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GIVING DIRT THE BRUSH-OFF

Easy-to-clean properties now available for epoxy resin systems. By Majdi Al-Masri, Wolfgang Griesel and Lin Xie, Byk.

A new hydrophobising additive for 2-pack epoxy systems has a polymer structure containing functional groups that lead to chemical bonding with the coating matrix. The additive reduces the effects of soiling and resisted repeated contamination/ hot cleaning cycles. Improvements were noted in several other properties.

Epoxy resin coatings (EP coatings) are characterised by their high chemical and mechanical resistance, and are generally applied in thick layers. The cured EP coatings also exhibit extremely high adhesion to the substrate. Epoxy resins generally refer to diglycidyl ethers of bisphenol A or bisphenol F. In this structure lies the reason for the limited UV resistance of EP coatings. This is why they are recoated for outdoor applications with a UV-stable topcoat such as polyurethane (PU).

Wherever the need for such a topcoat can be avoided, the benefits of EP coating compared with PU coatings are uncontested. They are admirably suited to coating machinery, plant, railway car parts, pipeline and tanks and for construction parts and concrete floors which experience high mechanical or chemical stress. For this reason, it is of great interest to develop customised surface additives for one-coat EP coatings. In addition to levelling additives, which are used to improve film formation, additives to prevent dirt pick-up and to simplify surface cleaning are becoming increasingly important. Particularly in applications where clean surfaces play a major role in preventing contamination, such as in containers, tanks and conveyor systems, or for safety or aesthetic reasons such as in tunnels and corridors (*Figure 1*), easy-to-clean surfaces bring huge economic and time advantages [1, 2].

TWO VERY DIFFERENT EASY-TO-CLEAN TECHNOLOGIES

The easy-to-clean effect can be achieved, for example, by using self-cleaning or easy-to-clean coatings. These easy-to-clean surfaces are created using two different technologies: there are (super) hydrophilic and (super) hydrophobic surfaces.

(Super) hydrophilic surfaces are characterised by a contact angle to water from 0° ('super') to 30° [3]. The water wets the surface, thus infiltrating the deposited dirt. These surfaces are manufactured either by embedding defined structures on the surface, for example using self-assembling monolayers, or by the best-known method, using photocatalytic TiO_2 [4]. In comparison, (super) hydrophobic surfaces have a contact angle of at least 140° to water, and water therefore simply drips off [5]. This behaviour means that the deposited dirt will be removed with the water. This effect can be achieved by creating hierarchical structures ('Lotus effect') which, however, is characterised by a time-consuming application process and may only last a short time due to loss of the surface structure [6].

IMPROVING THE PERFORMANCE OF HYDROPHOBIC ADDITIVES

It is a little simpler to use powerful surface tension reducing and hydrophobising additives for coatings, which include fluorinated hydrocarbon compounds and silicone oils. However, because of the ad-

RESULTS AT A GLANCE

➞ Existing easy-to-clean additives for epoxy topcoats tend to have only short-term benefits. A new hydrophobising additive for 2-pack epoxy systems has been developed, with a polymer structure containing functional groups that are compatible with epoxy resins and lead to chemical bonding with the coating matrix.

➞ The additive reduced the effects of both hydrophobic and hydrophilic contamination and resisted repeated cleaning in a dishwasher at 50 °C much better than a commercial silicone additive.

➞ Significant improvements were found in a number of other properties, including reduced carbamate formation, decreased ice adhesion and improved de-icing and greater UV resistance.

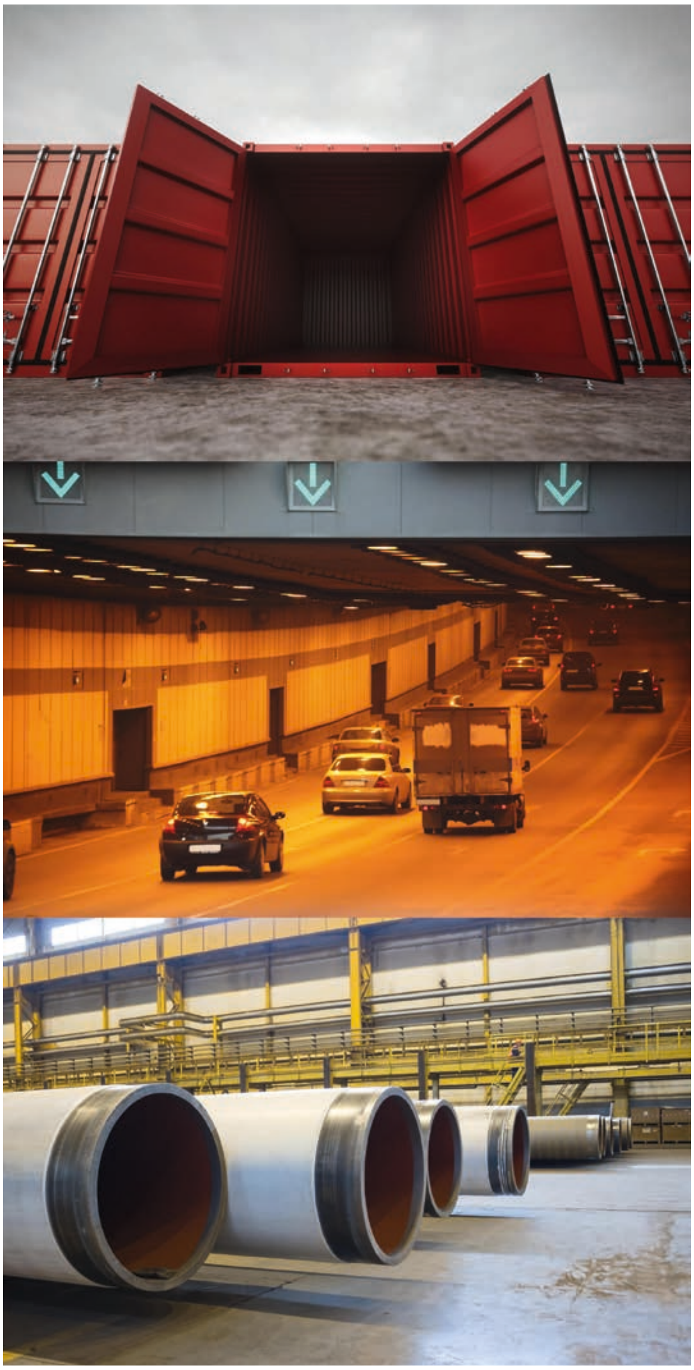
➞ Levelling was not affected and there was no evidence of cratering or increased foaming. Pot life is unaffected, and there is no reduction in intercoat adhesion.

verse environmental impact of fluorinated hydrocarbons, their use is undesirable [7].
Traditional silicone oils only display a short-term effect and may also cause levelling problems [8]. Silicones that are modified with polar groups result in better levelling. However, the easy-to-clean effect is only short term. These silicone additives lose their effect after a few (generally no more than two) cleaning cycles.
By making a wise and well-balanced structural selection such as the ratio of polar to non-polar groups, an additive was recently developed that combines the two properties of being easy to clean and having optimum levelling. Using silicone macromonomer technology, and by introducing groups that are compatible with epoxy resin that form covalent bonds with the coating (*Figure 2*), an additive with long-lasting easy-to-clean properties could be developed.
This additive is characterised by a strong surface orientation, so that the polar portion of the copolymer remains in the inside of the polymer film and the reactive groups form a covalent bond with the binder, thereby embedding themselves. The additive has also shown compatibility with most EP systems, whether conventional, high-solids or solvent-free.

COATINGS RESIST REPEATED SOILING AND CLEANING

The strong hydrophobic effect generated by the surface enrichment of the silicone block results in a surface that strongly repels dirt in solid, liquid or mixed form irrespective of whether the contamination is of a hydrophobic (oil-based) or hydrophilic (aqueous) nature. Metal sheets were coated with a conventional EP topcoat. In some sheets, the coating contained up to 2% of the new additive (all specified percentages are by weight). The sheets were contaminated in different ways, stored for one hour at 50 °C and then washed in a commercially available dishwasher on its standard program. The contamination was simulated with carbon black powder, with a 2% carbon black powder-water suspension and with 1% carbon black powder in hand cream. The carbon black powder was sprinkled on the surfaces. The aqueous carbon black suspension and the carbon black hand cream were applied to the surface using a laboratory paper towel that was wetted with the suspension or hand cream. After being washed using a standard dishwasher program (2.5 h at 50 °C), the samples were visually assessed, photographed and re-contaminated and washed again as described above. This process was repeated several times.
In addition to the 'control' (coating without additive) a conventional silicone additive was used in the tests as a comparison. *Figures 3*, *4* and *5* show the exceptional easy-to-clean effect and durability of the new additive, regardless of the polarity of the contamination. The ef-

Figure 1: Some possible applications of EP monolayer coatings (i.e. areas with limited UV light exposure). Source: 3dmentat/Fotolia Pavel L Photo and Video/Shutterstock and Kekyalyaynen/Shutterstock



fect could be demonstrated after up to ten cleaning cycles. Even if these simulated contamination and cleaning cycles do not entirely correspond to real-life conditions, they are nevertheless proof of the effectiveness of the additive under harsh conditions. In addition, these tests were able to demonstrate significant differences from the conventional silicone additives.

PULL-OFF TESTS SHOW INTERCOAT ADHESION IS RETAINED

The new additive was developed as an easy-to-clean additive and is therefore recommended for use in topcoats. However, as it is also a surface-active substance, it is important that there should be no adverse influence on the intercoat adhesion, i.e. no reduction in adhesion between the topcoat and the base coat.
A pull-off test in accordance with DIN EN ISO 4624 was used to confirm that the additive caused no intercoat adhesion problems. A red, conventional 2-pack EP primer was applied at 200 µm wet film thickness to sand-blasted steel (Sa 2½) and, after 30 days drying, it was coated with 100 µm of a white 2-pack EP topcoat containing 2% of the new easy-to-clean additive (*Figure 6*, *left*). After a further 14 days of drying, the pull-off test was performed according to DIN EN ISO 4624. *Figure 6, right* illustrates the result. Cohesive failure occurred only in the primer, which indicates extremely good adhesion between primer and topcoat.

SMOOTHNESS IS UNAFFECTED AND SLIP INCREASED

Another key property of coatings is film formation or film integrity, which is especially ensured by optimum levelling. Silicone additives can cause levelling issues as a result of high incompatibility with the system.
For this reason, the new additive was used at different concentrations in the EP coating systems, and the levelling was tested. Levelling measurements for the samples without the additive (control) and with 0.5% to 2% of the new additive show similar values. An additive quantity of up to 2% did not cause any levelling issues. Larger quantities were not tested as the easy-to-clean effect can be fully achieved at the 2% addition rate. To test surface slip, experiments were conducted with the same range of samples as for the levelling test. The results in *Figure 7* show, based on the coefficient of friction, a strong increase in slip even with a low quantity of additive. Even as little as 0.5% was sufficient to significantly improve the slip.

Figure 2: Schematic diagram of the modified silicone polymer structure.

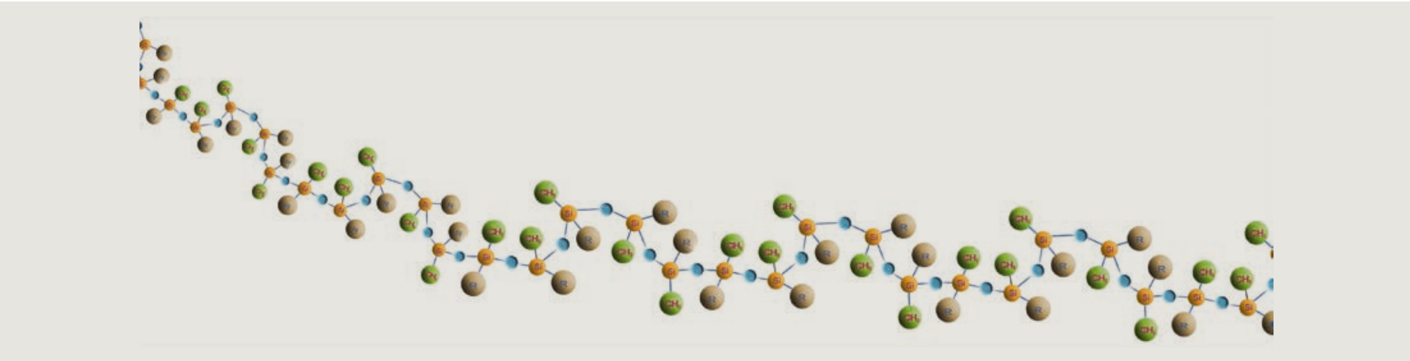


Figure 3: Easy-to-clean effect in conventional EP topcoat without additive, with 0.5% conventional silicone additive and with 0.5% new additive after contamination with carbon black powder and cleaning in washing machine.

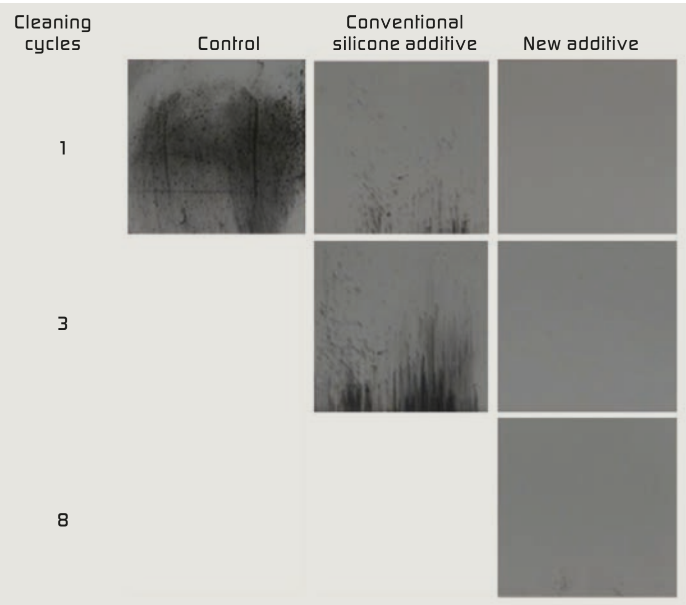
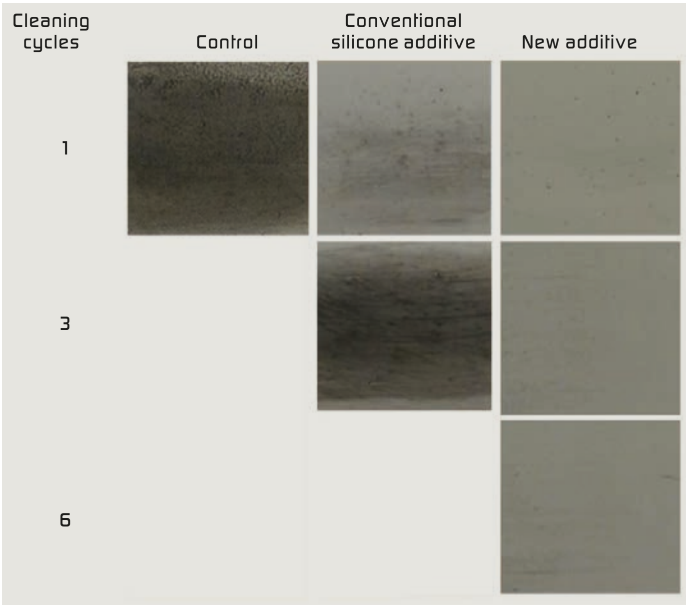


Figure 4: Easy-to-clean effect in conventional EP topcoat without additive, with 1% conventional silicone additive and with 1% new additive after contamination with 2% carbon black suspension in water and cleaning in washing machine.



SOME IMPROVEMENTS FOUND IN OTHER PROPERTIES

The defoaming property of epoxy systems is very significant as a result of their often relatively high viscosity. The additive was used at a proportion of 2% in a 2-pack epoxy system. A defoaming effect was observed in comparison with the sample without the additive. As a result of its specifically low incompatibility, the additive does not stabilise foam and can even improve defoaming.
In two-component systems, the pot life always plays an important role. When using the new additive, there may initially be a slight increase in viscosity. However, it has no impact on the pot life. When curing epoxy/amine two-component coatings, a significant reduction was observed in carbamate formation. Carbamates, which are also referred to as 'amine blush', are chemical compounds that form from air, especially with ambient curing EP systems under the influence of high air humidity and carbon dioxide. They result in haziness on

Figure 5: Easy-to-clean effect in conventional EP topcoat without additive or with 2% silicone after contamination with 1% carbon black powder in hand cream. A = directly after wiping B = after 10 contamination and cleaning cycles.

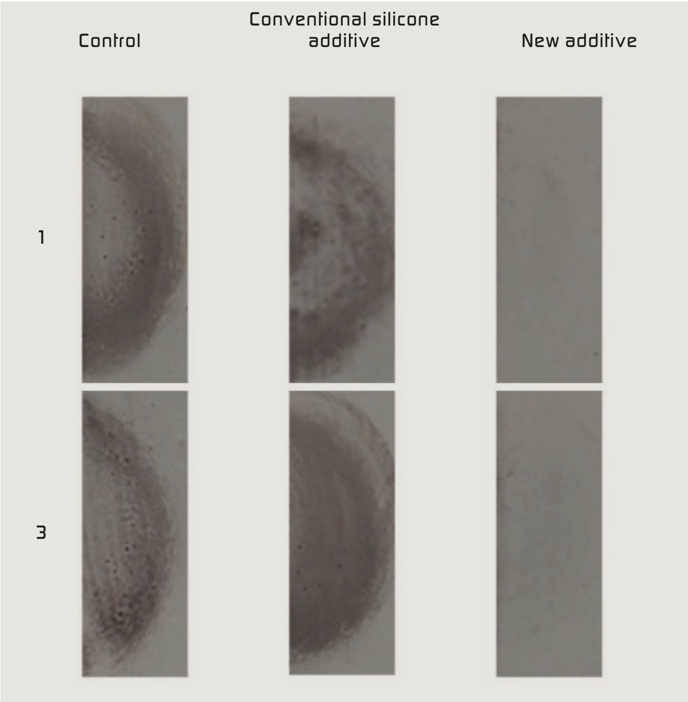


Figure 6: Schematic coating structure for the pull-off test (left) and pull-off test according to DIN EN ISO 4624 (right). No adverse impact on the intercoat adhesion.

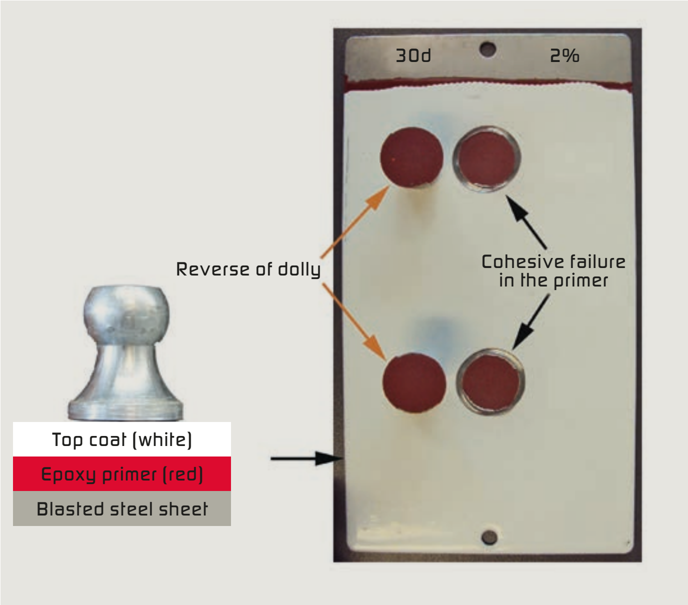


Figure 7: Influence of the new additive on slip for a conventional EP coating without additive (control) and with 0.5 – 2% additive.

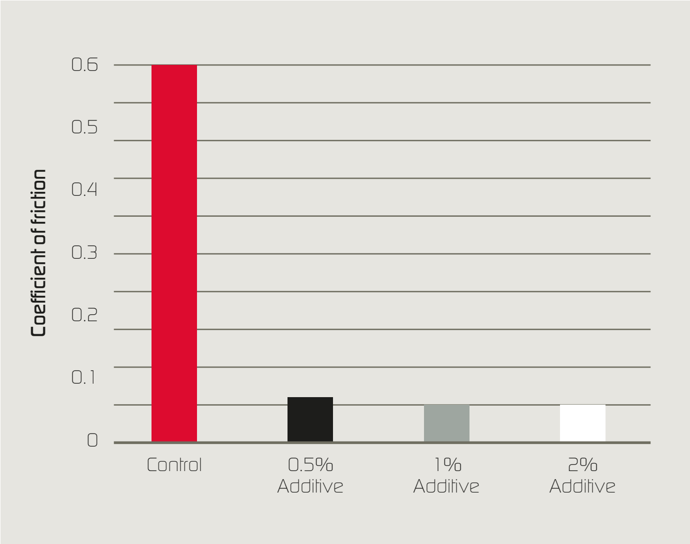
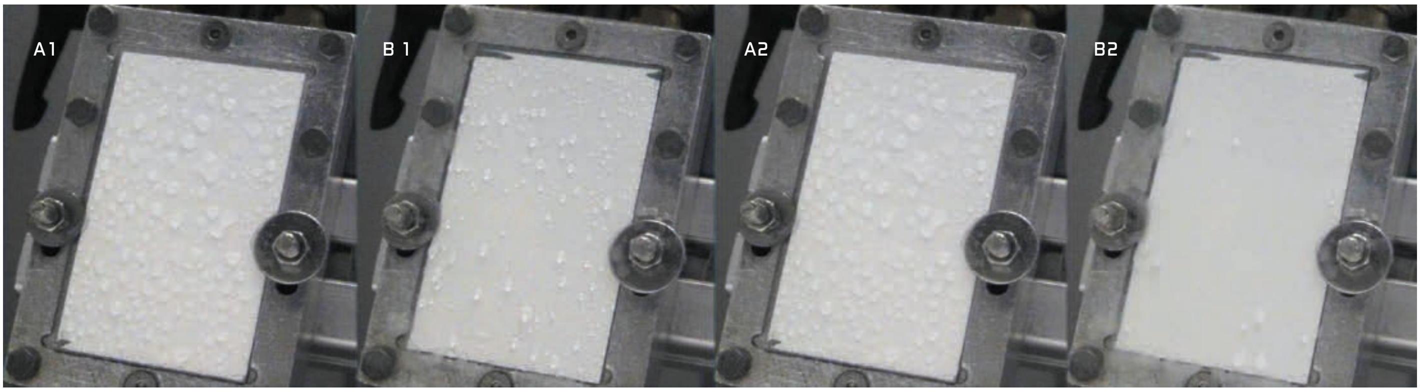


Figure 8: Use of the surface additive prevents ice formation in topcoats – immediately after sprinkling with ice water (A1 without additive, B1 with 2% additive) and five minutes after sprinkling with ice water (A2 without additive, B2 with 2% additive).



black or brilliant surfaces [9]. Three panels were coated with a black EP/amine coating. The samples were cured at room temperature and at an air humidity of 85%. Following curing, the colour of the sheet metal without the additive displayed strong greying. Adding 2% of a common silicone additive slightly reduced the grey discoloration. Using 2% of the new additive meant that there was virtually no greying.
This visual evaluation was also confirmed using measurements taken with the Byk-Gardner "colour guide" spectrophotometer. The whiteness L* values (in the CIELab system) of the control, of the sample with the silicone additive and of the sample with the new easy-to-clean additive are 33.7, 29.5 and 27 respectively, indicating that the new additive retained the darkest shade.

RESISTANCE TO UV EXPOSURE CONSIDERABLY IMPROVED

In addition to protection against carbamate formation, the EP coating with the new additive also survives 550 hours of QUV-B exposure with only minor alteration. The ΔYI values (the difference between the yellowness indices in accordance with ASTM E313) were determined with the same spectrophotometer for the samples without additive, with the conventional silicone additive and with the new additive, before and after QUV exposure. The differences were 17, 11 and 8.57 respectively.
The strong reduction in surface tension by the new additive led to another test, which was performed by an independent institute. A low surface tension can reduce the ice adhesion to coating films or improve the de-icing of the surface. For this purpose, investigations were performed in a defined atmosphere, in which ice water was sprinkled on the samples at -5 °C and a defined wind speed of 11.5 m/s and humidity of 66%.
Instantly and after five minutes, an image of the sprinkled samples was taken to evaluate the degree of icing (*Figure 8*). The sample that contained the additive displayed a considerably lower degree of icing. This phenomenon also suggests the additive could be used for surfaces that require de-icing for technical, economic or safety reasons.

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"The system can be readjusted by reducing the rheology additive level."

3 questions to Dr Majdi Al-Masri

Does the slight increase in viscosity show an impact on the spray application performance or levelling? *It depends on the coating system. As most coating systems contain rheology additives, the system can be readjusted by reducing the rheology additive level or other spray application parameters in order to maintain the coating performance.*
What methods of testing for easy-to-clean effects were used? Does the use of a standard dish washer program for testing entail the use of detergents? *The test was carried out by contamination with carbon black in different media, followed by visual evaluation. The results were documented by photographs. We believe that the long-term and recurring cleanliness of the coated panels is evidence for the presence of the surface additive over multiple cleaning cycles involving a common market detergent.*
Does a higher content than 2% of the product affect the surface similarly to regular silicones? *The addition of more additive is not always helpful. An excess of the additive in this case may form a liquid layer on the surface which is not chemically bonded to the matrix. This layer will act as regular silicon and could leave a greasy surface. In addition, it could also affect the appearance of the coating or its adhesion.*