Neuburg Siliceous Earth

in a polyester based

coil coating primer

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Contents

1 Introduction

Coil Coating is a process where rolled steel or aluminum bands are continually coated in big units. The Coil Coating industry is a market segment characterized by steady growth; in 2010, worldwide about 17 million tons of steel and 3 million tons of aluminum have been coated.

The special characteristic of coil coating is the ductility of the band after the coating step. This requires high flexibility of the coil and coating as well as an excellent adhesion of the individual layers.

The primer has to meet the following requirements:

- ✓ very high reactivity
- ✓ optimum adhesion to the substrate
- ✓ high flexibility
- ✓ long-term corrosion protection

The binder determines the primary properties of the system, but the fillers used can also exert an influence. This aspect has not found much attention in the past, which is why the following question needs an answer:

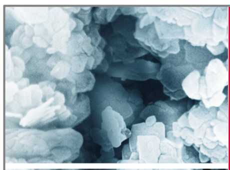
Are functional, high quality fillers as the Neuburg Siliceous Earth able to substitute the anti-corrosion pigment partly as well as the present filler and thereby maintaining the optical, mechanical and most notably the corrosion protective features?

This problem was studied in a polyester based primer formulation which contained 9.5 % anti-corrosion pigment and 5.7 % talc.

2 Experimental

2.1 Base formulation and variations

The guide formulation from the Evonik company, as given in *Fig. 1,* served as the base for the study.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

CUSTOMER FEEDBACK

Base Formulation *

Primer			%
A-component (grinding stage)	Dynapol LH 820-16	Binding agent (Polyester)	36.0
	Aerosil 200	Rheological additive (fumed silica)	0.2
	Heucophos SAPP	Corrosion protection pigment	9.5
	Kronos 2059	Pigment (Titanium dioxide)	6.6
	Talkum 10 M 0	Filler	5.7
	Methoxypropylacetate (MPA)	Solvent	13.5
B-component (let-down stage)	Dynapol LH 820-16	Binding agent (Polyester)	1.9
	Epikote 1004 (50% in MPA)	Epoxy resin	5.7
	Catalyst C 31	Catalyst	1.4
	Vestanat Hardener EP B 1481	Polyisocyanate	5.7
	Resiflow FL 2 (10% in Solvesso 150)	Levelling agent	2.8
	Nacure x 49-110 (5% in IPA)	Catalyst	1.0
	Cymel 202	Melamine resin	2.4
	Solvesso 150	Solvent	7.6
Total			100

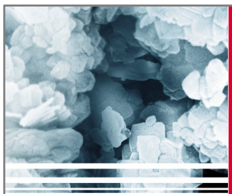
* by Evonik

VM-2/0811/04.2012

Fig. 1

Starting from this base formulation, 50 % of the anti-corrosion pigment and all the talc were replaced at equal weight with two grades of the Neuburg Siliceous Earth, i.e. Sillitin Z 89 and Aktifit AM.

The corresponding variations of the formulations are shown in *Fig. 2*. As a result of the replacement at equal weight, in view of the different densities of talc, anti-corrosion pigment and Neuburg Siliceous Earth, the pigment volume concentration increased slightly from 20.1 % to 20.8 %.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

CUSTOMER FEEDBACK

Formulations

HOFFMANN MINERAL

	Control	Sillitin Z 89	Aktifit AM
Dynapol LH 820-16	36.0	36.0	36.0
Aerosil 200	0.2	0.2	0.2
Heucophos SAPP	9.5	4.75	4.75
Kronos 2059	6.6	6.6	6.6
Talkum 10 M 0	5.7	-	-
Sillitin Z 89	-	10.45	-
Aktifit AM	-	-	10.45
MPA	13.5	13.5	13.5
B-Component (let-down stage)	28.5	28.5	28.5
Total	100	100	100
PVC [%]	20.1	20.8	20.8

VM-2/0811/04.2012

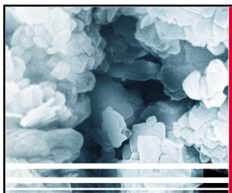
Fig. 2

2.2 Fillers used and their characteristics

Neuburg Siliceous Earth, extracted in the surrounding of Neuburg (Danube), 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 cryptocrystalline primary particles of about 200 nm diameter.

The calcination of the Neuburg Siliceous Earth helps to drive off the crystal water present in the kaolinite portion and to generate calcined kaolinite. The silica portion remains inert under the temperature chosen. Through an integrated air classifier process grain sizes > 15 µm are being removed.

Fig. 3 summarizes the typical properties of the talc and the two Neuburg Siliceous Earth grades, i.e. Sillitin Z 89 and the calcined, amino funktional treated Aktifit AM. The siliceous earth grades showed a somewhat lower density, considerably lower particle size, higher oil absorption and higher specific surface area than talc. In addition, Aktifit AM offers amino functionality due to the surface treatment with additive.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

CUSTOMER FEEDBACK

Filler Characteristics

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		Talc	Neuburg Siliceous Earth Sillitin Z 89	Calcined Neuburg Siliceous Earth Aktifit AM
Morphology		lamellar	corpuscular / lamellar aggregated	
Density	[g/cm³]	2.8	2.6	2.6
Particle size d_{50}	[µm]	6.8	2.0	2.0
Particle size d_{97}	[µm]	18.4	8.5	10
Oil absorption	[g/100g]	45	55	60
Specific surface area BET	[m²/g]	4.8	10	7.5
Functionalization		---	---	Amino

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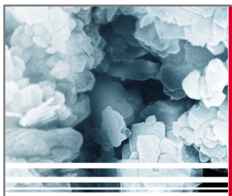
Fig. 3

The color values of the fillers are listed in *Fig. 4.* Aktifit AM showed the highest brightness with an L* value of over 95, followed by Sillitin Z 89 with 94. The talc with only 91.5 was clearly darker. The red/green parts a* for all fillers were comparable, around 0. For the yellow/blue parts b* there were the following differences: talc with 0 exhibits the highest color neutrality, followed by the Calcined Neuburg Siliceous Earth Aktifit AM with 0.9. Sillitin Z 89 is inherently characterized by a slight yellow tinge, as evident from the b* value of 4.1.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

CUSTOMER FEEDBACK

Filler Characteristics

HOFFMANN MINERAL

Color	Talc	Neuburg Siliceous Earth Sillitin Z 89	Calcined Neuburg Siliceous Earth Aktifit AM
L*	91.5	94	95.2
a*	-0.3	0.1	-0.1
b*	0.0	4.1	0.9

VM-2/0811/04.2012

Fig. 4

2.3 Preparation, application and stoving conditions

The ingredients of the A component were premixed in the sequence as listed in the formulation and dispersed in a dissolver-mounted agitator bead mill for 9 minutes at 6 m/s using glass beads as grinding media.

After adding the B component, the mix was homogenized for 1 minute at 6 m/s. The application of the primer was done with a wire wound rod (14 µm wet coating deposit) onto zinc plated steel substrate (hot dip galvanized, HDG), pre-treated with Bonderite 1303.

The primer films were stoved in an oven adjusted to 350 °C air temperature and a dwell time of 24 s, which resulted in a peak metal temperature PMT of 230 °C. The dry film thickness was 5 µm. Then a top coat from Akzo (PE-340-2027) was applied with a wire wound rod (32 µm wet coating deposit), in order to finally test the total system. The top coat was stoved in a continuous oven at 270 °C air temperature and a dwell time of 35 s, resulting in a PMT of 240 °C. The dry film thickness of the top coat came out at 20 µm.

3 Results

3.1 Optical properties

The optical properties of the top coat were determined in order to possibly find out effects of the different filler types in the primer formulation with regard to color and general optical properties (*Fig. 5*).

The gloss 60° with all formulations came out at 40 units. This confirms that the surface structure of the top coat remains unaffected by the primer.

The color values were determined with a spectral photometer (measuring geometry d/8°). Here too, no effect of the primer could be found, which means even with its slightly yellowish tinge Sillitin Z 89 did not affect the top coat.

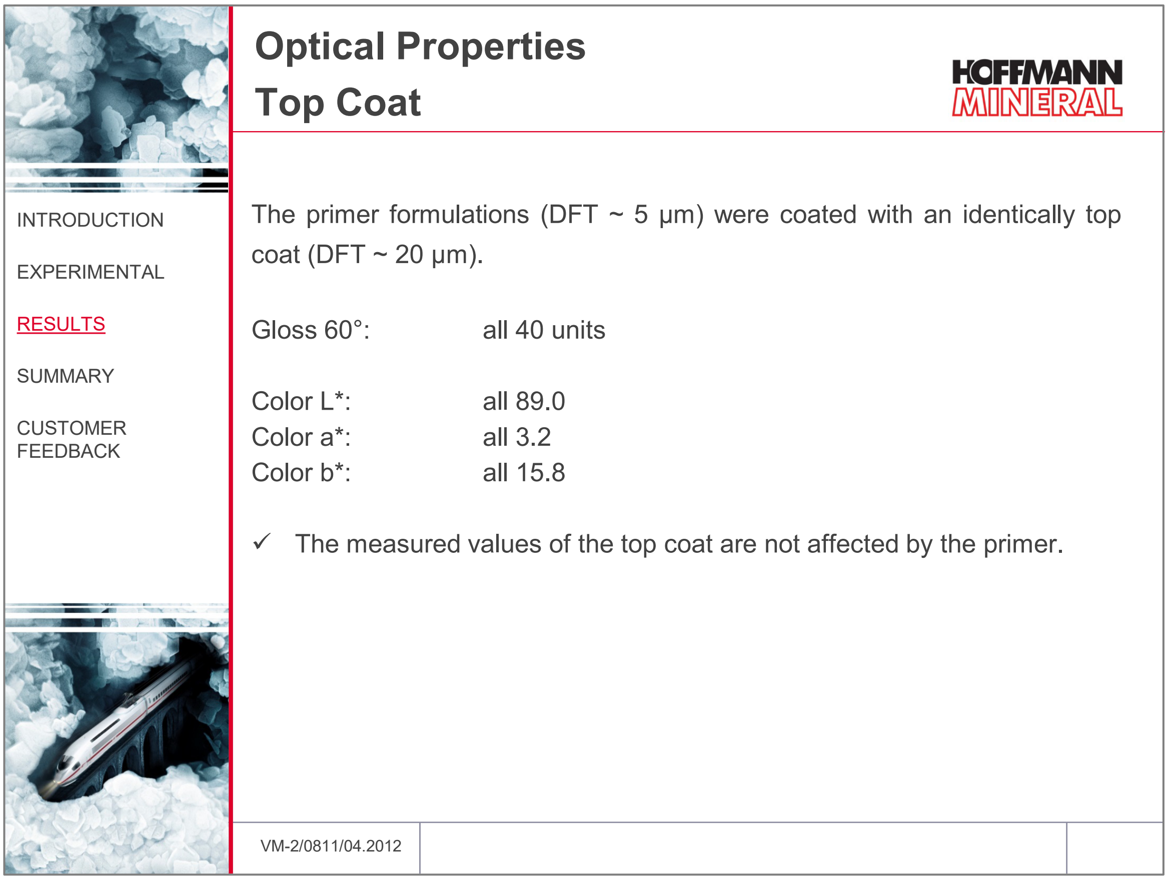


Fig. 5

3.2 Mechanical properties

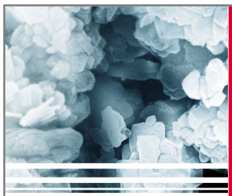
Also the mechanical properties were determined on the top coat in order to be able to assess the total system to exclude negative effects of the tested primer formulations (*Fig. 6*).

The hardness of the top coat was measured by the pendulum damping test according to DIN EN ISO 1522. It was found comparable for all samples with results between 64 and 66 s.

The determination of the adhesion followed the cross-cut test according to DIN EN ISO 2409 with a blade distance of 1 mm. All formulation variations showed an excellent adhesion with a cross-cut result of Gt 0. These results confirm that the adhesion of the primer to the substrate and to the top coat is maintained at an outstandingly high level.

As an indicator for the flexibility under slow deformation, the cupping test according to DIN EN ISO 1520 was used. The results in all cases with more than 11 mm were excellent.

The flexibility under rapid deformation was determined with the impact test according to ASTM D 2794-93. Here again, no detrimental effect of the primer variations could be found, as all results came out at a similar level between 52 and 54 inch pounds.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

CUSTOMER FEEDBACK

Mechanical Properties
Top Coat

HOFFMANN MINERAL

The primer formulations (DFT ~ 5 µm) were coated with an identically top coat (DFT ~ 20 µm) and afterwards the:

- Pendulum damping test (DIN EN ISO 1522)
- Adhesion by cross-cut test 1mm (DIN EN ISO 2409)
- Cupping test (DIN ISO 1520)
- Rapid deformation / Impact test (ASTM D 2794-93)

were carried out:

	Control	Sillitin Z 89	Aktifit AM
Pendulum damping test [s]	64	64	66
Adhesion [cross-cut test 1mm]	Gt 0	Gt 0	Gt 0
Cupping test [mm]	11.1	11.6	11.2
Impact test [inchpounds]	52	52	54

VM-2/0811/04.2012

Fig. 6

3.3 Corrosion protection

The test here again was applied to the total system primer plus top coat, as already indicated in the experimental section. In this context it should be noted that the anti-corrosion properties of a coil coating also depend on the metal pretreatment used.

Humidity test DIN EN ISO 6270-2, 1000 h

The assessment of the damages followed DIN EN ISO 4628/1-8 for a period of exposure of 1000 hours. For all formulations, no damages could be established:

- ✓ no blistering on the surface
- ✓ no blistering at scribe
- ✓ no rust at scribe
- ✓ no delamination
- ✓ no corrosion

The adhesion was assessed via the cross-cut test (1 mm) according to DIN EN ISO 2409 after conditioning the samples for 48 h at 23 °C and 50 % humidity. All formulations showed, after an exposure of 1000 hours, an excellent adhesion with Gt 0.

Also the mechanical properties after the exposure to moisture were largely retained, which was also verified with the cupping test as an index for the flexibility. After a conditioning for 72 h at 23 °C and 50 % humidity, the outstanding results between 9 and 10 mm did not indicate any differentiation between the various formulations.

By contrast, first differences showed up in the remaining pendulum hardness (*Fig. 7)*.

Aktifit AM gave right after the end of the test favorable results: 90 % of the original hardness was maintained, which means the exposure had hardly given rise to a softening of the coating, which also allows the conclusion that the functiional treated calcined filler is optimally bound into the binder matrix. The control as well as Sillitin Z 89, with around 60 %, came out markedly lower.

After conditioning the samples over a period for 72 h at 23 °C and 50 % humidity, all go up again to 100 % of their original level, with the Aktifit AM formulation even arriving at a somewhat higher hardness versus prior to exposure.

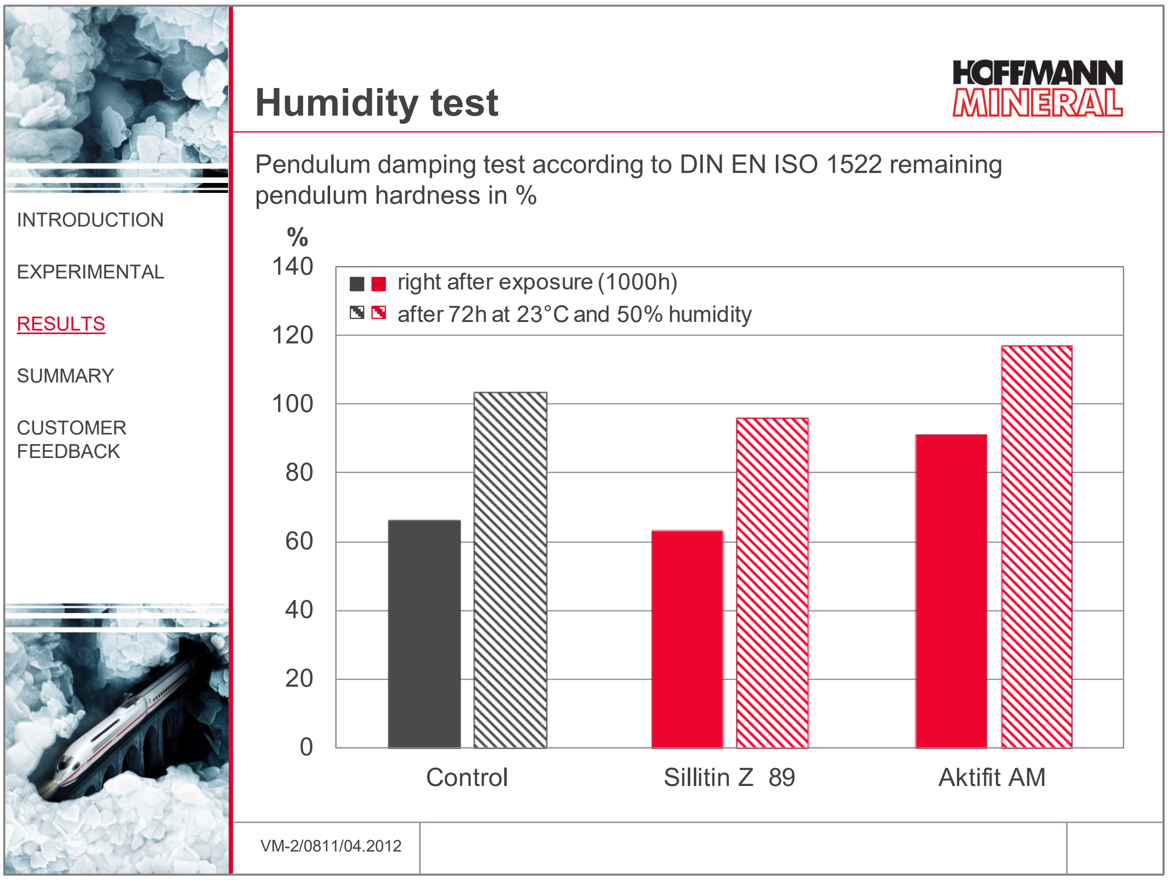


Fig. 7

<u>Salt spray test DIN EN ISO 9227, 1000 h</u>

To further assess the anti-corrosion properties, also the salt spray test was run over a period of exposure of 1000 hours.

The assessment of the damages followed DIN EN ISO 4628/1-2.
Rating the unscribed area, with the control there was not seen:

- ✓ any visible damages on the surface
- ✓ any blistering on the surface

Sillitin Z 89 and Aktifit AM showed some locally limited isolated and small blisters on the surface, however only near the edges or the scribe *(Fig. 8)*. As otherwise on the surface no further blistering was apparent, this sporadic and individual damage was not further taken into account.

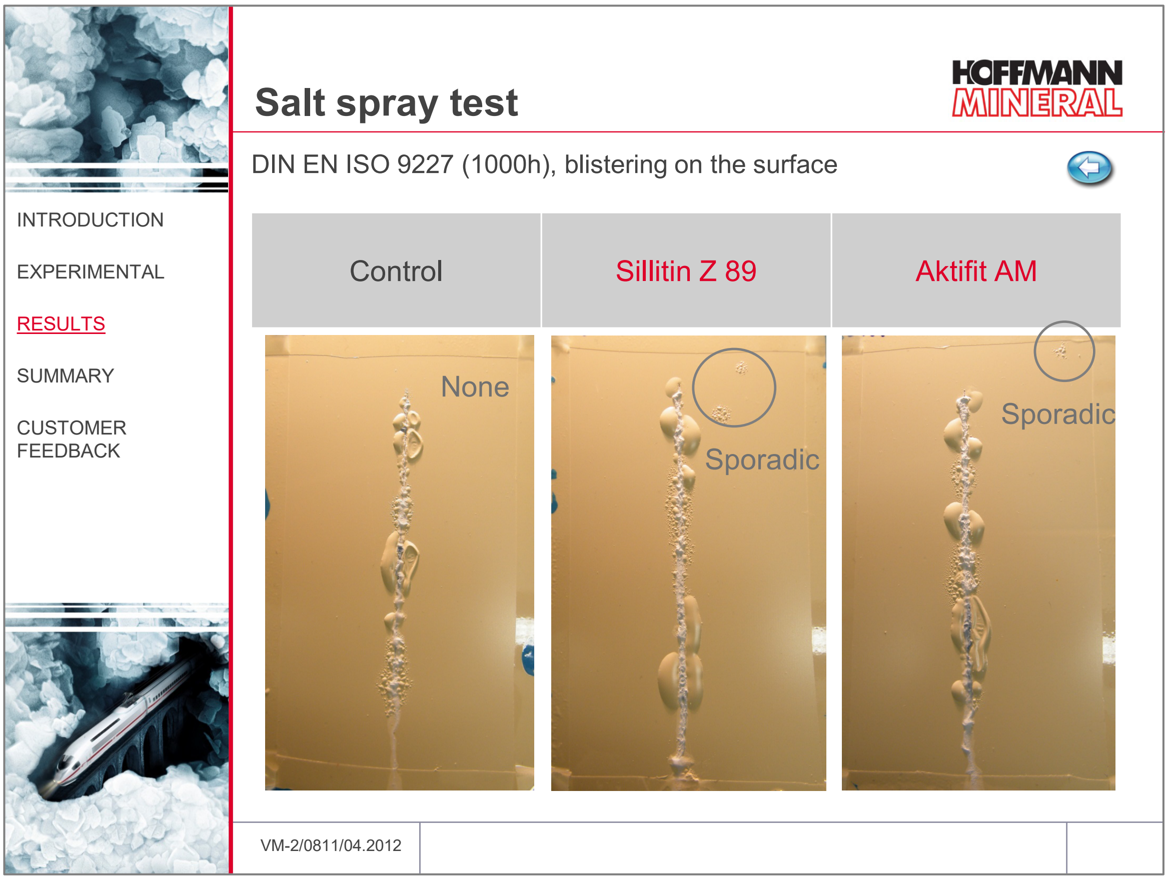


Fig. 8

Rating the behavior at the scribed area, blistering at scribe according to DIN EN ISO 4628/8 was evaluated.

After 1000 hours salt spray test all formulations showed blistering at scribe *(Fig. 9)*. Size and amount of the blisters were comparable in all cases.

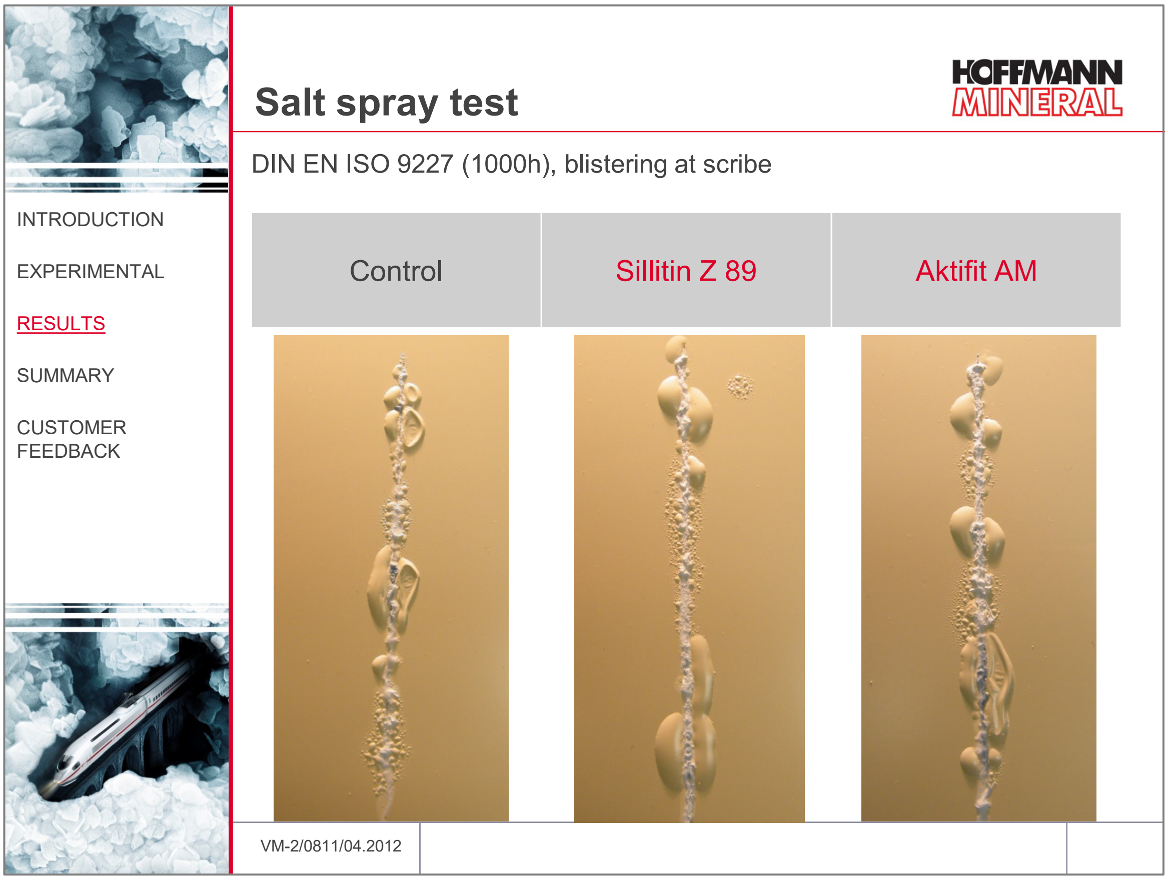


Fig. 9

For a further and more detailed assessment of the anti-corrosion properties, delaminated areas of the coating were removed starting from the scribe with a fine knife blade (*Fig. 10*). With this, a judgment of the disbonding/delamination and rusting/corrosion at the scribe was made possible.

The average width of delamination of the formulations with Neuburg Siliceous Earth was found in the range of 3.9 to 4.3 mm, which means despite the 50 % reduction of the anti-corrosion pigment, there has not occurred a severe setback.

The average width of corrosion, i.e. the white rust of the formulations with Neuburg Siliceous Earth was found between 2.7 and 2.9 mm, and this way despite the 50 % reduction of the anti-corrosion pigment only slightly higher than the control with 2.2 mm.

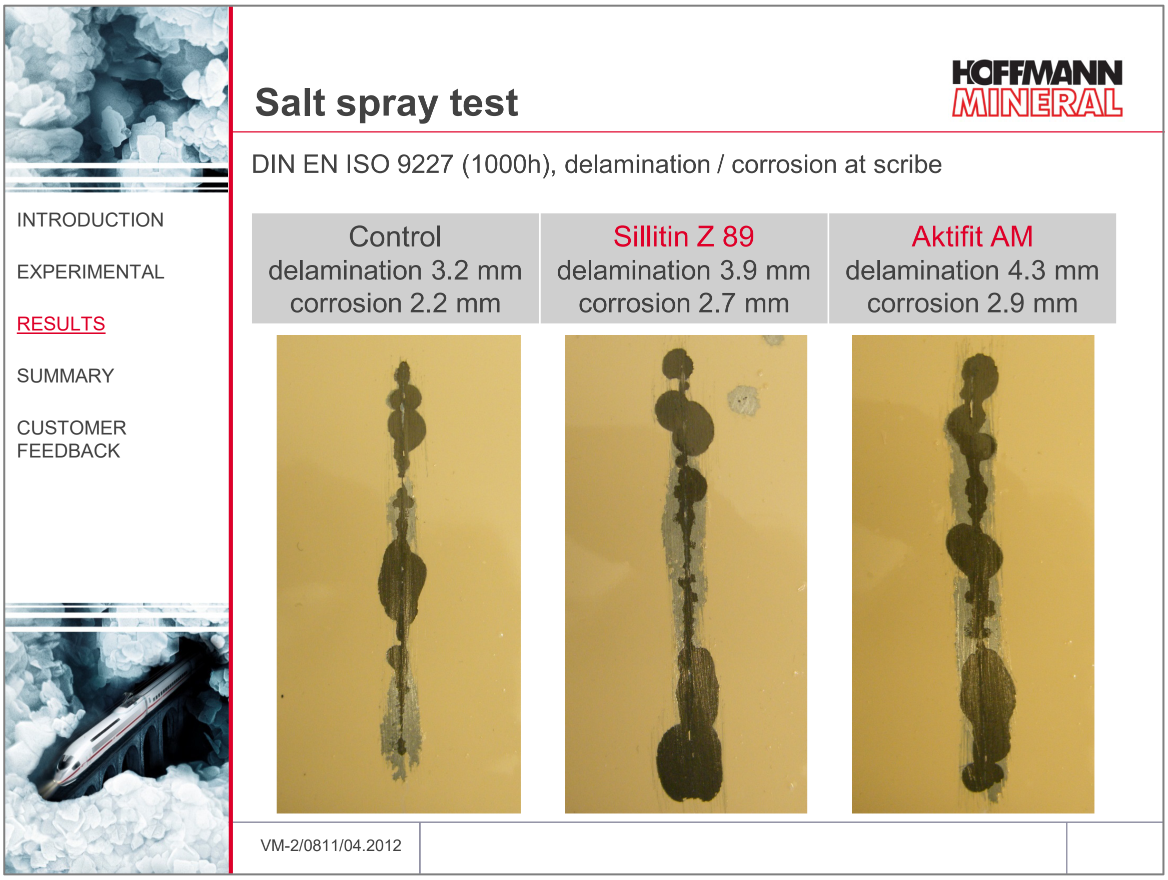


Fig. 10

In addition a coated test panel was cut on one side with a plate shear in order to obtain, close to industry conditions, a “fresh cutted edge” without any protective coating. This edge was arranged upwards in the salt spray cabinet with the consequence that the salt brine could easily enter defect areas at the metal/coating interface. *Fig. 11* illustrates the test samples after exposure for 1000 hours with an exposed delamination region. The average width of delamination is indicated by the lines in the pictures.

Contrary to the somewhat increased width of delamination at the scribed test panels, here the Aktifit AM shows a positive effect with respect to edge protection, as a lower mean width of delamination is seen compared with the control or with Sillitin Z 89.

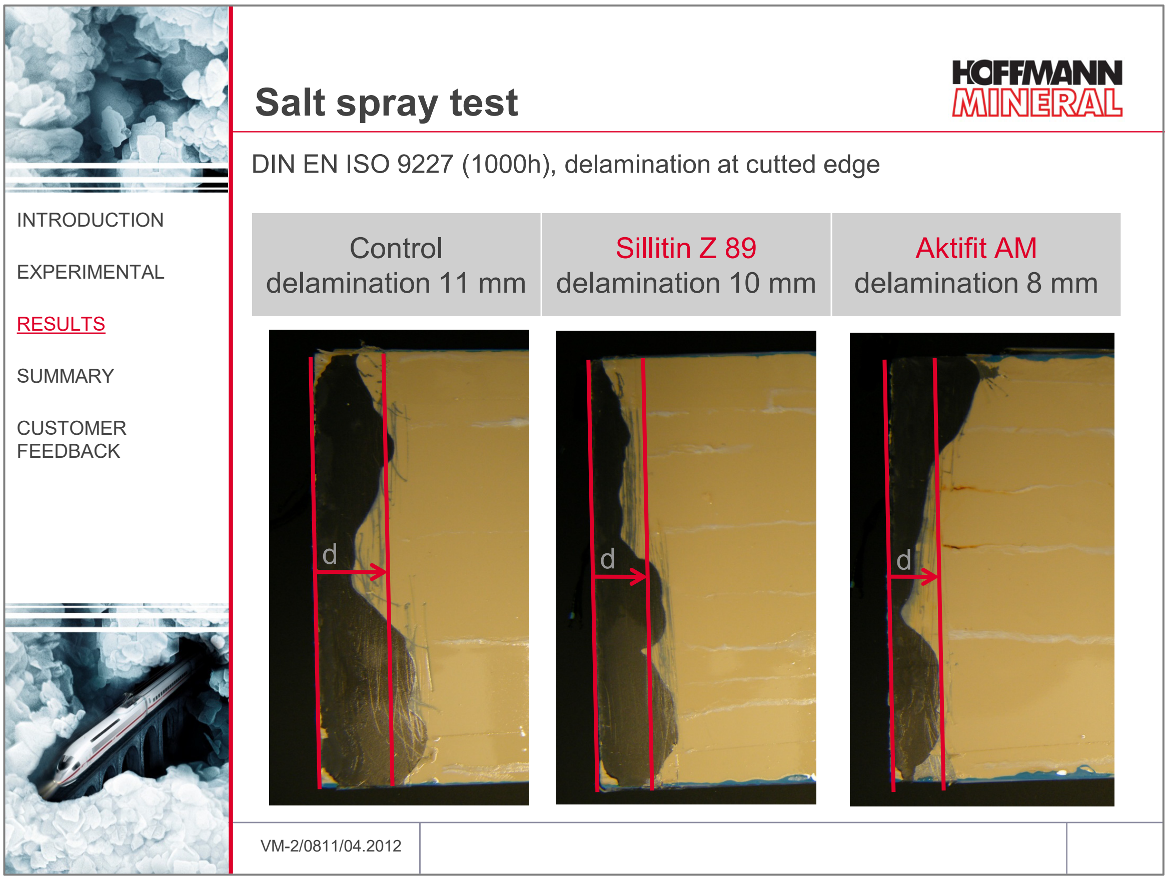


Fig. 11

Adhesion was monitored via the cross-cut test (1 mm) and a conditioning of 48 h at 23 °C and 50 % relative humidity. All formulations showed after an exposure to the salt spray test for 1000 hours an excellent adhesion with Gt 0.

The mechanical properties after the exposure were also checked with the cupping test. After conditioning for 72 h at 23 °C and 50 % relative humidity, outstanding results between 10 and 11 mm were registered.

Fig. 12 shows the retention of the pendulum hardness in percent after 1000 hours of salt spray exposure. Right after the end of the test, all formulations came out at least at 100 %. Thus the original hardness was maintained, which means no “softening” of the coating by the salt spray exposure could be observed. After a conditioning for 72 h at 23 °C and 50 % relative humidity, all coatings even go up above 100 %. Aktifit AM stands out, especially immediately after exposure, by a higher remaining pendulum hardness, whereas the Sillitin Z 89 could catch the Aktifit AM only after conditioning. In any case, both products reached higher values than the control.

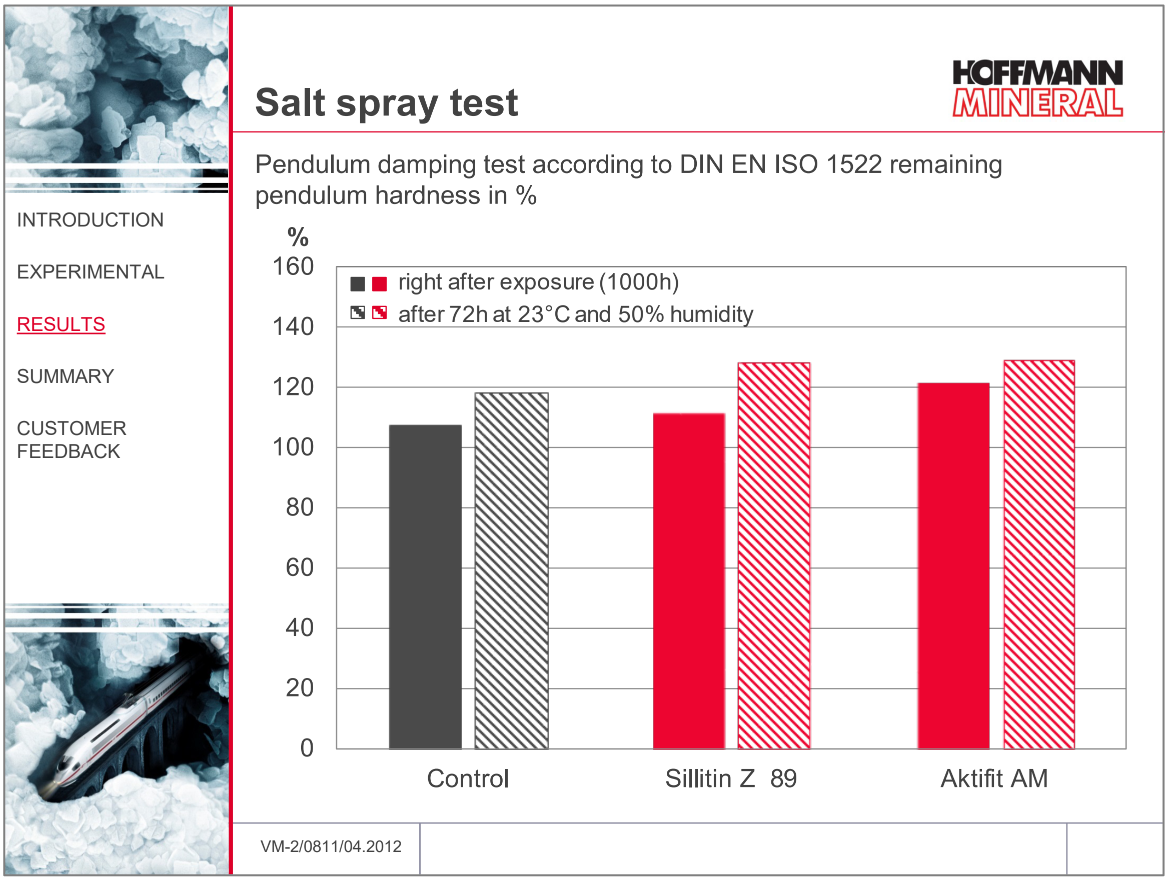


Fig. 12

4 Summary and outlook

The replacement of
50 % of the anti-corrosion pigment and
100 % talc
with Sillitin Z 89 or Aktifit AM leads to

- retained optical and mechanical properties
- very good adhesion prior to and after exposure
- retained corrosion protection at a high level
- according to the market situation, attractive potentials for cost savings

Sillitin Z 89 is recommended for cost attractive formulations.

Aktifit AM stands out by very easy dispersion and enables better resistance to wet conditions as indicated by a higher hardness after exposure.

Depending on the formulation and the substrate, it is suggested to adjust the reduction of the anti-corrosion pigment, for instance at 30 %.

5 Customer feedback

Customer feedback industrial application:
Further benefits of Aktisil AM mentioned below refer, divergent to the study, to the exclusively replacement of talc. The anti corrosion pigment is not replaced.

- good rheological properties, especially suitable for the direct roller coating process: considerably better leveling than talc, thus avoiding surface structures, which would be visible in the following topcoat and would deteriorate the appearance of the coating
- quick deaeration after roller application, thus a smooth surface is feasible
- improved hiding power, thus the amount of titanium dioxide can be reduced, which has a positive impact on costs