9 vinyl ester isomers. The \(T_g\)’s ranged from +10 to 119°C, leading to the conclusion that the high \(T_g\) of poly- VeoVa™ 9 is a cumulative effect of the shorter chain length and the higher degree of branching within the various isomer mixtures.
VeoVa™ 10 monomer is the vinyl ester of neodecanoic acid (ten carbon atoms) and has a homopolymer \( T_g \) of -3°C, making it a flexibilizing monomer. VeoVa™ EH monomer is the vinyl ester of 2-ethylhexanoic acid, a less branched acid, and therefore has a significantly lower \( T_g \) of -36 °C.

**WATER RESISTANCE**

Water resistance is one of the most important barrier properties of a coating. The water resistance of a coating is mainly governed by its polymeric binder and the monomers used to produce the binder. If water solubility is taken as an indication of hydrophobicity (Table 1) it becomes clear that VeoVa™ monomers are much more hydrophobic than other monomers commonly used in emulsion polymerization.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Water solubility at 20°C (g/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VeoVa™ 10 vinyl ester</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>VeoVa™ EH vinyl ester</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>2-ethylhexyl acrylate</td>
<td>0.01</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.03</td>
</tr>
<tr>
<td>Butyl acrylate</td>
<td>0.16</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>1.5</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>2.5</td>
</tr>
</tbody>
</table>

*Table 1: Water Solubility\(^5\) of Some Commonly Used Monomers*

**ACRYLIC RESINS MODIFIED WITH VEOVA™ VINYL ESTER**

VeoVa™ monomers readily copolymerize in emulsions with acrylates and methacrylates. The bulky and hydrophobic hydrocarbon structure of the VeoVa™ monomers enhances the polymer to provide a high degree of water repellence and hydrolysis resistance. VeoVa™/acrylic latices represent a large family of polymers with a wide range of possible polymer compositions and performance properties.

**WATER RESISTANCE OF ACRYLIC POLYMERs**

Because of their hydrophobic nature, both VeoVa™ 10 and VeoVa™ 9, can increase the water resistance of copolymers in which they are used. The amount of water absorbed and also the whitening of the polymer film after exposure to a drop of water can be used as a means to measure the water repellence of a coating. However, polymer \( T_g \) and the surfactants used can influence these tests. To demonstrate the effect of the VeoVa™ monomers independently of other variables, we tested a series of polymers having the same \( T_g \) and surfactant system. The \( T_g \) was kept constant at 20°C by adjusting the concentration of either the MMA or BA monomers. Figure 3 shows the influence of the VeoVa™ monomers on water absorption after 14 days immersion.
Whitening of the film was measured by the water spot test. A drop of water is applied on the clear film and the whitening of the water drop is rated visually after one day. Figure 4 shows the influence of the VeoVa™ monomers on water spot resistance after 24 hours of exposure.

Figures 3 and 4 show that incorporation of VeoVa™ monomers leads to significant improvements in water resistance and that the effect increases with increasing VeoVa™ content. For both water absorption and water spot resistance, the best results are obtained by using VeoVa™ 9, a harder monomer than VeoVa™ 10. At the same VeoVa™ concentration, more MMA is needed with the VeoVa™ 10 based systems to obtain the same Tg as with the VeoVa™ 9 polymer. Since MMA is a more polar or hydrophilic monomer than BA, an increased MMA content will increase water sensitivity of the terpolymer.
The water repellence effect can also be demonstrated visually by measuring water droplet contact angles. Figure 5 shows the spreading of equally sized droplets of water on various acrylic paints. Acrylic systems modified with 30% VeoVa™ had a high water contact angle of 79°. On the VeoVa™ modified acrylic paint the water beads to a small droplet while on pure acrylic systems containing either butyl acrylate or 2-ethyl hexyl acrylate the water readily spreads out over a large area of the paint surface.

![Figure 5. Beading effect and contact angle of VeoVa™/acrylic based paints](image)

Expensive additives such as special waxes or silicones are commonly formulated into coatings to provide them with a water beading effect. Often, the effect of these additives is only temporary as they will gradually leach out of the coating. When the hydrophobic component is bound chemically to the polymer backbone, such as is the case for VeoVa™ containing polymers, the efficacy is extended.

WATER VAPOR TRANSMISSION

Water vapor permeability is another important property of coatings and adhesives. For optimum substrate protection, a low transmission of water vapor is required. Water vapor transmission of VeoVa™/acrylic polymers was determined according to ASTM method D1653, with the dry cup method. The polymer consisted of MMA/2-EHA/VeoVa™ and the effect of VeoVa™ was determined by replacing equal amounts of the already relatively hydrophobic 2-EHA with VeoVa™ 10. Figure 6 shows that there is an almost linear correlation with the VeoVa™ content and the water vapor transmission rate. The more 2-EHA that is replaced by VeoVa™ the less water migrates through the polymer.

![Water vapor transmission for VeoVa™ modified acrylic polymers](image)
ALKALI RESISTANCE

Good alkali resistance is required for coatings designed for application on alkaline substrates, such as cement or plaster. Due to the bulky neodecanoate structure of VeoVa™ monomers, the ester bond is sterically shielded from alkali induced hydrolysis and furthermore, the neodecanoate structure also protects neighbouring monomer units within a polymer. To demonstrate this effect, butyl acrylate/methyl methacrylate copolymers were modified with two different levels of VeoVa™ 10 and clear latex films were cast and subsequently immersed in 2% aqueous sodium hydroxide for 8 weeks at 50°C. After immersion, the clear polymer films were rinsed, dried and weighed to determine the amount of polymer degraded by hydrolysis. As can be seen in Figure 7, the VeoVa™ containing polymers demonstrate superior resistance to alkaline hydrolysis when compared to the VeoVa™-free methyl methacrylate/butyl acrylate copolymer.

![Alkali extractables of clear latex film (50°C in 2% aqueous NaOH - 8 weeks)](image)

**Figure 7. Alkali extractables of clear latex film (50°C in 2% aqueous NaOH - 8 weeks)**

APPLICATIONS

Virtually all coating applications will benefit from increased water resistance. Very good performance of VeoVa™/acrylic polymers has been demonstrated in metal protection paints, wood coatings, concrete tile coatings, exterior architectural paints and water repellent systems; and also in adhesives such as pressure sensitive adhesives (PSAs). In addition, the global drive to decrease VOC levels requires polymers with low $T_g$ and reduced MFFT. As polymers with lower $T_g$ usually suffer from higher water sensitivity, VeoVa™ vinyl esters provide a tool to provide excellent water resistance in low VOC systems.

METAL PROTECTION

The excellent adhesion to metal and high hydrophobicity imparted by VeoVa™ monomers makes them very suitable for waterborne and VOC compliant industrial applications such as metal protection. An emulsion polymer was prepared, having a monomer composition of VeoVa™ 10/MMA/BA/AA in the following ratios 60:35:2:3 with an MFFT of 32°C, to investigate the performance of VeoVa™/acrylic binders in anti-corrosion paints. As a reference, a commercial styrene/acrylic latex (MFFT 30°C) advertised for use in anti-corrosion applications was also evaluated. The emulsions were formulated in a 23%
PVC paint that can be used as primer or eggshell topcoat. The paints were applied at 100 microns dry film thickness on cold rolled steel (Q-panel R46). Salt spray testing was performed according to the ASTM B 117-90 method. After 750 hours, the test was stopped and pictures of the panels were taken (Figure 8). One can see that the primer based on VeoVa™ only exhibited blistering around the scribe and that corrosion was confined to the scribe. On the other hand, the styrene acrylic primer shows very severe blistering and corrosion over the entire surface of the panel.

Figure 8. Salt spray resistance after 750 hours

ELASTOMERIC ROOF COATINGS

Elastomeric roof coatings have been used for many years to extend the useful life of many types of roofing substrates. The roof coatings market also has seen significant growth, driven by the cool roof movement. Thermoplastic polyolefin (TPO) roofing membranes are a popular roofing system in many regions. It has been a challenge developing a waterborne elastomeric roof coating formulation with sufficient adhesion to the polyolefin surface of weathered TPO roofing membranes. Since VeoVa™ monomers lower the surface tension and increase the hydrophobicity in which they are incorporated, VeoVa™ modified acrylics make good candidates for water resistant elastomeric roof coatings with good adhesion to polyolefin substrates.

A series of VeoVa™ modified (0, 15 and 30 wt%) acrylic polymers with the same $T_g$ of ~ -35 °C were formulated in an elastomeric roof coating and applied on UltraPly™ TPO from Firestone Building Products. Both wet and dry adhesion were tested (ASTM C794) at a peel rate of 2 inches/min. Wet adhesion was measured after the samples were immersed in water for 7 days.

Figure 9. Dry adhesion and wet adhesion of elastomeric coatings on TPO
As can be seen from Figure 9, the incorporation of VeoVa™ 10 has a positive effect on both the dry and wet adhesion of the roof coating to TPO, with higher levels of VeoVa™ 10 leading to further improvements in adhesion. The low surface tension of the VeoVa™ based polymers leads to an improved wetting of the TPO surface while the increased hydrophobicity allows the coating to maintain good adhesion under wet conditions.

**EXTERIOR WOOD COATINGS**

Without some type of protective surface coating, most woods deteriorate very rapidly during outdoor exposure. In addition to excellent resistance to weathering and UV, other features such as good adhesion to wood, protection against liquid water ingress and a good balance between hardness and flexibility are key requirements for exterior wood coatings. Moisture protection, however, remains a critical parameter still to be optimized in the field of waterborne acrylic wood coatings.

Self-crosslinkable core/shell acrylic latices with a fixed core $T_g$ of 54 °C and shell $T_g$ of 0°C were prepared, characterized and formulated into wood stains. The systems had a weight ratio of hard to soft material fixed at 30/70. The shells were composed of butyl acrylate, methyl methacrylate, acrylic acid, a wet adhesion promoter monomer and either VeoVa™ 10 or 2-ethyl hexyl acrylate as hydrophobic monomers at a level of 30 wt.% on total monomers.

Weathering performance of the wood stains was evaluated with an accelerated weathering test according to EN 927-6. Performance of the wood stains was also assessed by performing an outdoor durability test. This entailed exposure to continental European weather conditions in Belgium for a period of three years (Figure 10).

![Figure 10. Weatherability of exterior wood stains](image-url)

After 2000 hours, no blistering, cracking, flaking or chalking could be observed for wood stain based on the VeoVa™ modified polymer. Severe chalking was observed for the wood stain containing 30% 2-EHA as the hydrophobic monomer. Also, after three years of outdoor exposure the wood stain based on the VeoVa™ modified acrylic performed better than the 100% acrylic polymer containing 2-EHA. The superior combination of UV stability with increased hydrophobicity conferred by the VeoVa™ vinyl ester incorporated into the polymer backbone contributes to the improved weathering resistance of the coating.
VEOVA™ RICH MODIFYING POLYMERS

One way to enhance the performance of paints based on acrylic emulsions is to add modest amounts of VEOVA™ rich vinyl acetate/VEOVA™ copolymers. This concept simplifies the improvement of paint performance and one VEOVA™ rich blending polymer could potentially be used to upgrade many different coatings. In addition to enhancing performance, the use of these VEOVA™ rich vinyl acetate/VEOVA™ copolymers in acrylic paint systems provides an opportunity to reduce the system cost.

To demonstrate the performance enhancements made possible by adding VEOVA™ rich copolymers to coatings based on acrylic polymers, a VEOVA™ rich copolymer containing 60% vinyl acetate and 40% VEOVA™ was synthesized, along with a 100% acrylic polymer based on methyl methacrylate and butyl acrylate. Mixtures of the VEOVA™ rich copolymer and the all acrylic polymer where then used to formulate high quality 42% PVC paints and these paints were subsequently tested for scrub resistance versus the same paint formulation containing only the 100% acrylic binder and another paint using only the VEOVA™ rich copolymer. It is evident from the scrub testing results (Figure 11) that the VEOVA™ rich copolymer blending resins dramatically increased the scrub resistance of the paints to which they were added. Additionally, the testing shows that the VEOVA™ rich blending resin used as a sole binder provides superior scrub resistance.

CONCLUSION

The copolymerization of the hydrophobic vinyl esters of branched neo-carboxylic acids with acrylic monomers significantly improves the performance of acrylic binders. Manufacturing of acrylic polymers modified with VEOVA™ monomers is an easy process and yields polymers with exceptional performance characteristics including very high alkali and
UV resistance, excellent durability and adhesion, and outstanding water repellence. These high performance VeoVa™ modified acrylic polymers are ideal for a wide variety of very demanding coating applications including metal, elastomeric, and wood coatings, coatings for cementitious substrates, and high performance decorative coatings. In addition, the modification of acrylic emulsions by blending with VeoVa™ rich vinyl acetate copolymers enables a convenient route to enhancing coating performance while simultaneously providing a potential route for reducing overall system cost.

References

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7. N. Havaux, D. Vanaken and F. Simal, Paint & coating industry magazine, October 2010