

Breaking the tension

New substrate wetting additive simplifies formulation

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Waterborne coatings require effective substrate wetting additives, and any cosolvent reduction changes the requirements for these additives. It can be time-consuming to find an optimum single additive or mixture for individual coatings. A new polyether-modified substrate wetting additive permits simultaneous optimisation of many coatings properties in many different types of binders.

Despite their physical limitations, waterborne paints must be as easy to apply as solventborne types. Even the thinnest films of cosolvent-free or low cosolvent formulations are expected to wet the substrate completely, possess optimal flow and not be susceptible to cratering. In addition, there should be no build-up of foam, which could lead to other defects.

Substrate wetting additives are frequently added to coatings to optimise these properties. However, different combinations of additives are often required for different paint formulations. Certain additives achieve the best results in individual areas such as wetting, anti-cratering, atomisation during spray application or compatibility. Formulators have therefore often required several products and laboratory research to find the best solution.

Many formulators would therefore like a reliable “all-rounder” or universal additive, particularly for spray application of waterborne industrial finishes on plastics and critical metal substrates.

A new substrate wetting additive with universal qualities which provides reliable performance in the diverse areas related to substrate wetting is presented below. Ways of increasing production and application security by use of the new substrate wetting additives are also shown.

Theory of wetting summarised

The most obvious consequences of the high surface tension of water (73 mN/m) are the inadequate wetting of various, mainly low energy, substrates by waterbornes and the susceptibility of the coatings to cratering.

Due to surface tension, paint drops form a contact angle α on the substrate. According to Young's equation (Equation 1), substrate wetting depends on the surface tension (σ) of the wetting liquid, the surface tension of the substrate and the interfacial tension between the liquid and solid.

$$\sigma_{\text{substrate}} = \sigma_{\text{substrate/liquid}} + \sigma_{\text{liquid}} \cos \alpha \quad (\text{Eq. 1})$$

The following rules can be deduced from the equation:

- » A substrate with a high surface energy is relatively easy to wet;
- » A liquid with a low surface energy wets relatively well. [1, 2].

The addition of substrate wetting additives causes a change in the balance of forces on molecules interacting at the interface. Within this interface, they reduce the forces directed into the aqueous solution (Figure 1). This significantly reduces the surface tension of the waterborne coating.

The addition of a substrate wetting additive thus enables a waterborne coating to wet a low energy substrate, resulting in a closed film even at low film thicknesses. The coating is also less susceptible to cratering.

General requirements for substrate wetting agents

Substrate wetting additives are used for two main reasons: Optimising coatings properties such as:

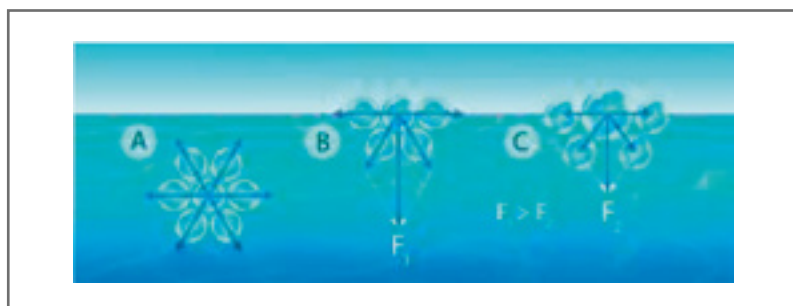


Figure 1: Surface tension: A: Balanced-out molecular forces in the aqueous phase, B: Directed force at the boundary layer, C: Minimisation of the directed force by surface active substances in the boundary layer

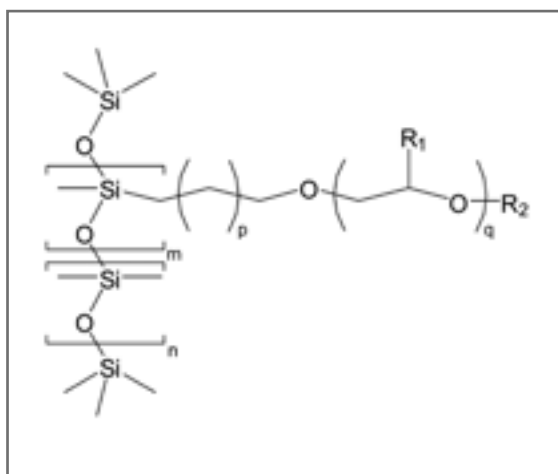


Figure 2: Schematic structure of a polyether siloxane

- » General application properties
- » Substrate wetting
- » Obtaining a closed film at low film thickness.

Increasing general security by:

- » Reducing susceptibility to cratering
- » Repairing contaminated coatings
- » Widening the application window.

Depending on the polarity of the coating and the tasks it must perform, different substrate wetting agents must be used. Products once established are not in general replaced. As a result, many coatings formulations contain different wetting agents. Because of the low concentrations used (between 0.01 and 0.5 %w/w), the raw material costs remain reasonable, so that comprehensive series of tests to optimise formulations are rarely carried out.

When there is a reduction in the cosolvent content in waterborne coatings, their polarity is changed. Established substrate wetting additives may no longer be reliable, and in addition, some may contain up to 50 % organic solvents which, although having a beneficial effect on foam characteristics, are detrimental to the VOC balance despite the small amounts used. The search for optimised substrate wetting additives is thus becoming an increasingly commonplace task in the laboratory.

Setting the targets for wetting agent development

The company's product development team has developed a new substrate wetting additive with the aim of achieving the following characteristics:

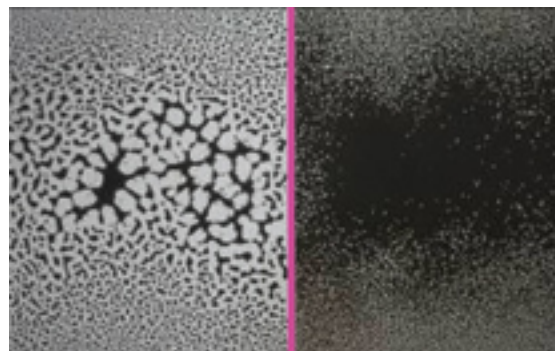


Figure 3: Substrate wetting by a black paint on a light background, One Spray Pass method (left: without; right: with substrate wetting additive)

Broad usability in:

- » All waterborne industrial coatings (particularly for plastics and metals)
 - » Cosolvent-free or reduced cosolvent binders
 - » Conventional binders
- Target: best performer in critical coatings formulations on low energy substrates

Increased production and application security through very good:

- » Ease of incorporation
 - » Wetting even with variations in the quality of plastics and metals
 - » Wetting even at very low film thicknesses
 - » Anti-cratering effect
 - » Recoatability
- Target: best performer in terms of reliability
- » High efficiency at low concentrations
 - » Low VOC content.



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Results at a glance

»» Waterborne coatings require effective substrate wetting additives, and the trend to cosolvent reduction changes the requirements for these additives. The primary objectives of such additives are optimisation of application properties, anti-cratering effect, wetting of the substrate and formation of a closed film at low film thickness.

»» Tailor-made substrate wetting additives or combinations of additives are often required for different coatings, and the search for an ideal solution is time-consuming.

»» The polyether-modified substrate wetting additive presented here permits optimisation of many coatings properties such as: defect-free wetting on plastics and metals, closed paint films in the thinnest coats, non-critical rewetting and adhesion in multi-coat application, high compatibility in the most diverse binders and a high anti-cratering effect.

»» The newly developed "all-rounder" thus ensures high production and application security.



Figure 4: Substrate wetting by a silver paint on a dark background, wedge application (left: without; right: with substrate wetting additive)

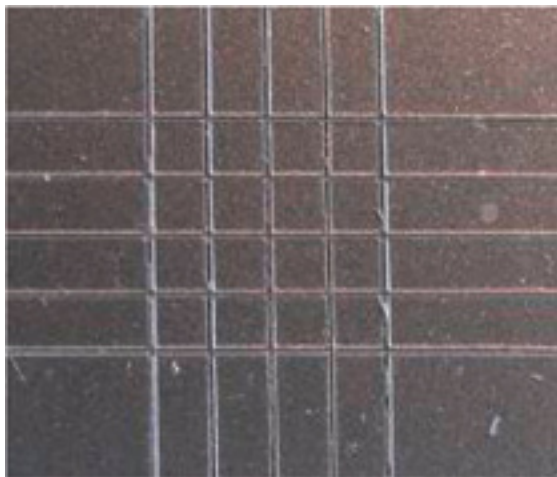


Figure 5: Cross-hatch test on the stoving filler with substrate wetting additive



Figure 6: Contact angle showing good rewettability

All in all, the additive to be developed should make a waterborne, solvent-free or low-solvent coating highly resistant to defects, thus offering the user the widest possible application window with maximum security in production and quality.

Chemical structure of substrate wetting additives

All substrate wetting additives can be regarded as surface active substances (surfactants), but these may originate from quite different chemical structure families. Common to almost all is the combination of a non-polar, often water-insoluble, part with a polar, often water-soluble part.

For printing inks, which make high demands on the dynamic behaviour of the additives, pure organic substrate wetting agents are firmly established. In industrial coatings, substrate wetting agents based on modified siloxanes permit reliable wetting even on very low energy substrates or contaminants.

Polyethers are frequently linked onto the hydrophobic siloxane segments. Varying the length of the siloxane chain and the polyether modification density opens up many possibilities in relation to the hydrophilic-hydrophobic balance of the molecule as a whole. The polarity of the polyether can also be adjusted over a wide range by selecting components such as ethylene-, propylene- and butylene-oxide, as well as by varying the chain length (Figure 2).

Modification of the siloxane backbone must be reliable since unmodified siloxanes can, for example, impair recoatability or intercoat adhesion. This modification is ensured by suitable control of the manufacturing process. By varying the various parameters, tailor-made polyether-modified substrate wetting additives have been developed which satisfied the requirements described above better than previous products.

Putting the new product to the test

Four low-solvent or solvent-free paints were used to differentiate various substrate wetting additives:

- » Polyester PU/acrylate dispersion, a primer and basecoat for plastics
- » PU modified polyester, a metal primer in OEM applications
- » Acrylic copolymer, a basecoat for refinish and OEM coating of plastics
- » Aliphatic PU dispersion, a topcoat for wood and plastics coatings

The main assessment criteria were:

- » Wetting during critical spray application
- » Wetting at minimal film thicknesses
- » Wetting on critical substrates such as plastics or contaminated steel
- » Anti-cratering effect
- » Gloss
- » Foam stabilisation
- » Recoatability
- » Flow.

The new substrate wetting additive was compared with several commercial products.

Measuring techniques summarised

Static surface tension was measured by the du Nouy Ring Method. In this test, a ring is immersed in a liquid and slowly withdrawn. The maximum force required to form a lamella between the ring and the liquid is measured. The lower this force, the lower is the corresponding surface tension of the liquid.

In spray application, atomisation of the paint into the finest droplets is decisive in achieving very thin closed films. In addition to viscosity, flow rate and atomising pressure, atomisation is decisively influenced by surface tension [3].

The use of effective substrate wetting additives enables the demand for ever thinner films to be met. To ensure good reproducibility, the paints were applied with robotic sprayers. Critical conditions for applying the paint were chosen to assist in differentiation:

- » Low pressure

Wetting agents

- » Medium flow rate
- » Slightly increased viscosity.

The paints were also applied by spray in a wedge (film thickness increasing between 0 and 15 μm). The minimum film thickness at which a closed film was formed (wetting limit) was determined. Because the application conditions were identical, the position of the wetting limit on the panel provides an indication of wetting characteristics.

Another spray technique used to evaluate paint quality is known as the One Spray Pass method. Here, the paint is applied very rapidly to a contaminated substrate using a spraying robot. Critical application parameters (pressure, amount of material, reduced spray fan) are again used. The width of the spray mist and the homogeneity of the droplet size on the substrate provide information on the quality of wetting.

To evaluate the anti-cratering effect, a defoamer incompatible with the formulation was deliberately added to the coating. This produced surface defects in the reference sample. The various substrate wetting additives were added, and their performance in eliminating surface defects and craters was ranked by examining the dried film visually.

Recoatibility is tested by adhesion and contact angle

Recoatibility was tested on a waterborne stoving filler. The coatings containing the additive were applied and after drying for 30 minutes were stoved at 165 °C. A second coat was then applied and stoved under the same conditions. Adhesion was evaluated by the crosshatch or pull-off test.

The unimpaired rewettability of a paint film containing additives can be assessed using the contact angle. Water droplets are placed on the dried paint film and the contact angle is measured after 1 and 180 seconds. The smaller the difference in contact angles between the coating surfaces with and without additive, the lower is its influence on the rewetting performance of a second coat.

Pigment stabilisation effects are also checked

Paints containing a mixture of pigments in which the densities of the pigments differ greatly were applied. After a short drying time – after which the paint must still be able to flow – part of the surface is rubbed out using a finger. The difference in colour between the rubbed and unrubbed area is determined spectrophotometrically (as total colour difference or ΔE).

The resulting difference in colour reflects the pigments' homogeneity and tendency to floating in the coating. Surface active additives can influence these properties. The lower the ΔE , the smaller is the influence of the substrate wetting agent on pigment stabilisation.

Positive results are obtained in all tests

"Pictures speak louder than words": The illustrations show the results of a series of laboratory tests on ad-

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Figure 7: Rub-out test shows colour stability of a mixture of pigments

ditives. The amount of additive added was 0.3 % (w/w) of the complete coating.

Wetting by a waterborne coating is a challenge if the substrate is contaminated with drawing lubricants or oils. The modified polyether siloxane is outstanding at dealing with this problem in the most diverse coating formulations, though results are only shown from one

of the series of tests carried out (see Figure 3, where the one spray pass technique was used).

In wedge application, an increasing film thickness is applied by spraying. The photograph shows two sections from the wedge (using the waterborne pigmented coating for plastics). With the substrate wetting agent described above, the minimal film thickness of the waterborne paint wets critical substrates while the reference sample exhibits beading. Furthermore, fine atomisation, good wetting on critical substrates and good flow in paint films with minimal thicknesses is achieved, as would be expected from any effective substrate wetting agent (Figure 4).

Many users fear that the use of polyether siloxanes will result in impaired recoatability. Like the reference sample without additive, the polyether siloxane achieved optimum adhesion results (GT 0). The surface active product is highly effective during application but does not impair the properties of the dried film (Figure 5).

Surface active additives can occasionally cause difficulties in wetting by a second coat of paint if they are used in the first coat. The newly developed polyether siloxane does not impair recoatability. Just like the reference sample without additive, the water droplet on the film with additive exhibits a contact angle of 70 ° (Figure 6).

The influence of the polyether siloxane on the colour stability of mixed pigment coatings was evaluated. The ΔE values of rubbed/unrubbed areas were determined before and after storage. The differences lay within measurement tolerances. Very high colour stability can thus be achieved, though no data is presented here to show how the commercial products affected this property (Figure 7).

Highly effective defoamers are necessary for the manufacture and application of waterborne coatings but can cause surface defects. The illustration shows coatings for plastics based on a solvent-free AC/PU hybrid with a defoamer concentrate. The polyether siloxane successfully removes surface defects (Figure 8).

High compatibility and storage stability

The properties described are achieved by modifying the siloxane chains with polyethers. To check whether these properties are retained, resistance to hydrolysis was tested.

The new substrate wetting additive was aged for two weeks in aqueous solution at 50 °C and the surface tension was measured before and after ageing. From the initial 20.0 mN/m of a 0.5 % aqueous solution, a rise of 0.7 mN/m was observed after two weeks storage. This simple test gives no quantitative indication of the extent to which the additive has been hydrolysed. The storage stability of the new substrate wetting additive is, however, considered to be adequate.

The substrate wetting additive described also exhibits particularly good compatibility in aqueous binders. This was determined visually and by measuring gloss and haze on the dried paint films. Used together with a low-foam binder, the highest gloss can be achieved.

All-round benefits

The new substrate wetting additive satisfies numerous requirements. Its all-round performance assists in the optimisation of spray-applied waterborne coatings, particularly on critical substrates. Where several products were previously necessary, one substrate wetting additive can ensure process security.

Comprehensive R & D has resulted in a molecular structure which provides the best performance in relation to the maximum number of properties. ◀

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Figure 8: Removal of contamination craters (left: without; right: with substrate wetting additive)



Video interviews on additives: www.european-coatings.com/videos