

# NEW WATERBORNE PRESSURE SENSITIVE ADHESIVES BASED ON SOFT AND HYDROPHOBIC VINYL ESTERS

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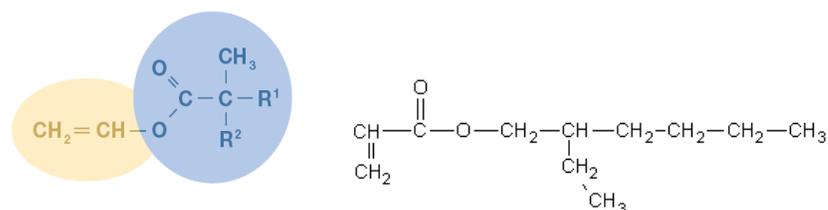
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## Introduction

Today, waterborne (WB) Acrylics are ubiquitous in the world of PSA thanks to the many advantages they offer over other technologies such as solventborne (SB) and other chemistries (*i.e.* Rubber based). Although great progress has been made to design WB Acrylic PSA with improved balance between peel strength and shear holding power<sup>1</sup>, these systems are still lacking the optimal performances that can be reached with SB Acrylics. Differences of molecular weight, cross-linking density, film formation processes and the presence of low molecular species (*i.e.* surfactants) typically account for the distinction of performance between the two<sup>2</sup>.

Due to their intrinsic nature, these dispersions suffer from the presence of small hydrophilic ingredients, which are necessary to produce and stabilize the dispersion. The distribution and accumulation of the surfactants at the polymer particle interfaces may prevent a complete coalescence and the inter-diffusion of the polymer chains across the particles which may result in non-homogeneous films lacking of mechanical properties, *i.e.* shear and peel. In most cases, the presence of these hydrophilic species also weakens the resistance of the product against moisture. Water resistance is not only needed in applications such as specialty tapes where the materials can be exposed to outdoor conditions and should maintain their level of performance but also in applications where clarity and aesthetic are key and which therefore require an excellent resistance against water whitening. Typically, the hydrophilic pockets created during the film formation process can swell when exposed to moisture. Above a certain size, light is scattered and leads to the whitening of the PSA film. Amongst the different strategies that have been developed over the years, the use of reactive surfactant has proven to be one of the most effective means to resolve water whitening drawbacks<sup>3</sup>.

In the decorative paint and protective coating markets, hydrophobization of the polymer backbone with a highly hydrophobic monomer is the standard practice performed in order to improve water resistance and, more generally, outdoor durability. In this respect, the incorporation into a polymer of moderately soft ( $T_g \sim -3$  °C) highly hydrophobic vinyl ester derivatives containing bulky alkyl groups (Figure 1) is well-known to greatly enhance the water resistance<sup>4</sup> of the final product.



**Figure 1: Chemical structure of VeoVa™ 10, 2-ethylhexyl acrylate (2-EHA)**  
(R<sup>1</sup> and R<sup>2</sup> = alkyl groups with a total of 7 Carbon atoms)

Despite the fact that most of the WB Acrylic PSA are based on 2-ethylhexyl acrylate, which is also a soft ( $T_g \sim -60$  °C) and hydrophobic monomer, these highly hydrophobic vinyl esters are likely to be ideal candidates to improve the water resistance of WB acrylic PSA (Table 1).

Interestingly enough, Yang<sup>5</sup> already studied the influence of such monomer in WB Acrylic PSA and concluded on its beneficial effect on the adhesion/cohesion balance.

**Table 1. Non-polar characteristics of VeoVa-10 and 2-EHA**

| Properties            | Units                           | VeoVa-10 | 2-EHA |
|-----------------------|---------------------------------|----------|-------|
| Surface Tension       | dyne/cm                         | < 28     | 30    |
| Oxygen Content        | %                               | 16.1     | 17.4  |
| Water Solubility      | g monomer/100g H <sub>2</sub> O | < 0.001  | 0.001 |
| Log K n-octanol/water | -                               | 4.9      | 3.9   |

The first part of this paper will aim at studying the effect played by a highly hydrophobic vinyl ester in a WB Acrylic PSA. More specifically, its influence on water resistance as well as on the fundamental PSA properties such as adhesion, cohesion and tack will be investigated.

The second part of the paper will introduce a totally new concept where the polymer backbone of the WB PSA has been designed on the basis of a judicious combination of soft and hydrophobic vinyl ester monomers.

## Experimental

### Latex preparation

The reactor is charged with water and KPS and heated to 85 °C. The pre-emulsion is fed for 2.5h, whereas the initiator solution is fed in parallel for 3h. This addition is followed by 0.5h of cooking. After this cooking period, a shot of monomer and initiator is then added followed by 0.5h of post-cooking. The latex is cooled down to 60 °C. The agitation is slowed down to about 100 rpm. A 10% solution of sodium carbonate and sodium hydrogenocarbonate (1/1) is added to adjust the pH to ~ 4 if needed. A first addition of Bruggolite®FF6 M solution is added in one shot. After 5 minutes, the remainder of Bruggolite®FF6 M and the tBHP are added via two separate lines over 90 minutes. Finally, the reactor is cooled down to room temperature and a biocide is added. The product is finally filtered over a 130µ filter. The final latex has a solid content of ~ 54%.

#### PSA film preparation:

The latex is adjusted to pH ~7 and applied with a bar coater on a 1 mil polyester film or white PVC film (monomeric phthalate-free from Mondoplastico). The gap of the bar coater is adjusted so that the dried PSA film has a thickness of 23 +/-2 µm. The film is dried for one hour at room temperature followed by 3 minutes in the oven at 110 °C. The film is then laminated on a release liner (Siliconized paper) and kept at least for 24 hours under 50% RH and 23 °C before testing.

#### PSA properties:

Adhesion – 180 ° Peel (20' – 24h, SS, HDPE, Glass) – according to Finat Testing Method (FTM-1), Tack – Loop Tack Test (1 x 1 inch, SS) – according to FTM-9, Cohesion – Static Shear (1 x 0.5 inch – 1kg, SS) – according to FTM-8

#### Water Whitening Test:

To assess the whitening, a piece of PSA film (5cm x 12cm) is immersed in 500 ml of demi water. After 24 hours, the film is removed from the water and applied directly on both black and white parts of the Leneta opacity chart. The opacity is measured immediately (*Ultrascan XE* from *HunterLab*) and compared to that of the non-exposed to water PSA film to obtain the delta opacity value. Each measurement is replicated 3 times. A lower Delta Opacity value means a higher resistance to water whitening.

#### Goniometry:

A-4 microlitre of demineralized water is applied to the clear polymer films applied on glass and the contact angle is measured after 30 seconds using a PG-X Measuring Head Goniometer. Ten measurements are made on each panel and the average is recorded.

#### Gel Content:

Specimen preparation: 1 ± 0.1 g of latex is placed into silicon paper box (15 x 40 mm) and dried during 4 days under 50% RH and 23 °C followed by drying at 120°C for 3 minutes. The dried specimen is placed in closed stainless steel mesh cell. The cell is placed into Soxhlet extractor for 8 hours of refluxing of THF. The sample is finally dried at 120 °C under vacuum oven for 3 hours. The gel fraction of PSA material is calculated as follows:  $C = m_{gel}/m_{PSA} \times 100\%$ , where  $m_{gel}$  is the mass of the material after extraction,  $m_{PSA}$  the mass of the material before extraction.

## **Results and Discussion**

### **Synthesis and characterizations of the modified acrylic latexes**

This study aims at understanding the effect brought by the selected hydrophobic monomer on the physical and chemical properties of the polymers and ultimately on the overall performance of the PSA derived thereof.

The compositions have been modified by varying the level (0 and 20 wt%) of VeoVa-10 (Latex 1-2, Table 2) and by increasing the  $T_g$  (Latex 3, Table 2). Thus, a series of latexes with a targeted  $T_g$  (~ -40 °C and ~ -30 °C) were prepared under the same polymerization conditions keeping the surfactants, functional monomers types and levels

constant. These were then characterized and tested as PSA. The detailed polymerization procedure is given in the experimental section of this paper.

**Table 2. Composition description of the latexes**

| <b>Latex</b> | <b>2-EHA<br/>(wt %)</b> | <b>MA<br/>(wt %)</b> | <b>EA<br/>(wt %)</b> | <b>Veova-10<br/>(wt %)</b> |
|--------------|-------------------------|----------------------|----------------------|----------------------------|
| 1            | 69                      | 12.5                 | 12.5                 | 0                          |
| 2            | 64                      | 5                    | 5                    | 20                         |
| 3            | 50                      | 0                    | 24                   | 20                         |

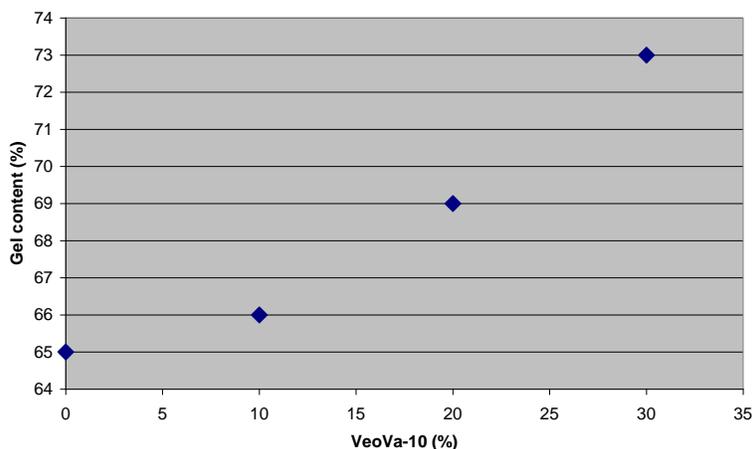
At this stage, a commercial latex (BM), marketed as permanent PSA for plasticized PVC films, was included in our study. All latexes were evaluated on solid content, particle size, viscosity, pH and  $T_g$  (Table 3).

In terms of solids content, the values measured for latexes 1-3 are in line with the theoretical values. Minor variations of the polymerization process have enabled us to prepare latexes with polymer content of ~60%. All latexes show a similar particle size, in the range of 200 nm which is expected from the combination of anionic and non-ionic surfactants used. The measurements of the  $T_g$  by DSC have revealed a good correlation with the predicted ones.

**Table 3. Latexes characterizations**

| <b>Latex</b> | <b>Solid<br/>Content (%)</b> | <b>Particle<br/>Size (nm)</b> | <b>Viscosity<br/>(mPa.s)</b> | <b>pH</b> | <b><math>T_g</math><br/>(°C)</b> |
|--------------|------------------------------|-------------------------------|------------------------------|-----------|----------------------------------|
| 1            | 53.1                         | 205                           | 150                          | 5.0       | -43                              |
| 2            | 53.3                         | 207                           | 255                          | 4.8       | -46                              |
| 3            | 53.2                         | 210                           | 215                          | 4.6       | -35                              |
| BM           | 51.5                         | 183                           | 118                          | 4.2       | -30                              |

Whereas the molecular weight of the soluble part of the latexes shows comparable values ( $M_n \sim 15$  kDa), the presence of the vinyl neoester seems to affect the gel content in these polymers (Figure 2). Gel content is known to significantly affect the fundamental PSA properties<sup>6</sup>, especially the cohesion level.



**Figure 2: Influence of VeoVa™ 10 level on the Gel content**

### Evaluation of the PSA properties

Next, the key PSA properties were evaluated. The adhesion levels measured on different substrates and after different dwell times are given in Table 4. From the first set of data (Latex 1-2), it appears that the modification of the polymer backbone by the hydrophobic vinyl ester monomer does not affect the adhesion levels on both polar and non-polar substrates. Similarly, no particular effect can be observed for the loop-tack on stainless steel.

Yet, the modification of composition from Latex 2 to Latex 3 leads to improved adhesion and tack, allowing PSA 3 to reach better overall properties compared to the commercial benchmark (BM).

Interestingly enough, the presence of the vinyl neoester in the acrylic polymer has a remarkable effect on the shear strength of the PSA. Confirming the earlier observations made by Yang, the presence of the branched alkyl vinyl ester in this series of model products allows for a substantial improvement of the adhesion/cohesion balance. The increased gel content obtained with the VeoVa modified latexes (Figure 2) may be taken into account to explain this trend.

**Table 4. PSA properties**

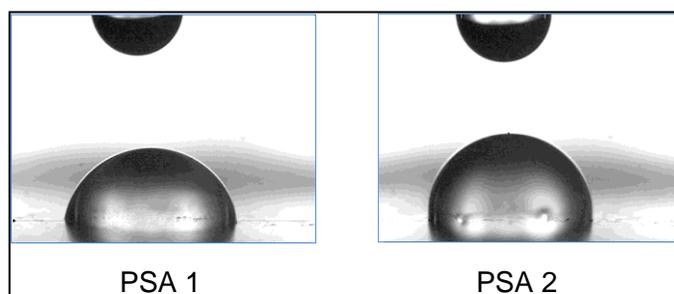
| PSA Properties              | Units | PSA 1 | PSA 2   | PSA 3   | BM   |
|-----------------------------|-------|-------|---------|---------|------|
| <b>Stainless Steel</b>      |       |       |         |         |      |
| Peel 20 min.                | lb/in | 1.54  | 1.37    | 1.52    | 1.43 |
| Peel 24 hr.                 | lb/in | 1.98  | 1.94    | 2.16    | 2.31 |
| Peel 7 days                 | lb/in | 2.07  | 2.16    | -       | -    |
| Peel 7 days (90% RH, 35 °C) | lb/in | 1.21  | 1.61    | -       | -    |
| Peel 20 min. (PVC)          | lb/in | -     | -       | 3.70    | 3.68 |
| Loop Tack                   | lb/in | 0.83  | 0.71    | 1.30    | 1.21 |
| Shear at 23 °C              | min.  | 3338  | >10.000 | >10.000 | 1377 |
| <b>HDPE</b>                 |       |       |         |         |      |
| Peel 24 hr.                 | lb/in | 1.08  | 1.10    | 1.83    | 1.59 |

At this stage, it is also important to mention that Latex 2 seems to be less affected by humid environment compared to Latex 1, as measured from the peel test after seven days under 90% relative humidity and 35 °C. On this basis, further investigation of the hydrophobic nature of the different latexes was pursued. A few specific evaluations related to the water resistance were performed (Table 5).

**Table 5. Water Resistance of the PSA**

| <b>Water Resistance</b>    | <b>Units</b>  | <b>PSA 1</b> | <b>PSA 2</b> |
|----------------------------|---------------|--------------|--------------|
| Water Contact Angle        | °             | 80.4         | 90           |
| Water whitening resistance | Delta Opacity | 16.2         | 12.5         |

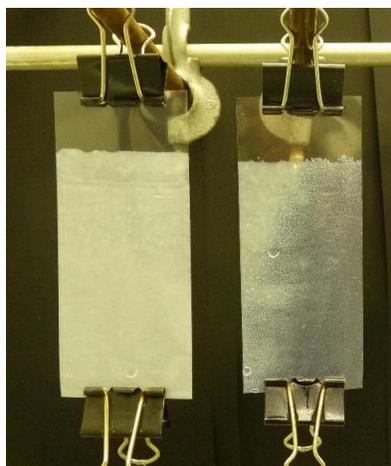
The water contact angle measurement is an easy way to assess the polar character of the PSA film surface. From the data obtained, it appears that the modification of the acrylic backbone by the hydrophobic vinyl ester is decreasing considerably the polarity of the PSA film surface. Despite the apparent lowering of surface tension brought by the vinyl versatate, no improvements of the adhesion on the low surface energy substrate (HDPE) could be observed between PSA 1 and PSA 2.



**Figure 3. Water Contact Angle**

As already mentioned, it is important that the PSA shows good resistance against water whitening when exposed to moisture. The details of the test are given in the experimental section and the results obtained are shown in Figure 4 where the pictures taken after 24 hours exposure clearly demonstrate the reduced water whitening provided by the sample containing 20% of the hydrophobic vinyl ester.

The delta opacity of the different samples was measured with a colorimeter in order to quantify the degree of whitening resistance (Table 5). Typically a lower delta opacity value indicates a better resistance against water whitening. The improvement brought by the hydrophobic vinyl ester can be determined and confirms the qualitative visual evaluation.



PSA 1      PSA 2

**Figure 4. Water whitening resistance after 24h in water.**

In the other series, a higher degree of whitening was observed for Latex 3 and BM (Fig. 5), perhaps due to the more polar composition of the PSA (Water Contact Angle  $\sim 77^\circ$ ). Interestingly enough, the replacement of the non-ionic surfactant used in Latex 3 by a polymerizable one (Modified PSA 3, Figure 4) leads to an outstanding water whitening resistance.

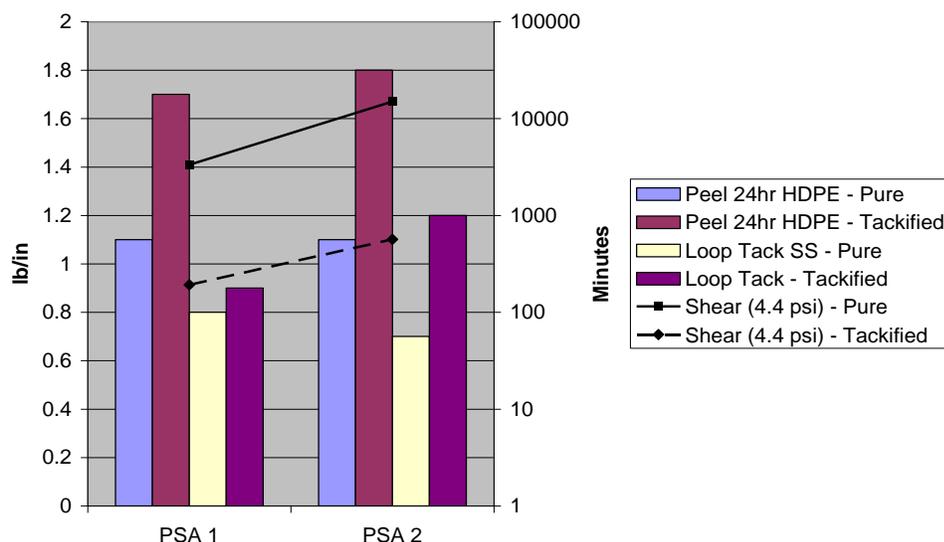


BM      Modified PSA 3

**Figure 5. Water whitening resistance after 24h in water.**

Finally, Latex 1 and 2 were tested in combination with a tackifier dispersion (20 wt%, Snowtack SE 724G). The two systems show a standard and similar response to the tackifier, i.e. increased adhesion to low surface energy substrates and tackiness (Figure 6). It is well-known that tackifiers have a detrimental effect on the shear resistance of PSA<sup>7</sup>.

Although this phenomenon could also be observed, the cohesion level of the tackified PSA 2 remains high thanks to the very high cohesion level of the base polymers.



**Figure 6. Peel, Loop Tack and Shear values of Pure versus Tackified PSA's**

### Synthesis and characterizations of the Vinyl Ester PSA

In light of the interesting properties obtained with VeoVa-10 in PSA applications and thanks to our access to softer hydrophobic vinyl ester ( $T_g \sim -40$  °C), we have been able to develop a new class of PSA based on a combination of vinyl ester monomers. This approach allows us to introduce a brand new class of materials, possibly showing different response and behavior compared to all-acrylic systems. The first step of this development aimed at synthesizing such latex with a targeted  $T_g$  of  $\sim -35$  °C. One model system was designed on the basis of a combination of 99 wt% of soft and hydrophobic Vinyl Esters and 1% of Acrylic Acid. The physical properties of the latex are given in Table 6 and are comparable to those obtained for the systems described in the first part of this work.

**Table 6: Latex characterizations**

| Latex | Solid Content (%) | Particle Size (nm) | Viscosity (mPa.s) | pH  | $T_g$ (°C) |
|-------|-------------------|--------------------|-------------------|-----|------------|
| 4     | 46.5              | 193                | 200               | 4.2 | -35        |

In the second stage, the PSA properties of this material were tested (Table 7). Interestingly enough, it can be observed that this material is behaving as a PSA showing a good cohesion coupled with a very high adhesion level on HDPE. To further assess the adhesion of such material on Low Surface Energy substrate, a peel test was performed on Teflon. Although the adhesion level is lower in this case, the value obtained is still quite remarkable as most WB Acrylic PSA tend to show adhesion levels in the range of 0.1 lb/inch.

**Table 7: PSA properties**

| <b>PSA Property</b>    | <b>Units</b> | <b>PSA 4</b> |
|------------------------|--------------|--------------|
| <b>Stainless Steel</b> |              |              |
| Peel 20 min.           | lb/in        | 1.51         |
| Peel 24 hr.            | lb/in        | 1.61         |
| Loop Tack              | lb/in        | 1.52         |
| Shear (2.2 psi)        | min.         | 2393         |
| <b>Glass</b>           |              |              |
| Peel 24 hr.            | lb/in        | 1.08         |
| <b>HDPE</b>            |              |              |
| Peel 24 hr.            | lb/in        | 2.25         |
| <b>Teflon</b>          |              |              |
| Peel 24 hr.            | lb/in        | 0.88         |

## Conclusions

Modification of a WB acrylic PSA by a branched and hydrophobic vinyl ester has proven to be straightforward, allowing the polymerization process and general characteristics of the latex to remain unaffected. Yet, the introduction of VeoVa-10 in the acrylic backbone has led to a clear reduction of the polarity of the polymer which has resulted in a substantial improvement of the water resistance, as demonstrated by the reduced water whitening. Although the water whitening resistance is also influenced by the use of a polymerizable surfactant, the combination of the two approaches has allowed the design of a PSA displaying an outstanding water whitening resistance. This study has also led us to confirm the improved adhesion/cohesion balance that the bulky vinyl ester can deliver to the acrylic system. Overall, from the study of these model systems, we can conclude that the modification of WB acrylic PSA by such hydrophobic vinyl ester may be considered as a valuable option to reduce the performance gap between WB and SB Acrylic PSA.

Finally, we have been able to develop a new class of products based predominantly on a combination of Vinyl Monomers. It has been demonstrated that these materials behave as PSA, showing a good cohesion level together with an excellent adhesion to low surface energy substrates plastics such as HDPE and Teflon.

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