LES IS MORE FOR NEW TECHNOLOGY

Novel silicone resin for high-performing, lower-cost facade paints and plasters. By Markus Vogel, Roger Reinartz and Daniel Brünink, Evonik.

Facade paints need to be both decorative and weathering resistant as well as meet increasing customer requirements. Extending the colour range and environmental compatibility at the same time as reducing costs poses a real challenge. However, researchers believe they have developed a new hydrophobing agent using silicone resin technology that sets a new standard.

For decades, facade paints have had two important functions: They lend an attractive appearance and offer protection from the effects of weathering. Therefore, producers of premium facade paints have worked hard to optimise these two properties in their products. Silicone resin paints are now state-of-the-art options for exterior applications. These paints contain emulsified silicone resins in addition to a primary binder, which is generally a styrene-acrylate dispersion. Such paints have excellent weathering resistance and a long service life. Over the last few years, however, customer requirements have increased. The colour selection needs to be larger. The facade needs to be slower to soil than before and all these performance characteristics need to be achieved by environmentally compatible means. Researchers have now developed a new silicone resin that meets these increased requirements. As an added bonus, it can be used in significantly lower concentrations than the established alternatives, thus saving costs.

HIGH WATER-VAPOUR DIFFUSION WITH SILICONE RESIN

Facade paints must promote good diffusion of water vapour so that moisture coming from the interior does not accumulate in the brickwork. Under some circumstances, this moisture may lead to a build-up of pressure that can cause coatings that are not permeable to water vapour to burst. High water vapour diffusion is achieved by the supercritical pigment volume concentration at which the binder, due to its low quantity, does not fill all the interstitial spaces of the filler and pigment particles, thus allowing a network of micropores to be formed. These pores create a surface that is prone to attack by penetrating water such as rain. Hydrophilic pores absorb water strongly. This absorption strength can be illustrated by modelling a pore as a vertical cylindrical capillary. The capillary rise, $h$, of the water is given by the capillary equation:

$$h = \frac{2\sigma \cos \Theta}{\rho g r}$$

where $\sigma$ is the surface tension and $\rho$ is the density of the water, $\Theta$ is the contact angle of the water on the capillary surface, $g$ is the gravitational constant, and $r$ is the pore ra-
RESULTS AT A GLANCE

→ Silicone resin facade paints offer excellent weathering resistance and a long service life, but they now need to meet ever-increasing requirements on the colour range, environmental compatibility and dirt pick-up.

→ A new silicone resin has been developed that achieves these properties as well as being highly effective at low concentrations.

→ The comparison of paints formulated with the novel resin with a commercially available standard suggests processing benefits such as a more homogeneous distribution and a sustainably lower viscosity, even after storage.

→ Thin paint layers and high colour paste uptake reduce the user’s material requirements and therefore costs. Along with high environmental compatibility, the new silicone resin presents a new standard for hydrophobing agents for facade paints and plasters.

dius. For a hydrophilic pore with a contact angle of 0° and a radius of 100 nm, the capillary rise is 157 metres, so the water column would be taller than Cologne Cathedral in Germany. This effect needs to be reduced, which is most effectively achieved through the surface chemistry of the capillary. When the contact angle θ > 90°, the water sinks instead of rising. Under the same conditions (but with a contact angle of 140°), the water sinks by as much as 100 metres. The pore surfaces must therefore be made hydrophobic — without heavily impacting the microporous structure that makes water-vapour diffusion possible. In practice, this is achieved by adding silicone resin emulsions.

FAST-DEVELOPING WATER RESISTANCE

Researchers have conducted trials to quantify the hydrophobic effect of the new silicone resin. They painted mineral substrates with a paint previously treated with the novel silicone resin and immersed the substrates in water for 24 hours. The water absorption during this period was found to be significantly lower than for formulations using commercially available reference products. The water absorption coefficient $w_{24}$ was below 0.1 kg/(m²*h½) and 60-80% lower at a silicone resin concentration of 4.8%. Even at a concentration of only 2.0%, the novel resin retains this $w_{24}$ value — something that has not been achieved to date (Figure 1). The $w_{24}$ value of a coating generally decreases upon additional exposure to water because the surface-active components that enable penetration of water into the pore network are washed out of the coating. In practice, it is best if the lowest possible $w_{24}$ value is obtained after minimal exposure to water. This property is termed “early water resistance”. The analysed silicone resin achieves its optimum $w_{24}$ after the second exposure to water. For the reference products, the results after the first two passes were inadequate and comparable performance was not achieved until there had been further exposure to water. For users, this means that paints formulated with the novel silicone resin show good water resistance directly after drying — not only after a few heavy showers.

HIGHLY EFFECTIVE AT LOW CONCENTRATIONS

To further investigate the distribution of the silicone resin in the paint, the developers obtained electron micrographs. By means of spatially resolved energy dispersive x-ray spectroscopy (EDX), they also determined the local distribution of the elements. To allow for identification of the silicone resin, no silicone-containing fillers or pigments (such as quartz or silica) were used; calcium carbonate and titanium dioxide were used exclusively. A commercially available styrene-acrylate dispersion was used as the primary binder. Paint layers with 2.0% and 4.8% silicone resin — based on the novel resin and on a commercially available standard — were removed from the substrate and embedded in an epoxy resin under vacuum. The researchers then prepared 180 nm thick sections and investigated these. Figure 2 shows a representative result. The paint contains 2.0% of the novel silicone resin and, as expected, has a porous, non-homogeneous structure. Micrographs of paint layers with another silicone resin at a higher concentration are almost identical at first glance. Three regions can be distinguished, which are denoted in the image by I, II, and III. Region I is pale in colour, amorphous, and homogeneous. EDX shows almost exclusively carbon (C) and oxygen (O), and this appears to be pure binder. Region II consists of dark, homogeneous structures of high electron density. EDX shows here titanium (Ti) and calcium (Ca) as well as other elements, therefore this must be pigment or filler. Finally, for the non-homogeneous region III, also with fairly high electron density, EDX shows silicone (Si) in addition to carbon (C) and oxygen (O). This appears to be silicone resin.

The distribution of silicone resin in the film is crucial to its effectiveness. Upon more detailed examination, striking differences are seen here between the novel silicone resin and the market standard. Figures 2A and 2B show higher-resolution micrographs; silicone resin can be seen in addition to the primary binder. Figure 2A shows that the commercially available silicone resin is encapsulated...
to a large extent by the primary binder, undoubtedly to the detriment of its efficacy. On the other hand, Figure 2B shows that with the novel silicone resin there is almost complete separation between the silicone resin and the binder, so the silicone resin is fully effective. This microscopic phase separation is likely due to the molecular structure of the silicone resin and the choice of emulsifiers used.

A second difference between the two silicone resins is observed in the EDX spectra of the pigments. (Figure 3) The EDX spectrum of the commercially available standard shows some calcium and titanium but no silicone. Alternatively, the EDX spectrum of the novel resin shows both titanium and silicone, indicating that the pigment particles have been coated with a silicone resin film. The high affinity of the novel silicone resin for pigments and fillers — in addition to the aforementioned phase separation — explains its particularly high efficacy at low concentrations.

**LOWER DIRT PICK-UP**

In an accelerated soiling test in the laboratory that simulates outdoor weathering, the researchers also found that facades with formulations based on the novel resin pick up dirt only half as much as the market standard. (Figure 4) A special machine was used for this test. Water is treated with a dirt mixture consisting of tar, carbon black, and Japanese Norm Dirt. Test plates coated with silicone resin paints are soiled with this water in the machine. The machine then heats the plates to 50 °C and washes them with clean water. This cycle is repeated several times over a defined period. After the simulated soiling, the formulation with the new silicone resin structure showed L values (which indicate the degree of soiling) up to 30% lower than formulations with other silicone resins. (Figure 5)

**GREATER COLOUR CHOICE WITH ORGANIC PIGMENTS**

The high pigment affinity of the new silicone resin is also important for pigment concentrate uptake. Tests have shown that colour paste uptake for paints formulated with silicone resin is better than pigment concentrate uptake for paints without silicone resin. This means that formulators can save on pigment concentrate while still obtaining the same tinting strength. The particular strength of the novel silicone resin lies in its versatility: It can also be used with pigment concentrates based on organic pigments.
pigments and therefore allows a far wider choice of colours than what has been previously possible with most silicone resins. (Figure 6)

**PROCESSING AND STORAGE BENEFITS**

The novel resin can be used for liquid plasters as well as facade paints. It offers additional advantages in processability because the usual flow limit on the market is currently significantly higher. Tests have shown that, particularly after storage, the flow limit of plasters formulated with the new silicone resin is only about one-third of that for plasters using the reference products, regardless of storage time.

Formulations with the new silicone resin structure have a very favourable rheological profile, which simplifies application for the processor. Moreover, the homogeneous distribution of the silicone resin results in a more uniform structure in the plaster (Figure 7). This enhances its visual appearance and also prevents the formation of fairly large grooves, which would strongly promote water absorption. The viscosity remains significantly lower than for other commercially available products, even if the paint is exposed to a temperature of 50 °C over a fairly long period. This facilitates application after storage. Tests showed no effect on viscosity even after 256 days of storage — in contrast to reference products and to paints without additive, where the viscosity increased by a factor of 50.

Analyses of the storage modulus $G'$ support this observation: After only one week of storage, this value was significantly lower than that of the reference product and of the formulation without hydrophobing agent. After 256 days of storage, the storage modulus $G'$ for the novel resin had doubled, while the standard product and the formulation without additive showed an 8-fold increase (Figure 8). While this data doesn't indicate that the standard product compromises the formulation’s stability, it does confirm that using the novel silicone resin provides a more stable product over time. This can be attributed to the novel resin's high affinity for pigments and fillers and is ultimately why formulations containing this product have a significantly longer service life.

**ENVIRONMENTALLY COMPATIBLE FOR BROAD MARKET ACCESS**

Because all these functions are obtained even with thin paint layers, the user’s ma...
The overall required use level is reduced. And the environment also benefits because, since the beginning, the developers have chosen the raw materials so that the finished formulation can satisfy high certification demands and easily surmount the regulatory obstacles in various countries. Possible certificates include Blue Angel, the Nordic Ecolabel, and the EU Ecolabel.

REDUCED COSTS AND GREATER PERFORMANCE

In conclusion, the newly developed silicone resin shows improved technical properties even at reduced concentrations. For the end customer, it offers a wider selection of colours and reduces maintenance costs. These benefits are combined with high environmental compatibility, so that the product sets a new technology standard on the market for hydrophobing agents for facade paints and plasters.

Figure 7: Surface structure of plasters. Formulations based on the novel silicone resin show a more uniform surface structure with the same filler package.

Figure 8: Storage modulus G’ as a function of time. With the novel silicone resin, G’ is lower by one third at the onset and increases only slightly over time. Without silicone resin, or with the market standard, G’ increases strongly over time.

“The overall required use level is reduced”

2 questions to Daniel Brünink

To what extent does the novel silicone resin influence a reduction of wetting and dispersing agents? Due to the novel structure of our silicone resin technology, we do increase the affinity to pigments and fillers, therefore the overall required use level is reduced and we achieve already a good stability. We have seen in our test that we increase especially the acceptance of colorants in the new system.

How does the reduced viscosity influence the application? Due to the new technology we do not just reduce the viscosity. The whole rheological profile can be improved which leads to a better stability of the paint or plaster. On the other hand it generates a better workability especially with plasters and at the end easier application and better appearance.

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