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STICKING TO POLYMERS

Wetting agent and substrate interactions in water-borne finishes for the automotive industry.
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Good substrate wetting may be particularly difficult to achieve on plastic substrates, which are increasingly used in the automotive industry. Tests with a range of different types of wetting agents showed pronounced and possibly unexpected differences. A fluorinated acrylic polymer gave the best overall results.

Appearance and adhesion are key performance characteristics for any coating, but in automotive coatings they are especially crucial. In this market segment in particular plastic substrates are becoming increasingly important for both interior and exterior parts.
Because of their rather low surface energies, plastic substrates are usually much more demanding in terms of wetting, especially for water-borne coatings. The study reported below was set up to investigate in detail the influence of different wetting agent chemistries on water-borne coating formulations.

SURFACE DEFECTS AND SUBSTRATE WETTING ISSUES

Formulating a defect-free coating is a challenge. It needs careful control of the surface chemistry of the coating. More specifically, local surface tension differences are the primary cause of many surface defects (for example, craters). These local differences can be minimised by the use of special wetting agents.
Substrate wetting depends primarily on the surface tensions of the coating and of the substrate to be coated. As a general rule, wetting takes place if the surface tension of the liquid is lower than the surface energy of the substrate's surface. This criterion for wetting is also known as the wetting condition.
Poor wetting (such as 'de-wetting') will occur if the surface tension of the paint is higher than the surface tension of the substrate. Thus, substrates with low surface tensions are not easy to wet with water or water-borne coatings. Special substrate wetting agents are required to lower the surface tension of the coating.
Therefore an effective wetting agent for a coating formulation should have surfactant characteristics in order to lower the surface tension of the liquid to allow the liquid to wet the surface. This is especially important if hydropbic subtrates

RESULTS AT A GLANCE

→ Good substrate wetting is essential for good appearance and adhesion. This may be particularly difficult to achieve on plastic substrates, such as those which are increasingly used in the automotive industry.

→ Wetting agents of varying chemical nature show large differences in surface tension and dynamic surface tension reduction if examined in water dilution. In combination with an acrylic dispersion however, these differences are less pronounced.

→ Different types of plastic substrates which have very similar surface energy yield large differences in adhesion. In this case, on average the best results were achieved on PA and worst results on ABS/PC.

→ From all the wetting agent technologies tested, a fluorinated acrylic polymer gave the best overall results.

(e.g. plastics) have to be coated with waterborne formulations.

MAIN WETTING AGENT TYPES AND THEIR KEY PROPERTIES

For this study, various wetting agents of different chemical structures were selected as shown in *Table 1*. The advantages and disadvantages of the main chemical types have been briefly summarised.
Sulfosuccinates like Product 3475 are highly dynamic, cost-effective wetting agents. Due to their excellent dynamic surface tension reduction and broad food contact compliance they are commonly used as substrate wetting agents in the printing and packaging industry. However, sulfosuccinates are also known to promote foam stabilisation.
Alkoxylated surfactants (Products 3120, 3650 and 3322) are usually cost-effective, non-ionic wetting agents. Depending on the alcohol used in their synthesis, the ratio of ethylene oxide to propylene oxide and the overall degree of alkoxylation their hydrophilic-lipophilic balance (HLB) can be varied widely. Some alkoxylated surfactants are particularly low-foaming wetting agents.
Star-shaped polymers, here represented by Product 3322, form a special class of alkoxylated surfactants The hyperbranched structure of these non-ionic surfactants was modified to give them additional wetting and defoaming properties.

Organo-modified silicones like Product 3221 are a widely used class of polymers. Depending on the degree of modification and on their overall silicone content they can be employed as substrate wetting agents, flow- and leveling agents and/or slip agents.
In general, silicone-based additives reduce the surface tension of a formulation rather drastically. Silicone surfactants, due to their short chain lengths, will not provide surface slip in most paint systems.
Fluorinated polyacrylates (Products 3370 and 3500) are another very versatile class of interfacially active additives. They are well represented in the coating industry as substrate wetting agents and flow- and levelling additives.

Table 1: Overview of the selected wetting agents and their chemistries.

Wetting Agent	Chemistry
Product 3475	Sulfosuccinate
Product 3120	Fatty alcohol alkoxylate
Product 3650	Synergistic blend including alcohol alkoxylates
Product 3322	Star-shaped polymer based on alkoxylated fatty alcohol
Product 3221	Silicone-based wetting agent
Product 3370	Fluorinated polyacrylate
Product 3500	Fluorinated polyacrylate

Figure 1: Dynamic surface tension at different bubble frequencies of various wetting agents in water.

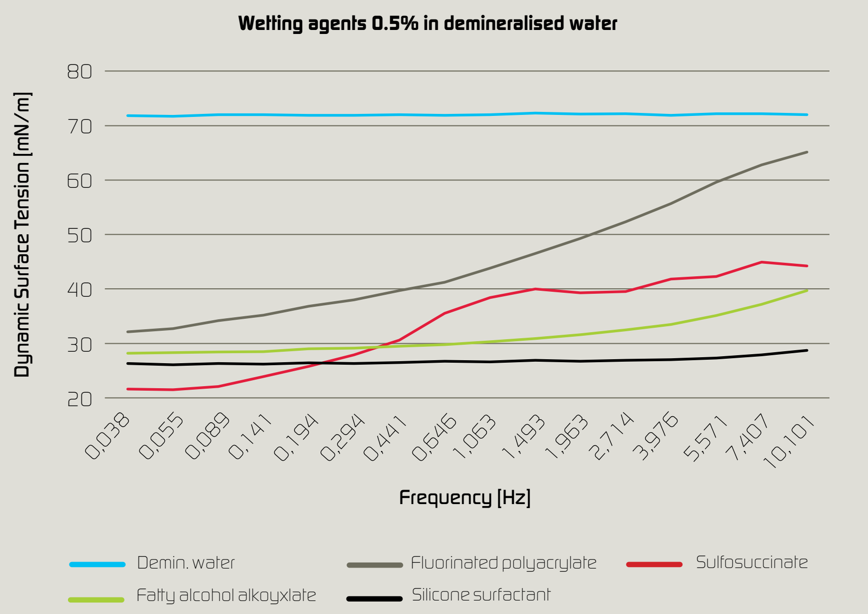


Table 2: Coating formulation used in Testing

Coating formulation	Parts by weight
Dispersion 8211	100.0
Butyl glycol	7.0
Texanol	3.0
Wetting agent (see Table 1)	0.5
Defoamer (silicone)	0.4
Ammonia 25 %	If necessary, add to adjust pH to 8-9

Table 3: Initial adhesion and appearance tests.

Tests after ageing (48 h @ 60 °C)	Target value (Norm)	Substrate	WE 3221 Silicone	WE 3500 Fluor. acrylate	WE 3650 Surfactant blend	WE 3322 Star polymer	WE 3370 Fluor. acrylate
Adhesion GT (crosscut) DIN ISO 2409	0-2	PA	0	1	0	1	0
		PC	0	0	0	0	0
		ABS	0	1	0	1	0
		ABS / PC, T65	0	1	0	1	1
Adhesion K (knife test) DBL7399-5.1	0-2	PA	1	1	1	2	3
		PC	0	0	0	1	1
		ABS	4	4	4	3	4
		ABS / PC, T65	3	3	3	3	3
Gloss 20°/60° **	0-2	ABS	90/96	88/96	90/97	92/97	87/97
		ABS / PC, T65	90/98	90/98	92/99	94/99	90/98
Haze **		ABS	144	221	87	88	131
		ABS / PC, T65	109	127	87	67	149
Appearance Specks		PA	2	2	2	2	2
		PC	2	2	2	2	2
		ABS	2	2	2	2	2
		ABS / PC. T65	3	3	3	3	3
Levelling	0-2	PA	1	1	1	1	1
		PC	1	1	1	1	1
		ABS	1	1	1	1	1
		ABS / PC, T65	0	0	0	0	0

** Gloss and haze not measured over PA and PC substrates. Note: Cratering 0 for all samples; norm specifies 0-2 rating

Table 4: Test results after Condensation Water Test according to DIN EN ISO 6270-2: 240 h duration; all tests after 1 h regeneration time unless shown otherwise. Note: degree of blistering (DIN EN ISO 4628-2): 0 for all samples; norm specifies zero.

Tests after Condensation Water test	Target value (Norm)	Substrate	WE 3221 Silicone	WE 3500 Fluor. acrylate	WE 3650 Surfactant blend	WE 3322 Star polymer	WE 3370 Fluor. acrylate
Adhesion GT (crosscut) DIN ISO 2409	0 - 2	PA	2	0	0	3	1
		PC	2	0	1	1	1
		ABS	2	2	2	2	1
		ABS / PC, T65	0	2	0	2	1
Adhesion K (knife test) DBL7399-5.1	0 - 3	PA	3	2	2	4	1
		PC	4	3	3	3	1
		ABS	4	4	4	4	2
		ABS / PC, T65	4	5	3	3	5
Appearance after humidity test + 1 h regeneration		PA	**clear**	**clear**	**clear**	**clear**	**clear**
		PC	whitish	whitish	whitish	whitish	whitish
		ABS	whitish	whitish	whitish	whitish	partially whitish
		ABS / PC, T65	whitish	whitish	whitish	whitish	whitish
Appearance after humidity test + 24 h regeneration		PA	**clear**	**clear**	**clear**	**clear**	**clear**
		PC	slightly turbid	slightly turbid	slightly turbid	slightly turbid	slightly turbid
		ABS	partially whitish	**clear**	partially whitish	partially whitish	**clear**
		ABS / PC, T65	whitish, after 48h clear	whitish, after 48h clear	whitish, after 48h clear	whitish, after 48h clear	whitish, after 48h clear

WE 3120 FA ethoxylate	WE 3475 Sulfo-succinate
0	0
0	0
0	1
1	1
0	1
0	0
3	3
3	3
91/97	86/96
91/98	88/97
102	163
93	136
2	2
2	2
2	2
3	3
1	1
1	1
1	1
0	0

WE 3120 FA ethoxylate	WE 3475 Sulfo-succinate
2	1
1	3
1	1
0	1
2	3
3	3
2	2
5	5
clear	**clear**
whitish	whitish
partially whitish	partially whitish
whitish	whitish
clear	**clear**
slightly turbid	slightly turbid
clear	partially whitish
whitish, after 48h clear	whitish (even after 48h)

These polymers have a polyacrylic backbone with fluorinated side chains which lower the surface tension of a formulation. They combine excellent flow and leveling with anti-cratering and good wetting behaviour.

APPLICATION TECHNIQUE MAY AFFECT SURFACTANT CHOICE

It should not be overlooked that diffusion and adsorption of surfactants at interfaces is a time-dependent process. New interfaces are produced extremely rapidly during spraying, printing or other coating application techniques and the mobility of the surfactants is an important factor here.
For fast-changing processes the use of highly dynamic surfactants is recommended, in order to ensure that the surface tension remains low even if new surfaces are formed very quickly. The different dynamic behaviour of wetting agents is illustrated in *Figure 1*.
The ability to lower the surface tension even under highly dynamic conditions (high bubble frequency) depends on the mobility of the surfactants. It can clearly be seen in *Figure 1* that low molecular weight sulfosuccinates and alkoxylated surfactants can cover newly formed interfaces very quickly. On the other hand, the fluorinated polyacrylate and the silicone surfactants are slower due to their higher molecular weight and different aggregation behaviour.
Unfortunately, surface tension measurements in pure water reveal little about the behaviour of wetting agents in real coating formulations. In 'real life' coating formulations the wetting agents interact with all the other ingredients such as emulsifiers and polymer dispersion particles. If the dynamic surface tension behaviour is measured in polymer dispersions, the results show that the differences between surfactant types are reduced, as revealed in *Figure 2*.

WETTING AGENTS SHOW PRONOUNCED DIFFERENCES IN FOAMING

Dispersion 8211 is a rheology controlled dispersion or 'RC dispersion' [1]. In this styrene-acrylic polymer dispersion a special acid-containing oligomeric emulsifier is used. Compared to conventional systems, RC dispersions impart enhanced stability (both steric and ionic stabilisation), good compatibility with formulation additives and a nearly Newtonian flow behaviour.
The particle sizes of RC dispersions are generally smaller than for conventional dispersions. The results discussed below are all based on the use of this product.
A much undesired side effect of wetting agents can be foam stabilisation. It is therefore recommended to check foam stabilisation if wetting agents are used in a new coating formulation. *Figure 3* provides an example in which different surfactants lead to very different foam levels. The results show density values after stirring of binder emulsions with wetting agents (180 sec at 5000 rpm). Higher densities indicate better defoaming and lower densities indicate foam stabilisation.
As can be seen from *Figure 3*, sulfosuccinate surfactants stabilise foam in this case, whereas products such as the star-shaped wetting agent 3322 used here have pronounced defoaming characteristics. The defoaming effect of star-shaped wetting agents has also been found by other scientific groups [2].

TEST FORMULATION AND APPLICATION DETAILS

Clearcoat formulations based on the RC dispersion and wetting agents were prepared next. The dispersion has a solids content of 44%, a Brookfield viscosity of 150 mPa•s at 25 °C and a minimum film forming temperature of 57 °C.
As shown in *Table 2*, the formulation was deliberately kept rather simple. Besides the dispersion it only contains the appropriate cosolvent, approximately 0.5% wetting agent plus defoamer. The liquid coating was filtered before application using an 80 µm metal filter mesh (to remove possible coagulum).
The coatings were applied by drawdown using a 150 µm applicator bar resulting in a dry film thickness of about 50 µm. After a flash-off time of 10 min at room temperature, the coatings were dried for 30 minutes at 60 °C. The films were routinely aged for 48 h at 60 °C before testing (which is a common procedure for automotive plastic testing, e.g. according to Volkswagen TL226 3.5).
Four plastic substrates relevant to the automotive industry were used for this screening: polyamide (PA), polycarbonate (PC), acrylonitrile-butadiene-styrene copolymer (ABS) and a PC/ABS blend known as T65.
Prior to using these substrates, they were wiped with isopropanol in order to remove dust and possible other contamination. No other forms of pre-treatment were applied. The surface tension of the plastic substrates ranges between 41.4 mN/m and 45.1 mN/m.

TEST PROCEDURES SUMMARISED

The films were evaluated in terms of gloss (at 20° and 60°), haze and optical appearance as well as for adhesion (crosscut adhesion and knife test). Crosscut adhesion was performed and rated according to DIN ISO 2409.
The knife test was performed according to DBL7399-5.1, a Daimler Benz test procedure. In this test a round knife blade is used to

scratch the coating on the plastic substrate while applying pressure on the blade. According to how hard it is to scratch off the coating and what the residual appearance of the scratch is, the results are rated from 0 to 5, with 0 being the best result and 5 the worst.
The initial results are summarised in *Table 3*. Significant differences could be observed with regards to the influence of wetting agents on adhesion. The knife test in particular proved to be a very valid differentiation criterion.
In this test the fluorinated polyacrylic wetting agent Product 3370 performed best. Fluorinated acrylic polymers are known for their excellent wetting performance and their very limited influence on (intercoat) adhesion.
Exposure to humid climate conditions and subsequent drying may have a significant impact on both appearance (whitening) and adhesion (through swelling and shrinking). That is why it should be routinely tested as well, using the humidity test according to DIN EN ISO 6270-2. Results after this exposure test are presented in *Table 4*.
Here the same picture is observed, the same fluorinated surfactant performed best. Despite swelling of the polymer by water vapour, adhesion must not be affected. Water uptake might also lead to whitening which has to be reversible. This reversibility was indeed observed for this system; only on the tested (transparent) PC substrate some turbidity does remain.

Figure 2: Dynamic surface tension at different bubble frequencies of various wetting agents in polymer dispersion 8211 (4:1).

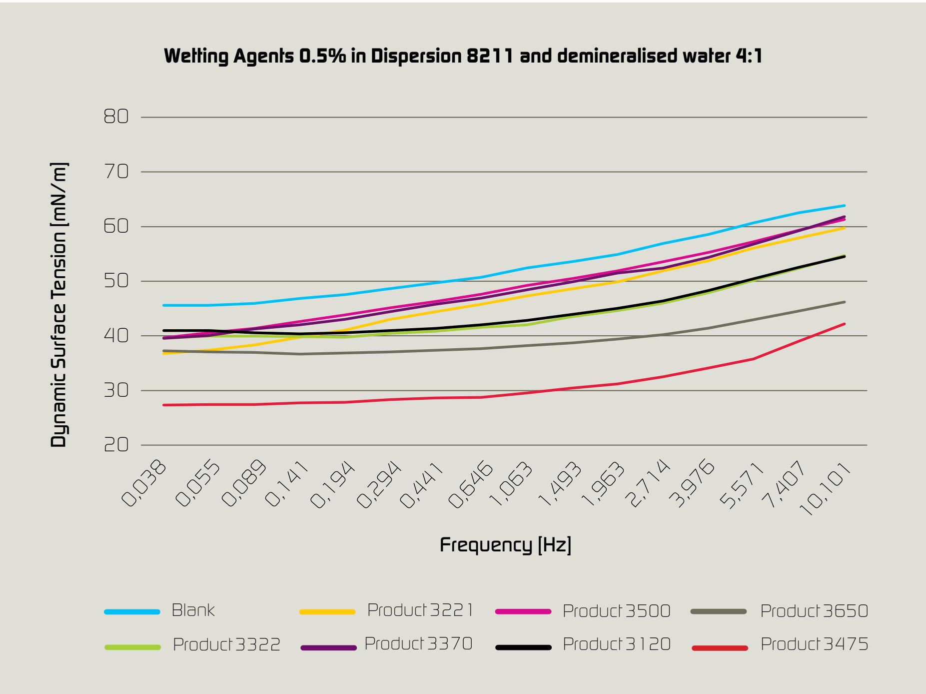
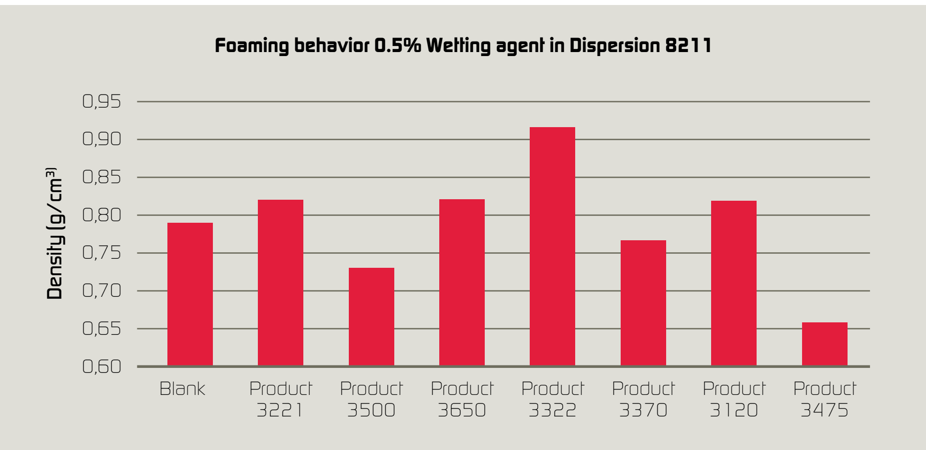


Figure 3: Results of foam tests with wetting agents and Dispersion 8211.



ADDITIONAL TESTS CONFIRM BEST PRODUCT

In a further test series spray application trials were also performed (not shown). In particular, what is called the wetting limit (the minimum film thickness where a complete film is formed) was evaluated. In this respect, too, the same fluorinated product showed excellent results. The wetting limit could be decreased to about 14 micrometres.
The RC acrylic dispersion already shows excellent gloss and appearance with only a very limited impact of the wetting agent, due to its chemical nature and very small particle size. Only some differences in haze are observed, especially on ABS, with values ranging from 87 to 221 indicating slight differences in compatibility of the polymer matrix with the respective wetting agent.
In general it is evident that the interaction of wetting agents with the given polymer dispersion is a key factor in order to achieve excellent adhesion and appearance characteristics. Wetting agents not only influence the wetting behaviour by lowering the surface tension, they also have significant influence on film formation and leveling. In addition they also have an effect on foam formation.
From all the wetting agents tested, a fluorinated acrylic polymer gave the best overall results. Product 3370 combines good wetting characteristics with very little influence on adhesion and defoaming characteristics.

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[2] Mojgan N.et al, Caught on camera, Europ. Coat. Jnl., 2015, No. 10, pp 30-36.

“The influence of emulsifiers should not be underestimated. “

3 questions to Sascha Oestreich

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In many cases the fluorinated polyacrylates seem to perform best. But what are their main limitations?

Indeed, fluorinated polyacrylates are a very versatile group of interfacially active additives. They combine excellent flow & leveling with anti-cratering and good wetting behavior. Additionally, they have clear advantages with respect to intercoat adhesion and foam stabilization. There are fluorinated polyacrylates with different fluorine content available on the market. This allows the formulator to select the right product for a specific binder type and application. Fluorinated polyacrylates are limited when strong surface slip and anti-blocking effects are required. Slip and anti-blocking effects can better be achieved by organomodified silicones, for example.

Your study used a well-defined rheology controlled dispersion with enhanced stability. In what way could your findings differ in “real life” coatings?

In this study we evaluated our wetting agents in increasingly complex formulations: We started with simple water, then we used a commercially available polymer dispersion and finally we used a simplified coating formulation based on the dispersion which additionally contained defoamer and coalescing solvents. The application tests with these coating formulations showed best results with fluorinated polyacrylates. We think that the biggest difference can be observed between measurements in pure water and measurements in a polymer dispersion. A wetting agent should always be evaluated in the respective binder system or in the final coating formulation. The influence of emulsifiers and internal surfaces (e.g. latex particles) on the behavior of the wetting additive should not be underestimated.

Your study shows that substrates with very similar surface energy yield large differences in adhesion. What is the explanation for this behavior?

Good wetting is only one prerequisite for good adhesion. Certainly the chemical composition of the substrate, the surface structure, possible pretreatment and many other factors influence adhesion of a coating film, too. It is essential to ensure optimal interaction of the polymer film with the substrate. Wetting is supporting physical and chemical adhesion because it increases the surface area of the coating which comes into contact with the substrate. On the other hand, a wetting agent should not have a negative effect on the (intercoat) adhesion. Also here, fluorinated polyacrylates are well known in the market for their marginal influence on (intercoat) adhesion.