

Neuburg Siliceous Earth in water-based corrosion protection DTM acrylate single-layer black

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1 Introduction

Homemaking is back in style and more popular than it has been for a long time. This is why the demand for "do it yourself" products is also increasing. For the paint sector, this means that products from the "direct to metal" (DTM) range are increasingly being used. But what does a DTM coating stand for and what requirements should it fulfill?

A DTM coating should combine the corrosion-protective effect of a primer and the high visual demands placed on a topcoat, which normally have to be achieved with the application of only one coat. In addition, the paint must be storage-stable and have good processing properties, since often no special equipment is available. DTM paint also stands for good adhesion on substrates that have not been specially pretreated. The good adhesive strength should then also still be present under corrosive stress. And the coating itself is expected to protect the substrate against corrosion for as long as possible. In addition, environmental aspects relating to solvents and other ingredients should also be taken into account.

These diverse requirements represent a challenge, which is why high development activities are necessary in the field of DTM coatings.

The aim of the following work is to demonstrate to developers the positive effect of the functional filler Neuburg Siliceous Earth in the field of waterborne DTM acrylate anticorrosion coatings and thus to contribute to a reduction of the development effort.

2 Experimental

2.1 Formulation lacquer

The results of this study were found with the black DTM acrylate formulation shown in *Fig. 1* as a single-layer system. In the control formulation, a natural barium sulfate is included in the filler paste. For the Neuburg Siliceous Earth formulation with Aktisil AM, the entire additive package of the control formulation was exchanged, which is why the total varies slightly between the formulations. The new additive package additionally contains an organic corrosion inhibitor. For this, no anti-corrosion pigment was used in the Aktisil AM formulation, details are given in section 2.2 Formulation Pastes. The test should be carried out at the same pigment volume concentration (PVC). This results in different concentrations for the paste filler in the formulation and a variation in the solids content by mass.

	Formulation	HOFFMANN MINIERAL		
Carlor Dist			BaSO ₄	Aktisil AM
	Setaqua DTM 6851	Acrylic dispersion	71.40	71.40
INTRODUCTION	Ammonia 25 %	Neutralizing agent	0.20	0.20
EXPERIMENTAL	IENTAL Filler paste		19.20	15.95
RESULTS	Pigment paste black		8.45	8.45
	Water demineralized		1.00	
SUMMARY	flashproTAC C4E	Flash rust inhibitor	0.20	0.10
	BYK 024	Defoamer	0.20	0.10
	Asconium 142 DA	Org. corrosion inhibitor		2.00
	AMP 90	Neutralizing agent		0.15
	Tego Wet KL 245	Wetting agent		0.20
	Tego Glide 494	Slip and flow additive		0.15
	Tafigel PUR 45 (1:1 in H ₂ O)	Thickener		1.00
	Additol VXW 6387	Anti-settling	0.20	
	Additol XW 6580	Wetting agent	0.25	
	Additol VXW 6388 (1:10 in H ₂ O)	Thickener	2.85	
	Total		103.95	99.70
	Pigment volume concentration [%]		12.3	
	Solids content w/w [%]	olids content w/w [%]		43.5
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2.2 Formulation Pastes

For the above formulation, one paste Filler and one paste Black are prepared, the quantities for which can be taken from *Fig. 2*.

The filler paste with natural barium sulfate contains an active anti-corrosion pigment which is not needed in the Aktisil AM formulation and has therefore been left out. Instead, an organic corrosion inhibitor is added. As already mentioned, the filler replacement was done with the aim of achieving a constant PVC, which, due to the density difference of Aktisil AM to the natural barium sulfate, means different mass fractions. Likewise, the corrosion inhibiting pigment was replaced by Aktisil AM in the same amount by volume. For the production of the Aktisil AM paste, a higher water content is required. Nevertheless, the paste is storage stable for several months without rheological additives and free from sedimentation or separation. The filler paste with natural barium sulfate is storage stable only with the aid of rheology additives.

The black paste formulation has not been changed. The pigment used is a particularly easily dispersible carbon black preparation for aqueous systems from Orion Engineered Carbons.

	Paste Formulation	HOFFMANN MINIERALL		
	Filler		BaSO₄	Aktisil AM
RODUCTION	Water demineralized		17.65	28.07
	Additol XW 6588	Dispersing additive	3.00	3.00
PERIMENTAL	BYK 024	Defoamer	1.60	1.60
SULTS	Dowanol DPM		3.00	3.00
	Aerosil R 972	Thickener	0.20	
IMMARY	Barium sulfate natural	Filler	55.10	
	Aktisil AM	Filler		47.41
	Nubirox 102	Anti-corrosion pigment	17.70	
	Additol VXW 6388	Thickener	0.25	
	Rheobyk 7420 ES	Thickener	1.50	
	Total		100.00	83.08
	Black			
	Water demineralized		74	1.90
	Surfynol 104 E	Surfactant	0	.40
	Colour Black OE 430W	Pigment black	24	l.70
	Total		10	0.00
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2.3 Filler Characteristics

Fig. 3 gives an overview of the most important characteristic values of the fillers used.

The classic Neuburg Siliceous Earth is a naturally formed mixture of corpuscular Neuburg Silica and lamellar kaolinite, a loose mixture impossible to separate by physical methods. As a result of natural aging, the silica portion exhibits a round grain shape and consists of aggregated primary particles of about 200 nm diameter. This unique structure is responsible for a relatively high specific surface area and oil number. The particle size is determined by the physical separation process. By surface functionalization of the classical Neuburg Siliceous Earth with aminosilane, the product named Aktisil AM is formed.

	Filler Characteristi	MINERAL	
INTRODUCTION		Barium sulfate natural (BaSO₄)	Aktisil AM
RESULTS	Particle size d ₅₀ [µm]	2.9	2.2
SUMMARY	Particle size d ₉₇ [µm]	14	10
	Oil absorption [g/100g]	14	45
	Specific surface area [m²/g]	0.8	9
	Density [g/cm ³]	4.4	2.6
	Functionalization		Amino
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2.4 **Preparative Methods**

The conditions for the production and application of the coatings as well as the drying conditions of the panels before the tests are shown in *Fig. 4*.

The addition sequence of the raw materials corresponds to their position in the corresponding formulations. Two pigment preparations were made for the anti-corrosion coating. The filler paste was ground in a bead mill adapted to the dissolver at 6.0 m/s for 10 minutes. The volume ratio of glass beads to filler paste was 1:1. The Black pigment paste was prepared by toothed disc dispersion at 4.2 m/s. The process of dispersive mixing is possible because the pigment used is a carbon black preparation that is particularly easy to disperse in aqueous systems. The mixing time was 20 minutes. The next day, the coating was prepared at the dissolver with toothed disc. After addition of all components, mixing was carried out for 5 minutes at 2.5 m/s and the finished paint was then filled into metal cans.

The application should be carried out at a viscosity of 400 to 500 mPa·s at 25 s⁻¹. Therefore, the Aktisil AM formulation was diluted with 10 percent deionized water before application. The barium sulfate formulation was applied undiluted. A doctor blade was used as application tool. The cold-rolled Q-Panel R 48 steel sheets were cleaned with solvent and then the lacquers were applied in one coat. The dry film thickness was approx. 80 µm.

Two variants were selected as drying conditions. Seven days drying at 23 °C and 50 % relative humidity for the gloss and adhesion tests. For the corrosion protection tests, dust drying at room temperature was followed by forced drying at 60 °C for 30 minutes. No significant difference was found between forced drying and drying at room temperature in the corrosion protection tests.

	Preparative	e Methods	
INTRODUCTION	Mixing	 <u>Filler paste:</u> Dissolver with adapted bead mill 10 min at 6.0 m/s beads v/v 1:1 	
RESULTS		 <u>Pigment paste black:</u> Dissolver with toothed disc 20 min at 4.2 m/s <u>Completition:</u> Dissolver with toothed disc After addition of all components final 5 min at 2.5 m/s 	
	Application	Doctor blade Application viscosity: 400 to 500 mPa·s at 25 s ⁻¹ BaSO ₄ -formulation: undiluted Aktisil AM-formulation: diluted with 10 % water Substrate: cold rolled steel, Q-Panel Type R 48 DFT ca. 80 μm	
	Drying conditions	Gloss, adhesion: 23 °C / 50 % relative humidity, 7 d Corrosion protection tests: dust-dry, then 30 min 60 °C	
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3 Results

3.1 Viscosity lacquer

The viscosity was determined in an MCR 300 rheometer with cylinder system CC17 via a logarithmic shear ramp. *Fig. 5* shows the viscosity values after 35 days of storage at room temperature. The viscosity curve of the barium sulfate formulation is clearly higher in the low shear range than that of the Aktisil AM formulation. This can be attributed to the rheological additives required to prevent sedimentation in the barium sulfate filler paste, as well as to other formulation components, such as the anti-corrosion pigment. Neither is needed in the Aktisil AM filler paste.



3.2 Storage Stability

The storage stability of the coatings was determined after 8 weeks of storage at 40 °C. The same measuring procedure was used as for 3.1 Viscosity lacquer. The result is shown in *Fig.* 6. The viscosity change of the barium sulfate containing formulation in the low shear range is shaded in gray. The circumstances already discussed for the viscosity can be considered as the reason for the increase in viscosity during storage. In contrast, with the formulation containing Aktisil AM, practically no change in viscosity is detectable over the entire measuring range and time period. Both coating formulations had no sediment after 8 weeks of storage.



3.3 Gloss

The gloss was determined with a micro-TRI-gloss instrument from Byk Gardner (*Fig.* 7). The barium sulfate formulation is in the satin matt range. In contrast, Aktisil AM in the corresponding formulation achieves a gloss increase in all three measuring angles.



Fig. 7

3.4 Adhesion

The adhesion of the coating to the substrate in the unloaded state was tested by cross-cut tests with adhesive tape according to DIN EN ISO 2409.

As can be seen in Fig. 8, both variants achieved a cross-cut characteristic value of 0 and so excellent adhesion to the substrate cold-rolled steel.



Fig. 8

3.5 Humidity test

After forced drying, the test sheets were loaded for 250 hours into a humidity test cabinet with constant climate (CH) at 40 °C according to DIN EN ISO 6270-2.

3.5.1 Adhesion

Adhesion testing was performed by means of 2 mm cross-cut test with tape tear-off. During the humidity test, an early intermediate evaluation of the adhesion strength was carried out. For this purpose, the panels were removed from the test after 18 hours of exposure and tested after 1 hour of regeneration at 23 °C and 50 % relative humidity in the thus still wet condition. At this point, the barium sulfate containing coating already showed no more adhesion to the substrate and was therefore rated with characteristic value 5. Although the Aktisil AM formulation does not contain any anti-corrosion pigment, the adhesion strength was completely present and was therefore rated as 0.

After 250 hours, the humidity test was terminated and again the adhesion strength was tested. In order to assess this in the dry state, the panels were regenerated for 24 hours. Here, too, the Aktisil AM variant achieved a characteristic value of 0 and thus unchanged excellent adhesion to the substrate. The barium sulfate coating was not able to fully restore the adhesion, and therefore achieved a characteristic value of 1. The pictures of the cross cut tests can be seen in *Fig. 9*.



Fig. 9

3.6 Salt spray test

The neutral salt spray test (NSS) according to DIN EN ISO 9227 was carried out. The adhesion strength was tested on the undamaged coating by means of a cross-cut test. To evaluate the delamination starting from a defined damage, a 10 cm long scribe was made in the middle of further panels with a scribe according to Sikkens (diameter 1 mm).

3.6.1 Adhesion

Analogous to the humidity test, an early intermediate evaluation of the adhesion strength after 18 hours of exposure was carried out by means of a 2 mm cross-cut test with adhesive tape tear-off. After a regeneration time of 1 hour at 23 °C and 50 % relative humidity, the test was still performed in the moist state. The result was the same as in the humidity test. The coating containing barium sulfate showed a complete loss of adhesion and thus a characteristic value of 5, while the coating containing Aktisil AM without anti-corrosion pigment showed unchanged complete adhesion to the substrate and thus received a characteristic value of 0.

After 250 hours, the salt spray test was finished and the adhesion strength was tested after 1 hour and 24 hours regeneration. Also after 250 hours, the Aktisil AM containing coating was found to have unchanged full adhesion strength to the substrate. The barium sulfate containing coating after 1 hour regeneration was unchanged poor as for the early intermediate evaluation. Only after 24 hours of regeneration, when the coating has re-dried, the adhesion to the substrate builds up again. *Figure 10* shows the cross-cut images.

	Salt Spray Adhesion	Test		HOFFMANN
	Cross-cut test 2 mm with tape			
INTRODUCTION	Test duration	Test duration 18 h 250 h		
EXPERIMENTAL	Regeneration time 23 °C, 50 % rel. H.	1 h	1 h	24 h
RESULTS				
SUMMARY	BaSO ₄			
	value	5	5	0
	Aktisil AM without anti- corrosion pigment			
	value	0	0	0
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Fig. 10

3.6.2 Delamination at Scribe

After completion of the salt spray test, the delaminated coating was removed mechanically with the aid of a cutter knife. Only the loose coating was removed to the point where adhesion to the substrate was restored.

As with the adhesion test, an earlier check was chosen for an intermediate evaluation of the delamination at the scribe. After 90 hours of loading and 24 hours of regeneration at standard climate, the coating no longer adhering to the substrate was removed. This showed that the delaminated area of the coating in the barium sulfate formulation with 10 mm was more than twice as wide as that of the Aktisil AM with only 4 mm.

After 250 hours, the salt spray test was finished. The early delamination after only 1 hour regeneration time, which approximately replicates the loaded condition, showed a complete delamination of the barium sulfate coating. In contrast, the Aktisil AM containing coating achieved only 8 mm delamination. After 24 hours of regeneration and thus evaluated in the dry state, the delamination of the barium sulfate containing coating was shown to be 16 mm. The Aktisil AM containing formulation remained at its good level with 7 mm delamination as shown in *Fig. 11*.



Fig. 11

In Fig. 12, the delamination range of both coatings is again shown as a time line of the load duration and compared. This clearly shows that with the Aktisil AM formulation, almost a triple lifetime is achieved.



Fig. 12

3.6.3 Cross Check: Barium Sulfate in the Aktisil AM Formulation

In order to exclude that the performance increase in corrosion protection of the Aktisil AM formulation is exclusively caused by the additive side formulation change, the barium sulfate in this formulation was also tested. The result is shown in *Fig. 13*. The photos were taken after 250 hours of neutral salt spray testing and the evaluation was made after 24 hours of regeneration in dry condition. Despite the long regeneration time, the coating detached completely in the cross-cut test with adhesive tape and received characteristic value 5. Likewise, the delamination of the coating starting from the scribe showed maximum deterioration. The natural barium sulfate in the Aktisil AM formulation without anticorrosion pigment thus showed even worse results than in the original formulation.

This cross-check shows very clearly how important it is to tailor the formulation to the specific filler.



4 Summary

By coordinated raw material selection and use of the surface-treated Neuburg Siliceous Earth Aktisil AM, a multiple of the corrosion protection duration was achieved in the acrylate single-layer system (DTM) tested here. In detail, the following was achieved:

- Storage stable filler paste without thickener (no sedimentation)
- Liquid laquer with higher rheological stability
- Higher gloss
- Good adhesion to the substrate, even in the wet condition during corrosion exposure
- Improvement of delamination at the scribe, even in the wet condition during corrosion exposure
- High performance with anti-corrosion inhibitor instead of anti-corrosion pigment

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