Neuburg Siliceous Earth in water-based corrosion protection acrylate primer red

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VM-0/1219/12.2019

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1 Introduction

Solvent-based coatings have always been the first choice for corrosion protection of metal by organic coatings. However, legislative pressure to reduce volatile organic compounds (VOC) and increasing consumer demand require the development of solvent-reduced, environmentally friendly formulations. Waterborne coating systems are therefore becoming increasingly important, but at the same time, they should fulfil the accustomed property profile and high performance level of classic systems. These include not only simple technical producibility and easy processability, but also especially the technical performance after application.

As the first protective layer, the primer is intended to create the basis for excellent corrosion protection, mainly through good adhesion to the substrate. In addition, the film formation process, which differs from that of solvent-based paints, not only requires the development of new binders, but also places increasingly higher demands on the use of modern functional fillers, particularly in corrosion protection.

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.

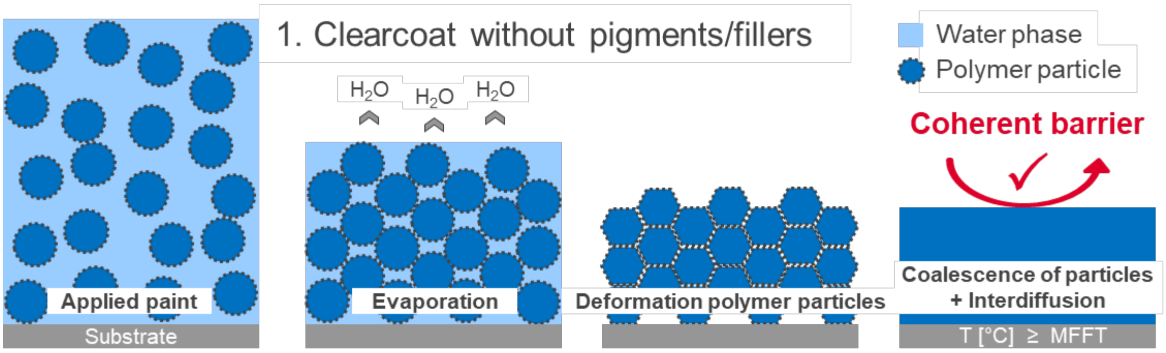


Fig. 1

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 %.

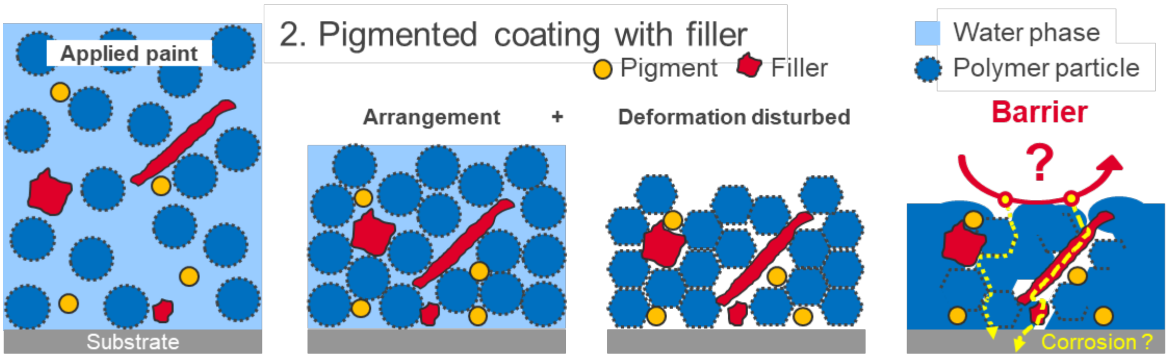


Fig. 2

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 primer by using Neuburg Siliceous Earth.

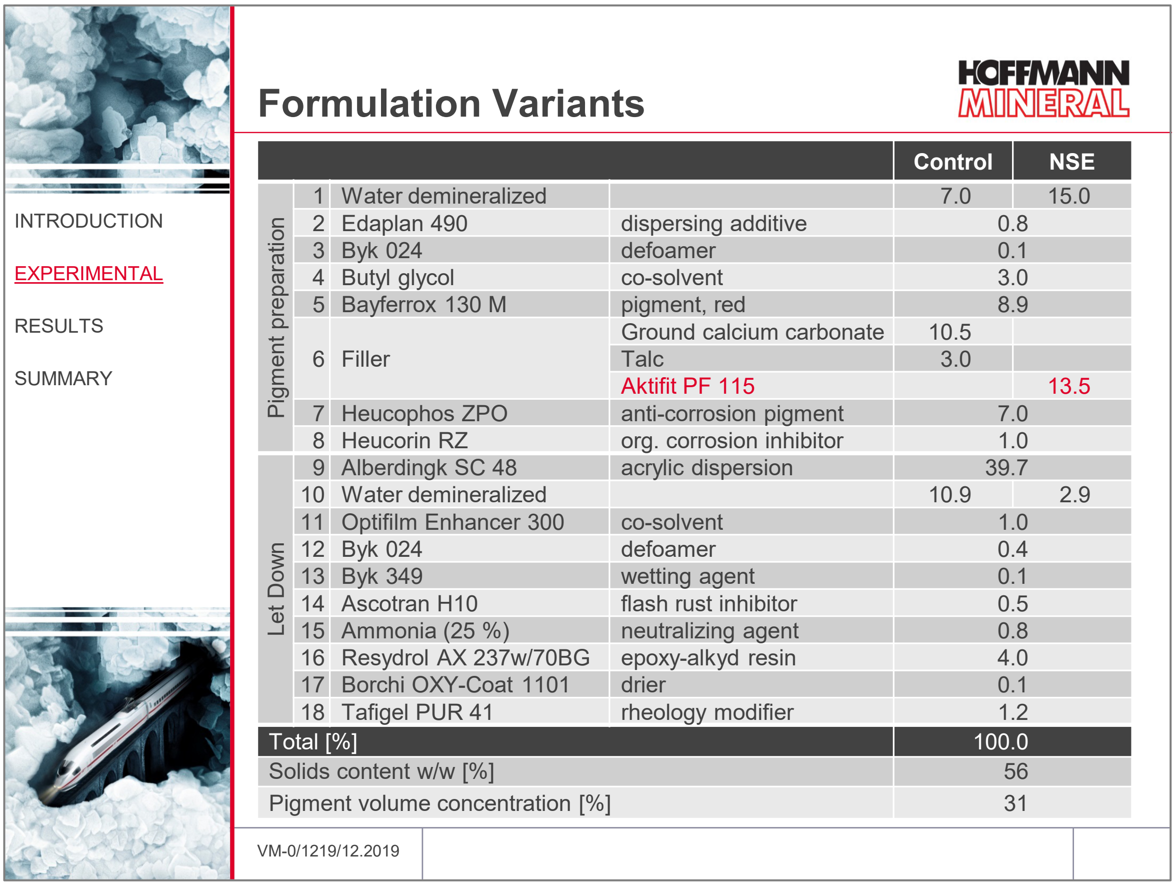
2 Experimental

2.1 Base formulation and filler variation

Fig. 3 shows the underlying base formulation (control), based on the formulation FP 48 02 from Alberdingk Boley.

The acrylate dispersion binder and formulation framework form the basis of a red-pigmented primer, as it is often used in the classical coating design for corrosion protection. The usual top and/or intermediate coating was deliberately omitted in order to emphasize the performance of the tested fillers in the primer with maximum differentiation.

In addition to an active pigmentation for corrosion protection and the coloring iron oxide pigment, the based control formulation contains 10.5 % natural calcium carbonate and 3 % talc. In the present study, this filler combination is replaced by the Neuburg Siliceous Earth grade "Aktifit PF 115" by equal weight. All other formulation ingredients remain unchanged. Only a part of the water in the Neuburg Siliceous Earth (NSE) variant is brought forward from the letdown stage into the pigment preparation, in order to ensure comparable conditions during filler incorporation and subsequent dispersion process.



Formulation Variants

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				Control	NSE
Pigment preparation	1	Water demineralized		7.0	15.0
	2	Edaplan 490	dispersing additive	0.8	
	3	Byk 024	defoamer	0.1	
	4	Butyl glycol	co-solvent	3.0	
	5	Bayferrox 130 M	pigment, red	8.9	
	6	Filler	Ground calcium carbonate	10.5	
			Talc	3.0	
			Aktifit PF 115		13.5
	7	Heucophos ZPO	anti-corrosion pigment	7.0	
	8	Heucorin RZ	org. corrosion inhibitor	1.0	
Let Down	9	Alberdingk SC 48	acrylic dispersion	39.7	
	10	Water demineralized		10.9	2.9
	11	Optifilm Enhancer 300	co-solvent	1.0	
	12	Byk 024	defoamer	0.4	
	13	Byk 349	wetting agent	0.1	
	14	Ascotran H10	flash rust inhibitor	0.5	
	15	Ammonia (25 %)	neutralizing agent	0.8	
	16	Resydrol AX 237w/70BG	epoxy-alkyd resin	4.0	
	17	Borchi OXY-Coat 1101	drier	0.1	
	18	Tafigel PUR 41	rheology modifier	1.2	
Total [%]				100.0	
Solids content w/w [%]				56	
Pigment volume concentration [%]				31	

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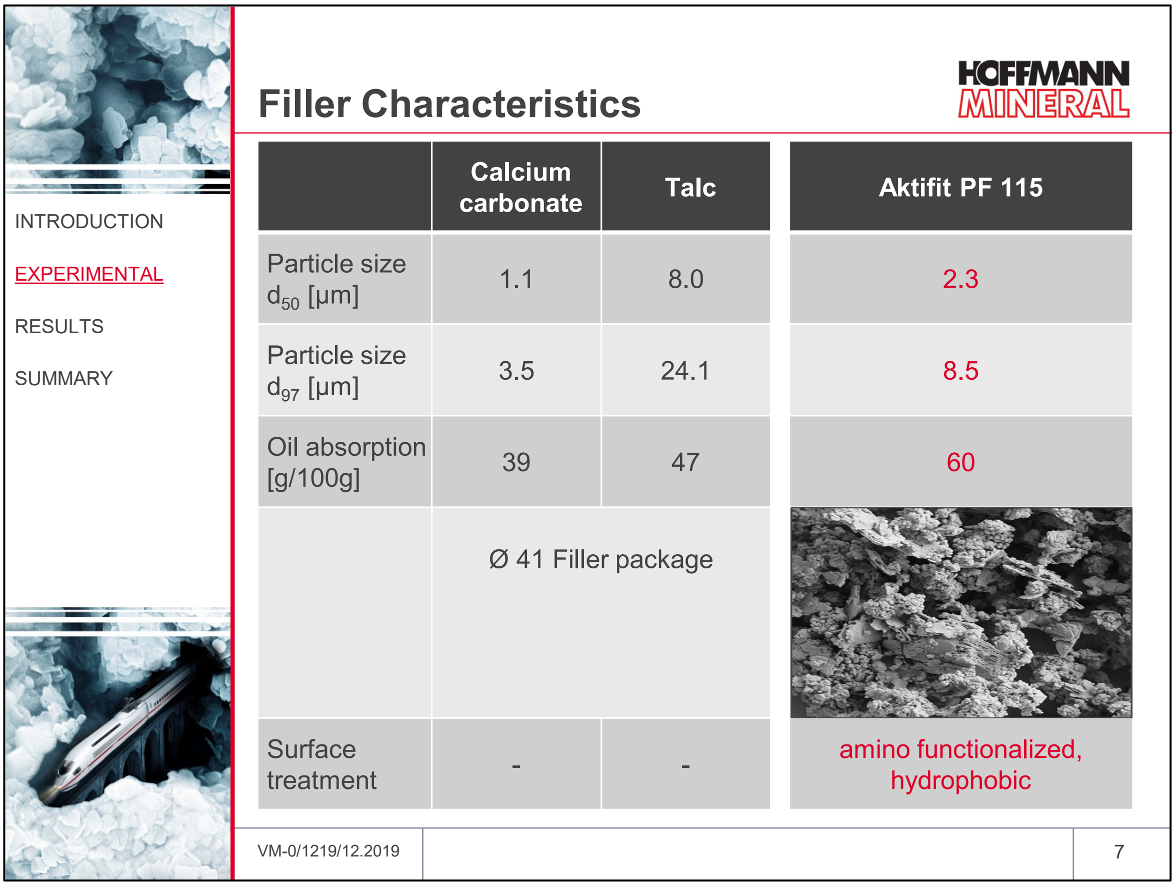
Fig. 3

2.2 Filler Characteristics

The fillers used in the control formulation are a very fine natural calcium carbonate and a smaller proportion of coarser talc (*Fig. 4*). The somewhat higher oil absorption of the talc has only a minor effect on the average oil absorption of the filler combination, which at 41 g/100 g is close to that of pure calcium carbonate.

Aktifit PF 115 is a calcined hydrophobic grade of Neuburg Siliceous Earth, produced by modifying the surface with a special amino functional group. Neuburg Siliceous Earth is a naturally occurring 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. Such a unique structure is responsible for a relatively high specific surface area and the higher oil absorption of 60 g/100g in the present case. In terms of particle size, Aktifit PF 115 is in the range between the two control fillers, but is closer to the very fine calcium carbonate.



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Filler Characteristics

	Calcium carbonate	Talc	Aktifit PF 115
Particle size d_{50} [µm]	1.1	8.0	2.3
Particle size d_{97} [µm]	3.5	24.1	8.5
Oil absorption [g/100g]	39	47	60
	Ø 41 Filler package		
Surface treatment	-	-	amino functionalized, hydrophobic

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Fig. 4

2.3 Preparation, Application und Testing

The preparation was carried out on a high-performance dissolver as shown in *Fig. 5* with a toothed disc ("Cowles Blade") according to the specified raw material sequence indicated in the formulation.
After the raw materials 1 to 4 have been supplied, the separately premixed ingredients 5 to 8 are incorporated at a peripheral speed of 5 m/s and dispersed as a pigment preparation for 10 minutes at 10 m/s under ice-water cooling.
For the let down process the binder is placed, diluted with water and the pigment preparation is added while stirring at 5 m/s. The other additives 11 to 18 are added successively at intervals of 5 minutes each. After the thickener has been added, final homogenization is done for a further 5 min, whereby air entry into the batch should be avoided if possible. The total production time is approx. 60 minutes.


Source: VMA-GETZMANN GMBH

Fig. 5

For the measurement of the rheological data of the wet paint a rheometer MCR 300 from Paar Physica at 23°C measuring temperature and with cylinder measuring geometry was used.

After 28 days of maturing time, cold-rolled steel test sheets of the type Q- Panel R 48 were coated. To ensure uniform dry film thicknesses and to exclude corrosion damage caused by pores and defects in the film, the formulations were first applied undiluted in two layers by means of a doctor blade and an automated film applicator equipment. The intermediate drying time was 4 hours in each case; the total dry film thickness was approx. 150 µm. For the planned corrosion protection tests, the wet paints were additionally sprayed as a single coat with a dry film thickness of approx. 80 µm (compressed air nozzle 3 mm, 2 bar) after dilution to a comparable viscosity level.

The drying and conditioning of the paint films took place in an air-conditioned laboratory at 23 °C and 50 % humidity (*Fig. 6*). Subsequently, the following tests were performed:

After 7 days
- Gloss measurement, DIN EN ISO 1522
- Light microscopic evaluation of the coatings surface

After 28 days
- Cross cut test, DIN EN ISO 2409
- Humidity test, DIN EN ISO 6270-2 CH
- Salt spray test, DIN EN ISO 9227 NSS

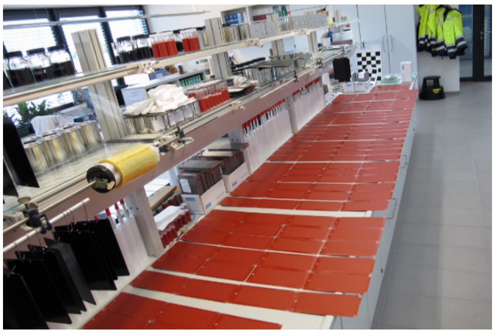


Fig. 6

Under both, condensation water climate and salt spray, the resistance of the coated test panels to blistering and corrosion phenomena in and under the coating was determined (*Fig. 7*). In addition, immediately before the start of the salt spray test, a scratch mark of 1 mm width was applied separately from the non-scribed area, in order to investigate the effects of this layer damage on the anti-corrosion behavior.

During the interim evaluations, the cross-cut adhesion after a short regeneration time of the coatings was determined in parallel.

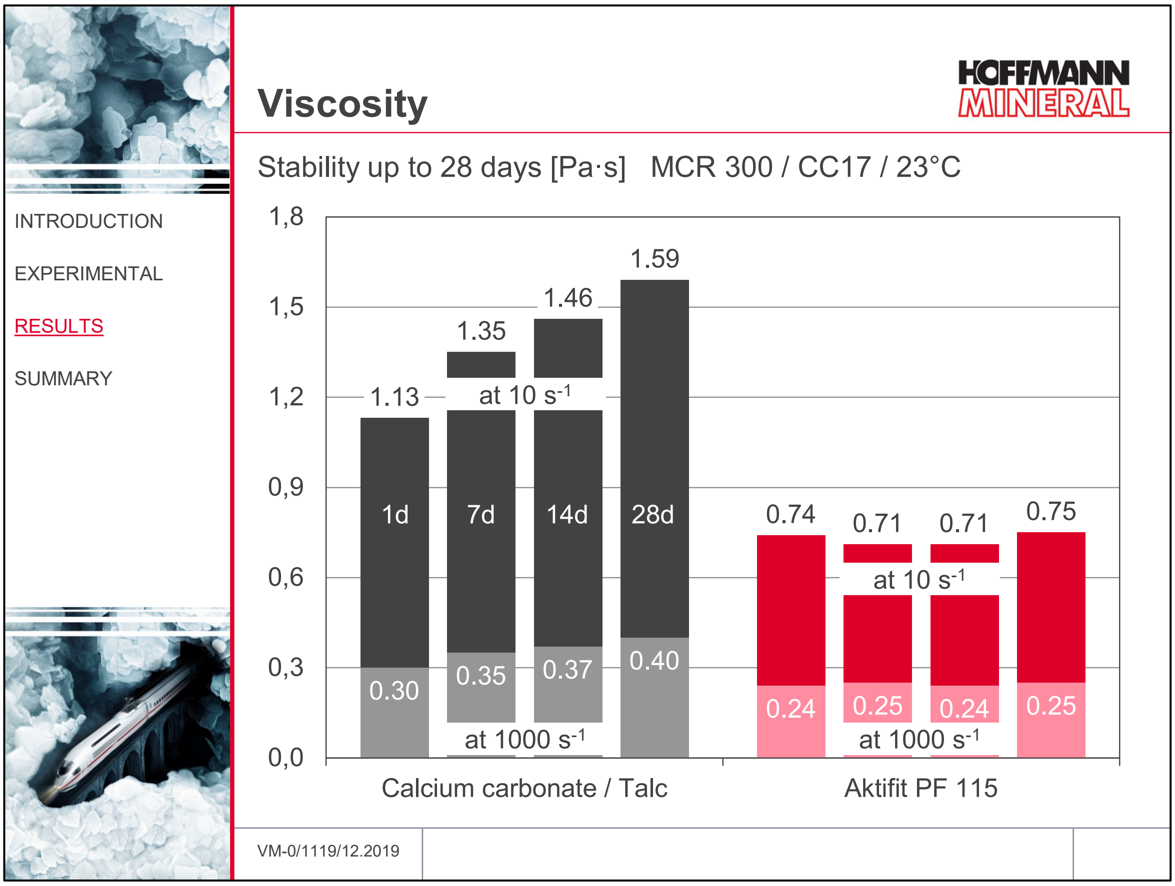
Fig. 7

3 Results

3.1 Processing properties

Both filler variants can be easily incorporated into the pigment preparations according to the formulation specifications. In the rheometer, as shown in *Fig. 8*, the anti-corrosion paints produced reveal highly shear-thinning flow characteristics. Greater differences arise when the rheological stability of the two formulations is considered. With the control fillers calcium carbonate and talc, there is a noticeable increase in viscosity over the entire shear rate range under storage conditions.

This behavior is not observed when using Aktifit PF 115: The viscosity is at a lower as well as constant level. From the beginning, this stability combines both a consistently good flow for brush or spray application and a sufficiently good storage stability of the wet coating.



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Viscosity

Stability up to 28 days [Pa·s] MCR 300 / CC17 / 23°C

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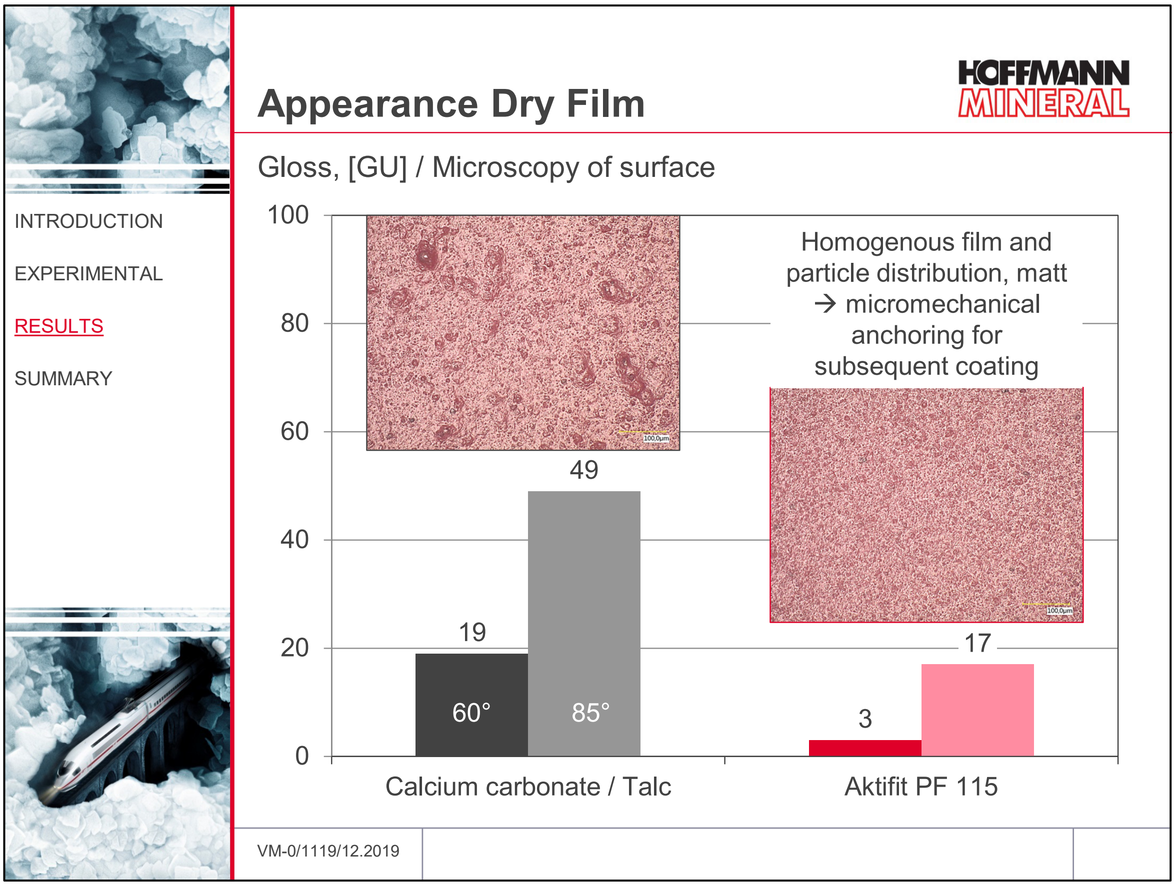
Fig. 8

3.2 Appearance dry film

In the present primer formulation, the variation of the fillers has no influence on the drying speed and hardness development, but on a microscopic level, it changes the texture of the coating surfaces (*Fig. 9*).

When using Aktifit PF 115, the narrow particle size distribution spectrum of the filler favors a much more homogeneous appearance compared to the control combination. Although in principle no optical demands are made on the regular film surface of the primer in a multilayer structure, the matte appearance of the coating with Aktifit PF 115 brings advantages. The superficially numerous, very well embedded filler particles form an optimal basis for the mechanical anchorage of a subsequent coating.



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Appearance Dry Film

Gloss, [GU] / Microscopy of surface

Homogenous film and particle distribution, matt → micromechanical anchoring for subsequent coating

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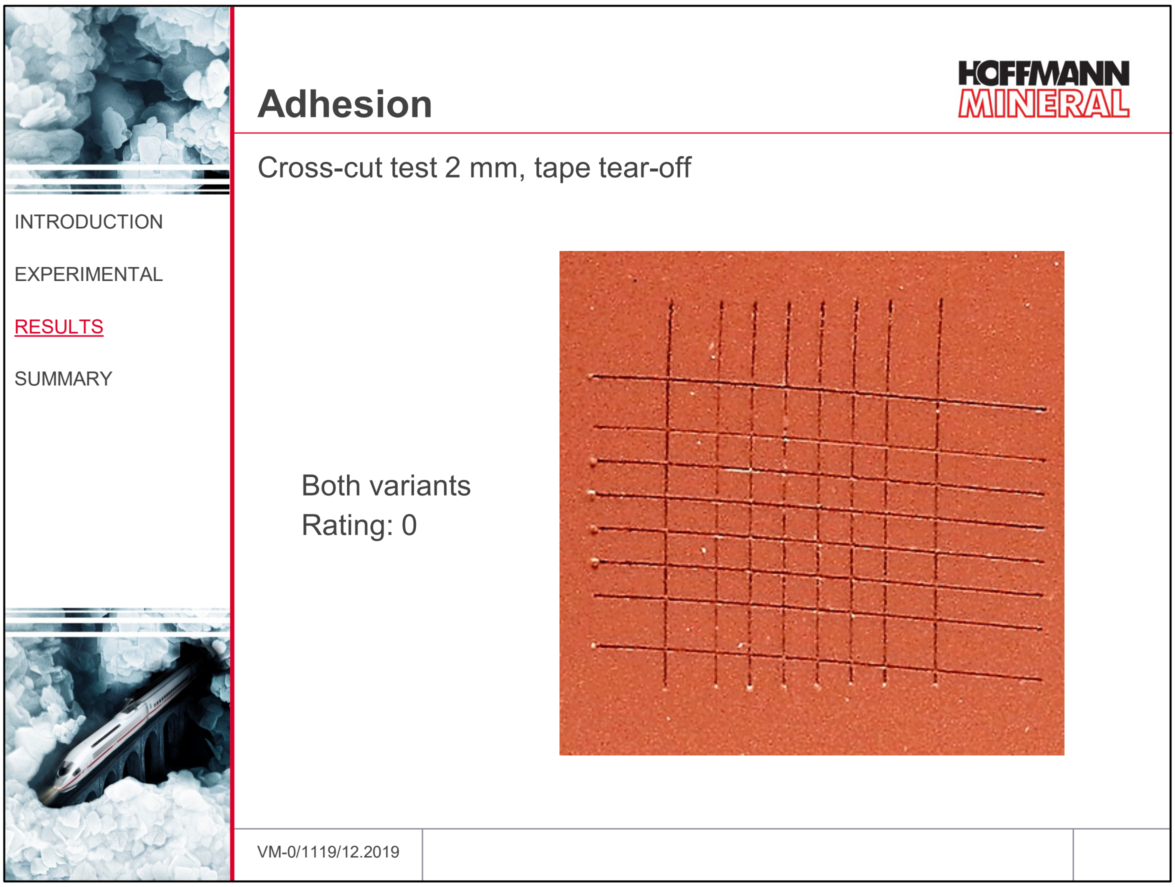
Fig. 9

3.3 Adhesion

Fig. 10 exhibits the results of the adhesion test 4 weeks after application. Before the corrosion protection tests are started, the cross-cut test after adhesive tape tear-off shows a perfect result for both formulation variants and thus the very good adhesion required for primers.



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Adhesion

Cross-cut test 2 mm, tape tear-off

Both variants
Rating: 0

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Fig. 10

3.4 Humidity test

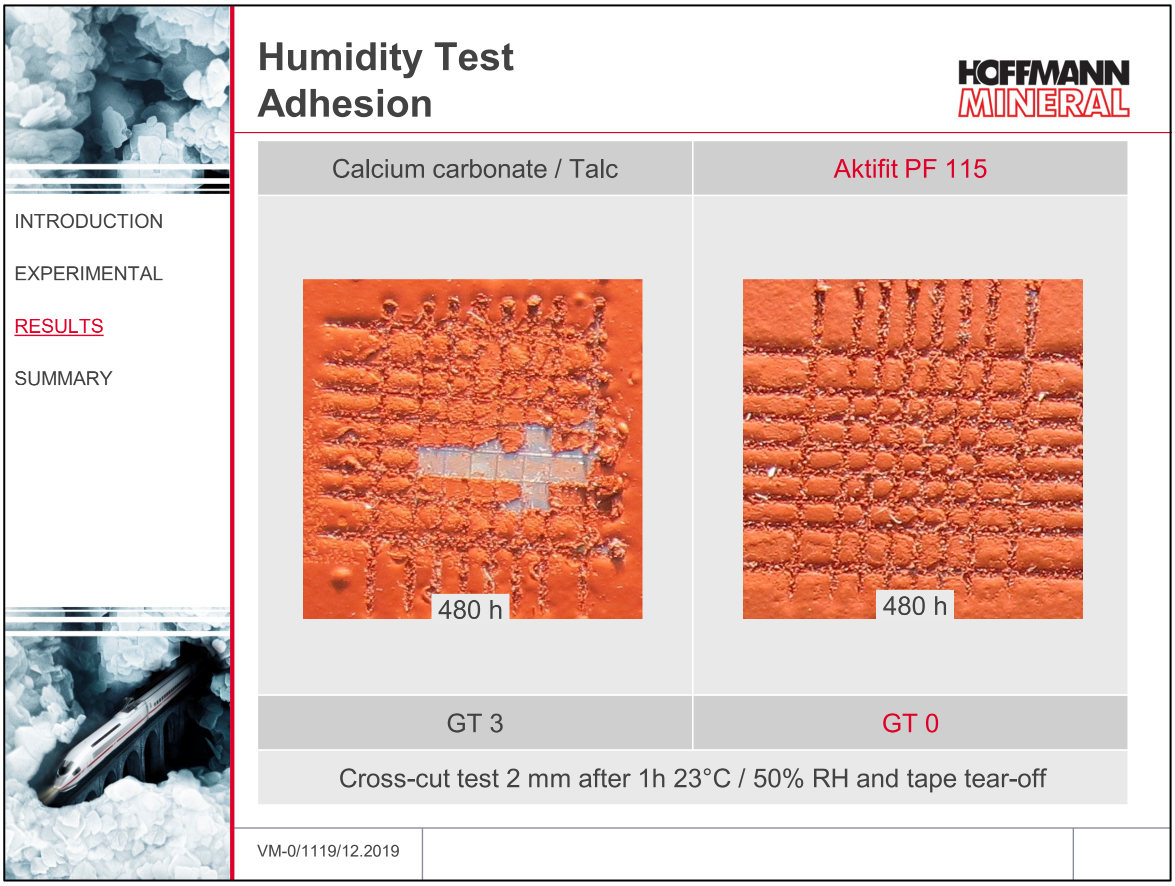
3.4.1 Adhesion

The cross-cut test was carried out just one hour after the end of the load. The short drying phase is adequate to build up sufficient adhesion for the adhesive tape tear-off and allows a statement to be made at this early stage about the wet adhesion performance of the coating.

Fig. 11 shows the results after 480 hours of humidity test. The absence of a topcoat exposes the coating surface directly to condensation water, which visibly swells the coatings following the osmotic principle.

In the case of the control fillers, noticeable losses in wet adhesion occur under this critical load. In the area of the cross-cut, squares of the coating film are partially completely removed and the metal substrate is exposed. In some cases, insufficient intercoat adhesion is also apparent due to adhesive tape tear-off of the upper layer.

Because of its hydrophobic character, Aktifit PF 115 already reduces the penetration of water into the coating and prevents premature adhesion loss. Very good intercoat adhesion and adhesion to the substrate remain intact despite the swelling effect and lead to a cross-cut rating value of GT 0.



Humidity Test
Adhesion

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Calcium carbonate / Talc	Aktifit PF 115
480 h	480 h
GT 3	GT 0

Cross-cut test 2 mm after 1h 23°C / 50% RH and tape tear-off

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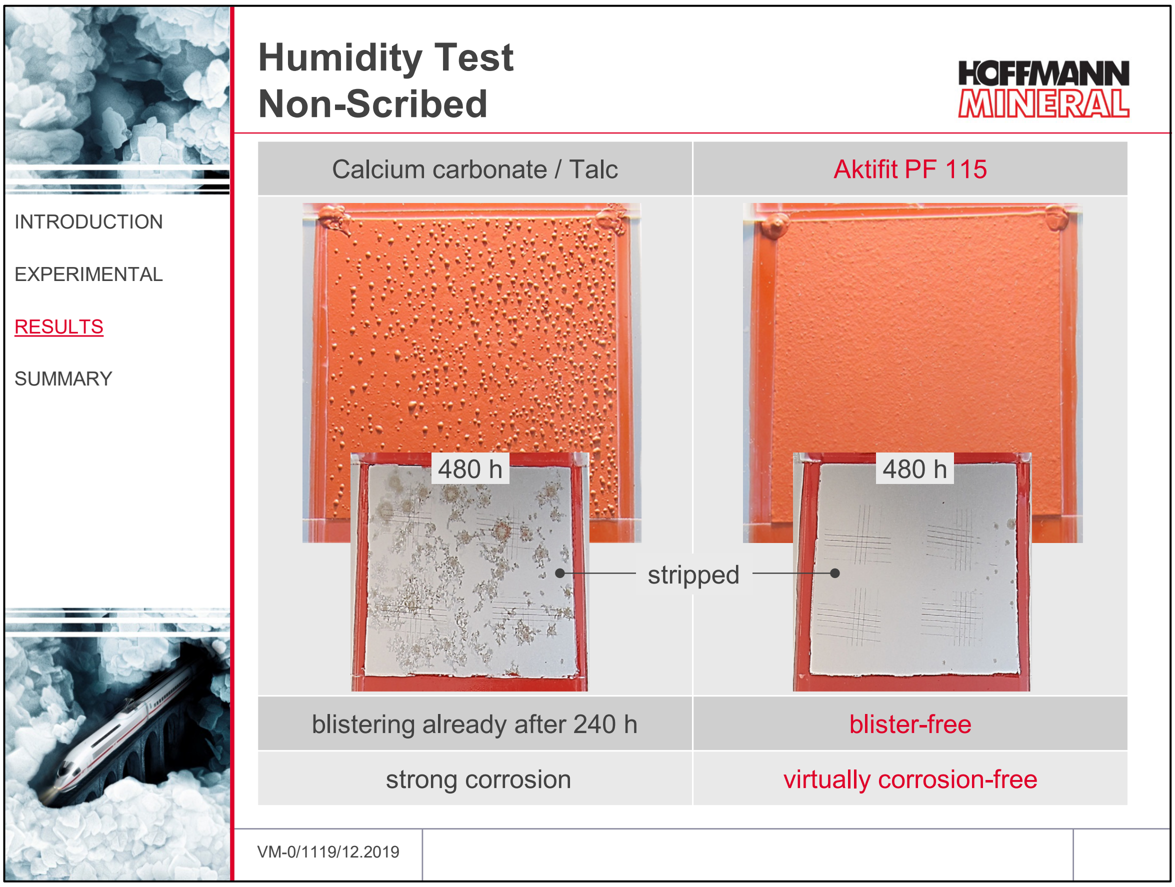
Fig. 11

3.4.2 Protection in non-scribed area

In the coating surface, the filler combination calcium carbonate / talc tends to blistering after only 240 hours, which increases visibly up to 480 hours as under-film corrosion sets in. The corrosion damage in the lower left part of *Fig. 12* primarily indicates reductive rust formation in the form of magnetite; locally, the first red rust cells are already forming.

If, on the other hand, Aktifit PF 115 is used, the barrier effect in the test surface is advantageously enhanced and not only the organic paint film, but also the metal substrate is protected against defects. The higher performance practically doubles the protective function and coating durability over time simply by using the optimized filler.



Humidity Test
Non-Scribed

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Calcium carbonate / Talc	Aktifit PF 115
blistering already after 240 h	blister-free
strong corrosion	virtually corrosion-free

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Fig. 12

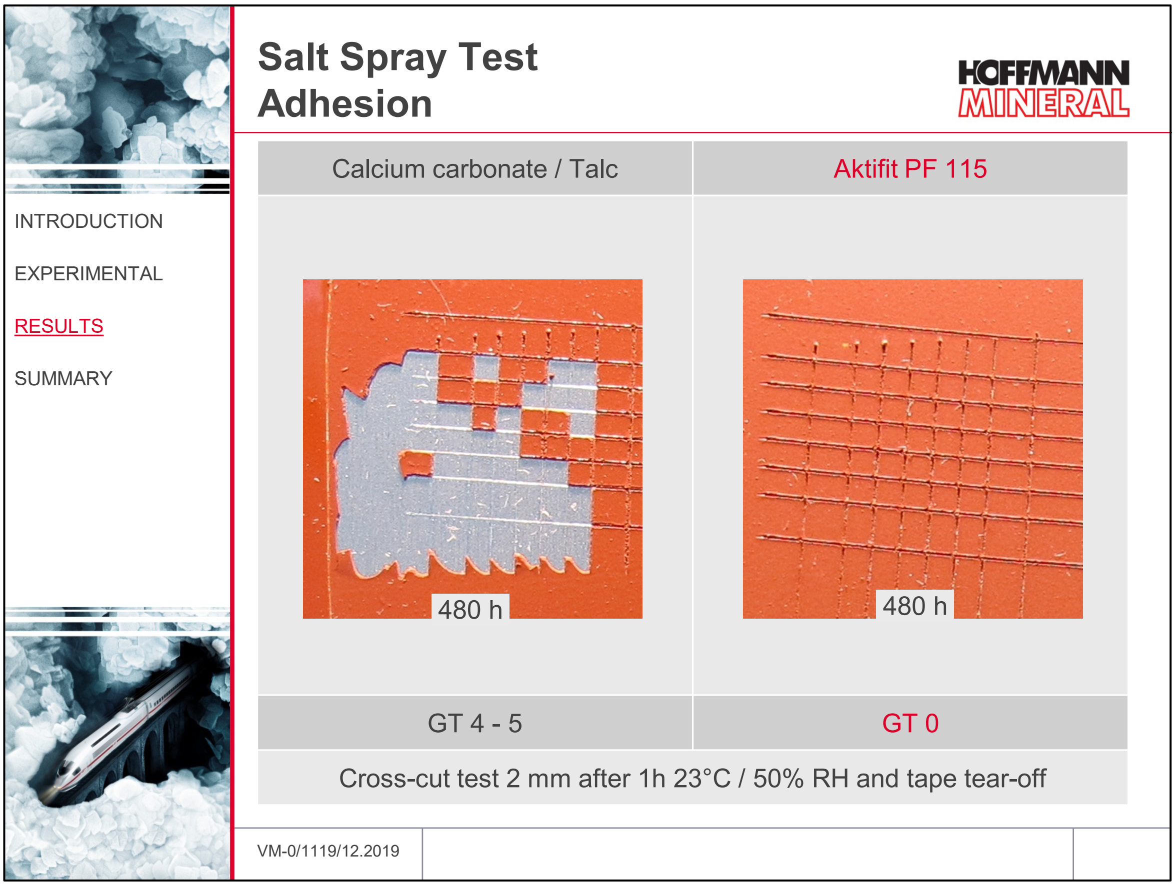
3.5 Salt spray test

3.5.1 Adhesion

The conditions in the neutral salt spray test make the necessity for the correct choice of filler even clearer. Due to the high sodium chloride electrolyte content of the test medium, strong water absorption and visible swelling of the coating film are avoided.

For the control formulation, the adhesion test with a cross-cut rating of GT 4-5 leads to an unsatisfactory result (*Fig. 13*, left). Problems of poor intercoat adhesion are not apparent, but the protective coating film is easily and almost completely removed by the adhesive tape.

In contrast, the variant with Aktifit PF 115 withstands the mechanical tear-off test much better and achieves maximum adhesion performance.



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Salt Spray Test
Adhesion

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Calcium carbonate / Talc	Aktifit PF 115
480 h	480 h
GT 4 - 5	GT 0

Cross-cut test 2 mm after 1h 23°C / 50% RH and tape tear-off

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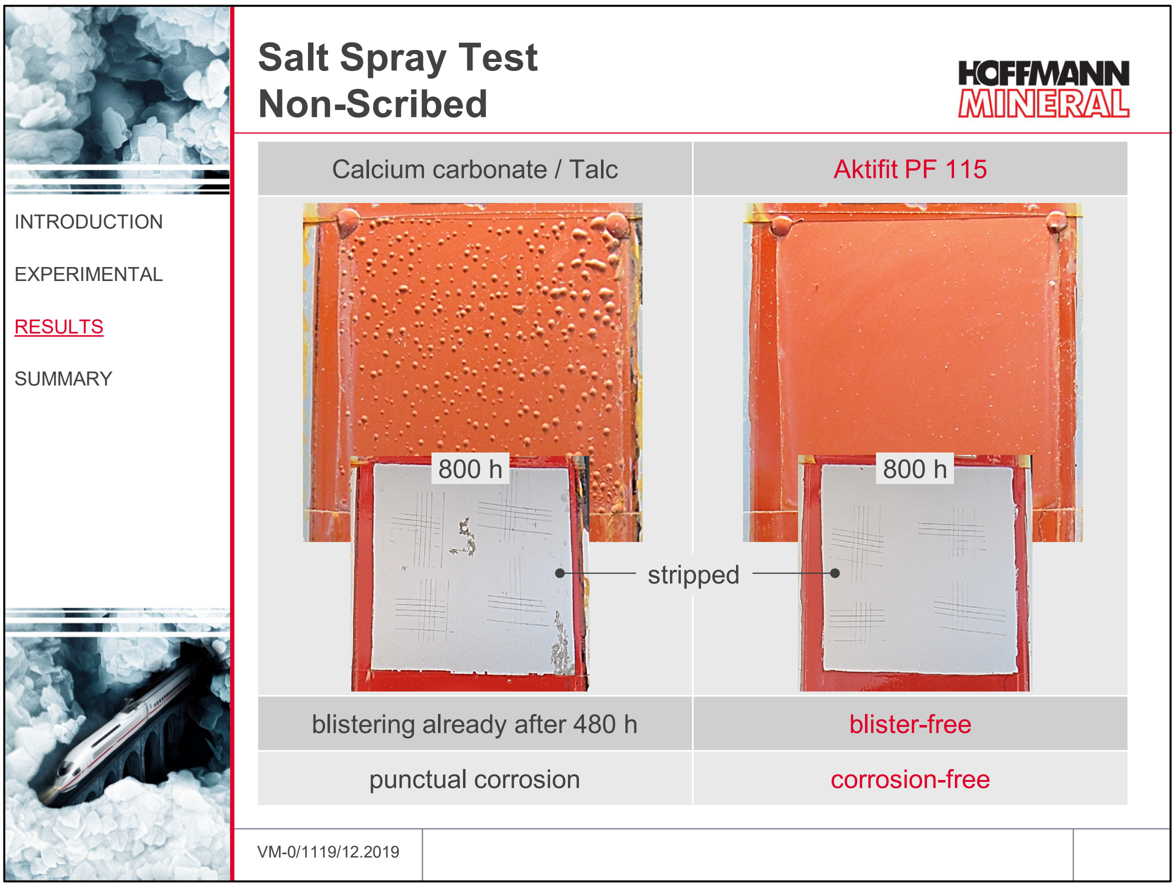
Fig. 13

3.5.2 Protection in non-scribed area

In corrosive salt spray, the performance of non-scribed coatings proves to be visibly more resistant than under water condensation in the humidity test.

Initial losses in performance occur in the control formulation after 480 h in the form of local blistering, which rapidly increases. After 800 hours of testing, the damage pattern is already present over the entire surface as shown in *Fig. 14*. The first areas of corrosion on the stripped substrate demonstrate the weakening and damage to the barrier against corrosion-promoting substances.

With Aktifit PF 115, the coating remains completely intact both optically and functionally even after 800 hours. This hydrophobic filler on base of Neuburg Siliceous Earth prevents the formation of blisters and the metallic substrate is still optimally protected against corrosion after the test period has expired.



Salt Spray Test
Non-Scribed

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Calcium carbonate / Talc	Aktifit PF 115
blistering already after 480 h	blister-free
punctual corrosion	corrosion-free

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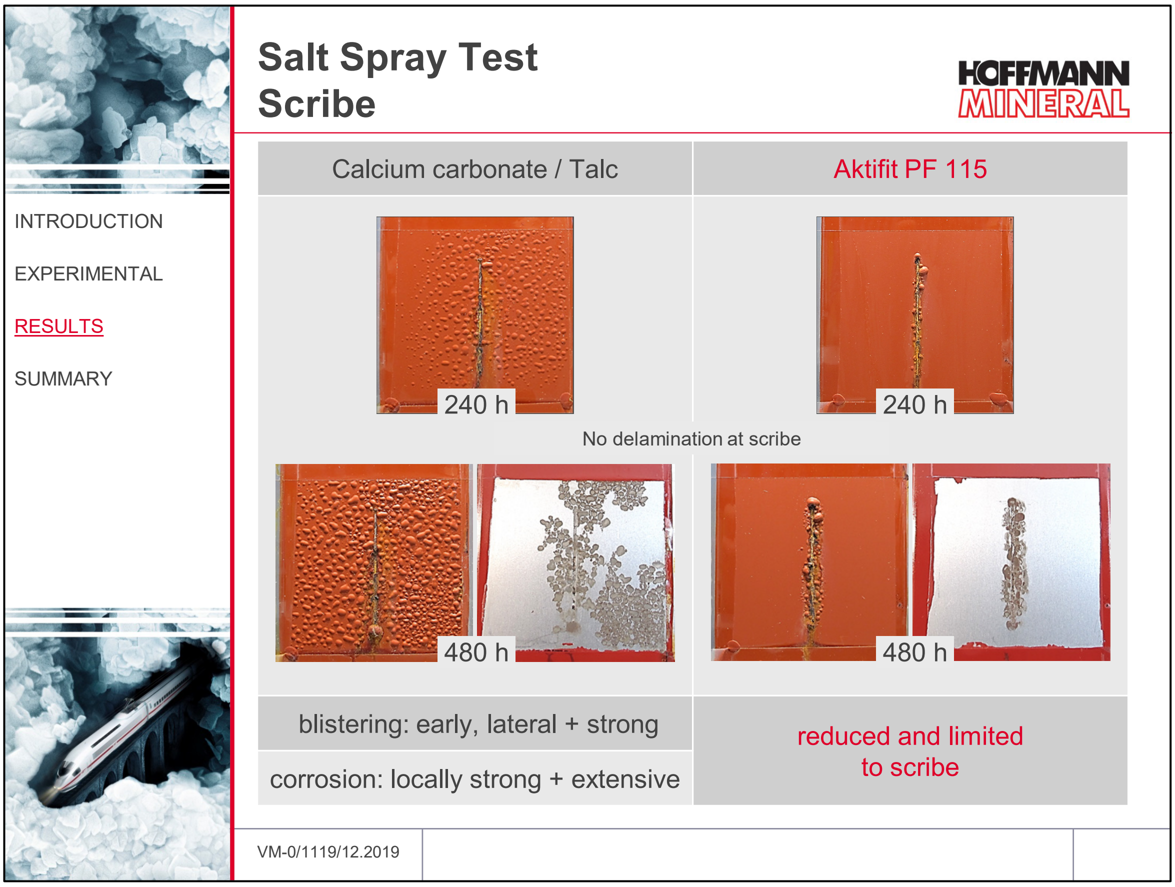
Fig. 14

3.5.3 Protection after scratching the surface

Completely different conditions arise when the coating film is exposed to mechanical damage, which is simulated in the laboratory by applying a defined scribe. Using a scratch stylus according to Sikkens, the coating films were therefore scribed over a length of 6 cm up to the metal substrate, thereby locally canceling the protective effect of the previously closed coating film.

The effects on the resistance are shown in the salt spray test to be significantly dependent on the selection of the suitable filler:
In the version filled with calcium carbonate and talc, the scribe becomes an early starting point for rapidly progressing, massive blistering. This circumstance prematurely undermines the barrier function of the entire adjacent surface, which would still be present at this point in time if non-scratched. The poor adhesion behavior is probably partly responsible for the penetration of further water and corrosion products of the electrochemical reaction starting from the scribe along the coating/substrate interface. Correspondingly, partial areas with strong corrosion of the underlying metallic substrate result, as the stripped test sheet in *Fig. 15* displays.

The formation of a separate delamination area by loss of adhesion at the scribe could not be observed on any of the test sheets.



Salt Spray Test
Scribe

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Calcium carbonate / Talc	Aktifit PF 115
240 h	240 h
No delamination at scribe	
480 h	480 h
blistering: early, lateral + strong corrosion: locally strong + extensive	reduced and limited to scribe

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Fig. 15

Aktifit PF 115 counteracts both the strong blistering and their lateral progress and limits the corrosion damage to the actual scribe area. The barrier effect of the surrounding surface remains intact and the substrate is protected against progressive corrosion.

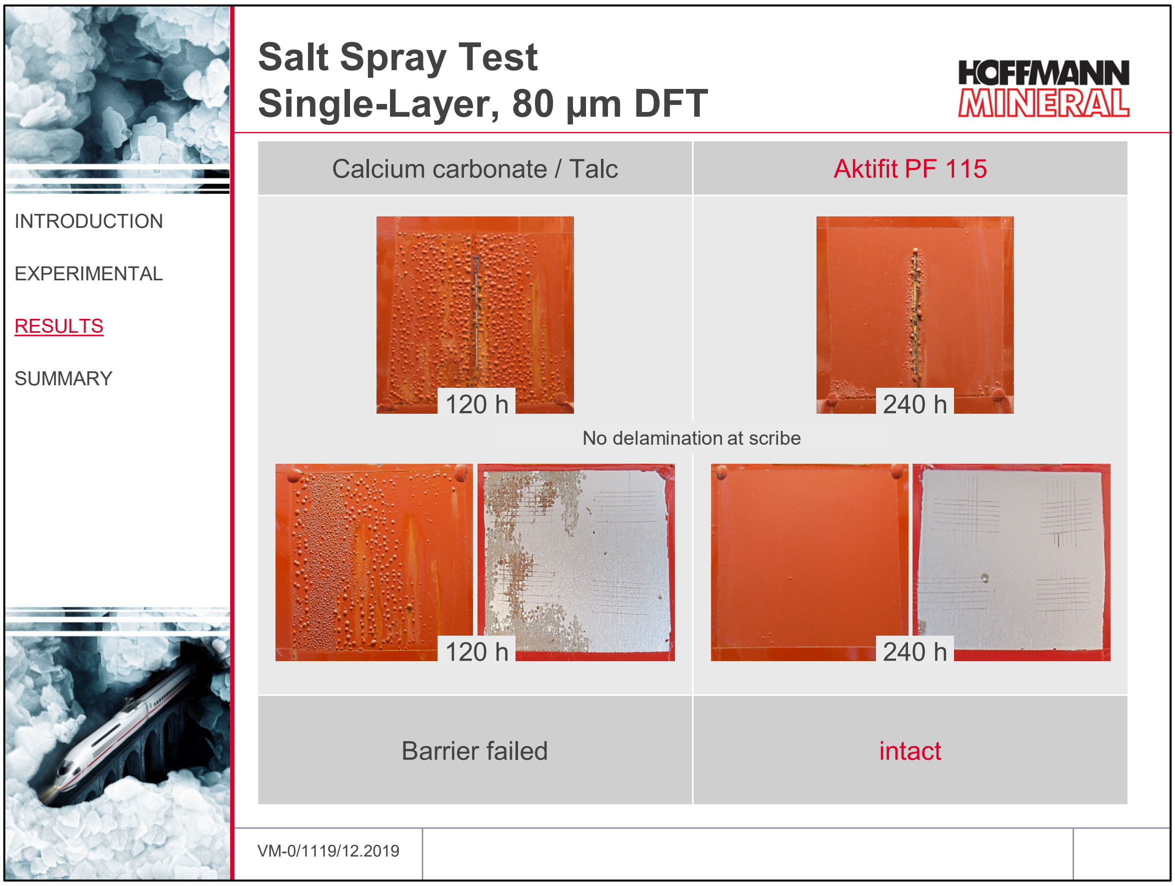
The very positive results with the functional filler Aktifit PF 115 led to the decision that further tests should also be carried out in spray-coated monolayers with reduced film thickness.

3.5.4 Performance in single-layer coating

The effects already described above were confirmed in both corrosion tests in the single coat, which is much more critical with regard to the protective effect. Exemplarily, the results of the salt spray test are illustrated in *Fig. 16* below.

The approximate halving of the dry film thickness to 80 µm has a diametrical effect on the resistance and temporal protective effect of the control fillers. Consequently, a damage pattern comparable to the two-layer coating with strong blistering and corrosion becomes visible early after 120 h. In a similar way, the non-scribed test panel fails prematurely under the salt spray load.

Aktifit PF 115 offers a much better result than the control fillers, even after an extended exposure time. Despite the greatly reduced layer thickness, the performance with Aktifit PF 115 hardly decreases. It is even higher in the single layer than the original performance of the control in the double layer (see *Fig.15*, page before). Blistering again occurs only in the immediate area of the scribe. Because of the well-integrated filler and its hydrophobicity, the surrounding coating area is strengthened in its protective function for the metallic substrate to such an extent that the technical lifetime of the coating can be more than doubled.



Salt Spray Test
Single-Layer, 80 µm DFT

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Calcium carbonate / Talc	Aktifit PF 115
120 h	240 h
No delamination at scribe	
120 h	240 h
Barrier failed	intact

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Fig. 16

4 Summary

Suitable, surface-treated Neuburg Siliceous Earth improves the performance of the present acrylic corrosion protection primer. Compared with a filler combination of fine, natural calcium carbonate and talc, the calcined and hydrophobic Neuburg Siliceous Earth grade Aktifit PF 115 is recommended preferably by the following properties:

- Lower viscosity and better stability under storage
- Higher wet adhesion and intercoat adhesion in humid and ionic environments
- Significant improvement in resistance to blistering and surface corrosion
- Strongly inhibited corrosion progress after coating damage

The optimized barrier properties with Aktifit PF 115 offer

- VOC-compliant corrosion protection based on only a single filler
- Doubling the duration of protective effect without loss of technical performance
- Coating thickness reduction for more material, time, energy and cost savings
- Leave out one layer: Strong performance even for economical, noticeably more critical single coat

Aktifit PF 115 proves to be the ideal partner within the complex film forming process, which lays the foundation for good corrosion protection in advance. Without the need for a filler combination, but equipped with the synergy of high hydrophobicity and good adhesion properties, Aktifit PF 115 can more than compensate for the weaknesses still occurring in waterborne coatings when using conventional fillers. The plus in performance not only offers enhanced, longer corrosion protection, but also contributes to more environmentally friendly, material-saving and economical coating methods in metal protection.

Whether the filler effects described above can also be advantageously extended to the much-noticed area of DTM corrosion protection was examined in further investigations. In such applications, the known protection requirements of the classic multilayer system must be bundled in a single coating layer and, in addition, sometimes meet aesthetic requirements. The results are the subject of the technical report "*Neuburg Siliceous Earth in Water-based Corrosion Protection Acrylate Single-layer White* ". In this clearly different binder and formulation, the likewise hydrophobic Aktifit Q achieves the best results.