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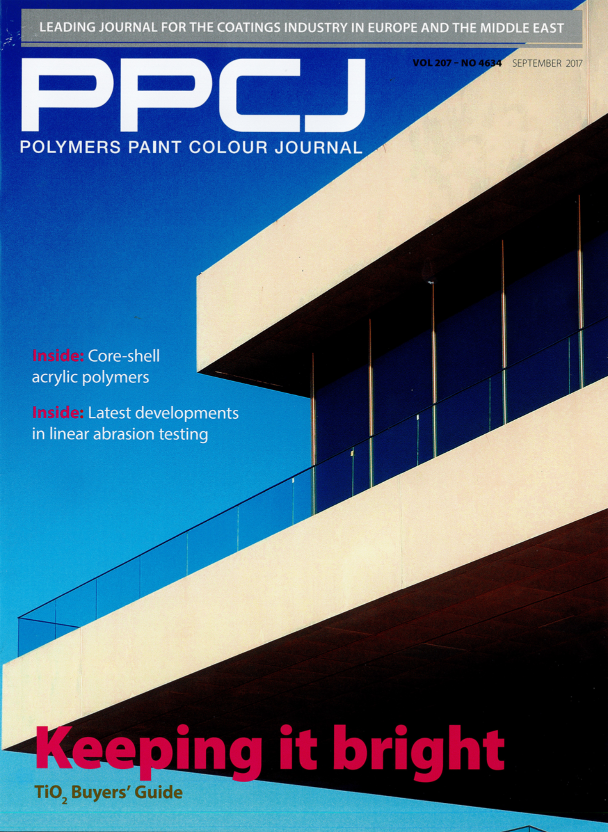
# PPCJ

## POLYMERS PAINT COLOUR JOURNAL



**Inside:** Core-shell acrylic polymers

**Inside:** Latest developments in linear abrasion testing

# Keeping it bright

**$TiO_2$ Buyers' Guide**

**TEST & WEATHERING • ADDITIVES • SURFACTANTS • WATERBORNE • ADHESIVES & SEALANTS**

*Jorge Moniz, Susana Carvalho, Bharat Odedra* and *David Graham*, Resiquímica, discuss their research into the development of core-shell acrylic lattices suitable for wood, metal and plastic surfaces

# Core-shell acrylic polymers for multi-surface coatings

The development of binders for multi-surface applications is a difficult task as the adhesion to surfaces of different energies is not straightforward.

In this work, we have studied acrylic core-shell lattices suitable for wood, metal and plastic surfaces that exhibit high hydrophobicity for exterior applications.

A careful balance of the core and shell polymers' composition and a suitable self-crosslinking system were key parameters in achieving a low minimum film forming temperature (MFFT) with excellent blocking resistance, while keeping a good elasticity. High performance was thus achieved with low VOC requirement. The crosslinking system works in conjunction with wet adhesion functionality to give excellent multi-surface adhesion properties. Additionally, high hydrophobicity was also given by the use of VeoVa10 monomer.

Interior and exterior construction areas increasingly require hydrophobic products in order to reduce water sensitivity to the coating materials. In particular, bathrooms require water protection in shower surroundings before painting or tiling. Decks, balconies and exterior walls also require waterproofing.

The development of a waterborne binder capable of addressing these application requirements is not straightforward. A simple sum of crosslinking and adhesion promoting agents to the main polymer can lead to severe stability issues or may not be sufficient in terms of performance.

In this work, we have studied a latex system based on an acrylic core-shell approach with a 0°C MFFT. VeoVa10 monomer was used to impart hydrophobicity. Wet adhesion and crosslinking monomers were added for multi-surface adhesion and blocking resistance.

## POLYMER DEVELOPMENT

The development of the required latex binder started with two VeoVa10 acrylate core-shell compositions **(Table 1)**. A moderate hard acrylic core was followed by a soft shell containing VeoVa10 monomer.

**Table 1. Data and results for VeoVa10 acrylate core-shell compositions**

| | #1 | #2 |
|---|---|---|
| Core Tg (°C) | 47 | 44 |
| Shell Tg (°C) | -7 | -1 |
| MFFT (°C) | 0 | 0 |
| Average particle size (nm) | 132 | 119 |
| Viscosity (mPa.s) | 58 | 66 |
| Solids content (%) | 46.6 | 46.6 |
| Sieve residue (%) | 0.020 | 0.030 |

Two different crosslinking mechanisms and a wet adhesion monomer were distributed in both stages of the polymerisation.

Both recipes produced products with 0°C MFFT and adequate particle size and viscosity. However, these VeoVa10 acrylate emulsions showed severe grit issues. After filtration the products still exhibited high sieve residues. Therefore, manufacturing conditions and recipes for the polymers were reviewed and modified. Radical initiation and residual monomer conversion were addressed to reduce grit formation. In addition, different emulsifier systems were screened to improve particle stability. A new method was thus tested in formulation #3 starting with monomer composition from #1 and several monomer adjustments were tested in #4 to #6 **(Table 2)**.

Results show that the main monomer composition is also relevant to grit formation, as only emulsions #3 and #6 show low sieve residue values. These results should be analysed together with the corresponding average particle sizes, since smaller particles tend to cause higher grit.

## WOOD STAIN

The improved lattices #3 to #6 were tested as binders in a wood stain formulation **(Table 3)** and compared to a low blocking pure acrylic core-shell latex.

For this wood application, blocking resistance is one of most significant properties to evaluate, in order to check if the low MFFT compositions are not detrimental. The results displayed on **figure 1** show that small variations in monomer composition have strong impact on the blocking resistance. Lattices #5 and #6 show clear improvements compared to the pure acrylic core-shell, however #5 having an MFFT of 10°C is not an option.

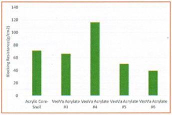
**Table 2. Data and results for grit improved VeoVa10 acrylate core-shell compositions**

| | #3 | #4 | #5 | #6 |
|---|---|---|---|---|
| Core $T_g$ (°C) | 47 | 50 | 50 | 48 |
| Shell $T_g$ (°C) | -7 | 4 | 11 | -2 |
| MFFT (°C) | 0 | 0 | 10 | 0 |
| Average particle size (nm) | 87 | 73 | 89 | 112 |
| Viscosity (mPa.s) | 85 | 147 | 63 | 255 |
| Solids content (%) | 49.0 | 47.7 | 48.3 | 47.9 |
| Sieve residue (%) | 0.006 | 0.018 | 0.012 | 0.0 |

As a further screening test, gloss was measured as core-shell compositions can lead to lower gloss levels due to the film forming process. **Figure 2** shows all the test formulations performed at least at the same level as the acrylic core-shell control.

The best blocking formulation (#6) was then chosen for application onto wood panels and tested in outdoor exposure for three years. **Figure 3** clearly shows the excellent ageing properties obtained with

**Figure 1. Wood stain blocking resistance for grit improved VeoVa10 Acrylate binders at 1kg/1h, 23°C (ISO 4622)**



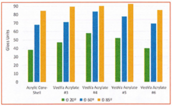



**Figure 2. Wood stain gloss levels for grit improved VeoVa10 acrylate binders (ISO2813)**

**Table 3. Wood stain formulation**

| | |
|---|---|
| Water | 24.65 |
| Wetting agent (Surfynol 104E) | 0.25 |
| Defoamer (Xynburst 9615) | 0.20 |
| Biocide (Preventol A-14D) | 0.20 |
| Thickener (Acrysol RM 825) | 0.24 |
| Binder | 68.36 |
| Wax | 2.30 |
| Pigment (Hostafine Transoxide Yellow R) | 2.30 |
| Pigment (Hostafine Transoxide Red B) | 1.50 |
| Total | 100.00 |
| **Solids content** | **35** |

**Table 4. Barrier coating formulation**

| | |
|---|---|
| Binder | 56.90 |
| Filler (Baryte) | 42.65 |
| Thickener (Xynpol AX 200R) | 0.40 |
| Defoamer (Xynburst 9615) | 0.05 |
| **Total** | **100.00** |
| Adjust to pH9.5 with Xyndisp 4500AD Solids content (%) | **70.6** |

**Table 5. High gloss paint formulation**

| | |
|---|---|
| Water | 16.12 |
| Dispersing agent (Additol VXW 6200) | 0.64 |
| Biocide (Preventol D-12) | 0.20 |
| Defoamer (Agitan E 256) | 0.03 |
| Propyleneglycol | 2.00 |
| Pigment (Kemira RDI-S) | 21.00 |
| NaOH 10% | 0.60 |
| Binder | 57.00 |
| Thickener (Aquaflow NMS 450) | 1.00 |
| Texanol | 1.50 |
| **Total** | **100.00** |
| **Solids content (%)** | **50** |
| **PVC (%)** | **18** |
| **VOC (%)** | **2.2** |

**Figure 3. Wood stain outdoor exposure after three years south facing: left, VeoVa10 acrylate #6. Right, acrylic core-shell**

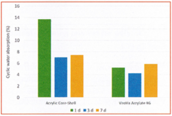



**Figure 4. Barrier coating cyclic water absorption (DIN 53495)**

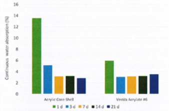



**Figure 5. Barrier coating continuous water absorption (internal method)**

this VeoVa10 acrylate binder compared to the pure acrylic control.

## BARRIER COATING

Given the good results on blocking and ageing, latex #6 was tested as a barrier coating. A suitable formulation to seal water-permeable substrates was developed. As can be seen in **Table 4**, no dispersant was used so that water sensitive ingredients are avoided.

Three different methods were used to assess water barrier properties. First, cyclic water absorption according to DIN 53495 was measured and the results clearly show a low water uptake **(figure 4)**.

Next, a continuous water absorption test was carried out where the test sample was not dried between measurements **(figure 5)**. Again, a much lower water absorption was obtained.

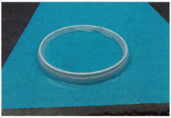


**Figure 6. After three months there was no loss of water into the plasterboard**

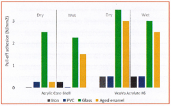



**Figure 7. 18% PVC white paints dry and wet pull-off adhesion after seven days drying (ISO 4624)**

Finally, a demonstration test on a plasterboard was performed using the same barrier coating composition but blue tinted for easier evaluation **(figure 6)**. After two barrier coats were applied, plastic cylinders were stuck to the plasterboard and filled with tap water. After three months, no loss of water was observed into the plasterboard.

## HIGH GLOSS COATING

In order to address multi-surface adhesion properties, latex #6 was evaluated in a high gloss paint formulation, with a PVC of 18% and a low VOC requirement **(Table 5)**.

The dry and wet pull-off adhesion tests carried out confirmed the multi-surface properties of latex #6 **(figure 7)**. Glass and old alkyd surfaces showed the biggest improvement compared to the pure acrylic core-shell. Adhesion to iron and PVC surfaces was also enhanced. Latex #6 can also improve adhesion performances under both dry and wet conditions. The crosslinking system gives highly coherent films with intimate molecular contact to surfaces with different energies.

Besides multi-surface adhesion, other high gloss paint properties were assessed. The gloss levels obtained were similar to the pure acrylic control values **(figure 8)**, while the hardness had a lower start but similar figures after 14 days **(figure 9)**.

Blocking resistance needs to be evaluated. Results shown in **figure 10** show the chosen pure acrylic core-shell has an outstanding blocking resistance but the VeoVa10 acrylate latex ▷31

compared to the alternatives. **Figure 5** shows that the multifunctional neutralising agents AMP and glucamine demonstrate a comparable shift of shades in the L and +b axis for all pigment pastes used and, therefore, allows these products to be interchangeable in mixing systems. (Note: a shift of shade of 0.1–0.2 is not evaluated as a significant deviation since it is still in the measurement tolerance.)

## PIGMENT COMPATIBILITY

For this test, a standard low VOC emulsion paint with various neutralising agents was adjusted to a pH-value of 8.5 and subsequently tinted with a water-based iron oxide red pigment paste (3% each). After the homogenisation using a paint shaker, the paints were stored for 24hrs; then 200µm was applied and subjected to a rub-out test.

As can be seen in **figure 6**, glucamine increases the tinting strength in the water-based paint system by more than 50%.

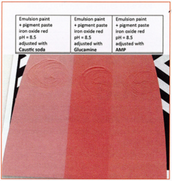



**Figure 6. Pigment compatibility in a water-based system**

## CONCLUSION

Neutralising agents are only used in small quantities in water-based paints. However, their effect is of significant importance. Not only do they regulate the pH-value, they also interact with paint ingredients and influence the stability of the paint during storage. This article compares the new glucamine with the most frequently used neutralising agents available to the paints and coatings industry – caustic soda, ammonia and AMP. Glucamine consists of up to 75% renewable raw materials, does not require labelling and is VOC/SVOC free.

In assessing the performance attributes, glucamine as a multifunctional additive is shown to improve the storage and freeze-thaw stability, reduce flash-rust discolouration and enhance the compatibility with pigments. These properties can be achieved in low PVC acrylic paints and high PVC indoor and outdoor emulsion paints. Such multifunctionality can help to reduce the number of components in the paint formulation and contribute to process and logistics cost savings. **PPCJ**

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Glucamine for paints and coatings features at 2017 tradeshows: Abrafati, October 3-5, São Paulo, Brazil; Western Coatings Show, Oct 15-18, Las Vegas, USA; ChinaCoat November 15-17, Shanghai, China.

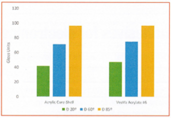


**Figure 8. 18% PVC white paints gloss levels**

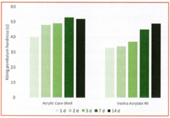


**Figure 9. 18% PVC white paints hardness levels (ISO 1522)**

◁ 28 also exhibits a very good performance, as typical values for standard acrylics with an average MFFT of ~13°C usually present blocking resistances above 300g/cm². An interesting result was the low blocking resistance did not imply low elongation properties **(figure 11)**. The obtained value of 103% is high enough for exterior wood applications.

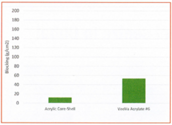


**Figure 10. 18% PVC white paints blocking resistance at 1 kg/1h, 23 °C (ISO 4622)**

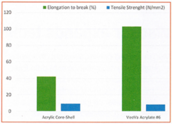


**Figure 11. 18% PVC white paints elastomeric properties (ASTM D 2370)**

## CONCLUSIONS

A VeoVa10 acrylate latex with crosslinking and wet adhesion functionalities has been developed.

The performance of the latex was evaluated in a wood stain, a barrier coat and a high gloss white paint.

Results compared to a pure acrylic control show improved adhesion to different substrates, especially old alkyd and glass.

Excellent water resistance properties were found in cyclic and continuous water absorption tests, as well as in a practical plasterboard impregnation method.

In addition, the core-shell approach could account for a high blocking resistance while maintaining gloss levels.

Overall, the results indicate that this product can be an excellent choice for interior and exterior coatings in cases where adhesion and barrier properties are necessary. **PPCJ**

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