

Rheology guides the way.....

Influence of balanced rheology modifier ratios on the optical and rheological properties of aqueous metallic coatings



Key Benefits

- ❖ BENTONE® DE provides
- ❖ Highest flop indices
- ❖ Optimum metal orientation
- ❖ Excellent humidity resistance

Introduction

The orientation of the metal flake pigments, e.g. Aluminum pigments are playing a major role to achieve the optimum optical properties in the formulation of metallic coatings.

The commercially used metallic pigments are shaped differently and differ in their properties.

Leafing pigments are orienting themselves in the wet film directly to the surface. Such pigments are causing a very metal like impression which is, however, often less wash or scratch resistant. Leafing pigments typically find application in aerosol coatings and inks. Non-leafing pigments spreading after the application homogenously through the film. This causes better effect protection in the case of chemical or scratch attack. On the other hand, the resulting coating are appearing more greyish and less metal like. Main applications are automotive, plastic and general industrial coatings.

Standard metallic pigments are shaped like cornflakes. The plates are irregularly shaped and might have an uneven surface. Pigments with rounded edges and smothened surfaced are being called „Silverdollar“. In comparison to cornflake shaped pigments they appear more brilliant and brighter in the final coating. The third class, so called VMP's (vacuum metallized pigments) are extremely thin and have very strong hiding power and provide mirror or chrome like effects. The shape differences have been visualized in *Figure 1*.



Figure 1: Available metallic pigment shapes

However, not only the shape and the surface of the used pigments will influence the optical effect of the final coating. Also, the drying behaviour and the characteristics of the liquid coating play a major role.

In an ideal case the pigments are orienting themselves parallel to the coatings surface. To achieve this, the pigments need to be brought in the described position and, directly afterwards, to be immobilized. In this case, an optimised reflection of entering light from every view angle can be obtained. If the metallic pigments remain in disorder after application and immobilisation a scattered reflection of the light is the results indicating poor metallic effect (*Figure 2*).

The immobilization of the pigments in aqueous systems is much more difficult compared to solvent based systems. The reason is the much slower drying time of aqueous systems in which the pigments need to be protected from either floating or sedimentation.

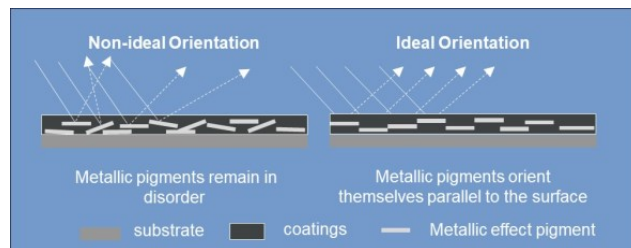


Figure 2: Mechanism achieving metallic effect

The resulting optical properties are typically being defined and measured as a flop index. The flop index can be described as the change of reflectance of the metallic coating during the measurement through a range of viewing angles. The typical value range starts from 0 up to approximately 17. Very high flop effect pigment based clear coats/basecoats are acting in a range in between 15 and 16.

As explained initially, the orientation and the immobilisation of the effect pigments plays a major role in achieving optimum effects. This is typically explained as a result of processes which are running throughout the drying process of the coating. The redissolve resistance as also the shrinkage of the drying film minimizes the disorientation at the basecoat/topcoat interface and the alignment of of the effect pigments. It can also be concluded that a rapid shrinkage of the film forces the orientation of the pigments.

However, to achieve the right orientation of pigment a correctly adjusted rheology plays a major role. This means the right balance between pseudoplasticity and thixotropy are key to obtain optimum results. The differences are schematically represented in *Figure 3*.

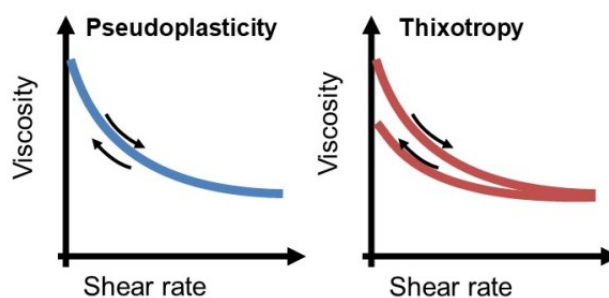


Figure 3: Difference Thixotropy/Pseudoplasticity

In fact, both, pseudoplasticity as well as Thixotropy are describing shear thinning flow. This means the viscosity of a system decreases with increasing shear rate. However, the main difference can be found in the recovery behaviour. Whilst in the case of the pseudoplastic flow up and down curves are identical, recovers the

This is indicated by a lower level of the return curve. The area in between up and down curve is call Hysteris. Larger areas are indicating increasing pseudoplasticity and elongating recovery time of the system after the influence of shear.

Translated to the requirement of a metallic coating and the orientation of the metal pigments this means that in case of a purely pseudoplastically adjusted system does not support the optical properties. This has been caused by the fact the viscosity and structure are recovering immediately after the spray application. This is also causing an immediate immobilization of the metallic pigments without allowing them to orient as desired.

The implementation of Thixotropy in a metallic coating allows a better orientation of the pigments by time shifted structure recovery. However, care must be taken. If the recovery time becomes too long also pigment sedimentation effects might depress the optical properties.

As a consequence, the the rheological characteristics of metallic coating need to be well balanced in order to obtain the optimum recovery time window allowing optimum pigment orientation parrallel to the coatings surface. However, the immobilization of the pigments need to be fast enough to prevent unwanted sedimentation effect.

To achieve this, the right combination of rheology modifiers need to be figured out. Ideally, this can be done by a combinations of ASE (alkali swellable emulsion) based thickeners with Hectorite clay based rheology modifiers.

Hectorite clay

Hectorite clay belongs as also Bentonite to the Smectite group and is swellable in water. The name Hectorite guides to the location of Hector, in the Moave desert in souther California, where this clay has so far only been found as a natural resource.



Hectorite is a layered clay what means that it consists of many microfine platelets stapled on top of each other. Individual platelets are negatively charged on their surfaces by mineralogy. In the natural form,tThe charges are neutralized by sodium ions (*Figure 4*).

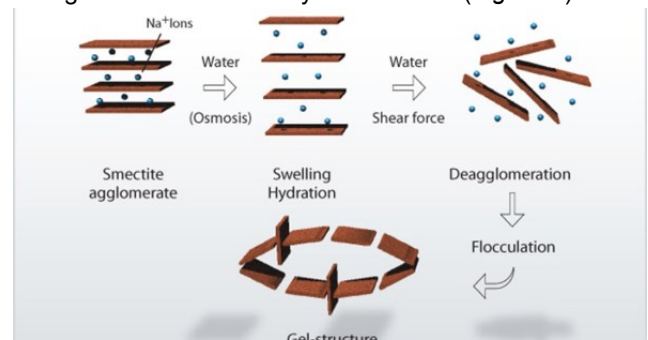


Figure 4: Mechanism activation of Hectorite clay

Hectorite clay can be activated by delamination of the platelets driven by swelling in pure water with high shear dispersion. The sodium ions hydrate, pushing the platelets apart and the clay swells. The high shear forces during dispersion cause the platelets to move away from each other as colloidal, slightly charged particles. After removal of shear, double-layer effects, van der Waals forces of attraction and electrostatic repulsion result in the flocculation edge-to-edge, which is visible as the desired viscosity is formed.

Hectorite clays are providing after the activation Thixotropic flow alongside with very high low shear viscosities.

Apart from the natural sources, Hectorite can also be manufactured synthetically in a solid state process.

Further details on the Hectorite clay chemistry and technologies can be found in the specific technical leaflets.

BENTONE® DE has been based on highly beneficiated, easy dispersible natural Hectorite clay. Due to its fine particle size and the special beneficiation process the product can be easily dispersed and activated without the need for high shear forces. Another advantage is the possibility to make a high solid pregel. A pregel can be made at concentrations of up to 14% solids in water that is still pourable. This allows for easy handling and formulation flexibility during paint production.

BENTONE® DE

Composition	Highly beneficiated Hectorite clay
Form	Milky white, soft powder
Active concentration[%]	100
Density [g/cm ³]	2.5

Alkali swellable thickeners

This group can be splitted in two parts, ASE (**A**lkali **S**wellable **E**mulsions) and HASE (**H**ydrophobic modified **A**lkali **S**wellable **E**mulsions). Both consist of long chain water insoluble acrylic polymers dispersed in water. The acrylic backbone surrounded with functional acid/carboxylic groups.

To become rheologically active all alkali swellables require pH in a range in between 8 and 10. When the pH is raised to around 7, the acid groups start to dissociate and the polymer chains uncoil or swell driven by magnetic repulsion (Figure 5).

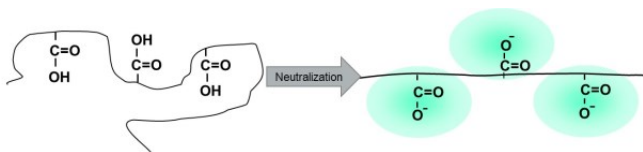


Figure 5: Neutralization of alkali swellable emulsions

A complete dissociation is typically reached at a pH of around. The chains reach their maximum extension and develop viscosity by macromolecular entanglement.

In case of HASE, additional hydrophobic groups are part of the molecule to implement additional associative functionality.

However, in this market segment usually traditional ASE grades have been formulated. The reason is the effective low shear build alongside with a strong shear flow which is required especially for spray applied systems.

Contrary to the previously described rheology provided by Hectorite clay, alkali swellable emulsions (ASE) are providing predominately pseudoplastic flow, so have no time shifted viscosity recovery after shear removal.

Effect on optical properties and rheology

Experience has shown that by a proper combination of BENTONE® DE and ASE thickeners, the optical properties of metallic coatings can be optimized. Rheological properties are showing an additional clear guideline on suitable concentration ratios.

In the following case study, a water based base coat (WBBC) has been equipped with various ratios of BENTONE® DE and a standard ASE thickener in order to visualise the effect on the flop indices and the rheological characteristics.

In the following *Figure 6*, the effect of various rheology modifier combination on the optical properties, determined as flop index, is shown.

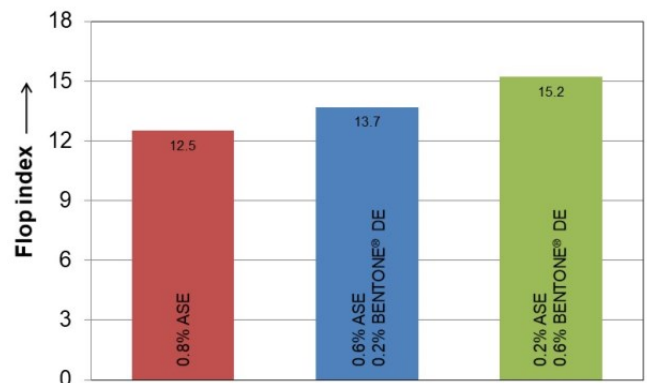


Figure 6: Flop indices

It is obvious that with increasing clay content alongside decreasing ASE concentration, the flop indices of the cured coatings are significantly increasing.

As it was said, rheology measurements play a very useful role in adjusting and forecasting this effect.

In *Figure 7*, the effect of various BENTONE® DE /ASE combinations on the flow characteristics is shown. The standard material contains 0.2% of the ASE. In the following this concentration has been stepwise replaced by the BENTONE® DE. The target viscosity of the system in all cases was a flow out time of 30 seconds measured in a DIN 4 cup.

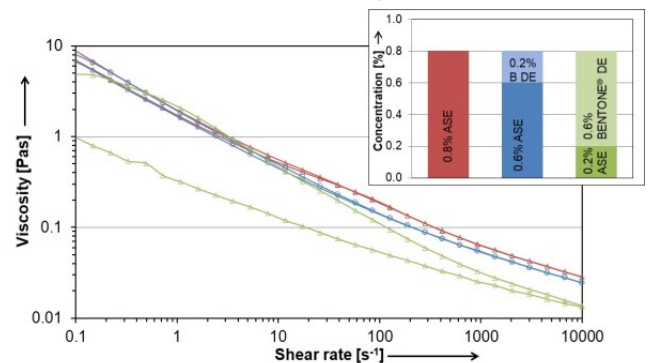


Figure 7: Rheology curves

In the shown graph, the shear rate was first increased from 0.1 s^{-1} up to 10000 s^{-1} . In the second measuring step the shear rate had been decreased in the same manner. It becomes visible that with increasing content of BENTONE® DE, the viscosities at higher shear rates are decreasing. In addition, the area in between down and up curve, the so called Hysteresis, is enlarging. This is typically indicating an increasing Thixotropic flow character.

Both observed effects are in line with the increase findings in the flop indices of the applied and cured coatings shown in *Figure 6*.

However, this measurement does not allow to predict the exact recovery time. For this purpose, a different setup needs to be utilized (Figure 8). In a first step the viscosity has constantly been measured at a low shear rate of 0.1 s^{-1} to simulate the conditions of the coating material prior to the influence of shear. In the second step the viscosity has been risen to high shear rates of 1000 s^{-1} as simulation of application. As a third part of the determination, the initial conditions of 0.1 s^{-1} were repeated. This last step allows the material to relax and to recover in viscosity. As the entire graph has been plotted on a time scale, this also allows measurement of the recovery time.

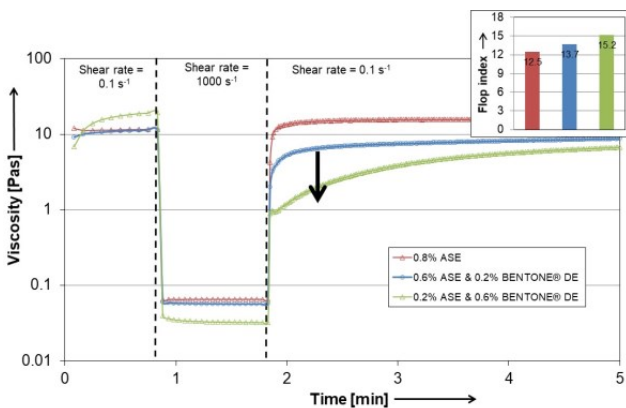


Figure 8: Viscosity recovery

With increasing replacement rates of ASE by BENTONE® DE the recovery time elongates. Also, the already mentioned lower high shear viscosity is visible. A maximum elongation time of the viscosity recovery is visible at the concentration ration 0.2% ASE and 0.6% BENTONE® DE. With a further replacement of the ASE thickener by BENTONE® DE no further elongation could be detected.

In the second graph in upper right corner of Figure 4, the flop indices have been repeated. The data shown are again in line with the rheological findings.

Noticeably increasing flop indices alongside with increasing recovery time are achievable with all tested ratios of ASE thickener and BENTONE® DE.

As the viscosities of the coatings is quite low in all measured shear rate areas, the detection of viscoelastic data is useful. Contrary to the pure viscosity, viscoelasticity allows a view in the structure of the material at rest and its controlled destruction or recovery. In this case structure recovery tests were utilized and are shown in Figure 9.

As already performed in case of the viscosity recovery, the measurements to simulate the post application behavior are splitted. The structure of the coating was disrupted in a rotational measuring step by high shear rates of 1000 s^{-1} (left of the black arrow). As in this step no viscoelastic data are generated, the part in the graph remains empty. In a second, oscillatory step, the viscoelastic behavior of the coating after the removal of initially applied shear is visualized, to analyze the properties of the coating after impacting the substrate (right of the black arrow).

This oscillatory part has been displayed as Modulus G' and G'' . G' , the storage modulus, indicates the elasticity. G'' , the loss modulus, shows the fluid characteristics. This means also, that every individual sample has been represented by two lines in the graph! Those moduli which are higher on the modulus scale (Y), are dominating the other one. Means, if G' acts higher on the moduli scale than G'' the elastic character dominates and vice versa.

Plotting of G' and G'' on a time scale allow a clear prediction of changes of the viscoelastic conditions of the sample and of the recovery time. This is the time, in which the viscose modulus (G'') remains dominant over the storage modulus (G'). If G' dominates immediately after the removal of high shear, as it is the case with the sample manufactured with pure ASE thickener, the sample immediately behaves elastic.

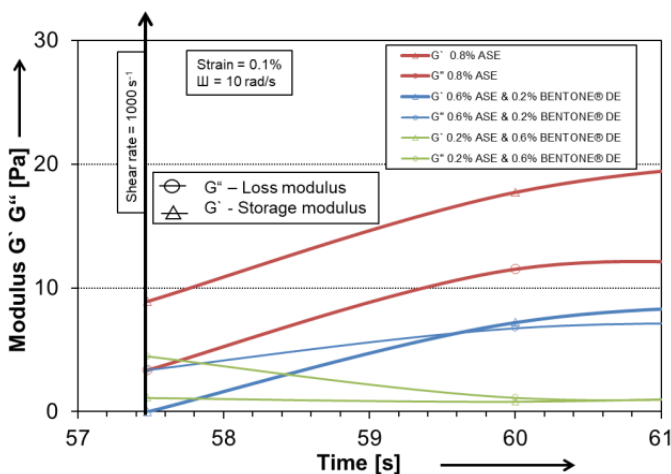
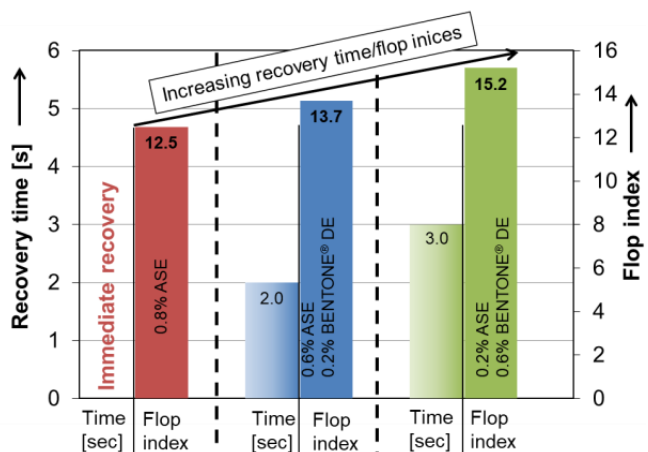


Figure 9: Structure recovery



The detected recovery times have been extracted and are shown separately in the right part of the present figure alongside the relevant flop indices.

The sample formulated with 0.6% ASE and 0.2% BENTONE® DE displays a significant increase in of the recovery time alongside with improved optical properties displayed by flop indices. Another noticeable step in this direction could be seen with an increase of the Hectorite concentration up to 0.6%.

However, not only the optical and rheological characteristics of the tested samples are important. In *Figure 10* further characteristics of the cured samples are visualized.

	0.8% ASE	0.6% ASE 0.2% Hectorite (DE)	0.2% ASE 0.6% Hectorite (DE)
Gloss 20°	89	90	91
Cross hatch test before exposure 6 x tape pull off	Gt. 0	Gt. 0	Gt. 0
3 days 40°C, 100% humidity			
Gloss 20°	86	86	90
Cross hatch test after exposure 6 x tape pull off	Gt. 0	Gt. 0	Gt. 0
Blisters	none	1 / 1	none
Micro structure, initial	OK	slight	slight
Micro structure, 2h	OK	OK	OK
Micro structure, 24h	OK	OK	OK

Figure 10: Humidity resistance BENTONE® DE

All samples display equal gloss at 20° measuring angle and stable results in blistering and adhesion (crosscut) after moisture curing. All sample panels tested were exposed two weeks at 100% humidity at a temperature of 40°C. In these cases, only minor changes of the tested parameters have been detected.

Also, synthetic Hectorite materials are being used in this market to achieve the desired optical properties. Therefore, a comparison of the influence of the flop index was carried out. All tests samples in *Figure 11* contained equal loadings of ASE thickener and Hectorite.

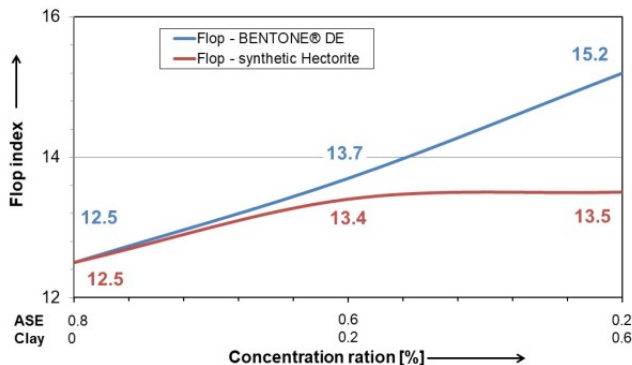


Figure 11: Flop indices comparison

In this test results remarkable differences between the performance of BENTONE® DE the synthetic Hectorite material are shown. The flop index is constantly inclining with increasing rates of BENTONE® DE . The maximum rate achievable is a flop value of 15.2. Contrary to these results, the synthetic Hectorite achieved only a maximum flop level is 13.8. The high levels of BENTONE® DE could not be obtained with any of the synthetic Hectorite/ASE combinations.

However, also the applied coating performance after high humidity storage are strongly differing to those with BENTONE® DE (*Figure 12*).

	0.8% ASE	0.6% ASE 0.2% synt. Hectorite	0.2% ASE 0.6% synt. Hectorite
Gloss 20°	89	90	89
Cross hatch test before exposure 6 x tape pull off	Gt. 0	Gt. 0	Gt. 0
3 days 40°C, 100% humidity			
Gloss 20°	86	87	87
Cross hatch test after exposure 6 x tape pull off	Gt. 0	Gt. 0	Gt. 0
Blisters	none	none	none
Micro structure, initial	OK	medium	strong
Micro structure, 2h	OK	medium	slight
Micro structure, 24h	OK	slight	slight

Figure 12: Humidity resistance synth. Hectorite

Already from the lowest concentration of synthetic Hectorite, the humidity stability suffers remarkably. The ratio 0.6% ASE thickener combined with 0.2% synthetic Hectorite the panels show already strong microstructure in the top layer. In case of the ASE and BENTONE® DE combinations, all optically beneficial ratios are providing excellent humidity stability. It should also be mentioned, that with further two weeks of testing at 40°C, a further deterioration could be observed.

Apart from the shown data, the generation of gas and the stability of the samples over storage was tested. However, in none of the tested samples, issues with excessive gas production have been noticed.

Storage stability, an important factor, with all tested combinations of ASE and BENTONE® DE is good. Only in case of the very high clay loadings, slight syneresis has been observed after 30 days at 50°C. In no case sedimentation could be detected. The samples formulated with synthetic Hectorite display a slightly higher tendency to syneresis.

Conclusion

	Clay product	Low shear viscosity	Structure recovery	Flop index	Gloss		Micro-structure top coat	Cross hatch	Syneresis after storage	Gassing
					Initial	Aged				
0.8% ASE	no	0	0	0	0	slight	0	Gt 0	OK	0
0.6% ASE	Hectorite (DE)	+	+	+	+	slight	slight	Gt 0	OK	0
0.2% clay	synt. Hectorite	++	+	+	+	slight	medium	Gt 0	OK	0
0.2% ASE	Hectorite (DE)	+	++	++	+	0	slight	Gt 0	OK	0
0.6% clay	synt. Hectorite	++	+	+	0	slight	strong	Gt 0	slight	0

excellent
good
neutral
slightly inferior
inferior
poor

Excellent balanced ratios of ASE based rheology modifiers and BENTONE® DE are optimizing the properties of aqueous metallic coatings

- Highest flop indices in the entire study
- Optimum metal orientation and optical properties
- Significantly higher flop values achievable than with synthetic Hectorite clay
- Excellent humidity resistance also at higher clay loadings

The market reference synthetic Hectorite provides also optimized optical properties, however

- Lower flop values than with super dispersible Hectorite
- Increasing clay loading do not result in inclining optical properties/flop indices
- Poorer humidity resistance than with super dispersible Hectorite, esp. at higher loadings

In general, the rheological characteristics of the system are in all tested cases a clear indication for the optimizing metal orientation. It has been visualized that increasing Thixotropy and elongating structure recovery times can be utilized as an indicator for the optical properties.

No tested samples showed issues with gas generation on storage.

Gloss and crosshatch results are remaining unaffected independently from the clay concentration



Appendix

Water based Base Coat (WBBC)

Raw material	Function	Concentration [%]
Daotan VTW 1262	Resin	39.00
Demin. water	Solvent	44.40 - X
Butylglycol	Co-solvent	0.70
n-Butanol	Co-solvent	1.30
DMEA (10%)	pH-adjustment	2.50
Rheological additive	Rheological additive	X
Aluminium-slurry	Effect	12.10
Total		100.00

Aluminum pigment slurry

Raw material	Function	Concentration [%]
Stapa IL Hydrolan 8154	Al-pigment	43.80
Butylglycol	Co-solvent	38.8
NUOSPERSE® W 30	Dispersing agent	4.1
n-Butanol	Co-solvent	13.3
Total		100.0

Preparation rheology modifiers

ASE Thickener (10% active dilution)		
Raw material	Function	Weight in %
ASE thickener (25%)	Rheological additive	40.0
Demin. water	Solvent	57.5
DMEA (10%)	pH-adjustment	2.5
Total		100.0

BENTONE® DE & synth. Hectorite (Pre-Gel 10%)		
Raw material	Function	Weight in %
Demin. water	Solvent	90.0
BENTONE® DE	Rheological additive	10.0
Total		100.0

Test methods

Rheology data

Determined using the Anton-Paar MCR 301 rheometer, equipped with PP 50 measuring geometry at a gap width of 1 mm, at a temperature of 23°C. KU viscosity.

All tested samples were adjusted to a flow out viscosity of 30 seconds from a DIN 4 cup at a temperature of 23°C.

Preparation of panels

All samples have been applied at a dry film layer thickness of 11-15 µm on metal panels. All panels have been overcoated with Permacron 2K-MS Brilliant clear coat at a layer thickness of 50 µm

Flop index

Measured with MA 68 XX from X-Rite

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