

# Maintaining protection

## How dispersants affect corrosion resistance of waterborne paints

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**By utilising different test methods the impact of several different chemical types of wetting and dispersing agents on the sensitivity of a waterborne primer towards water and moisture as well as anticorrosive properties has been evaluated. Clear performance differences depending on the chemistry utilised have been found. However, the results obtained with the five different evaluation methods did not correlate too well. This made it evident that the test procedure has to be selected according to the final requirements that have to be improved.**

In the protective and marine coatings market, great efforts are being made to reduce the amount of volatile organic compounds (VOCs) emitted during application. Many paint customers have been switching to high-solids and solvent-free paints that combine low VOC content with the advantages of conventional paint systems. Another option to reduce VOCs is the use of waterborne paints. Because of the demanding requirements and often uncontrolled application conditions, the use of waterborne systems in the protective paint market is still very limited. Indeed, in this market sector, it is estimated that globally the share of waterborne paints is around 6 %, while solventborne, high solids and solvent-free systems retain 94 % [1].

One key reason for this limited use is that waterborne systems restrict the temperature and humidity conditions under which the paint can be applied. Low temperature and high humidity prevent proper and sufficient curing of the coating. Additionally, the high surface tension of water can cause problems with certain substrates or impurities and lead to improper wetting, cratering and other paint defects.

Next to the application challenges, the formulation of waterborne anticorrosive paints is also quite challenging. To ensure proper film formation after application, paint components must be carefully selected. To overcome some limitations, the use of additives is essential.

### The impact of wetting and dispersing additives

Wetting and dispersing additives are an important class of additives. They provide three main features that are vital to produce coatings with good storage stability, application properties and optical appearance:

- » Wetting of the pigment and filler particles;
- » Dispersion of pigments and fillers;
- » Prevention of the re-agglomeration of the primary particles.

These aspects are almost impossible to achieve without the aid of additives due to the high surface tension of water.

Since the additive remains in the coating after drying, it may influence the overall hydrophilicity of the coating film and therefore affect certain coating characteristics such as early water resistance and corrosion protection. To study this effect on the final coating, relevant test methods must be compared.

### Mode of action and general structure of dispersants

The process of the dispersion of solid particles as pigments and fillers falls into three stages: wetting of the particles, dispersion and stabilisation. To understand the first process it is necessary to understand the circumstances under which a liquid properly wets a solid. This process is described by the Young equation:

$$\frac{\gamma_s - \gamma_{sl}}{\gamma_l} = \cos \theta \quad [1]$$

Where

$\gamma_s$  = surface tension of solid  
 $\gamma_{sl}$  = interface tension solid/liquid  
 $\gamma_l$  = surface tension of liquid  
 $\theta$  = contact angle liquid/solid

For complete wetting of a solid by a liquid, the contact angle becomes 0 °, which is the case when:

$$\gamma_l = \gamma_s - \gamma_{sl} \quad [2]$$

To achieve proper wetting, the surface tension of the liquid must be less than the surface tension of the solid [2]. Wetting and dispersing additives directly influence the wetting process by adsorbing on the surface of the solids and thus changing the surface tension.

### How the additives function during dispersion

In the dispersing process the agglomerates of pigments and fillers are broken down into so-called 'primary particles'. This process is carried out by introducing energy to the system, for example by high-speed dispersion with an agitator disk. The amount of energy needed to separate the particles from each other and so increase the surface area that needs to be wetted by the surrounding liquid is described by the following equation:

$$dW = \gamma \cdot dA \quad [3]$$

$W$ : introduced work  
 $\gamma$ : interfacial tension  
 $A$ : interfacial surface

Thus, the amount of work needed to generate a certain amount of surface area by breaking down the agglomerates into primary particles is directly linked to the specific surface tension. Wetting and dispersing additives reduce the work required by lowering the interfacial tension between liquid and solid.

Stabilisation is then vital to prevent re-agglomeration of the dispersed particles. Two major stabilising mechanisms are utilised: electrostatic and steric stabilisation, which may be combined. In summary, it can be said that wetting and dispersing additives always consist of two domains, one of which interacts with the pigment surface ('pigment affinitive group') and one which interacts with the binder ('binder affinitive group').

The main currently available wetting and dispersing additives with these characteristics are based on the following chemistries:

- » fatty acids
- » polyurethanes
- » phosphoric acid esters
- » polyacrylates

Different additives based on these chemistries were included in the evaluations below.

### How dispersants affect waterborne coatings

For the dispersant to be compatible with the system and able to interact adequately with the liquid matrix, the binder compatible groups need to have hydrophilic properties. These properties can be obtained by using polar chemical domains, such as polyethers or polyesters, or certain hydrophilic co-monomers.

Various wetting and dispersing additives use ionic salt structures to obtain sufficient solubility of the additive

#### Results at a glance

» Waterborne paints hold only a very small share of the market for protective and marine coatings, as they have stringent requirements for good surface preparation and drying conditions.

» Wetting and dispersing agents play a critical role in the formulation of waterborne coatings in particular. However, they are necessarily partly hydrophilic, and this can impair the protective properties of the cured film.

» Tests are reported on the impact of several different chemical types of dispersing agent on the anticorrosive properties of a styrene-acrylic based primer.

» The best results were given by two polyacrylates and a polyurethane-based additive. However, a notable result is that there was a poor correlation between the five different tests for protective performance that were used. Thus, it is important to ensure that the tests selected are appropriate for the planned end-use.

or its binder-affinitive domains in the paint matrix. Alternatively, salt structures may be introduced, for example by neutralising acidic groups with bases. The chemical nature and volatility of the base also both influence the resistance of the final coating to corrosion stimulants and water.

The effect of the additives on parameters such as early water resistance, water uptake and corrosion resistance must be evaluated in the search for an optimum wetting and dispersing additive.

### Evaluation of wetting and dispersing additives

To evaluate the influences of wetting and dispersing additives, a standard primer formulation based on a styrene-acrylic dispersion was used. Five test procedures were chosen to compare the effects of the products.

To determine water uptake, the paint was applied at a specific film thickness to a polyethylene (PE) foil, dried for a fixed time interval, carefully removed from the foil and weighed. Next it was immersed in distilled water. At fixed time intervals, the paint film was removed from the water, and water droplets were removed with a cloth. The weight gain was then established and the water uptake was determined as a percentage of the original dry film weight.

To check this method for reliability, some samples were evaluated by differential scanning calorimetry (DSC). After immersion in distilled water for 24 hours, a sample was cooled down to -60 °C and heated up to +80 °C. The melting peak of water and its melting enthalpy were used to calculate the amount of water inside the coating and this was compared to the values generated by the gravimetric method (see Figure 1).

To measure water diffusion, a free coating film was produced by the PE foil application method, a small plastic cup was attached to its surface then filled with distilled water (see Figure 2). At certain time intervals, the IR absorption was evaluated at wavenumber 3400 cm<sup>-1</sup> by means of an ATR (Attenuated Total Reflectance) measurement and compared to the absorption of a paint film without water contact.

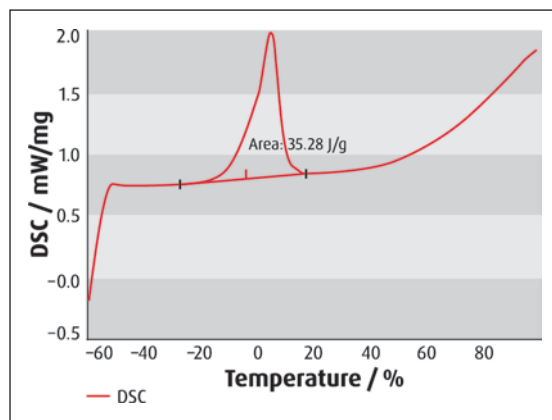


Figure 1: Sample of DSC result to determine water uptake and melting peak of water

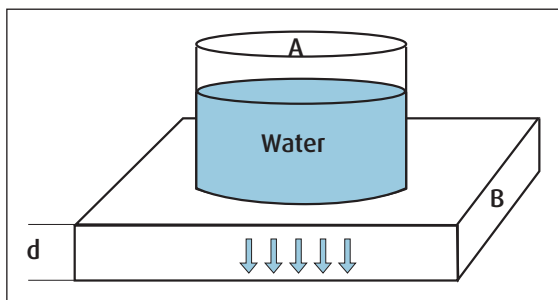


Figure 2: Experimental setup for water diffusion test

The salt spray test was carried out according to DIN EN ISO 9227. The test paint was applied to cold-rolled steel panels which were exposed in the salt spray chamber after drying. The panels were then checked for the amount of blistering according to DIN EN ISO 4628-2 and for delamination/rust creep according to DIN EN ISO 4628-8. Free films of the test paint were also fixed in a permeability cup. The test was carried out according to DIN EN ISO

7783. At certain time intervals, the weight lost by diffusion of water vapour through the coating was determined. To determine early water resistance, the test paint was applied to cold-rolled steel panels. Four and 24 hours after application, a cotton wool ball drenched with distilled water was placed on the coating then covered with a small plastic beaker to prevent the water from evaporating. After 24 hours, a cross-cut test was carried out according to DIN EN ISO 2409.

### Formulation, application and choice of additives

Several common pigments and fillers were incorporated to obtain a pigment volume concentration (PVC) of 28 %. The dry film thickness of the coating was fixed at 80 µm on cold-rolled steel panels and on PE foil to produce the free films. Drying conditions were set at seven days, at 23 °C ± 2 °C and a relative humidity of 50 % ± 5 %. As regards the choice of additives, the aim was to represent a large variety of different chemistries and variations. At least one representative from the groups of phosphoric acid esters, fatty acids, acrylates, polyurethanes, and controlled-polymerisation acrylates was picked initially. The chosen additives were used at an amount of 1.5 % active substance calculated on pigments and fillers.

### Results in summary

In the early water resistance test, the best results in *Table 1* are shown by two acrylate-based additives, AC-4 and AC-5, and the PU-based additive, PU-1. Their good performance can be explained by their hydrophobic nature, although AC-5 contains a considerable additional number of hydroxyl groups. The very non-polar domains/co-monomers in the additive molecules make it far more difficult for water to penetrate the coating, reach the interface between coating and panel and lead to adhesion loss.

In the water uptake test (see *Figure 3*) the parallel measurement of the water content by DSC in four samples shows that the values from both methods are the same within their variations. The tendency to absorb water can be correlated quite well with the hydrophilicity of the additives used.

The reference sample without additive shows the lowest water absorption, while the most polar additives AC-1, AC-3 and AC-5 (with a high content of hydroxyl groups) show the highest water uptake. The other additives range between the values of the control and AC-3, except for additive AC-4.

After 24 hours of water exposure in the diffusion test, it can be seen that AC-1, AC-2 and AC-3 show the highest diffusion and that almost all additives show a higher diffusion rate than the control, except for AC-4 and PU-1 (*Figure 4*). While the lower value of AC-4 can be explained by its hydrophobic nature, the good performance of PU-1 is surprising because of the high number of hydroxyl groups it contains. Further investigations are needed to explain this effect, but it can be said in general that a more hydrophobic additive leads to better diffusion behaviour.

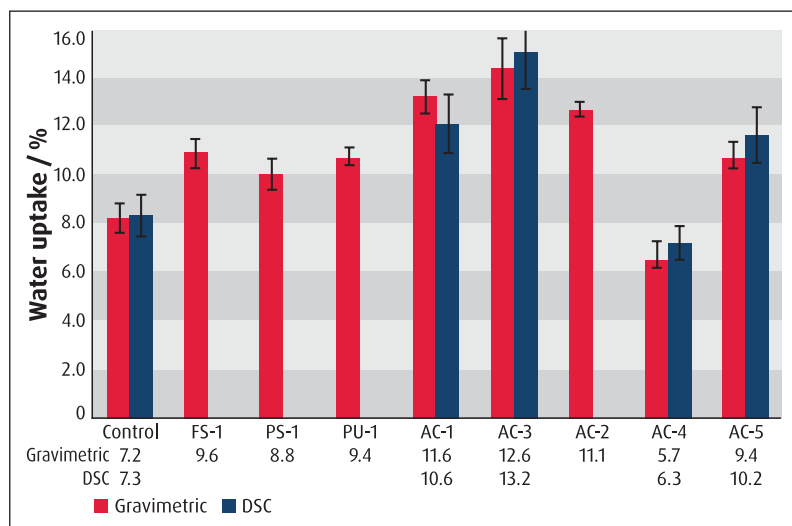


Figure 3: Water uptake after 6 hours of water immersion (gravimetric and DSC test)

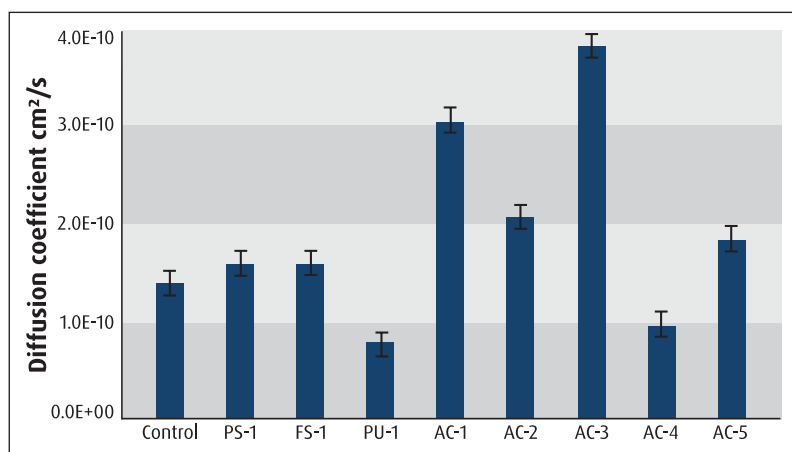


Figure 4: Diffusion coefficients after 24 hours of water exposure, evaluated by ATR-IR

Once again, the acrylate-based additives AC-1 and AC-2 show poor results in the permeability test (Table 1). AC-3 shows a medium level of performance, while all other additives exhibit values comparable to the control. It is hard to explain the poor result of additive AC-3. However, many factors could have increased the diffusion of water vapour: the additive itself, poor film formation or pin-holes generated by foam bubbles.

Finally, in the salt spray test (see Table 1) the acrylates AC-1 and AC-2 again gave the worst results, and were removed from the test after 140 hours due to severe blistering and delamination at the scribe. The products FS-1, AC-4 and PS-1 exhibited medium performance and were removed after 384 or 500 hours. The best performance was shown by PU-1, AC-3 and AC-5, which endured the test for 700 hours.

### Test results show some poor correlations

Summarising all the results in one overview with a view to drawing conclusions is rather difficult, as the results of the different methods do not necessarily correlate with each other. This can be seen in Figure 5.

An initial observation is that only three samples show the same tendency in all of the tests: the control, AC-1 and AC-2. The control shows very good results in all aspects, and it could be asked why a wetting and dispersing additive should be used at all.

The reason is quite obvious, as outlined in the introduction: the additive is needed to ensure good storage stability, application properties and optical appearance. In fact, the control paint without any additive was barely producible due to its extreme high viscosity and bad wetting. It was impossible to apply it by spray, and its storage stability was very poor.

This means that, although efficiency might be lost in the known parameters, a wetting and dispersing additive is necessary to be able to produce a stable and usable paint. The chemistry utilised for these types of additives has to be carefully selected to obtain additives with a minimal impact on paint film properties.

Additionally it can be said that the different test methods do not necessarily correlate with each other. This is a major finding, as it makes it very evident that, for example, a bad result in water uptake and diffusion does not necessarily indicate a bad result in the corrosion test (see additive AC-3), while, on the other hand, a good result in all other parameters can still mean a medium performance in the salt spray test (see additive AC-4). It is therefore important to carefully select the evaluation methods with regard to the subsequent use of the coating and the parameter of greatest importance.

### Test methods must be matched to end uses

This work has shown that several testing procedures must be used to evaluate the effect of additives and to compare them with each other as there is no clear correlation, for example, between water uptake and corrosion resistance.

Figure 5: Overview of additives and their performance in different tests

Code	Neutra- lisation	Water uptake	IR diffusion	Permea- bility	Early water res.	Salt spray test
Control						
FS-1	Amine 1					
PS-1	Amine 2					
PU-1	Amine 1					
AC-1	Amine 3					
AC-2	Base 1					
AC-3	Base 2					
AC-4	Amine 3					
AC-5	Base 2					

Table 1: Summary of some results in three tests

Name	Chemistry	Early water resist- ance: cross-cut test after water exposure		Permeability test (24 hours)		Salt spray test (hours)
		After 4 hr. drying [GT]	After 24 hr. drying [GT]	R2	V [g/ (m <sup>2</sup> /d)	
Control		1	1	0.9994	26.3	600
FS-1	Fatty Acid	5	1	0.9991	26.4	384
PS-1	Phos. Acid Ester	2	2	--	--	500
PU-1	Polyurethane	0	0	0.9984	24.0	700
AC-1	Polyacrylate	5	5	0.9949	46.2	140
AC-2	Polyacrylate	5	5	0.9995	38.0	140
AC-3	Polyacrylate	2	3	0.9979	29.1	700
AC-4	Polyacrylate	0	0	0.9983	24.3	384
AC-5	Polyacrylate	0	0	0.9987	26.5	700

Several structural elements that affect the overall performance of the additives could be identified. These structural parameters are range from the basic "backbone" elements via specific co-polymers to the bases used for neutralisation.

Although further work on these issues is required, it can be said that by deliberate variation of structural elements, additives can be developed which have only a limited impact on the critical parameters specified or which in future will even be able to improve the performance of waterborne coatings. ◀

## REFERENCES

- [1] Marktstudie, European Protective Coatings Markets, M39E-39.
- [2] Heilen W., Additive für wässrige Lacksysteme, Vincentz, 2009.