

Neuburg Siliceous Earth in

water-based corrosion protection

acrylate single-layer white

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1 Introduction

Corrosion protection is a major area of the coating industry and has always been dominated by solvent-based formulations. Despite their high solvent content and the associated occupational health and safety requirements, these coatings are considered the first choice for high resistance requirements.

Due to international environmental regulations that focus on limiting VOCs and increasing consumer demand for environmentally friendly solutions, water-based systems are considered the future for this coating sector as well.

Specially developed raw materials are needed to formulate water-based coating systems as efficiently as solvent-based systems. In most cases, these have a hydrophobic character, with the help of which the resulting film can form a barrier against moisture.

Another way to prevent corrosion is to prevent the diffusion of water, ions and oxygen to the metal surface. This can be realized with the help of a suitable filler.

The incorporation of pigments or fillers into solvent-based anti-corrosion paints is usually no problem. The binder is molecularly dissolved and the solids are wetted with additional additives if necessary. After application of the paint, the solvent evaporates and the freely moving polymer chains of the binder become entangled during the drying process, embedding the pigments and fillers homogeneously and firmly anchored in the polymer matrix.

In contrast, film formation in water-based coatings (*Fig. 1*) involves a critical phase change. The finely dispersed emulsified binder, which is insoluble in the hydrophilic, liquid environment, must be converted into a preferably comparable mechanically strong and resistant solid polymer layer. The prerequisite for this is that the minimum film-forming temperature is exceeded so that the polymeric binder particles, which have initially been isolated, can flow together after moving closer together and deformation beyond their boundaries (interdiffusion). Ideally, a compact composite is formed in this way, which already has high hydrophobicity on the raw material side as an additional barrier function for corrosion protection.



Fig. 1

Both fillers and pigments are subject to this process, which requires a complete transition from the aqueous phase to the polymer phase (*Fig. 2*).

However, the actual wetting by the binder is only noticeably possible in the last two steps of the film forming process. And here of all places, as particulate, usually larger, heterogeneous solids, they fundamentally disturb the orderly sequence of further film formation. In addition, new interfaces between polymer and filler are created, which must permanently withstand the internal stress build-up after volumetric film shrinkage of often more than 50 %.





Both effects influence the formation of the homogeneous structure within the coating. They do not necessarily have to be negative when using fillers, but are to be seen as increasingly critical in waterborne coatings if the number and size of particles rises and the wettability and compatibility with the polymer decreases. The increase in viscosity, that usually occurs, has an additional kinetically unfavorable effect on particle mobility and ideal arrangement. With higher pigment/filler content, the embedding in the polymer matrix and the homogeneous film forming can be impaired to such an extent that a massive weakening of the barrier layer occurs. Corrosion stimulators therefore penetrate more easily through areas of disordered gusset phases (*Fig. 2*, left yellow arrow) or directly through pore defects or the non-wetted filler surface (right yellow arrow) to the metal substrate.

To compensate for exactly this disadvantage is the minimum task of a good filler. Even better, the filler provides a performance capability from which the final coating additionally benefits.

The present report follows this approach with the aim of optimizing the performance of a water-based corrosion protection coating in the particularly challenging single-layer application by using Neuburg Siliceous Earth.

A classic corrosion protection coating consists of several layers applied one after the other. Defects in one layer, such as craters, air inclusions and pinholes, are usually completely levelled out by the next layer. In single-layer systems (DTM), however, each defect remains as such in the coating. Corrosion stimulators such as water, water vapor and ions of dissolved salts can penetrate the coating through these spots and migrate to the substrate. Over a longer period of time, blisters and corrosion develop at these points.

2 Experimental

2.1 Base Formulation

The present formulation is based on the guide formulation FP 2403-44 from Alberdingk Boley (*Fig. 3*). The paint is white pigmented and can be used as a single-layer system (DTM). The basis is a hydrophobic acrylate binder with good corrosion protection properties, all other raw materials are matched to the binder. There is no active anti-corrosion pigment, but an organic corrosion inhibitor. The good corrosion protection performance of this formulation is, among other things, due to the hydrophobic character of the formulation.

The solids content of the formulation is approx. 56 %, the pigment volume concentration (PVC) is approx. 21 %.

Target is to further improve the already good corrosion protection resistance of the base formulation with the Neuburg Siliceous Earth products Sillitin Z 89 and Aktifit Q. For this purpose, the fine, natural calcium carbonate (pos. 7 Filler) was replaced by equal weight.

	Bas	se F	or	mulation		HOFFMANN
	C	1	Wa	ter demineralized		5.90
INTRODUCTION	Itior	2	Edaplan 490		Dispersing additive	1.20
	ara	3 A		P 90	Neutralizing agent	0.02
	rep	4	Byk 024		Defoamer	0.10
RESULTS	Ц Ц	5	Byk	349	Wetting agent	0.18
	ner	6	Kronos 2190		Pigment white	17.70
SUMMARY	Pigr	7	Filler			7.50
	ш.	8	Water demineralized			2.90
	Let Down	9	Alb	erdingk AC 2403	Acrylic dispersion	57.90
		10 Byk	024	Defoamer	0.15	
		11	11 xillaria	Asconium 142DA	Org. corrosion inhibitor	1.90
		12		AMP 90	Neutralizing agent	0.15
0		13		Water demineralized		1.90
		14	Opt	ifilm Enhancer 300	Co-Solvent	1.50
		15	Asc	otran H10	Flash rust inhibitor	0.50
		16	Taf (10 %	igel PUR 60 solution 6 PUR 60; 20 % DPM; 70 % Water)	Thickener	0.50
	Total					100.00 %
	Solids content w/w					56 %
	Pigm	nent volume concentration (PVC)				21 %
as the s	VM-0/1219/12.2019					



2.2 Filler Characteristics

Fig. 4 gives an overview of the most important characteristic values of the fillers used. The natural calcium carbonate used in the control formulation was a very fine grade with an average particle size d_{50} of 1.1 µm. The oil absorption was 39 g per 100 g powder, and the specific surface area (BET) was determined to be 10 m²/g. Both oil number and specific surface area are quite high for a ground calcium carbonate.

With Sillitin Z 89 and Aktifit Q, two products from the same grain fraction were selected with an average particle size d_{50} of about 2 μ m. Sillitin Z 89 is a very bright and color-neutral grade of the classic Neuburg Siliceous Earth.

The classic Neuburg Siliceous Earth is a natural combination 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 absorption.

With Aktifit Q, a product from the range of calcined Neuburg Siliceous Earth was selected which offers highest brightness and color neutrality. After calcination, the product is modifying with a methacrylic functional group, giving it its hydrophobic character, which is intended to further improve the corrosion protection performance of the paint.

	Filler Characteris	HOFFMANN MINERAL		
		Calcium carbonate	Sillitin Z 89	Aktifit Q
	Color L*	96	94	94
RESULTS	Color a*	-0.1	0.1	-0.1
	Color b*	-0.1	4.0	1.0
	Particle size d ₅₀ [µm]	1.1	1.9	2.0
	Particle size d ₉₇ [µm]	3.5	9	10
	Oil absorption [g/100g]	39	55	65
	Specific surface area BET [m²/g]	10	11	9
	Surface treatment			methacrylic functionalized
	VM-1/1219/07.2020			7



2.3 **Preparative Methods**

The conditions for the production and application of the coatings and conditioning of the panels before the tests are shown in *Fig. 5*.

The preparation of the corrosion protection coatings was carried out on a dissolver with toothed disc under water cooling. First the pigment preparation was prepared, which was dispersed at 10.0 m/s for 10 minutes. This was added to the binder and the remaining components were mixed in, all at 5.0 m/s. After the thickener was added, the mixture was finally homogenized for 5 min at the same circumferential speed and then filled into metal cans.

The grain fineness of the finished varnish, measured with a grindometer, was less than 15 µm for all formulations. Further details on the manufacture can be found in the appendix.

The application was carried out after 35 days maturing at room temperature. On cold rolled steel (Q-Panel type R 48) the coatings were sprayed with a Walther compressed air spray gun at 1 bar pressure and a nozzle diameter of 3 mm. To achieve a good flow and defect-free film, all formulations were diluted with 10 % deionized water before spraying. All tests were carried out on single-layer sprayed panels with a dry film thickness of around 70 μ m.

All sheets were conditioned at 23 °C and 50 % relative humidity. Seven days after application, the appearance (colour and gloss) and adhesion were tested by using a cross-cut test. After 28 days the corrosion protection tests were started.

	Preparative	Methods MINERAL		
	Mixing	<u>Pigment preparation:</u>Dissolver with toothed disc		
EXPERIMENTAL		• 10 min at 10.0 m/s Let Down:		
RESULTS		Submission of binder		
SUMMARY		Addition of remaining ingredients at 5.0 m/sAfter dosing thickener finally 5 min at 5.0 m/s		
	Application	After 35 d maturing time Substrate: cold rolled steel, Q-Panel Typ R 48 Spray application: 10 % diluted with water, nozzle size 3 mm Dry film thickness: ~ 70 μm, <u>single-layer</u>		
	Conditioning	 Drying conditions 23 °C / 50 % relative humidity Appearance, adhesion: 7 d Corrosion Tests: 28 d 		
23 200	VM-0/1219/12.2019			



3 Results

3.1 Viscosity

The viscosity was determined in an MCR 300 rheometer with cylinder system CC17 via a logarithmic shear ramp. *Fig.* 6 shows the viscosity values after 35 days of storage, which corresponds to the time of application. The evaluation was carried out at shear rates of 0.1 s^{-1} and 100 s^{-1} . At both shear rates no significant difference could be found between the different fillers.

The storage stability, tested undiluted at room temperature, is comparably good for all variants.

For spray application, all formulations were diluted with 10 % deionized water in order to achieve a better surface result, especially flow. The viscosities of the formulations were then around 1.1 Pa·s at the low shear rate and around 0.1 Pa·s at the high shear rate.





3.2 Color

The color was measured with an X-Rite device and geometry $d/8^{\circ}$ (*Fig.* 7). The brightness L* is very high with values between 96 and 97. The a* values remain unchanged at around -1. The b* values are in the slightly yellow range with Sillitin Z 89 at the top, which means a slight increase compared to the calcium carbonate used here. In contrast, Aktifit Q achieves the lowest value and thus the best color neutrality.



Fig. 7

3.3 Gloss

The gloss was determined with a micro-TRI-gloss instrument from Byk Gardner (*Fig. 8*). The values of the corrosion protection varnishes are in the silk gloss range for all formulations. The slight shift in the 60° gloss with the Neuburg Siliceous Earth products is due to the slightly higher particle size and special morphology.

In the 85° measuring angle, the differences are less pronounced, here the calcium carbonate has 93 GU, Sillitin Z 89 lies at 87 GU and Aktifit Q by 82 GU.



Fig. 8

3.4 Adhesion

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

As shown in Fig. 9, all variants achieved the cross-cut rating of 0 and thus excellent adhesion to the substrate of cold-rolled steel.



Fig. 9

3.5 Humidity test

After 28 days drying at 23 °C and 50 % relative humidity the test panels were loaded for 1000 hours in a constant condensation water environment (CH) at 40 °C according to DIN EN ISO 6270-2. Two sheets without scribe were tested.

In preliminary tests there was no blistering, corrosion or delamination on sheets with scribe, so no such defined injuries were made in the main tests.

The non-scribed coating was checked for adhesion, which was evaluated by cross-cutting, and the degree of blistering. The coating was then stripped to examine the metal surface for under-film corrosion.

3.5.1 Adhesion

At the end of the humidity test, conditioning for 24 h at 23 °C and 50 % relative humidity followed, before the adhesion was tested by means of cross cut and adhesive tape tear-off. As shown in the pictures in *Fig. 10*, part of the coating flaked off along the cutting line of the calcium carbonate-containing coating. Based on the DIN EN ISO 2409 standard, the result could be classified with a cross-cut rating of 1 to 2.

A good adhesion of the coating to the substrate and thus a permanent protective layer for the metal, has to be guaranteed even after long exposure to moisture. This is the only way to further protect the metal in case of renewed contact with moisture or salts.

With Sillitin Z 89 and Aktifit Q, a characteristic value of 0 to 1 was achieved, thus improving the adhesion to the metal and the expectation of service life compared to calcium carbonate.



Fig. 10

3.5.2 Blistering

The degree of blistering was evaluated according to DIN EN ISO 4628-2. As shown in *Fig. 11*, all formulations were free of blisters and thus assigned a rating of 0-0(S0). This indicates a defect-free coating and thus underlines its special performance.



Fig. 11

3.5.3 Under-film Corrosion

After the cross-cut test and assessment of the degree of blistering, the coating was removed with the aid of a paint stripper so that the metal surface was exposed. In the case of calcium carbonate, discoloration and thus signs of incipient corrosion are visible (*Fig. 12*). Under the coating with Sillitin Z 89 and Aktifit Q, bare metal was visible without any changes or corrosion. This suggests that the coatings with the two Siliceous Earth products have a very strong barrier against water and water vapor, and this was still completly intact after the test period of 1000 hours.



Fig. 12

3.6 Salt Spray Test

In the neutral salt spray test (NSS) according to DIN EN ISO 9227 the test panels were placed in after 28 days drying at 23 °C and 50 % relative humidity for 1000 hours. Three panels were tested for each formulation variant, one of them without scribe, on which the blistering, the adhesion test by cross-cut and the under-film corrosion after paint stripping were assessed. On the other two panels, a 10 cm long scribe according to Sikkens (diameter 1 mm) was attached in the middle. These specimen were used to evaluate the formation of blisters as well as delamination and rust creep at the scribe.

3.6.1 Adhesion

After the end of the salt spray test, the non-scribed panels were conditioned for one hour at 23 $^{\circ}$ C and 50 % relative humidity. This was followed by the cross-cut test with adhesive tape tear-off. This early stage of testing is often a challenge for water-based coatings. The results are shown in *Fig. 13*. Calcium carbonate was rated with a characteristic value of 0 to 1, as the coating was partially detached at the intersections of the cross-cut lines. Sillitin Z 89 and Aktifit Q received a characteristic value of 0 and thus the best rating.

The two Neuburg Siliceous Earth products impress again with excellent results in the humidity test and salt spray test.

	Salt Spray Test Adhesion	HOFFMANN MINIERAL		
	Cross-cut test 2 mm with tape, after 1 h at 23 °C / 50 % RH			
INTRODUCTION EXPERIMENTAL	Calcium carbonate	Sillitin Z 89	Aktifit Q	
<u>RESULTS</u>				
SUMMARY				
	GT 0 - 1	GT 0		
1000	VM-0/1219/12.2019			

Fig. 13

3.6.2 Blistering and Under-film Corrosion

As can be seen in *Fig. 14*, all formulations were free of blistering after 1000 hours of the neutral salt spray test and were therefore rated 0 - 0(S0) according to DIN EN ISO 4628-2. In order to be able to examine the substrate for under-film corrosion, all coatings were stripped. In all formulation variants, the metal surface was free of corrosion, thus offering excellent protection.



Fig. 14

3.6.3 Blistering at Scribe

The coating must compensate for the mechanical damage of the scribe in the best possible way and thus protect the exposed metal from corrosion and blistering. Furthermore, a loss of adhesion (delamination) starting from the scribe to the surrounding area must be avoided as far as possible.

As can be seen in *Fig. 15*, the calcium carbonate-containing coating resulted in a lot of rust at the scribe and a wide area with blisters. Sillitin Z 89 was able to reduce rust formation and the blister area width. With Aktifit Q, rust at the scribe was further minimised and blistering could be completely prevented. Thus Aktifit Q clearly achieved the best result.



Fig. 15

3.6.4 Delamination and Rust Creep

After completion of the salt spray test, the delaminated coating was removed mechanically by using a cutter knife. Only the loose coating was removed up to the point where adhesion to the substrate was unaffected.

As shown in *Fig. 16*, the delaminated area of the calcium carbonate-containing coating was very wide (see long white arrow in the middle of the corresponding photo). With Sillitin Z 89 this can already be significantly reduced. With Aktifit Q the delamination can be reduced to a minimum, which achieves maximum protection.

In addition, the rust creep at the scribe was evaluated (see short white arrow in the middle of the left photo). This shows how far the corrosion at the scribe was progressed and the substrate was damaged. The photos of the test panels show that with calcium carbonate as filler, the rust creep was significantly wider than with Sillitin Z 89 or Aktifit Q.



Fig. 16

To quantify the properties delamination and corrosion the panels were evaluated according to DIN EN ISO 4628-8. For this purpose, the delamination width and rust creep were measured at nine positions at a distance of 1 cm. The mean value was calculated from these values and the width of the scribe graver of 1 mm was deducted and then divided by two. This gives the value for delamination and corrosion on one scribe side.

The diagram in *Fig. 17* and *18* shows the mean value of the two tested panels, the error indicator in the bars represents the span of the two panels.

For the coating with calcium carbonate, an average delamination of 26.3 mm could be determined, whereas with Sillitin Z 89 an improvement with a value of 17.9 mm was already observed. The clearly best result, however, was achieved by Aktifit Q with only 4.8 mm. In practice, this means that a damaged coating with Aktifit Q has a significantly longer service life than with calcium carbonate.

The rust creep of 1.4 mm for calcium carbonate was reduced to about half with the two Neuburg Siliceous Earth products, 0.7 mm with Sillitin Z 89 and 0.6 mm with Aktifit Q. In *Figs.* 17 and 18 the values for delamination and rust creep are graphically depicted.



Fig. 17



Fig. 18

4 Summary

In the aqueous acrylic corrosion protection lacquer presented here, applied in single-layer system (DTM), Neuburg Siliceous Earth was able to achieve an additional performance gain compared to fine calcium carbonate. The following enhancements were achieved in detail:

Sillitin Z 89 and Aktifit Q

- Improvement of the adhesion after humidity test and salt spray test
- Avoidance of under-film corrosion in the humidity test

Sillitin Z 89

- Reduced blistering at scribe in the salt spray test
- Less delamination and rust creep at scribe

Aktifit Q

- Avoidance of blistering at scribe in the salt spray test
- Lowest delamination and rust creep at scribe

With the Neuburg Siliceous Earth products presented here, the corrosion protection performance of the coating was significantly enhanced, and thus the service life of the component extended. Also, the high level of aesthetic requirements in the DTM sector, such as the color white here, can be maintained. In addition, the products presented here are characterized by simple and label-free processing.

Whether the filler effects described above can also be advantageously extended to the area of the classic primer was examined on the basis of further internal investigations. The results are the subject of the technical report "Neuburg Siliceous Earth in water-based Corrosion Protection Acrylate Primer red".

Mixing instruction

The formulation was produced on a dissolver with toothed disc under water cooling. For the pigment preparation, the raw materials from items 1 to 5 were presented and the solids from items 6 to 7 were stirred in (*Fig. 19*). The mixture was then dispersed for 10 min at 10.0 m/s, then completed with item 8. The binder (pos. 9) was submitted and the pigment paste was added while stirring at 5 m/s. The other raw materials were also added. A premix was prepared from items 11 to 13, which was added as a clear mixture within 10 minutes to the let-down. If the premix became cloudy, the mixture was to be discarded. The thickener components of pos. 16 were also mixed together in advance. After adding the thickener, mix for a further 5 min at 5 m/s final, then fill.

	Bas	se F	or	mulation		HOFFMANN MINERAL
	_	1	Wa	ter demineralized		5.90
INTRODUCTION	tior	2	Eda	aplan 490	Dispersing additive	1.20
EXPERIMENTAL	ara	3 AM 4 Byk 5 Byk		P 90	Neutralizing agent	0.02
	rep			: 024	Defoamer	0.10
RESULTS	μ			349	Wetting agent	0.18
	ner	6	Kro	nos 2190	Pigment white	17.70
SUMMARY	Pigr	7	Filler			7.50
		8	Water demineralized			2.90
	Let Down	9	Alb	erdingk AC 2403	Acrylic dispersion	57.90
		10	Byk	: 024	Defoamer	0.15
		11	emix	Asconium 142DA	Org. corrosion inhibitor	1.90
		12		AMP 90	Neutralizing agent	0.15
0		13	pr	Water demineralized		1.90
		14	Opt	ifilm Enhancer 300	Co-Solvent	1.50
		15	Asc	otran H10	Flash rust inhibitor	0.50
		16	Tafigel PUR 60 solution (10 % PUR 60; 20 % DPM; 70 % Water) Thickener		Thickener	0.50
	Total				100.00 %	
	Solids content w/w					56 %
	Pigment volume concentration (PVC)				21 %	
ES CON	VM-0/1219/12.2019					

Fig. 19

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