Neuburg Siliceous Earth

in high solid epoxy coatings for

heavy duty corrosion protection

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1 Introduction

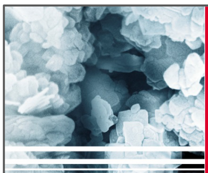
Functional fillers, along with selected binder systems and anti-corrosion pigments, today play an important role by contributing to the protection of metals with organic coatings. The multitude of the fillers offered, and the different surface treatment methods offer starting points to develop ever better performing formulations. While in earlier times predominantly conventional formulations with high solvent content were used, present-day developments are preferably directed towards aqueous or solvent-free systems. Such studies are being pushed by intense efforts to limit the emission of volatile organic compounds, as stipulated in the European VOC Directive. The use of high solids coatings represents an appropriate step in this direction, because the lower solvent content results in reduced emission of volatile compounds.

The objective of the present study is the assessment of the property profile of functional fillers in a typical High-solids coating. Based on the example of Neuburg Siliceous Earth, filler effects are followed in a two-part epoxy resin anti-corrosion formulation in comparison with talc and barite, two fillers well established in corrosion protection. In particular, it is intended to demonstrate the effects of an organic modification of the NSE filler surface with silanes. With respect to Neuburg Siliceous Earth the performance of the untreated base product Sillitin Z 86 and the surface-modified (coated) types Aktisil AM and Aktisil PF 777 will be presented and evaluated.

2 Experimental

2.1 Fillers

The fillers tested represent just a small fraction of functional fillers used in paints and coatings. However, talc and barite are very common fillers in anticorrosion coatings. Some of the most important characteristics are compiled in *Tab. 1*.



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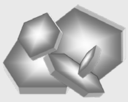
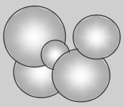
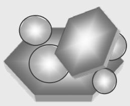
Filler Characteristics

HOFFMANN MINERAL

Filler	Morphplogy	Particle size [µm]		Surface area	Oil absorption	Density
		d_{50}	d_{97}	[m²/g]	[g/100g]	[g/cm³]
Talc		6.8	18	5	45	2.8
Barite		4.3	15	1	15	4.2
Neuburg Siliceous Earth (NSE)		1.8	8	12	50	2.6

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Tab. 1

Talc as a layered magnesium silicate is characterized by a pronounced plate-like, lamellar structure of its primary particles. Barite, the natural form of barium sulfate, offers a simplified corpuscular grain shape.

The unique morphology of Neuburg Siliceous Earth is due to its composition as a natural combination of corpuscular Neuburg silica and lamellar kaolinite. By means of different geologic processes both minerals sedimented 80 million years ago forming a loose structure which cannot be separated by physical methods.

The particle size distributions were measured by laser light diffraction, and for talc indicated a mean particle size of 6.8 µm. Barite and especially Neuburg Siliceous Earth showed lower figures. The high density of barite along with compact particle structure is reflected in low oil absorption and low specific surface area. Neuburg Siliceous Earth is distinguished by a markedly higher specific surface area as compared with the reference fillers. The oil absorption and density are in the range of the talc.

2.2 Surface modification

With the aim of improving the performance properties of the fillers, Neuburg Siliceous Earth is chemically aftertreated by the methods illustrated in *Fig. 1*. The electron microscope photograph again gives evidence of the lamellar structure of the kaolinite which partly occurs in stacks, and of the naturally aged rounded grain shape of the silica portion.

The modification is obtained with different alkoxy silanes. Via hydrolysis of the alkoxyl groups and reaction with the silicate hydroxyl groups, chemical bonding can be achieved onto the inorganic filler surface. In total, by these reactions the filler will become more organophilic which tends to improve wettability and integration into the polymer matrix. In addition a reaction of the amino groups with the binder will take place with formation of covalent chemical bonds. Such a coupling action cannot take place with Aktisil PF 777. However, the filler surface will be changed to strongly hydrophobic.

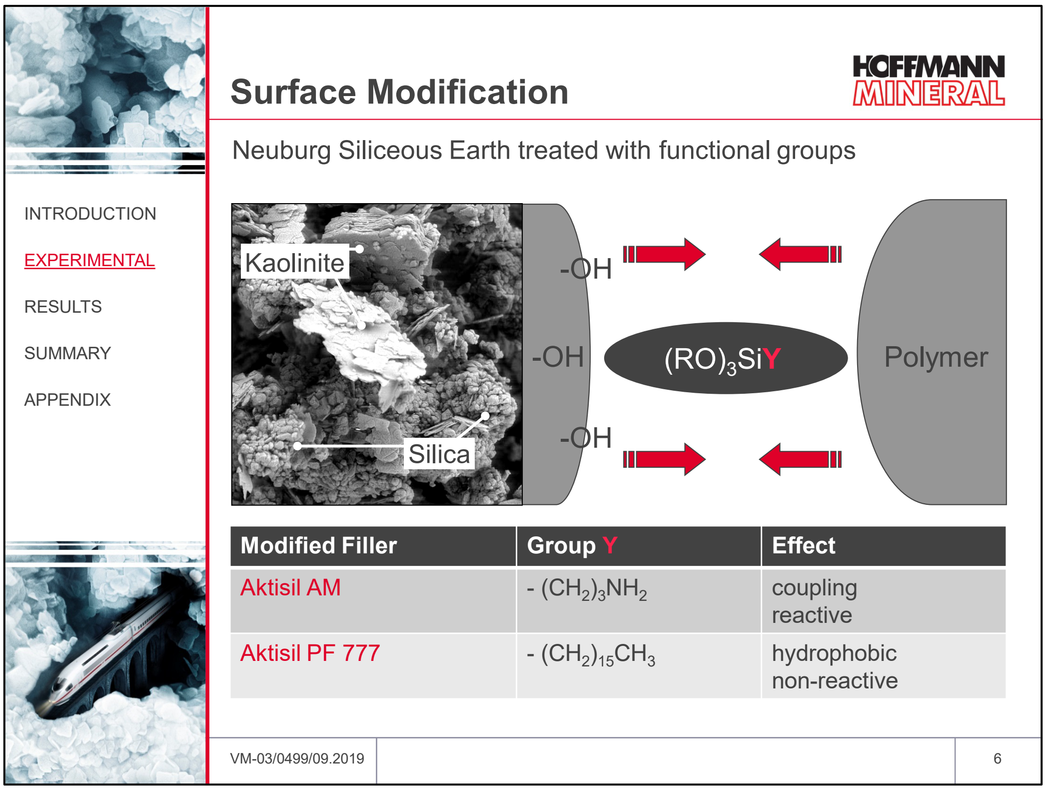
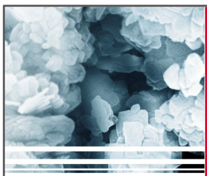


Fig. 1

2.3 Formulations

Tab. 2 shows the composition of the two-part anti-corrosion primer based on a guide formulation issued by Huntsman Advanced Materials (formerly Vantico). The solids content of 85 % and the VOC content of approximately 250 g/l give evidence of the low solvent character of the formulation.



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Base Formulation

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			Parts by weight
A	Araldit GZ 7071/75X	Solid epoxy resin based on bisphenol A, disssolved 75 % in xylene; EEW 635	178
	Araldit GY 783	Reactive-diluted epoxy resin on basis bisphenol A/F, EEW 190	134
	n-Butanol	Solvent	54
	Byk 057	Antifoam / deaeration agent, silicon-free	5
	Luvotix P 25 X	Rheology modifier	1
	Bayferrox 222	Red pigment, synthetic alpha-Fe_2O_3	49
	Zinc phosphate ZP10	Trizincbis(orthophosphate)	73
	Talc	Hydrated magnesium silicate	244
	Barite	Barium sulfate natural	98
B	Aradur 450	Preparation based on a modified Polyamidoamine adduct, HEW 115	111
	Shellsol A	Solvent, 80% aromatics	53
Total			**1000**
Solids Content [w/w %]			85
PVC [%]			29
VOC [g/L]			250

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Tab. 2

The study included, at constant Pigment Volume Concentration (PVC), the variation of the composition of the fillers, which make up 17 % by volume of the total formulation. The volume portion of the active anti-corrosion pigment represents 3 % of the total formulation. The starting point is a blend of the reference fillers talc and barite, which were originally used in a volume ratio of 79 : 21 in the system (*Fig. 2*). In a first variation, talc and barite were replaced by Neuburg Siliceous Earth. In further trials, Neuburg Siliceous Earth was tested in a blend with low amounts of talc and barite respectively. Finally, analogue formulations with identical volume filler composition were included with replacement of the anti-corrosion pigment.

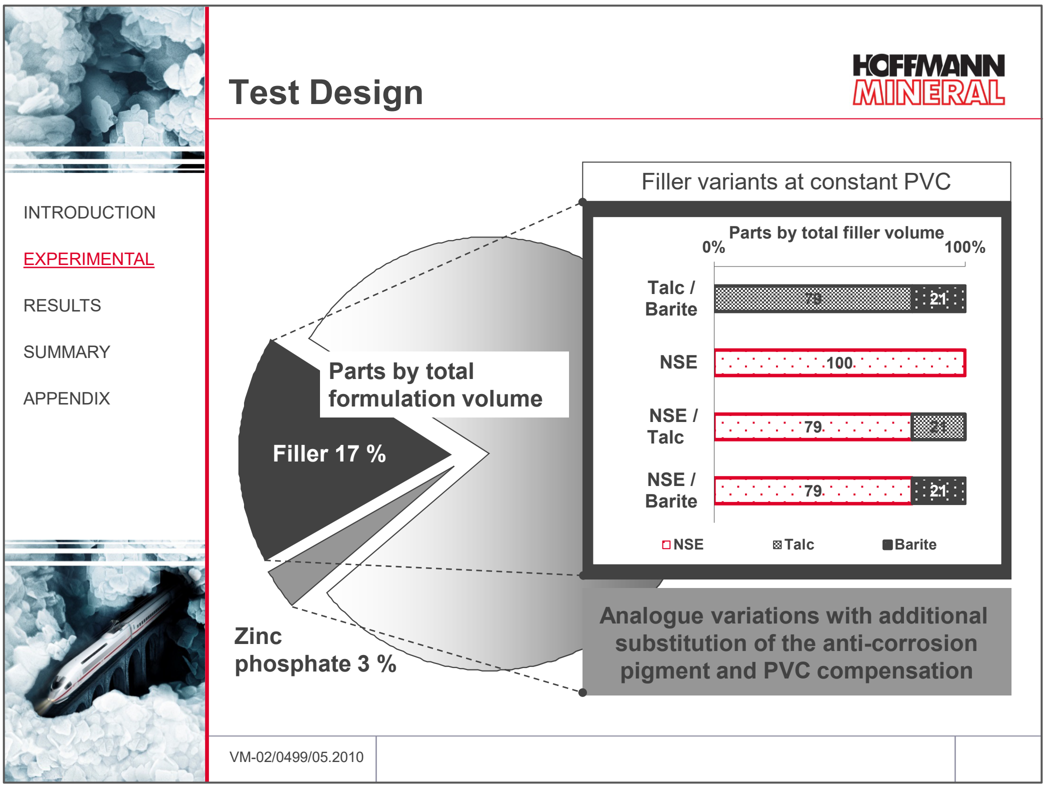


Fig. 2

2.3 Preparation, application and testing

Preparation, application and tests were carried out for all formulations in the same manner according to detailed information listed in *Fig. 3* and *Fig. 4*. All tests followed pertinent standards. In order to better assess the resistance to neutral salt spray fog, the study also includes films with a lower dry film thickness of approx. 130 µm.

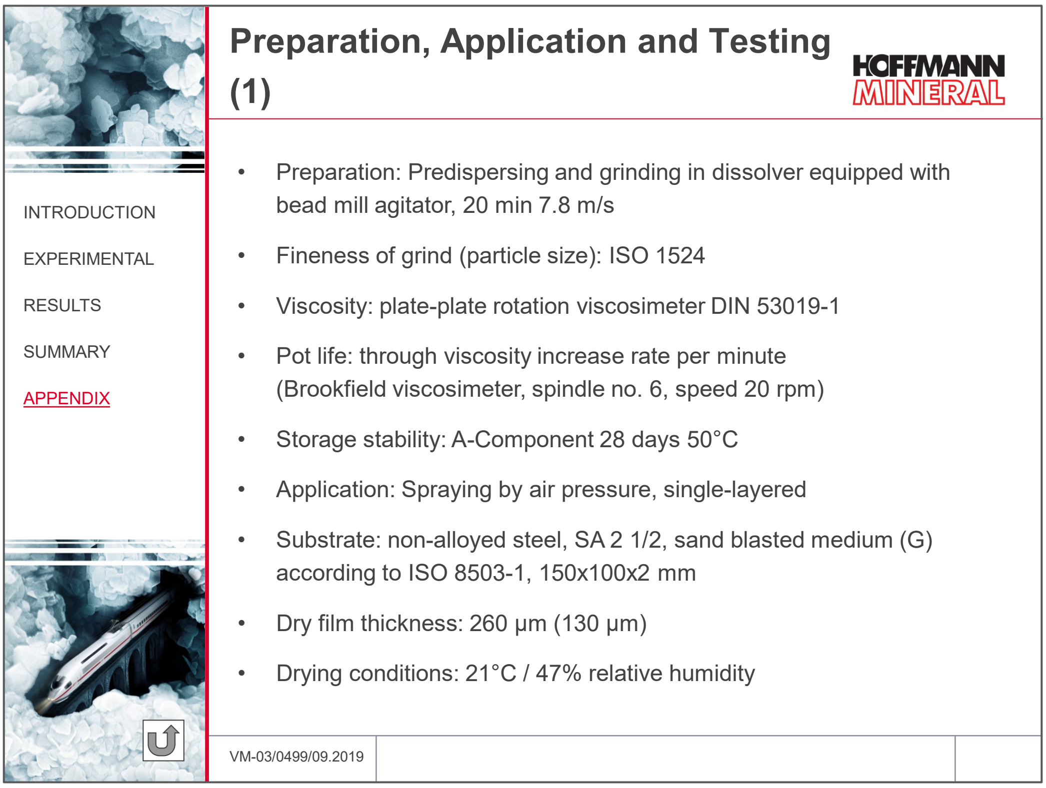


Fig. 3

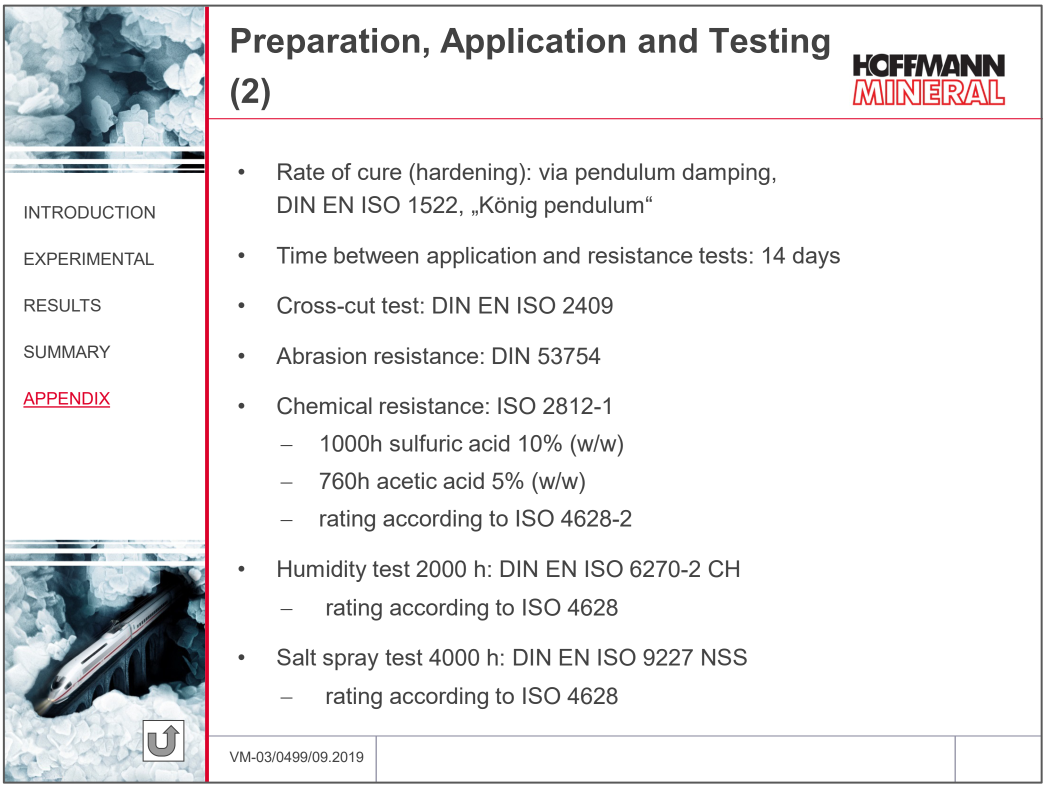


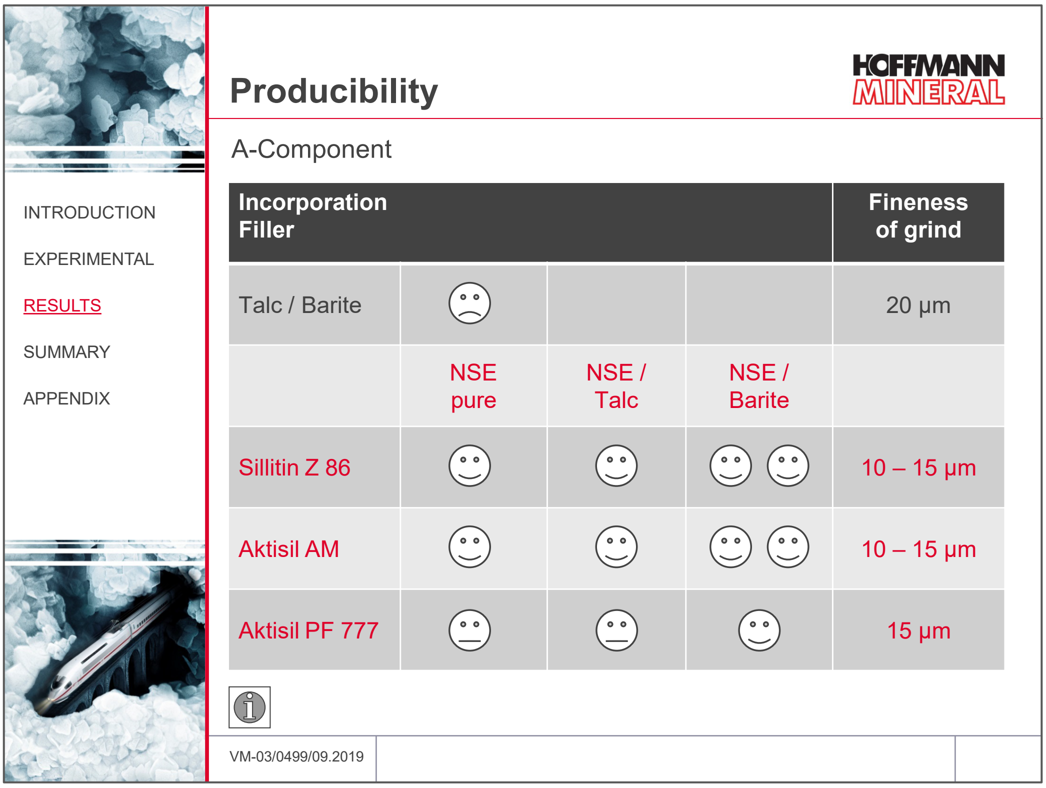
Fig. 4

3 Results

3.1 Processing properties

Producibility

Significant filler effects already became evident during the preparation of the formulations. A high amount of the hydrophobic talc in conjunction with the barite was difficult to incorporate and took a long time. The resulting grain fineness, according to grindometer tests, remained on a level of 20 µm (*Fig. 5*). Neuburg Siliceous Earth, by contrast, allowed an accelerated incorporation with improved grain fineness, a combination with talc showed no negative effects. The combination with barite even came out positively with respect to the incorporation of the filler. As for the surface modification of the Neuburg Siliceous Earth, differences become apparent only with Aktisil PF 777. The hydrophobization of the filler tends to decrease the compatibility with the polar binder system, and consequently its wettability and dispersibility. In comparison with the other fillers studied, as a result of the somewhat inferior ease of incorporation, the grain size was slightly higher at a level of 15 µm.



Incorporation Filler				Fineness of grind
Talc / Barite	☹			20 µm
	NSE pure	NSE / Talc	NSE / Barite	
Sillitin Z 86	☺	☺	☺ ☺	10 – 15 µm
Aktisil AM	☺	☺	☺ ☺	10 – 15 µm
Aktisil PF 777	😐	😐	☺	15 µm

Fig. 5

Storage stability

Concerning the storage stability of the A-component of the formulations the talc / barite filler system generates a lot of hard sediment during testing time of 28 days at 50 °C. This effect is most evident already after a short storage time. The formulations containing Sillitin Z 86 gives delayed and reduced amount of sediment (*Fig. 6*). A combination with talc or especially barite favors the sedimentation tendency, and generates hard sediment. With Aktisil AM or Aktisil PF 777, a sedimentation of particles can be totally avoided as a result of relatively high zero-shear viscosity.

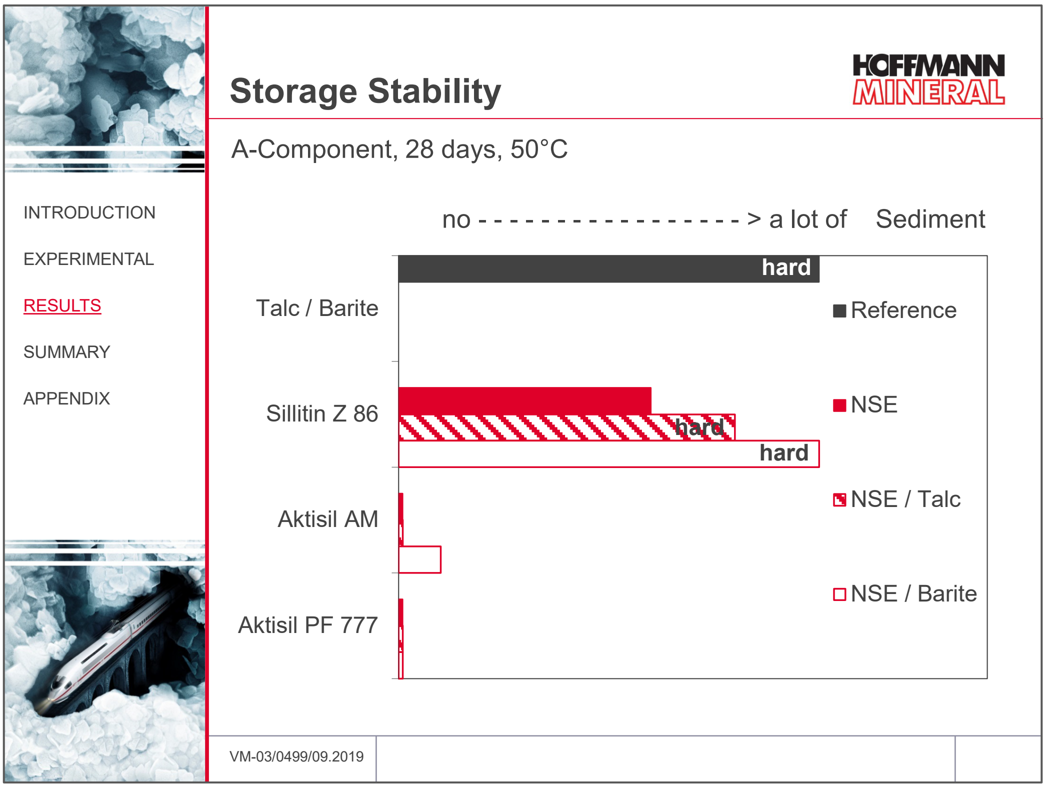


Fig. 6

Viscosity

After addition of the hardener, the formulations were checked for rheological properties (*Fig. 7*). The tests were carried out under rotation in a plate/plate rheometer. The evaluation of the viscosity curves for Sillitin Z 86 shows lower levels and close to Newton-type flow behavior in comparison to the reference fillers. The latter with a high talc portion increases the viscosity level markedly over the whole test range, with flow behavior at low shear rates indicating pseudoplasticity due to the lamellar structure of the talc. A considerably higher viscosity in the lower shear range is imparted by Aktisil AM or Aktisil PF 777. Both fillers also generate measurable yield points. With higher shear rate, however, significant shear thinning leads to a viscosity decrease to levels below the talc / barite blend.

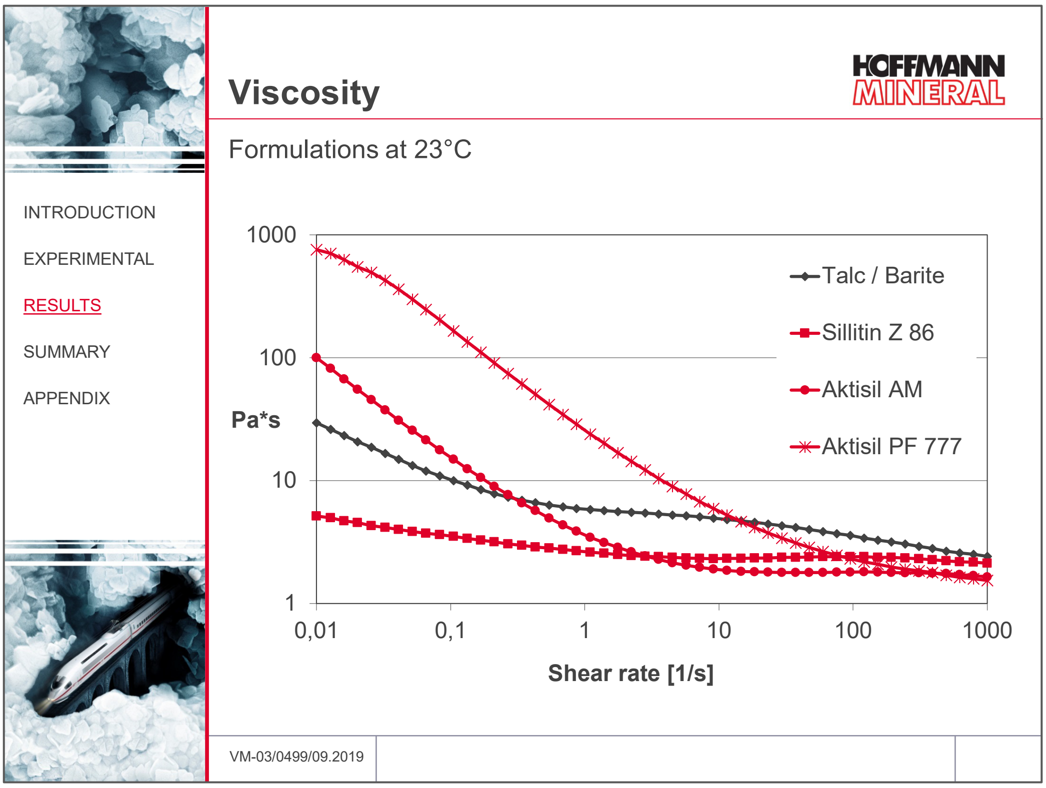


Fig. 7

Pot life

The use of a Brookfield viscosimeter at low shear strain conditions is common practice to calculate pot life. Usually the time necessary to double the original viscosity level of the formulation is regarded as pot life. In terms of the rheologic behavior of Aktisil AM and Aktisil PF 777 this would lead to disproportionately high and less meaningful results. Thus the mean viscosity increase rate per minute after hardener addition was assessed as a way to characterize pot life. According to *Fig. 8* higher figures indicate a shortened open time for coating application.

Compared with Neuburg Siliceous Earth, the use of talc and barite brings about a markedly faster rise reducing the pot life of the formulations. The accelerating effect of talc onto the viscosity increase rate is also confirmed in those cases where Neuburg Siliceous Earth is combined with talc. In contrast a portion of barite along with Neuburg Siliceous Earth has no effect.

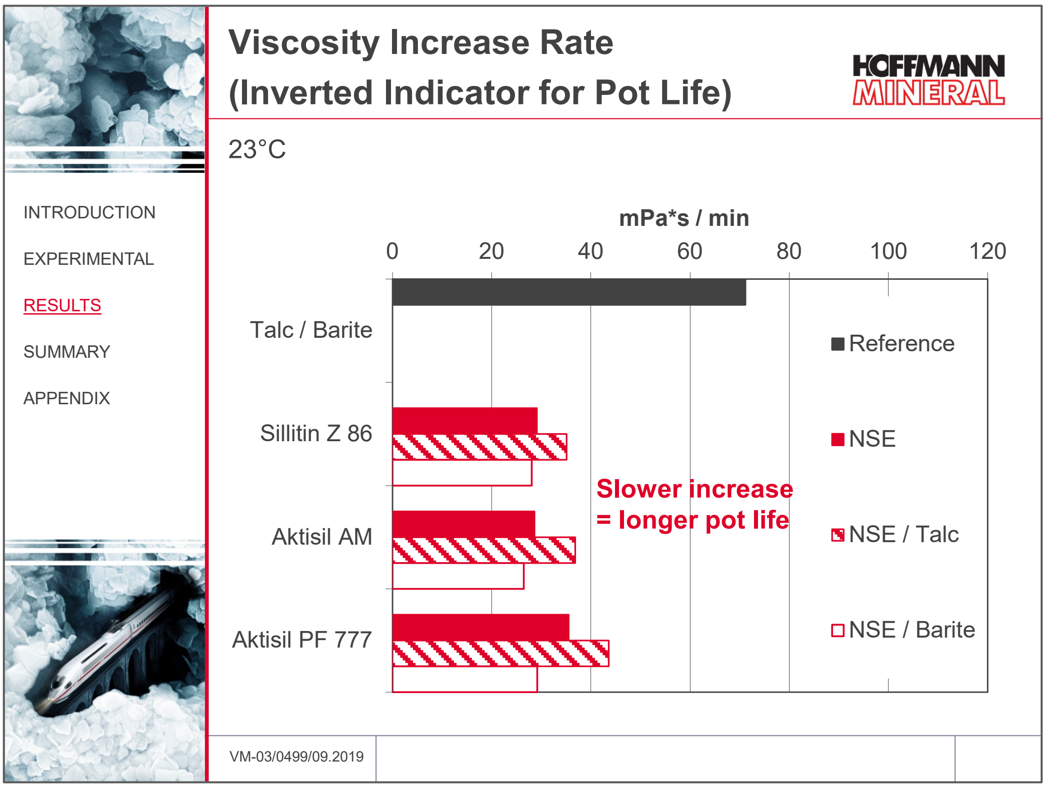


Fig. 8

3.2 Mechanical properties

Pendulum hardness

Characterizing the hardening process at room temperature, the surface modification with silanes markedly affects the mechanical properties of the coatings (*Fig. 9*). While formulations with untreated Neuburg Siliceous Earth or with the talc / barite blend give nearly the same pendulum hardness, the use of Aktisil AM leads to a more rapid hardness increase to a higher level. As a result of surface treatment, Aktisil AM is able to interact with the binder polymer via functionality of the organosilicon group, and thus favors the crosslinking process. As already discussed, such an effect has to be excluded for Aktisil PF 777, but all the same this system gives a similar level of coat hardness.

A possible reason might be the inherent modification of the original hydroxyl groups bound in the silicate through the silanization, which tend to restrain the potential competing reaction of the hardener's amino groups with the filler surface. This way, the effective amount of hardener available for the crosslinking reaction would be increased, as well as the crosslink density.

A combination of Neuburg Siliceous Earth with talc or barite does not give rise to noticeable changes in the coating hardness.

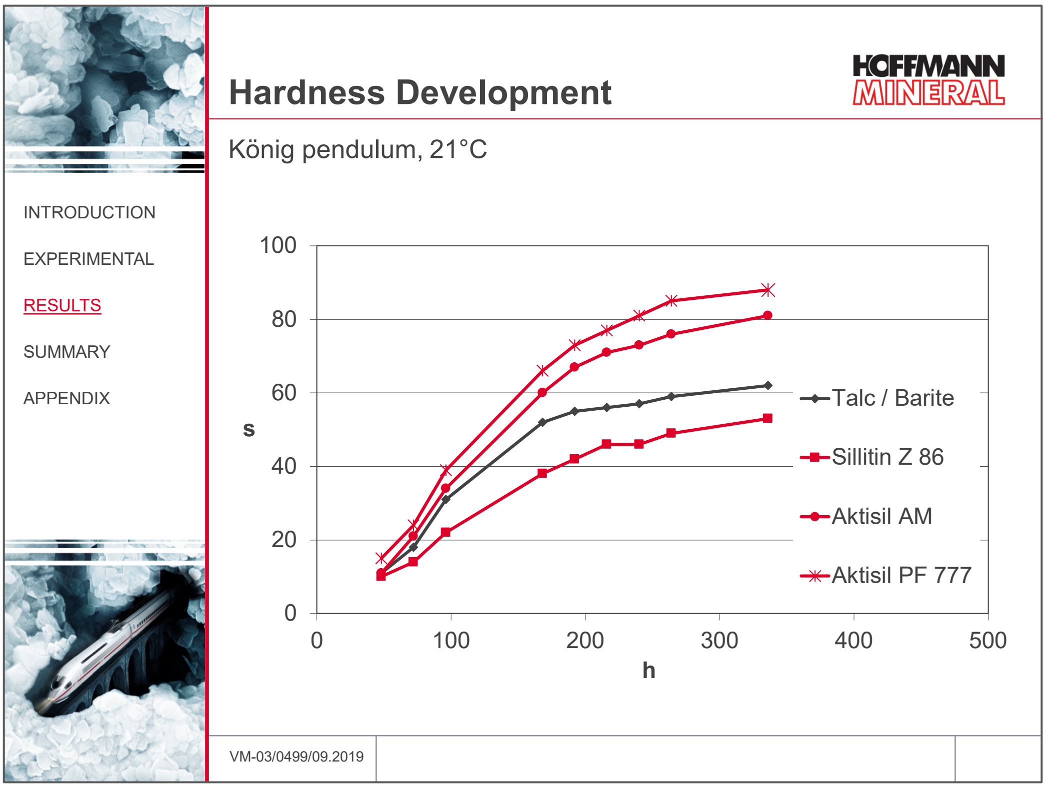


Fig. 9

Adhesive Strength

The adhesive strength of the coatings was determined by 3 mm cross-cut adhesion test according to ISO 2409. Due to the good substrate adhesion of the talc, the best results were obtained with the talc / barite blend (*Fig. 10*). All variations on basis Neuburg Siliceous Earth attained slightly lower adhesive strength but with a rating of 0 to 1 fulfill the requirements of ISO 12944 (Corrosion protection of steel structures by protective paint systems).

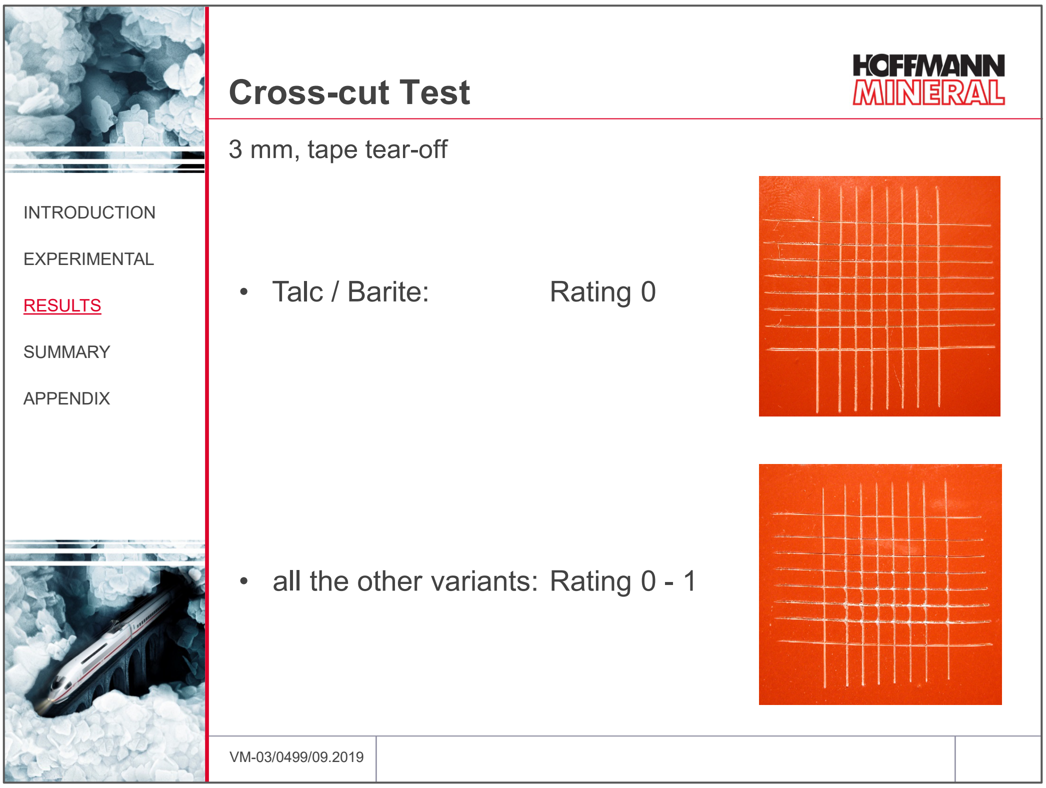


Fig. 10

Abrasion resistance

Abrasion properties were determined in an abrader wheel test (Taber) by abrasive paper type S-42 according to DIN 53754. This method measures the abrasive loss of the coating surface under defined grinding conditions. The higher the abrasion loss, the poorer the wear resistance of the coating. The results are presented in *Fig. 11*.

In the talc / barite formulation, the portion of the fairly soft talc under the test conditions gives rise to a high abrasion loss of 250 mg per 100 revolutions. Neuburg Siliceous Earth, even the untreated base material Sillitin Z 86, is able to reduce this loss figure by up to 50 %. Even in a combination with a portion of talc or barite similar results are obtained. Only modification with alkyl silane tends to reduce the abrasion resistance. The poorer compatibility of Aktisil PF 777 with the binder system, as well as the absence of a reinforcing effect of the hydrophobic filler surface appear to favor the abrasion process: filler and pigment particles can be detached more easily from the coating, in particular in the additional presence of talc.

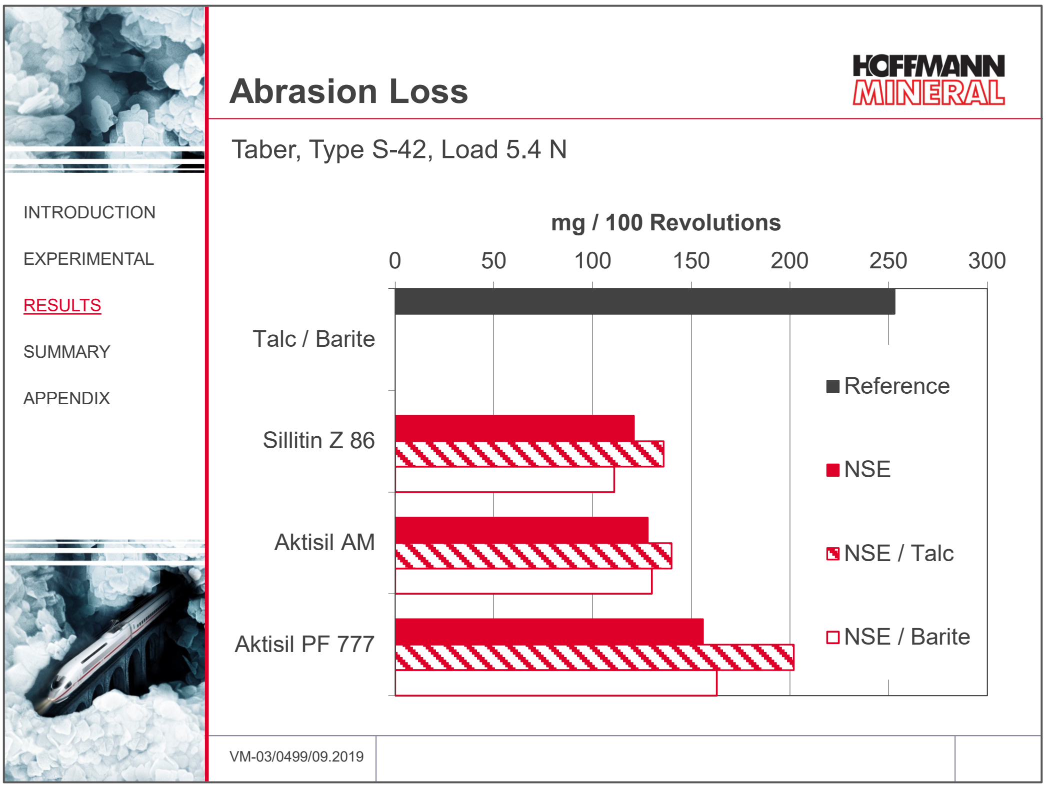


Fig. 11

3.3 Acid resistance

For assessment of the chemical resistance of the coatings, their response was tested by immersion in diluted sulfuric acid as well as acetic acid in accordance with ISO 2812-1.

Sulfuric acid

After 250 hours of immersion, the talc / barite formulation begins to show the first blisters. A similar effect is observed only after 620 hours with Sillitin Z 86 more than doubling resistance properties.

Fig. 12 shows the performance results for the coated test panels and the blister formation after 1000 h of exposure. The best resistance is obtained by Aktisil AM and Aktisil PF 777. The surface waves in the coating with Aktisil PF 777 are not caused by acid but based on the high sag resistance of the formulation after spray application. There is no evidence of blister formation, loss of adhesion or corrosion, whereas the formulation with the talc / barite blend partly peels off from the substrate.

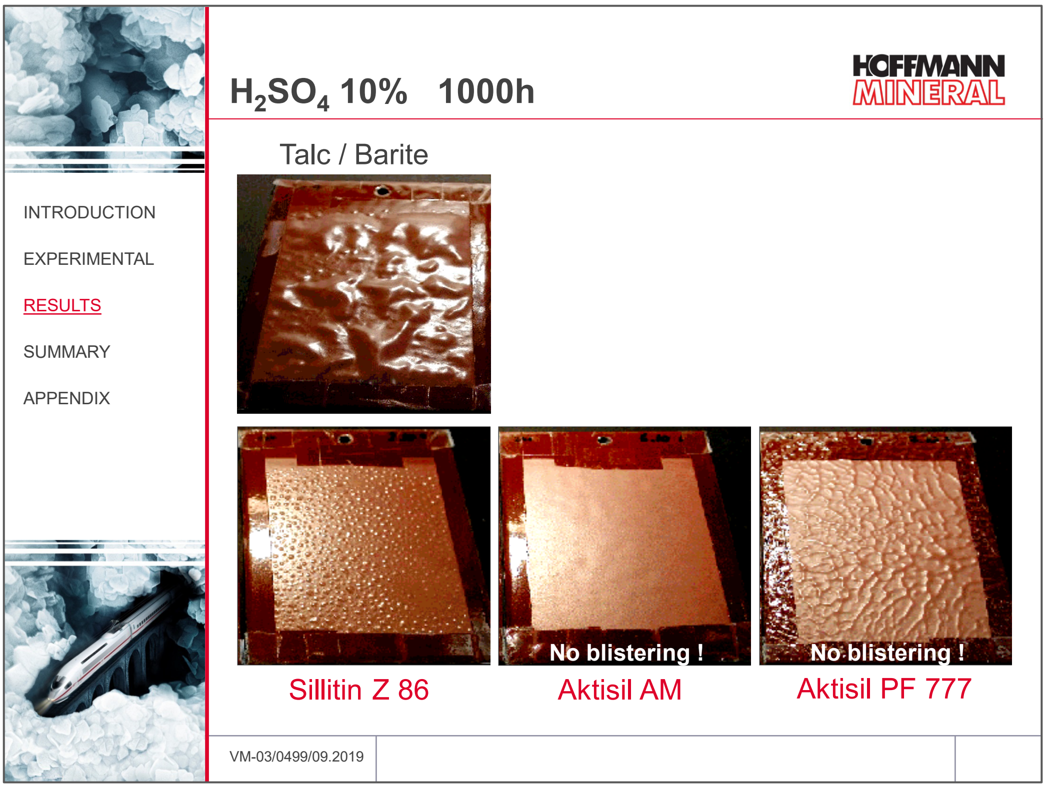


Fig. 12

Acetic acid

Compared to immersion in sulfuric acid all formulations tend to premature blistering when exposed to acetic acid for 168 h. Nevertheless, with respect to the reference fillers, Neuburg Siliceous Earth came out favorably as can be seen in *Fig. 13*.

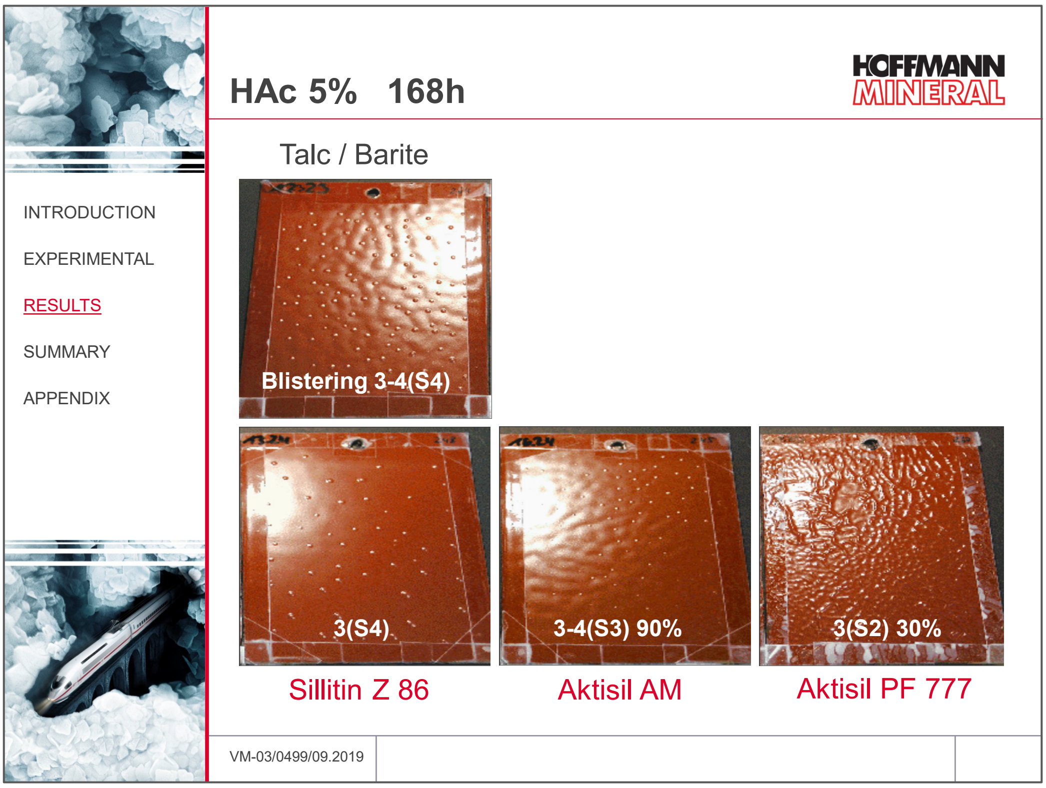
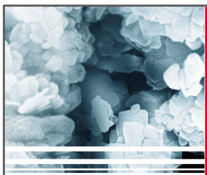


Fig. 13

For optimization, in addition to the reference hardener a formulated polyamine adduct with cycloaliphatic base amine (Variation 1) and a blend of formulated amine adducts with aromatic nature of the base amine (Variation 2) were tested and evaluated. Up to now types of the latter system are most commonly used to provide improvement of resistance to organic acids but within present-day developments have to be considered carefully because of toxic and environmentally hazardous classification.



HOFFMANN MINERAL

HAc 5%

Hardener variation

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Hardener	Characteristic	Base amine
Reference	formulated Polyamidoamine adduct	aliphatic Dimethyldiaminopropane (DMAPA)
Variation 1	formulated Polyamine adduct	cycloaliphatic Isophoronediamine (IPD)
Variation 2	Blend of formulated amine adducts	aromatic Diaminodiphenylmethane (DDM)

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Tab. 3

The test results are illustrated in *Fig. 14* and *Fig. 15*.

The use of a polyamine adduct based on IPD basically affects acid resistance positively. More than ever the choice of suitable fillers like Aktisil AM allows to reduce blistering. With the benefit of enhanced long-term protection the formulation nearly reaches the level of the reference coating cured with aromatic hardener.

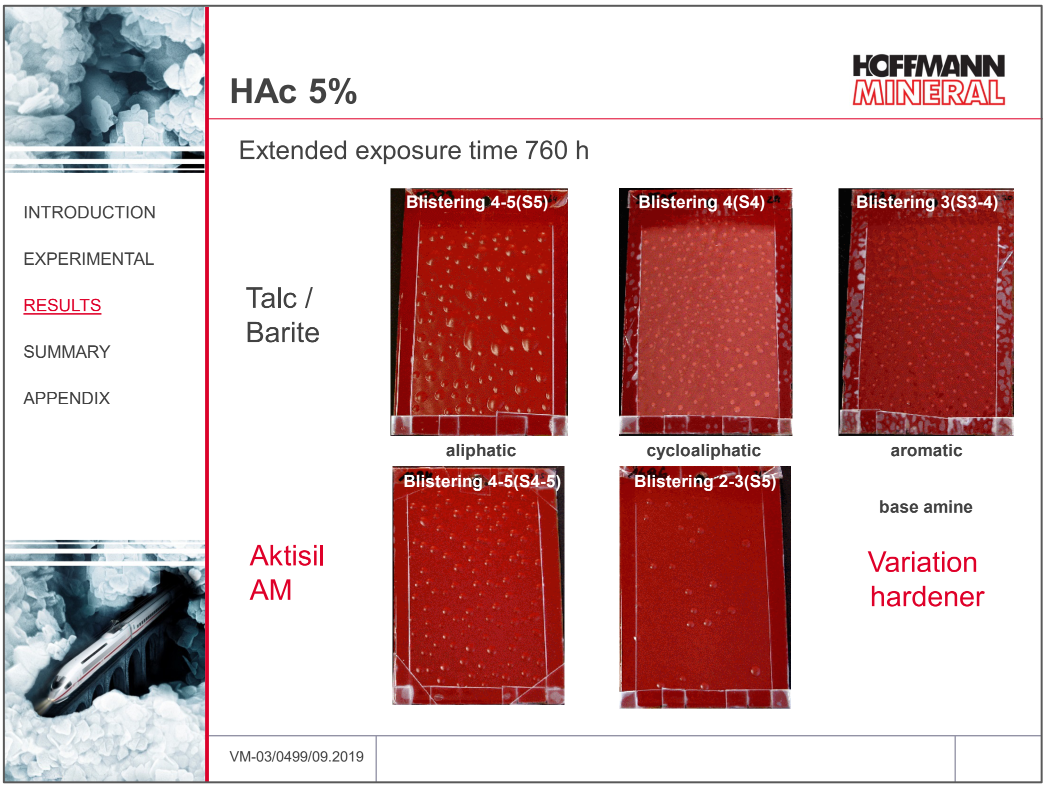


Fig. 14

Aktisil PF 777 is highlighted without any surface defects in the corresponding coating after 760 h of immersion. The reference fillers talc and barite markedly promote blistering and even with a hardener containing aromatic amines do not match the performance level of the combination Aktisil PF 777 / cycloaliphatic hardener.

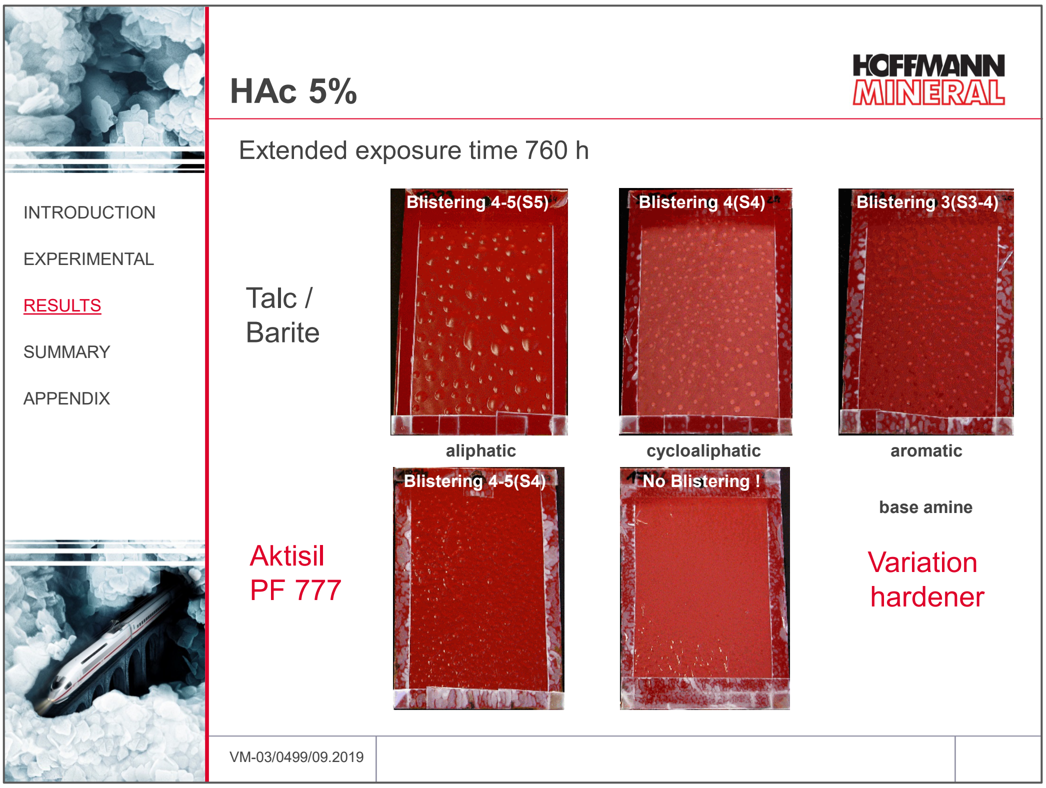


Fig. 15

3.4 Humidity test

Contrary to acid resistance, the coated test panels are not affected by exposure to condensed water. All formulations are resistant to an exposure over 2000 h to constant condensation climate conditions according to DIN EN ISO 6270-2 CH, without any defects apparent on or under the coating. In addition, coated test sheets were scratched in a defined manner with a scribe needle. After exposure, again no blister formation could be observed close to the damage area. Minor corrosion occurred only in the scribe track, and the mean rust creepage for all coatings reached max. 0.5 mm. No delamination starting from the scribe could be observed.

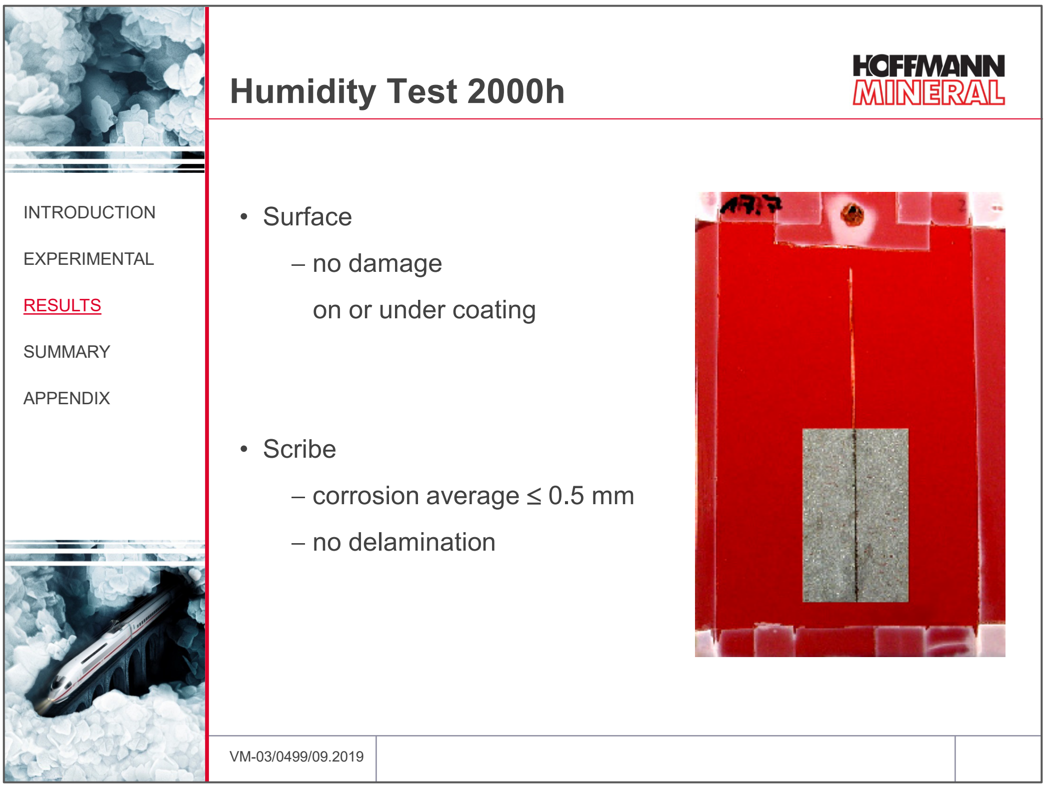


Fig. 16

After condensation exposure, coated sheets were conditioned for 24 h at 23 °C and 50 % relative humidity, in order to determine adhesion strength. The best results, with cross-cut ratings of 0.5 after adhesive tape pull-off, were obtained by coatings formulated with the talc / barite blend and Aktisil AM. The two other versions gave slightly poorer adhesion with a rating up to 1.

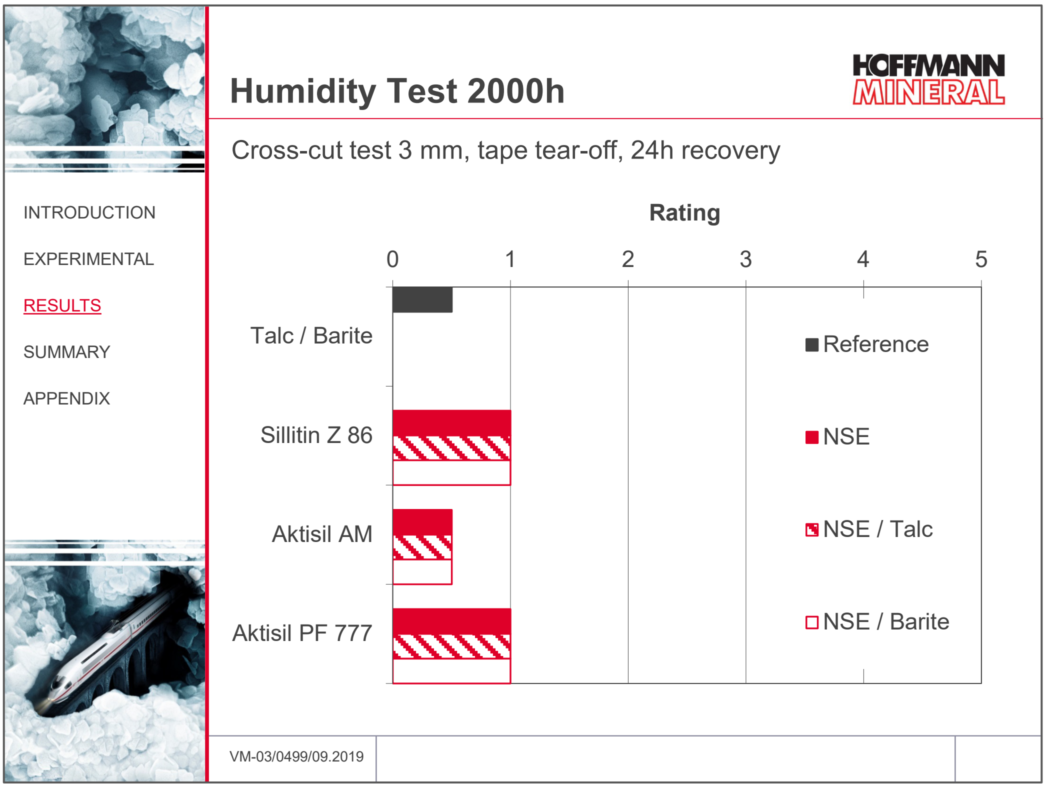


Fig. 17

3.5 Salt spray test

The exposure of all tested anti-corrosion coatings to neutral salt spray fog according to ISO 7253 did not lead to any visible defects in or below the film. There are, however, more complex effects of the electrochemical corrosion processes at the scribe. The studies showed in an early stage that, apart from the fillers, the amount of the anti-corrosion pigment markedly affects the damage incurred. This is why also the performance of formulations was studied in which the zinc phosphate at constant Pigment Volume Concentration was replaced by the fillers tested. *Fig. 18* demonstrates the corrosion defects for the reference fillers and the pure Neuburg Siliceous Earth grades.

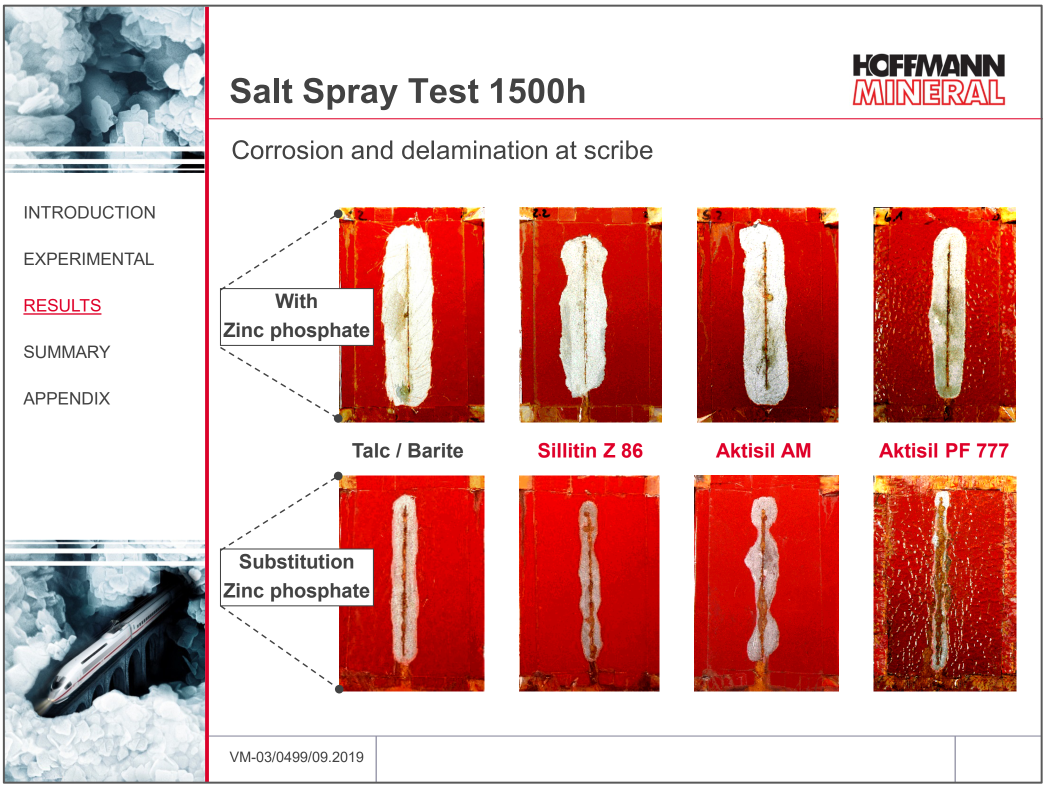


Fig. 18

According to the formulation, around the scribe an area of different width becomes exposed. This area corresponds to the corrosive delamination, where due to oxygen reduction of the cathodic step of the electrochemical process alkalination takes place with the result of reduced adhesion on the substrate. No rust formation is found here because of the passivation of the metal surface – corrosion is limited to the immediate scribe area with anodic iron dissolution. The total delamination width cannot be recognized from outside, and has to be exposed with the help of a thin knifeblade at a very flat angle. This allows the conclusion that loss of adhesion takes place, but it does not lead to complete delamination with total separation of all contact points between substrate and coating. The delamination front is sharply defined and clearly indicates the area of retained adhesion.

A more comprehensive assessment of the damage patterns is possible via direct quantitative comparison of corrosion and delamination at the scribe (*Fig. 19*). All formulations containing zinc phosphate show strong delamination but comparably little corrosion. Compared with the talc / barite blend, this effect can be minimized by using modified Neuburg Siliceous Earth grades (Aktisil). Conspicuous results are obtained when replacing the anti-corrosion pigment by fillers. Apart from the expected increase of rust formation at the scribe, delamination is markedly reduced. It looks possible that the solubility of small amounts of zinc phosphate favors the entry of water into the coating/substrate interface, and thus facilitates the advancement of the delamination during the corrosion process. A similar effect might be caused by the hydrophilic amino groups of Aktisil AM.

The coating with Aktisil PF 777 gives little evidence of delamination. The hydrophobization of the filler surface obviously provides an effective protection against the introduction of water at the filler / substrate interface.

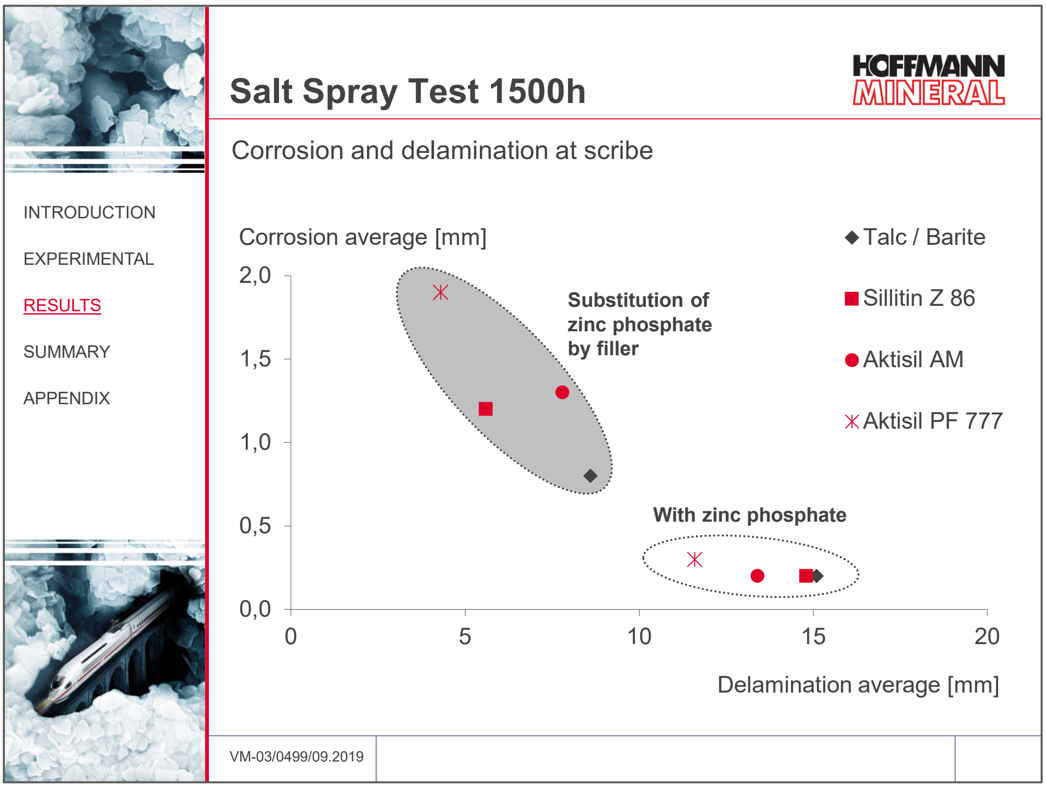


Fig. 19

The cases discussed illustrate how far the obviously reciprocal relationship between corrosion and delamination can be shifted within certain limits by functionalizing the filler surface. The strong increase in delamination due to the use of zinc phosphate becomes distinctly reduced by Neuburg Siliceous Earth without negative effect on corrosion at scribe.

The examination of the advancement of the delamination with time indicates for the talc / barite formulation a continuing strong increase even after 1000 h of exposure. The behavior of systems containing Neuburg Siliceous Earth, by contrast, shows a tendency to level off.

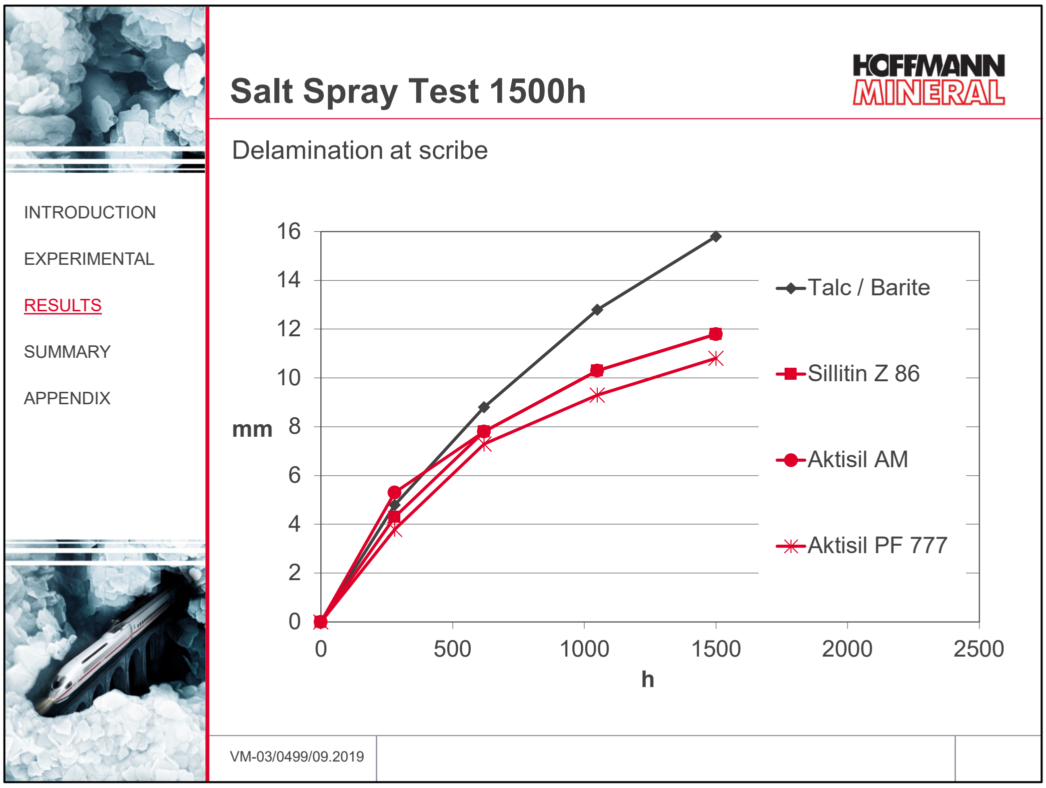


Fig. 20

Without scratching the coating surface, all undamaged polymer films after conditioning 24 h at 23 °C and 50 % relative humidity offer good adhesion with cross-cut ratings between 0.5 and 1.

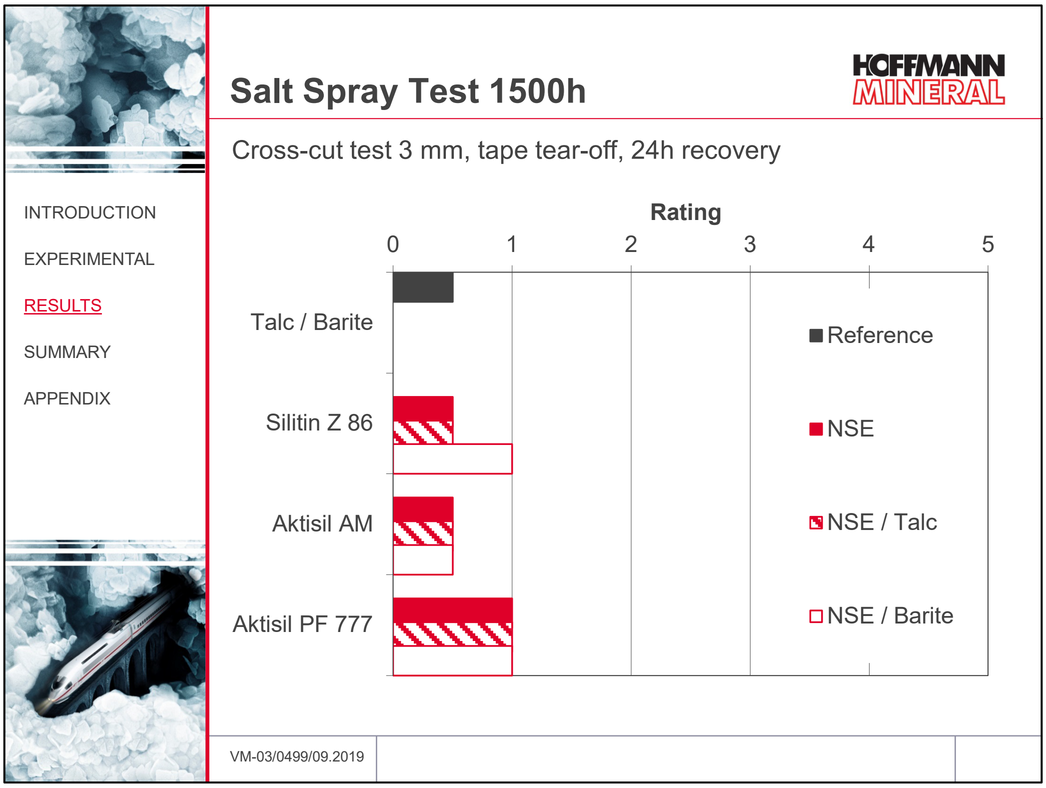


Fig. 21

For evaluation of filler performance in long-time protection further tests with extended exposure times were carried out. Besides, formulations with reduced dry film thickness (DFT) were subjected to the salt spray test. As the absence of anticorrosive pigment leads to strong corrosion at scribe, investigations were focused on formulations containing zinc phosphate.

The results are presented in *Fig. 22* and confirm the benefit of Neuburg Siliceous Earth on corrosion protection at scribe. Now, even with the untreated Sillitin Z 86 the delamination becomes markedly reduced. The overall picture remains unchanged when formulations are applied in lower film thickness.

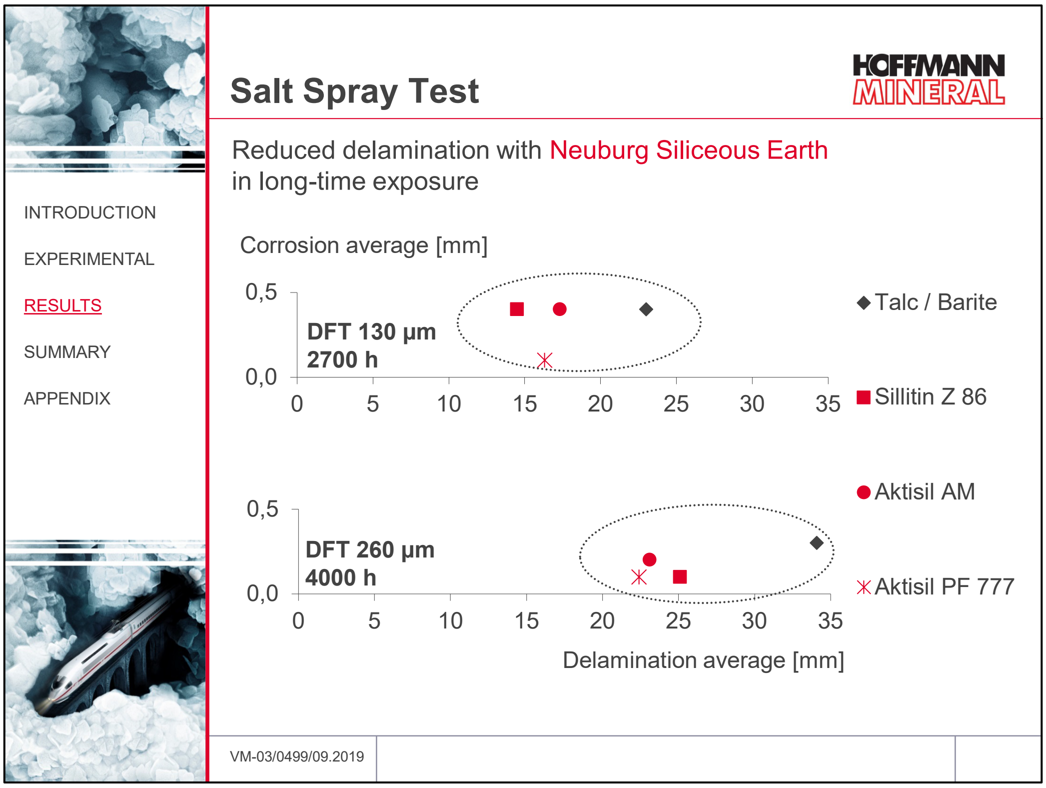


Fig. 22

3.6 Film morphology

In order to look for the cause of high delamination rate of the talc / barite formulation, scanning electron microscope (SEM) images of cross-sections of unstressed coatings were prepared. In addition the morphology of the films was subjected to elemental analysis by Energy Dispersive X-ray Analysis (EDX) to identify the local distribution of the fillers and pigments in the polymer film.

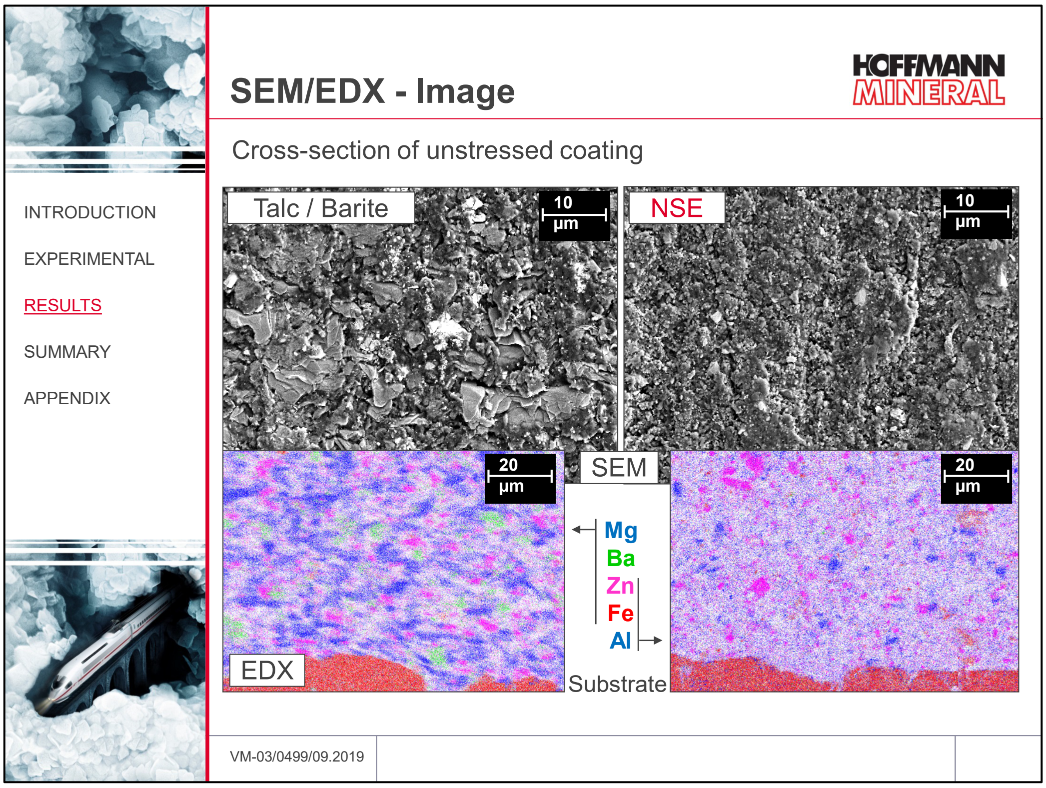
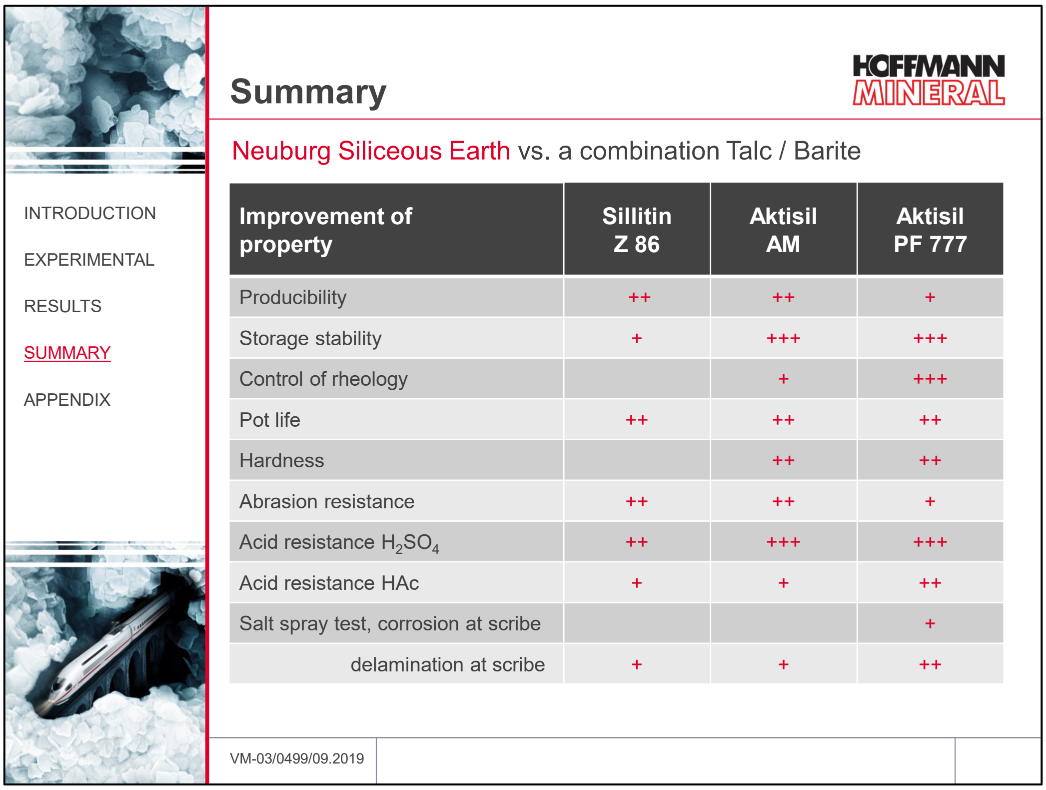


Fig. 23

In the case of the talc / barite coating a poorer embedding of the fillers was found (*Fig. 23*). The SEM micrographs exhibit a lot of single talc particles without contact to the surrounding polymer matrix. A contribution of the talc platelets (EDX, Mg signals) to passive corrosion protection via a barrier effect through fully parallel orientation relative to the substrate could not be detected. The SEM micrographs confirmed in parts a very irregular orientation pattern of the lamellar filler particles and an overall highly heterogeneous grain size distribution of the fillers in the polymer film. Micrographs of coatings with Neuburg Siliceous Earth, both for the untreated base material as well as for the functionalized grades, give evidence of a more homogenous packing density. It can be shown that due to the intense shear action during the preparation of the A-component not only the kaolinite stacks are partly broken up, but also the silica portion comes out largely disintegrated down to primary particles with sizes of 200 nm. In the EDX image, the kaolinite components of the Neuburg Siliceous Earth only present few resolvable aluminum signals; specific silicon signals of the silica cannot be detected separately due to the particles fineness. A comparison of the dispersion of the anti-corrosion and red iron oxide pigments does not show any significant differences.

4 Summary and conclusions

The investigations as presented, demonstrate on the example of Neuburg Siliceous Earth fillers how far the properties of anti-corrosion coatings can be influenced and improved in a different manner of weighting by the filler and an organic surface modification respectively. According to this, the use of untreated Neuburg Siliceous Earth grade Sillitin Z 86 inherently leads to a distinct improvement in view of producibility, pot life, abrasion resistance and acid resistance (*Tab. 4*).



Summary

HOFFMANN MINERAL

Neuburg Siliceous Earth vs. a combination Talc / Barite

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Improvement of property	Sillitin Z 86	Aktisil AM	Aktisil PF 777
Producibility	++	++	+
Storage stability	+	+++	+++
Control of rheology		+	+++
Pot life	++	++	++
Hardness		++	++
Abrasion resistance	++	++	+
Acid resistance H_2SO_4	++	+++	+++
Acid resistance HAc	+	+	++
Salt spray test, corrosion at scribe			+
delamination at scribe	+	+	++

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Tab. 4

The better dispersibility of the Neuburg Siliceous Earth fillers compared with a blend of talc and barite does not only enable a more economical production and give improved storage stability, but also offers an option towards reduction of solvent content, and thus a contribution to environmental protection. The use of additional rheology additives may become redundant in case modified Neuburg Siliceous Earth like Aktisil PF 777 is part of the formulation. Via suitably controlled rheological properties and a longer pot life, an optimum and resources-saving adjustment to conditions and requirements at the application site comes within reach using a cost effective, single-layered coating.

Aktisil AM and especially Aktisil PF 777 provide excellent acid resistance without the need of harmful aromatic amine hardeners, protection against organic acids included. The performance properties in the salt spray test concerning delamination at scribe can be distinctly improved with Sillitin Z 86 and Aktisil PF 777. Neuburg Siliceous Earth with suitable functionalization imparts to the coatings high hardness and abrasion resistance. Hence it creates the conditions for mechanical damage not to occur at all.

In view of such a property profile, modified Neuburg Siliceous Earth fillers should find selected application areas in heavy duty corrosion protection under critical conditions, e.g. where a maritime environment or an aggressive industrial atmosphere call for high protection efficiency. In particular cases a filler combination may be of use to meet the coating requirements.

Apart from classical application areas such as shipbuilding or steel constructions, the use of surface modified Neuburg Siliceous Earth fillers looks of interest in applications where besides corrosive exposure also high mechanical wear and acid attack are to be expected. Examples are loading areas, platforms and decks, container and tank linings as well as pipelines.