Chained to the surface

Polymeric additive bonds coatings even to contaminated substrates

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Paint performance can be adversely affected in many different ways by poor adhesion. High solids and waterborne coatings are especially liable to adhesion failures. A novel type of adhesion promoter was tested in a liquid epoxy system on different substrates, including deliberately contaminated or rusted steel. Significant improvements to flexibility, adhesion and corrosion resistance were noted.

When coatings are applied to substrates such as metal, the adhesion of the cured paint to the substrate is always a vital parameter affecting the final performance of the paint film. This adhesion affects many properties of the paint, including optical appearance, anticorrosive performance, flexibility, resistance to scribing and scratching, delamination, blistering and more besides.

Many steps can be taken to influence and improve the adhesion of a coating to a substrate. Several procedures can be carried out: on the substrate itself, by adding an additional coating layer or by the use of certain additives that can be incorporated into the paint.

Modifications to the substrate itself might involve, for example, sandblasting of a metal substrate. In this case the surface topography is influenced in such a way that, because of the higher surface roughness and the resulting "anchoring effect", the adhesion of the paint is enhanced, and impurities such as rust and scale are removed.

The process of sandblasting can be considered time-consuming. Moreover, the process needs to be properly carried out. Improper treatment of the surface can result in local failure of the paint film due to an inappropriate or too great an increase in the surface roughness or the incorporation of impurities due to the use of unsuitable blasting material.

The use of a primer can also be considered, which helps to prepare the substrate as a good base for the subsequent coatings. Primers show good adhesion to the substrate, are relatively insensitive towards impurities, or can prepare the substrate by removing impurities and generating higher surface roughness by etching the substrate. Again, the step of applying the primer is both time and material-consuming.

An adhesion promoter which is incorporated into paint can improve the adhesion of various paint systems to various substrates, usually by generating chemical bonds between binder and substrates.

Polyester/Rosin ester	COOH	OH
Phosphoric acid ester	$PO[OR]_3$	Alkyl, Aryl, Epoxy, COOH
Silanes	$Si[OCH_3]_3$, $Si[OC_2H_5]_3$	Amino, Epoxy, Methacryl, Vinyl,...
Titanates/Zirconates	$Ti[OR]_4$, $Zr[OR]_4$	$Ti[OR]_4$, $Zr[OR]_4$
Surface reactive group		Binder reactive group

Figure 1: Currently available adhesion promoter technologies

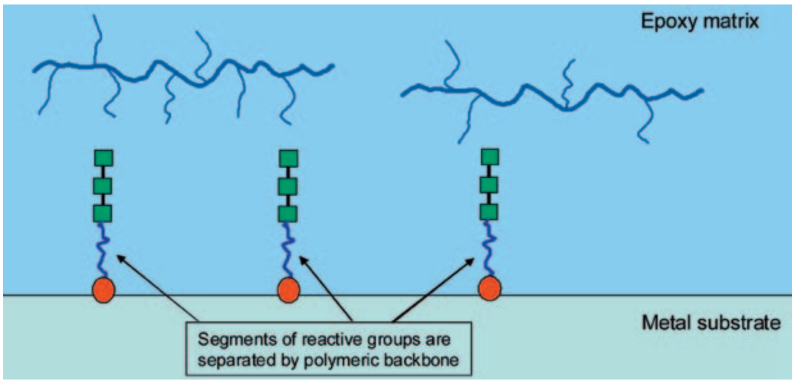

Figure 2: General concept of the orientation of new adhesion promoter in an epoxy matrix

Surface preparation: always important, today critical

As already mentioned above, the process of surface preparation is essential to producing a paint film that shows a good overall performance.

Many impurities on the surface such as rust, scale, oil, fat, dirt, etc. can affect the film formation and the wetting process of the paint. To achieve proper wetting by the paint, the surface energy of the paint needs to be lower than or equal to the surface energy of the substrate. If impurities present on the surface affect the wetting process, this can lead to poor overall performance of the coating system.

Various ways exist to remove the impurities from the surface. One can be sandblasting, as mentioned; other methods are sweeping, ultrasound, hand solvent cleaning, and so on.

The importance of a properly cleaned surface is growing with the increasing use of high-solids, solvent-free and waterborne systems. While solventborne systems are relatively uncritical when impurities are present, the properties of waterborne and high-solids/solvent-free systems lead to reduced acceptance of improperly prepared surfaces. Additionally, because of the use of binders that are lower in molecular weight, coating films become more brittle, leading to less flexibility and so reduced adhesion.

Three types of bonding affect coating adhesion

To understand the mode of action of adhesion promoters, the possible chemical and physical forces at work at the paint–substrate interface and their energy should first be considered.
Three basic forces are responsible for ensuring the adhesion of the paint to the substrate: chemical bonding (approximately 150-800 kJ/mol), hydrogen bridging (approximately 10-150 kJ/mol), and Van der Waals (VdW) forces (approximately 0.5-5 kJ/mol).
In most cases all these forces are present when paint adheres to a substrate but, as can be seen from the different values above, chemical bonds have a much greater impact than hydrogen bonds or VdW forces.
The difference in bonding energy suggests that an adhesion promoter should preferably be able to generate ionic or covalent bonds between the binder matrix and the substrate material. Thus adhesion promoters have at least one site which reacts with the binder and one which reacts with the surface. After the reaction, these additives should establish a covalent bond between the substrate and the binder matrix.

Adhesion promoter technologies and their enhancement

As mentioned, it is important for the function of the adhesion promoter that the latter contains two kinds of functional groups, where one group interacts with the substrate and the other with the binder matrix. *Figure 1* gives an outline of the combinations of functional groups that are currently being used in commercially available adhesion promoters.
Titanates and titanium chelate complexes are mostly used as adhesion promoters for stoving enamel systems, while amino silanes, for example, are utilised for ambient curing and 2-pack materials.
Since commercially available silane adhesion promoters do not provide a consistent performance for all systems and under all application conditions, a new type of adhesion promoter has been developed with multiple binder-reactive groups connected by a polymeric chain as a backbone (*Figure 2*). This is marketed as "BYK 4511".
The major difference from common amino silanes can be clearly seen in the multiple binder-reactive groups and the polymeric backbone, which separates the binder-reactive from the surface-reactive sites. This leads to the following major advantages:
» A flexible polymer chain ensures orientation of binder-reactive groups;
» Multifunctionality ensures higher reactivity and stronger linkages to the reaction partner groups in the binder matrix;

Results at a glance

››› Paint performance can be adversely affected in many different ways by poor adhesion. The use of high solids and waterborne coatings makes careful cleaning of the substrate, priming and/or the use of adhesion promoters more critical than in the past.

››› A novel type of adhesion promoter has been developed, using a polymeric chain to space the substrate-bonding groups from multiple groups that interact with the binder, so as to enhance flexibility and resistance to impact.

››› Tests were carried out on several substrates, including deliberately rusted or oil-contaminated panels, using a liquid bisphenol A epoxy with polyamide hardener. The tests included salt spray, mandrel bend, water immersion, pull-off adhesion and cross-cut tests.

››› Significant improvements were noted on all tests, confirming that the new adhesion promoter improves both flexibility and resistance to corrosion on contaminated surfaces.

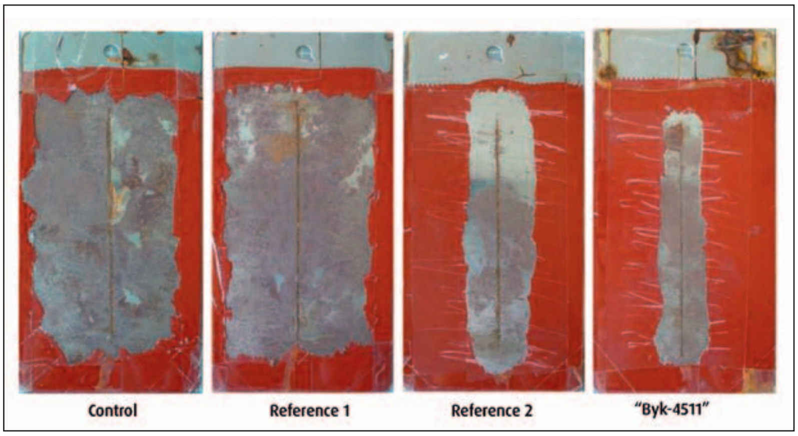

Figure 3: Performance of adhesion promoters on smooth steel after 168 hr. in neutral salt spray test

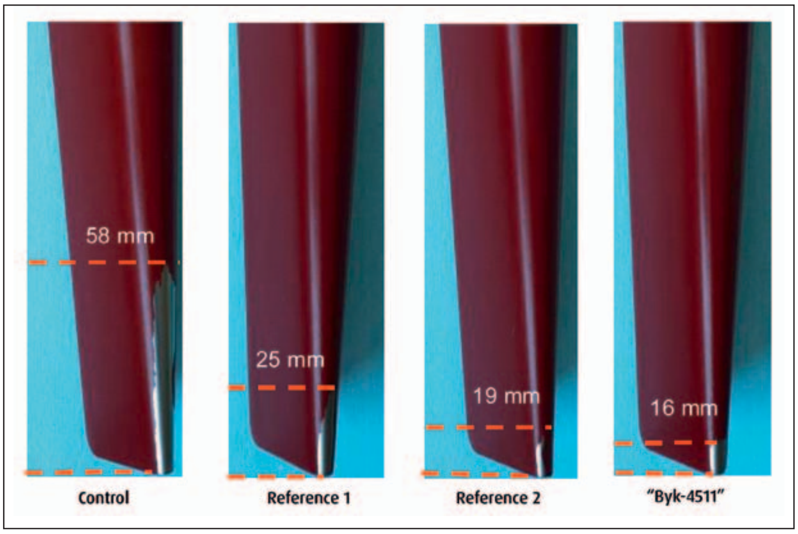

Figure 4: Results of mandrel bending test

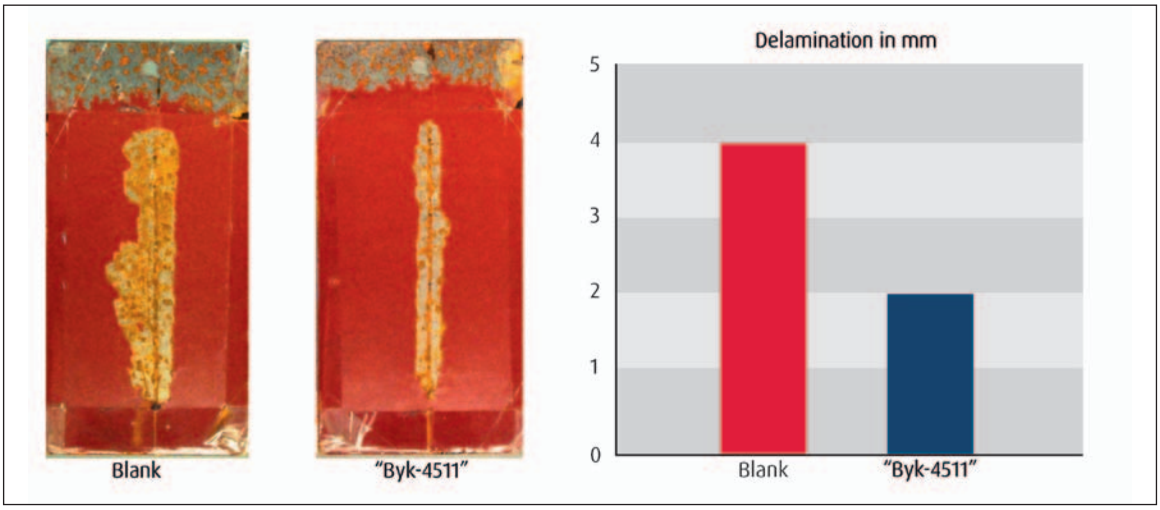

Figure 5: Performance of novel adhesion promoter on pre-rusted steel panels

» A degree of flexibilising introduced by the polymeric backbone improves adhesion/durability under mechanical stress.

Test substrates and preparation procedures

Test substrates of the following types were used:
» Smooth steel: Q-Panel, "QD-36" smooth steel finish, 0.5 x 76 x 152 mm;
» Sandblasted steel, Krüppel "DC04 B", 230 x 165 x 2 mm;
» Smooth panels as above, but with machine oil on the surface;
» Smooth panels as above but with strong rust contamination (one week on weathering stand).

Clean smooth steel panels were obtained by cleaning for five minutes in 2 % wt. in water of "Mucasol cleanser" (Brand GmbH & Co KG, Wertheim/Main) in an ultrasonic bath (Bandelin "Sonorex RK 100"), rinsing with demineralised water, then cleaning with ethyl acetate solvent. The panels were coated 24 hours after cleaning.

The sandblasted steel panels were visually examined for contamination. If no contamination or rust was present, they were used without cleaning.

Smooth steel panels were also wiped with an oily cloth and coated directly without cleaning.

Rust contamination was induced by placing the smooth steel panels on a weathering stand for one week during rainy weather. Strong contamination by rust was visible.

Test formulations and application procedures

The new additive was designed particularly for solvent-free systems and was evaluated in a typical liquid bisphenol A type epoxy primer using a polyamide-based hardener. For the two-layer system, the same primer was overcoated with a standard solventbased 2K-PU system.

The epoxy base was prepared by mixing all components of Part A except for the solvent (benzyl alcohol) and was dispersed for 20 minutes at 8000 rpm with a laboratory dissolver. After the grinding step, the solvent was added under low shear.

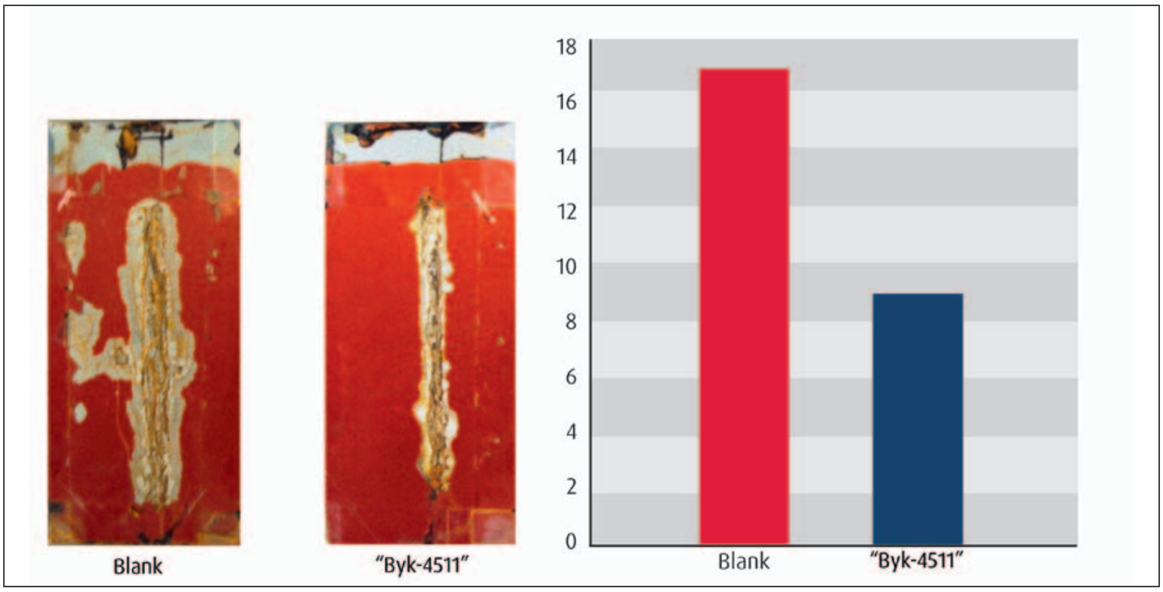

Figure 6: Performance of novel adhesion promoter on panels with oil contamination

Although the performance could be confirmed for solvent-free systems, to ensure the applicability of the system with lab methods by lowering viscosity, a small amount of benzyl alcohol was added to the paint.
To evaluate additive performance, 1 % active substance of the adhesion promoter was added to the curing agent (Part B). The curing agent was then mixed with the epoxy base (Part A) with a dissolver for 2 minutes at 2,000 rpm. After 5 minutes' resting time, the primer was applied to the respective test panels with a 175 µm wire applicator and dried for 16 hours at room temperature and 8 hours at 50 °C. After curing, the dry film thickness (dft) was measured.
The same primer was used for the system build-up. The PU paint was prepared by mixing all components of Part A and dispersed for 20 minutes at 8,000 rpm with a laboratory dissolver. The hardener was added and incorporated for 2 minutes at 2,000 rpm.
Application of the primer was carried out by HVLP spray with a 1.6 mm nozzle at a pressure of 3.5 bar. After drying at room temperature overnight, the topcoat was applied under the same conditions. The drying time for the full build-up was one week at room temperature with an additional drying time of one day at 50 °C.

Several corrosion test procedures are used

Before carrying out the salt spray test, the panels were scribed (10 cm lengthways and 1 mm wide) with a Sikkens cutting tool. For all the tests, adhesive tape was attached to the edges and the back of the panels to prevent corrosion.
To protect the back of the sandblasted steel panels, a PVC/ alkyd system was applied.
In order to evaluate the performance of the additive, the following tests were applied:
» Neutral salt spray test (EN ISO 9227)
» Flexibility/ mandrel bending test (EN ISO 1519)
» Water immersion test (EN ISO 2812)
» Pull-off adhesion (EN ISO 4624)
» Cross-cut test (EN ISO 2409).
After artificial ageing of the panels, they were evaluated by scratching the surface of each panel with a knife to remove all detached paint around the scribe. The width between the edges of the remaining coating was measured at six points along the length of the scribe. The delamination at the scribe is calculated as follows:
Where w(Del.) is the delamination width in mm.

$$Wd(mm) = \frac{(w(Del.) - 1mm)}{2}$$

To evaluate the two-layer system, a pull-off adhesion test was carried out. For this purpose, a metal block was glued to the upper right-hand corner using a basic epoxy adhesive. After curing, the metal block was removed with a hammer to determine the adhesion of the paint.
Figure 3 compares a control test piece without an adhesion promoter to two conventional adhesion promoters and the new polymeric type. It can clearly be seen that the total adhesion loss occurring at control and one of the references is improved significantly (Wd = 4 mm), even in comparison to the second working reference (Wd = 6 mm).

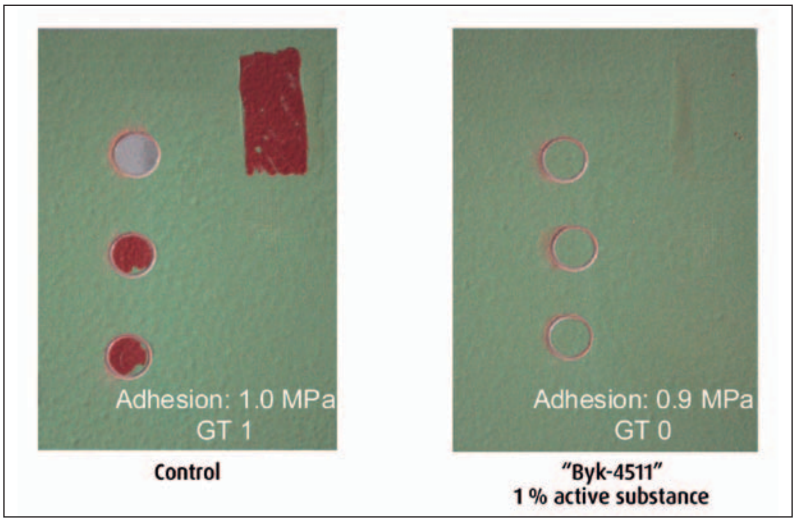

Figure 7: Adhesion of topcoat and base coat after 10 weeks of water immersion test

Figure 4 shows how the flexibility of the paint can be improved by the use of a polymeric adhesion promoter. The adhesion and the flexibility of the paint at the interface are clearly improved.
It is clear from *Figures 5* and *6* that the new adhesion promoter increases the surface tolerance toward two major types of contamination.
In the two-layer system, both intercoat adhesion and adhesion to the substrate are improved. As can clearly be seen, both substrate and intercoat adhesion show signs of failure on the blank, while in the sample containing the new adhesion promoter the coating is unharmed. In the two-layer system, both intercoat adhesion and adhesion to the substrate are improved (*Figure 7*).

Flexible performance from a flexible additive

These test results show that significant improvements can be achieved in the field of adhesion promoters by creative molecular design and the use of a new, innovative molecular structure. This new additive technology is suitable for increasing the adhesion of solvent-free epoxy primers to metal substrates, even when contaminated with oil and rust.
» It improves adhesion to several metal substrates, such as sandblasted steel and smooth steel;
» It improves the surface tolerance when the paint is contaminated, for example with oil or rust;
» It improves the overall performance of multi-layer systems;
» It increases the flexibility of the paint film;
» It improves the anticorrosive performance.

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