Neuburg Siliceous Earth

in cathodic electrodeposition

coatings

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VM-2/0609/09.2019

Content

1 Introduction

In the present work, the property profile of Neuburg Siliceous Earth was evaluated in a common light-colored automotive electrodeposition coating in comparison with a conventional reference filler.

Cathodic electrodeposition coatings represent a modern and highly effective technology to apply organic coatings in particular onto intricately shaped metal parts with the aid of direct current.

The project was carried out in cooperation with the University of Applied Science Fachhochschule Niederrhein and DuPont Performance Coatings GmbH (DPC), Wuppertal, between July 2001 and April 2003. The focus of the studies concerned Low Density Formulations with a markedly reduced titanium dioxide content.

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 formation, the silica portion exhibits a round grain shape and consists of aggregated, crypto-crystalline primary particles of about 200 nm diameter.

2 Experimental

2.1 Pigment paste

The individual ingredients of the premix for the pigment paste are listed in *Fig. 1*.

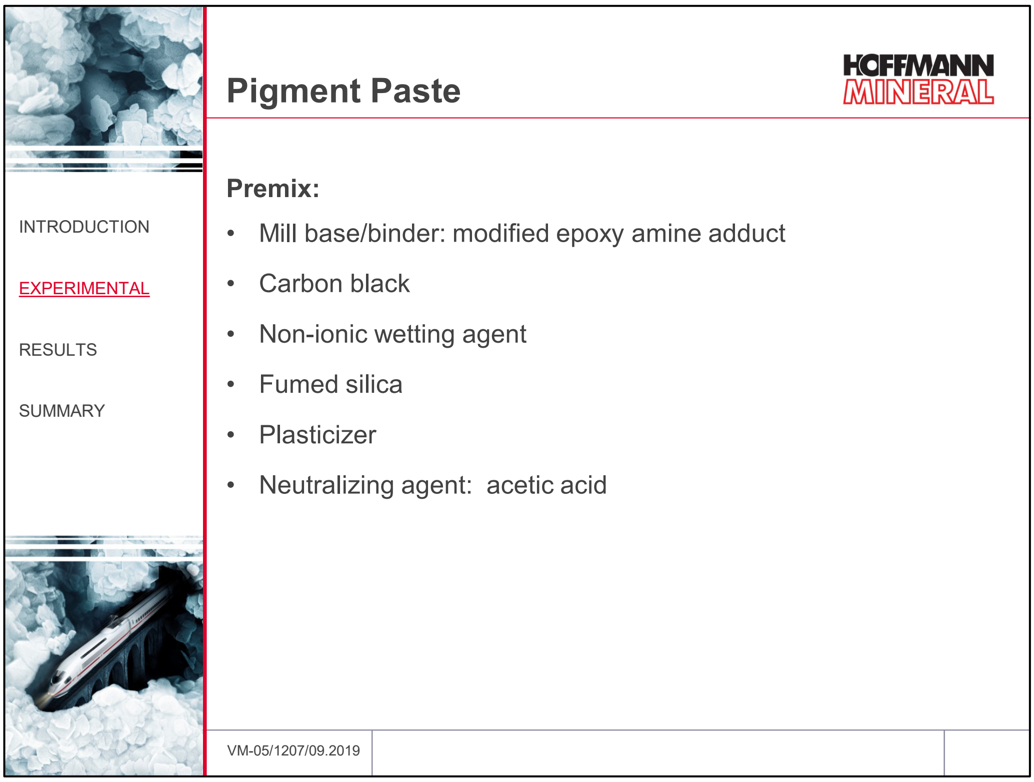


Fig. 1

This premix served as the base for the subsequent pigment pastes with different fillers and titanium dioxide concentrations. These variations, at constant pigment volume concentration (PVC), are shown in *Fig. 2*.

The following pigments and fillers were evaluated:

- Titanium dioxide (standard quality)

- American clay (standard clay)

- Sillitin Z 86 (Neuburg Siliceous Earth)
- Sillikolloid P 87 (finer particle size compared with Sillitin Z 86)
- Aktisil PF 777 (Sillitin Z 86, alkyl functionalized)
- Aktisil MM (Sillitin Z 86, mercapto functionalized)
- Talc (standard talc)

The typical properties of the fillers and the pigment are summarized in the appendix.

According to the guide formulation, batches of 0.7 to 1 kg were mixed and dispersed at about 40 °C in a dispersing vessel equipped with Dissolver and SAZ pearls (1.6 to 2.5 mm, weight ratio to grind feed 1:1).
In order to adjust to a viscosity of 60 to 80 seconds (DIN Cup 4 mm), up to 4 % deionized water were added.

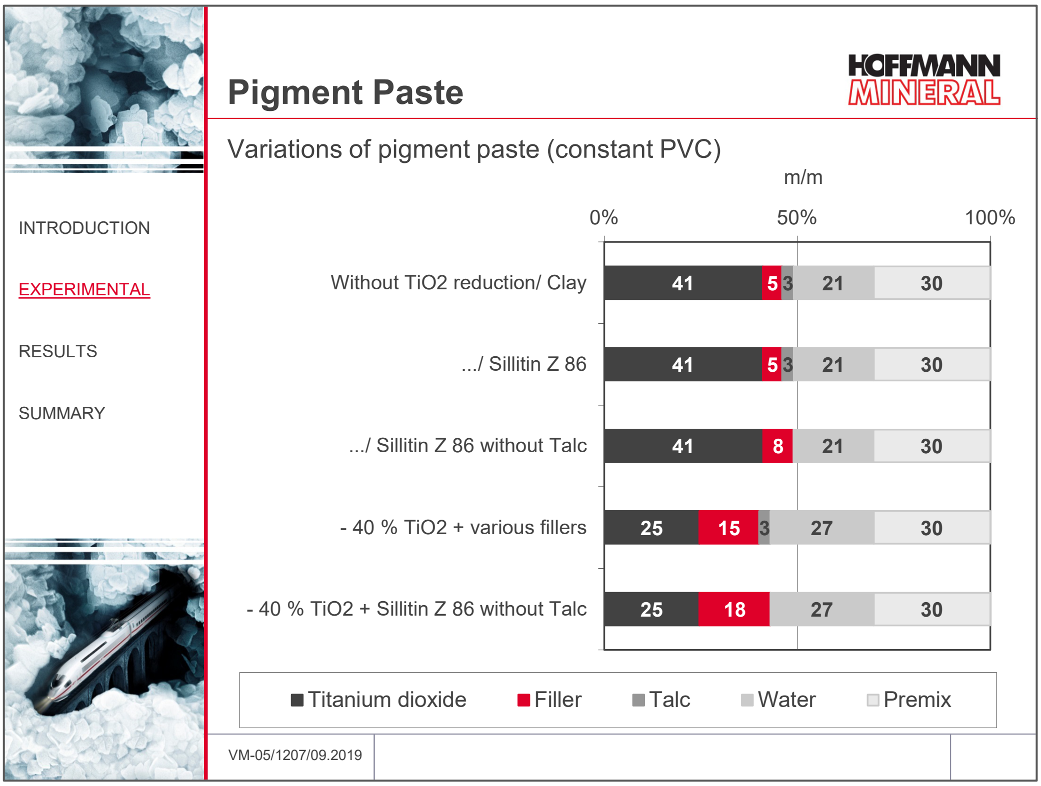
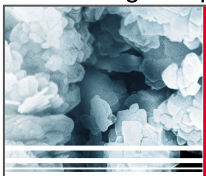


Fig. 2

2.2 Bath formulation

Upon addition of the dispersion, water and butylglycol/Texanol (1:1) the individual pigment pastes led to the Low Density bath formulations illustrated in *Fig. 3.* The usual batch weight was 3.5 kg. After homogenizing the raw materials, for “conditioning” (matching practical conditions with respect to concentrations of solvent and low molecular weight ingredients) the mixes were stirred for 16 to 24 hours with a magnetic stirrer at room temperature. Also during further storage, the mixes were stirred with a magnetic stirrer, as usual and necessary under industrial conditions. After sieving through a nylon gauze (30 µm) the properties of the bath formulations were determined (*Fig. 4*). Sieving trials through 15 µm sieves did not show any residues.



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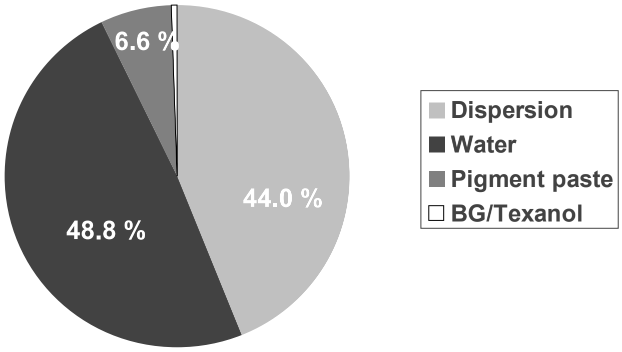

m/m	Without TiO_2 reduction	- 40 % TiO_2
paste	6.7	6.7
filler incl.)/	0.20	0.18

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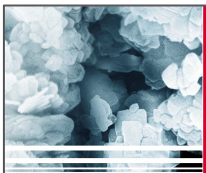
Fig. 3



Bath Properties

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SUMMARY

	Unit	Intended bath properties	Attained bath properties
Solid content	%	18 -19	17.5 – 18.5
pH value		6.3 ± 0.2	5.7 – 6.0
Electrical conductivity	µS/cm	1300 ± 200	1200 - 1500

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Fig. 4

2.3 Substrates and film thickness

The steel panels provided by Chemetall GmbH were all phosphatized with a nickel-free phosphate process on the basis of zinc phosphate. Considering the trend for zinced car bodies steel panels were first one sided electrolytically zinc plated before phosphatized. The panels and their dimensions for the individual testings are itemized below:

- **<u>Gardobond 2650T/6800/OC</u>**

Material: steel
Surface pretreatment: zinc-manganese phosphatized
Rinsing: chromate free

19 cm x 10.5 cm x 0.85 mm:
- Cupping test
- Impact and reverse impact test at -20°C
- L effect / Gloss (14 + 5 cm x 10.5 x 0.85 mm)

Perforated with 9 holes each (d = 1 cm), 20 cm x 10 cm x 0.9 mm:
- Edge covering assessment via salt spray test

30 cm x 10.5 cm x 0.9 mm (collar, “Ford box”):
- Throwing power

- **<u>Gardobond 2650T/6800/OG</u>**

Material: steel, electrolytically zinc-plated
Surface pretreatment: zinc-manganese phosphatized
Rinsing: chromate free

19 cm x 10.5 cm x 0.85 mm:
- Impact test at -20°C
- Adhesion (cross cut test)
- Cyclic corrosion test according to VDA

Cutter knives (from Lutz Industria, Solingen; no. AB 10, width 9 mm) were coated for assessing the edge covering via film thickness profile over the cross-section of the backward edge.

The film thickness for all testings was between 20 and 25 µm. Only for testing the edge covering on the cutter knives the film thickness was even higher from 28 to 34 µm.

2.4 Deposition and stoving

Fig. 5 and *Fig. 6* summarize the relevant parameters. In all cases, complete deposition curves were registered (voltage and amperage). As all these graphs came out identical no individual comments were possible, they are not shown here.

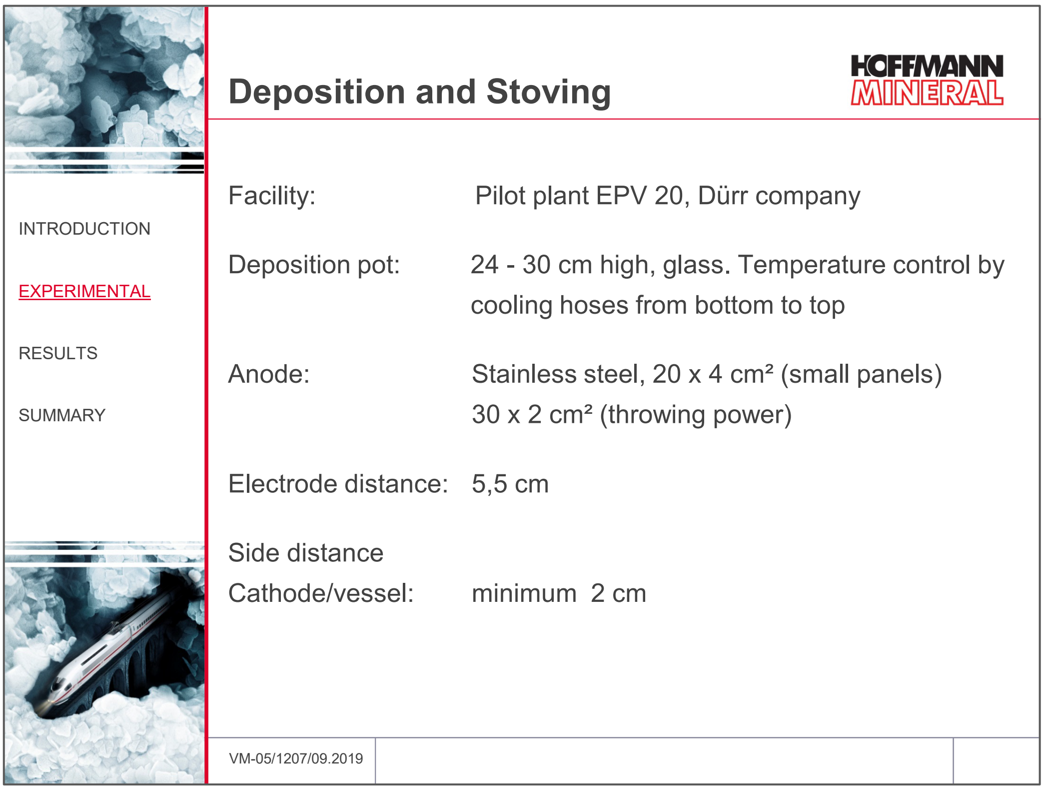


Fig. 5

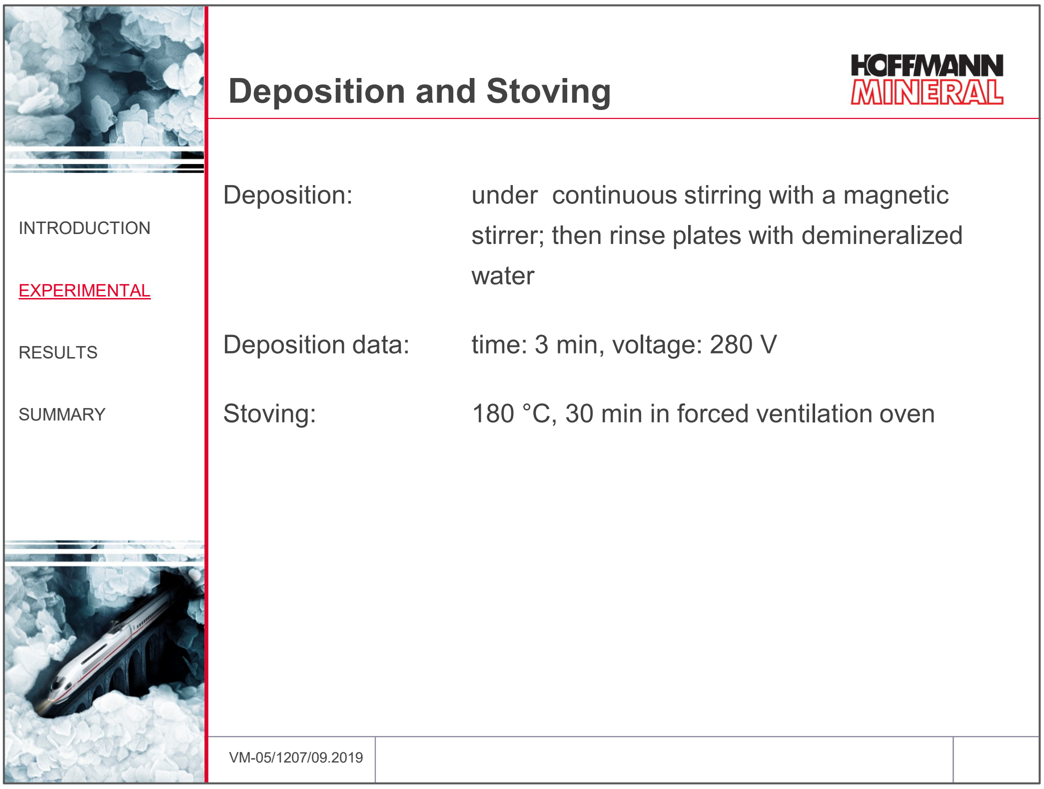


Fig. 6

3 Test methods and test results

3.1 Grain fineness

The grain size was determined with the aid of a Grindometer (DIN EN ISO 1524). The pigment pastes gave results between 6 and 12 µm, however a direct correlation to a type of filler could not be observed.

3.2 Flow time

The flow time was determined with the aid of a DIN Cup 4 mm according to DIN 53211-4. The pigment pastes without reduced titanium dioxide content gave flow times between 100 and 150 seconds, the reduction of the titanium dioxide content resulted in lower flow times between 23 and 56 seconds. This will be also due to the increased water content of the formulations, and should be adjusted according to needs.

3.3 L effect / Gloss

The L effect is to show quality differences with respect to degree of dispersion and deposition quality. In this test, the four different sides of a L-shaped test panel, in particular the critical side 2 (horizontal, upper side), were assessed. Informations about the sedimentation rate and other filler effects can be obtained.
The test followed the routine of dipping the panels, 15 minutes rest, then deposition without stirring.
Fig. 7 reports the gloss results at 60° (DIN 67530) of the four sides of the L-shaped panels. Without titanium dioxide reduction, clay and Sillitin Z 86 give comparable results, while the variants without talc and with Sillitin Z 86 show markedly higher gloss on side 2, and therefore come off much more favorably. Apparently Sillitin and talc enter into negative interactions which follow in reduced gloss results on the critical side 2. This means when working with Neuburg Siliceous Earth, talc as a co-filler should be excluded from the compounds.
The substitution of 40 % titanium dioxide gives a similar picture. Sillikolloid P 87 apparently does not react as strongly to the presence of talc, followed by the Aktisil grades MM and PF 777.

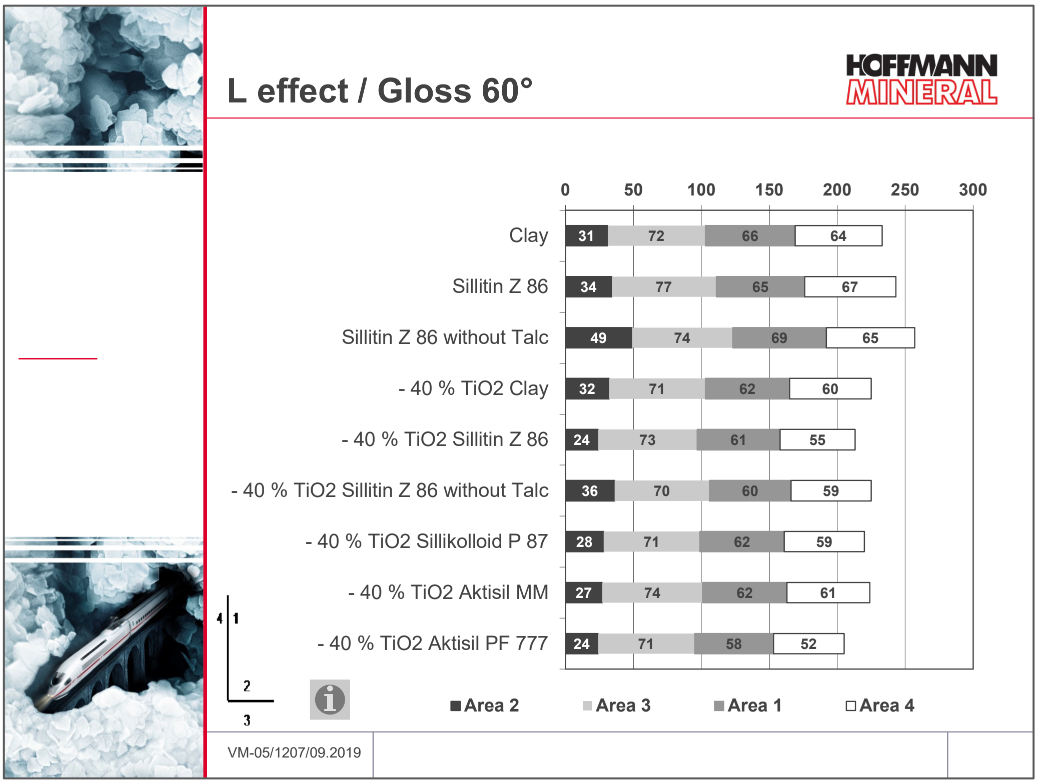


Fig. 7

3.4 Throwing power

One of the most important properties of electrodeposition coatings is the ability to coat the difficult areas in cavities, in order to obtain a good corrosion resistance. For the evaluation of the throwing power, steel panels were arranged as a collar “Ford box”. The distance between the two plates was 4 mm. *Fig. 8* overviews the scheme of the box and the position of the film thickness measuring points.

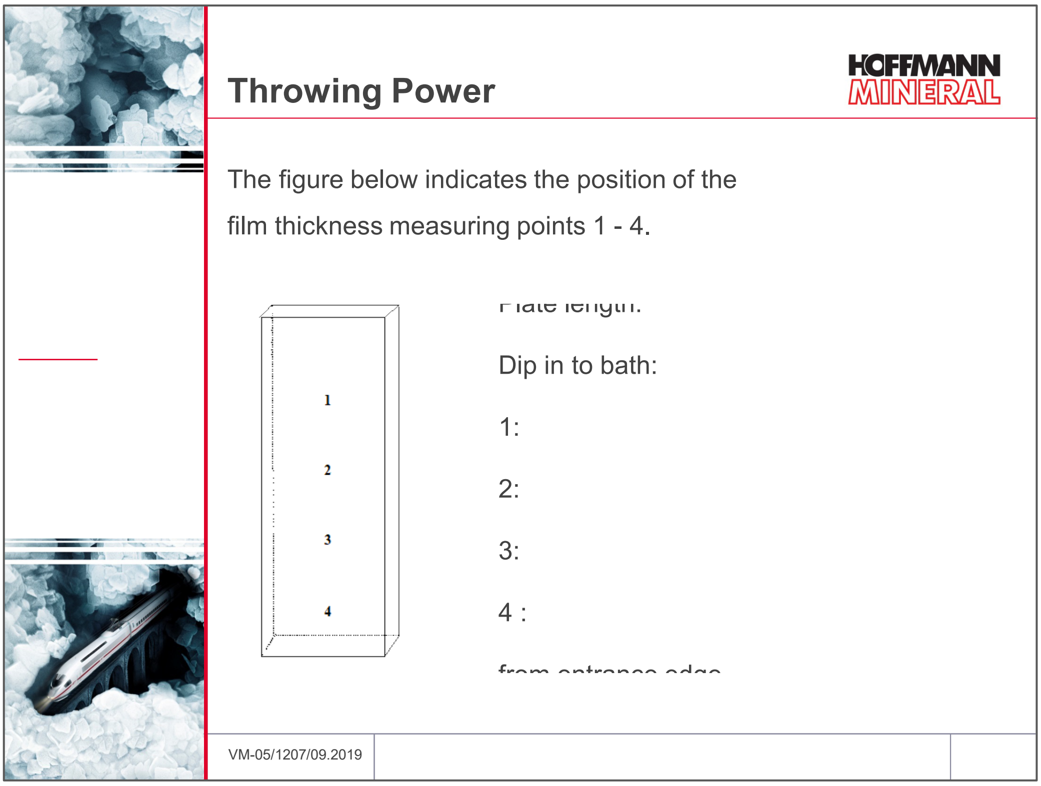


Fig. 8

Fig. 9 illustrates the film thickness versus the distance from entrance of the cavity (10 to 20 cm from the entrance opening). The highest film thicknesses are obtained with Sillitin Z 86 with approx. 18 to 2 µm, while the clay only results in approx. 13 to 1 µm. Upon substitution of titanium dioxide, a clear trend cannot be established.

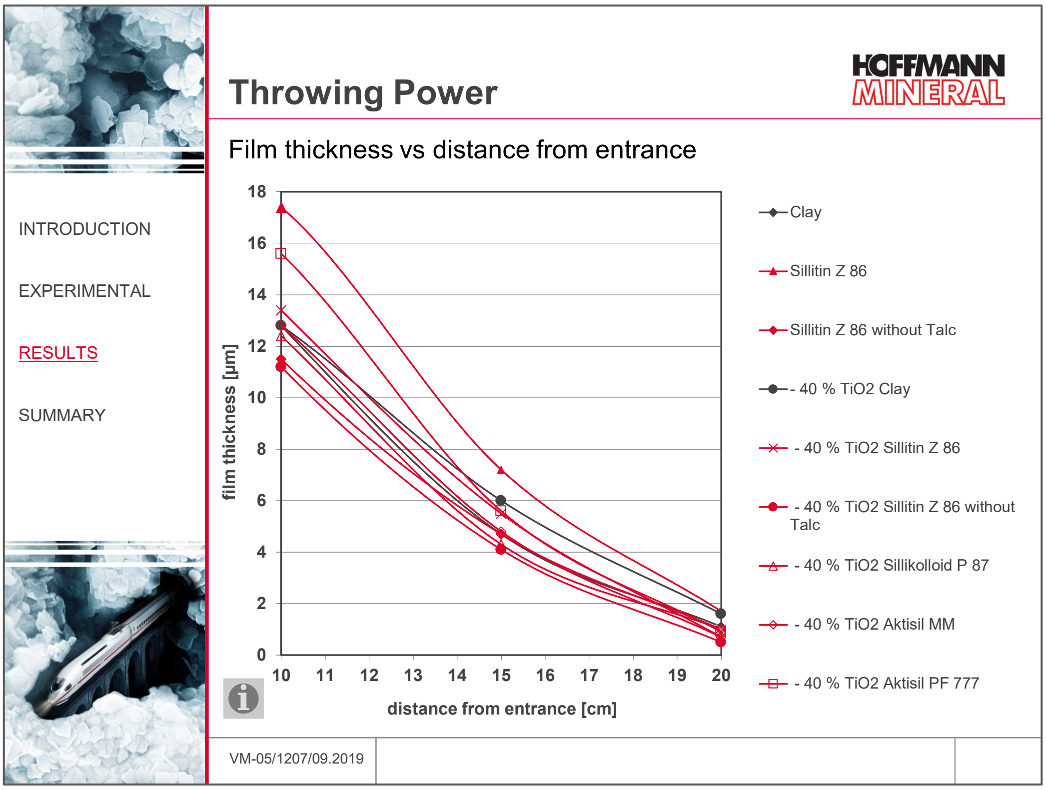


Fig. 9

In order to determine the inherent and most important function of the coating, i.e. corrosion protection, in this case via the required minimal film thickness for the pertinent protection against rusting, the throwing power panels were exposed for 1000 hours to the salt spray test (DIN EN ISO 9227).

Fig. 10 shows the film thickness as determined in the throwing power test at 15 cm from the entrance opening, and the coating length in centimeters which is found free from corrosion damage (rusting limit). Despite their different film thicknesses, all formulations practically show identical rust limit distances of about 16 cm from the entrance opening. This allows to conclude the determing role of the binder used.

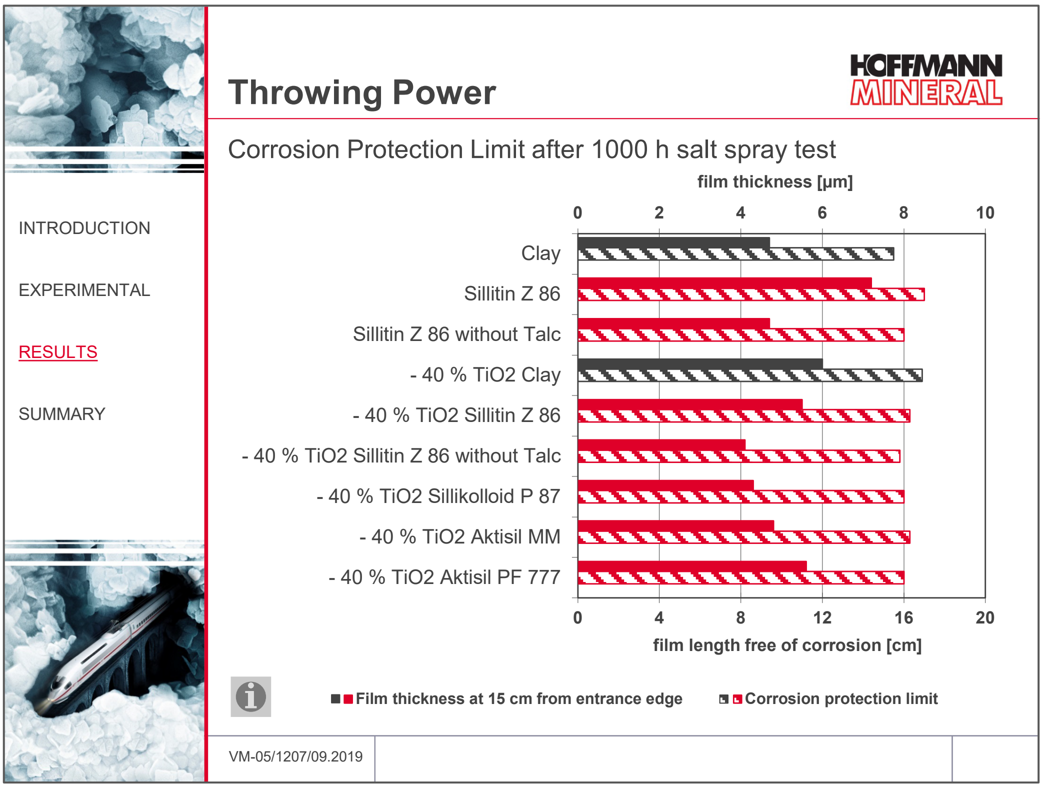


Fig. 10

3.5 Edge covering

The edge covering was determined by exposing perforated panels for 1000 hours to the salt spray test (DIN ISO 9227). The panels served to assess the rusting tendency at the edges on the burred side via determination of the degree of rusting (*Fig. 11*). The formulations with Sillitin Z 86 and Sillitin Z 86 without talc showed small areas around the holes free from rust damage. With the other fillers which had to be judged moderate, no intact (rust free) areas were seen around the holes.

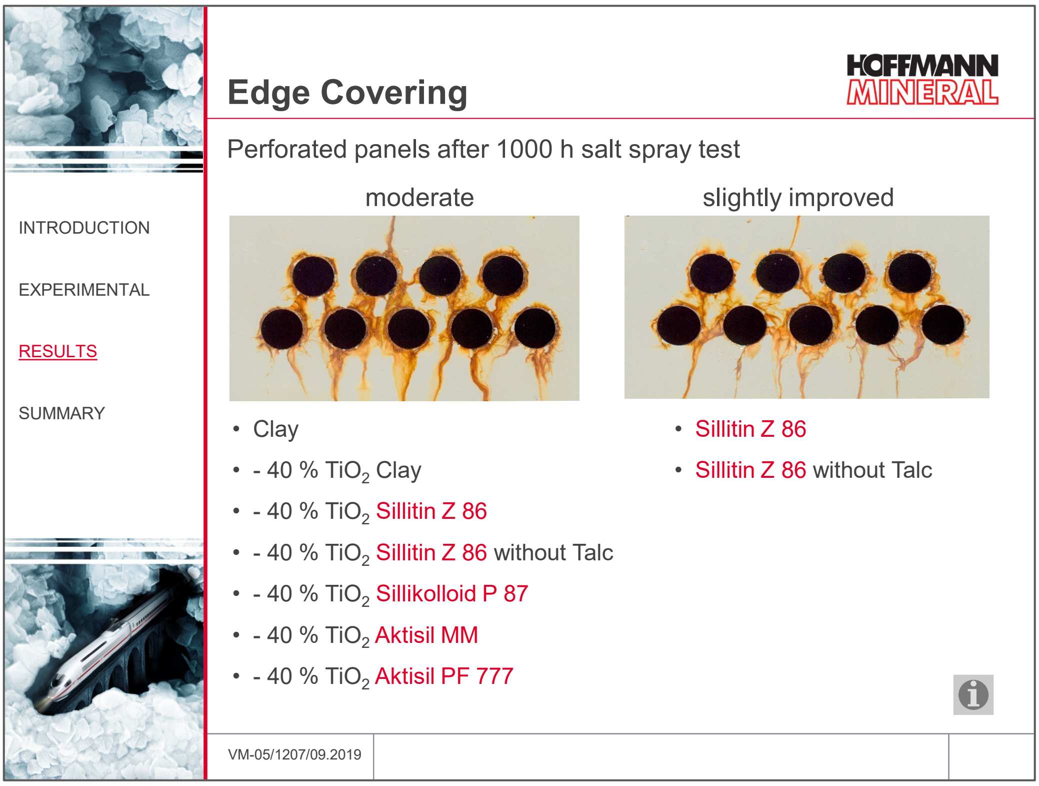


Fig. 11

In addition, the edge covering was assessed with the aid of coated cutter knives through the coating thickness profile over the cross-section of the backward edge. The cutter knives were coated, broken and slightly post-abraded at the cross-section. The fillers judged moderate showed almost no coating at the edges. With clay, Sillitin Z 86, the 40 % titanium dioxide reduction and Aktisil PF 777 some improvement was evident, as there was found a thin coating film at the edges as well as a higher film thickness in the neighborhood (*Fig. 12*).

The cutter knives together with the perforated panels were exposed to the salt spray test for 1000 hours. No significant differences were found between the individual components.

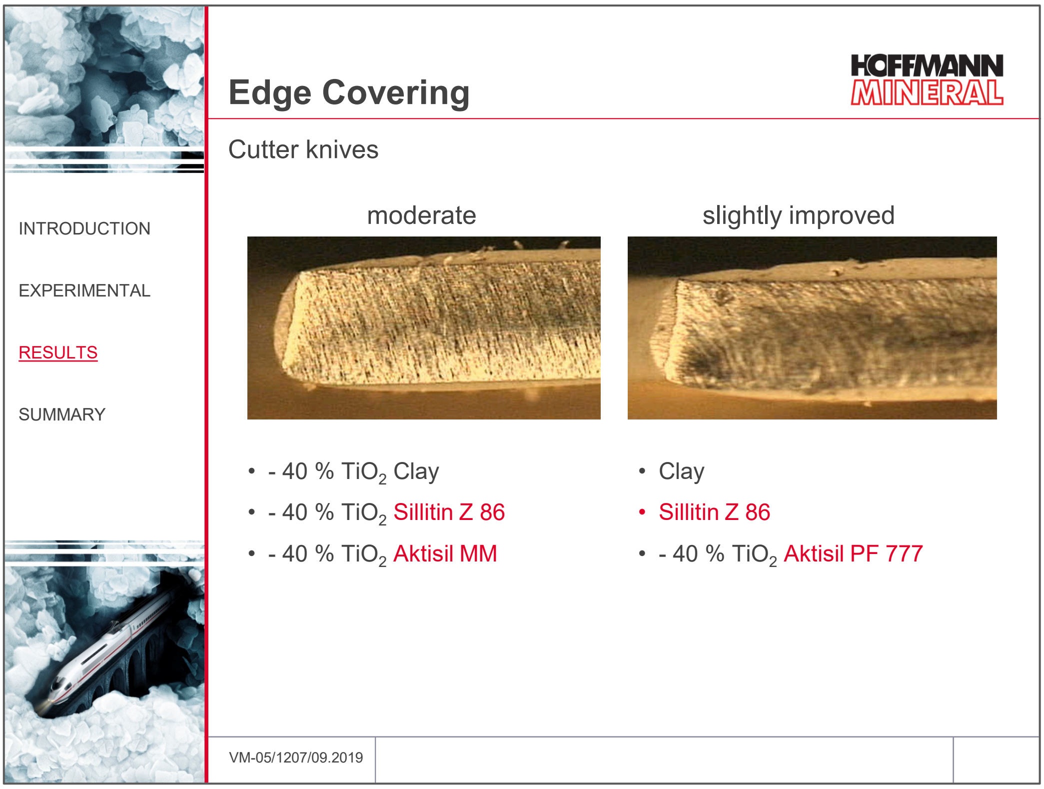


Fig. 12

3.6 Cupping test

In order to assess the ductility at low speed, the cupping test (DIN EN ISO 1520) was carried out (*Fig. 13*). Sillitin Z 86 enables to arrive higher values and thus indicates a superior deformability compared with the clay, in particular in the formulations without talc and upon substitution of the titanium dioxide. Also the other Neuburg Siliceous Earth grades led to a better ductility than the control with clay.

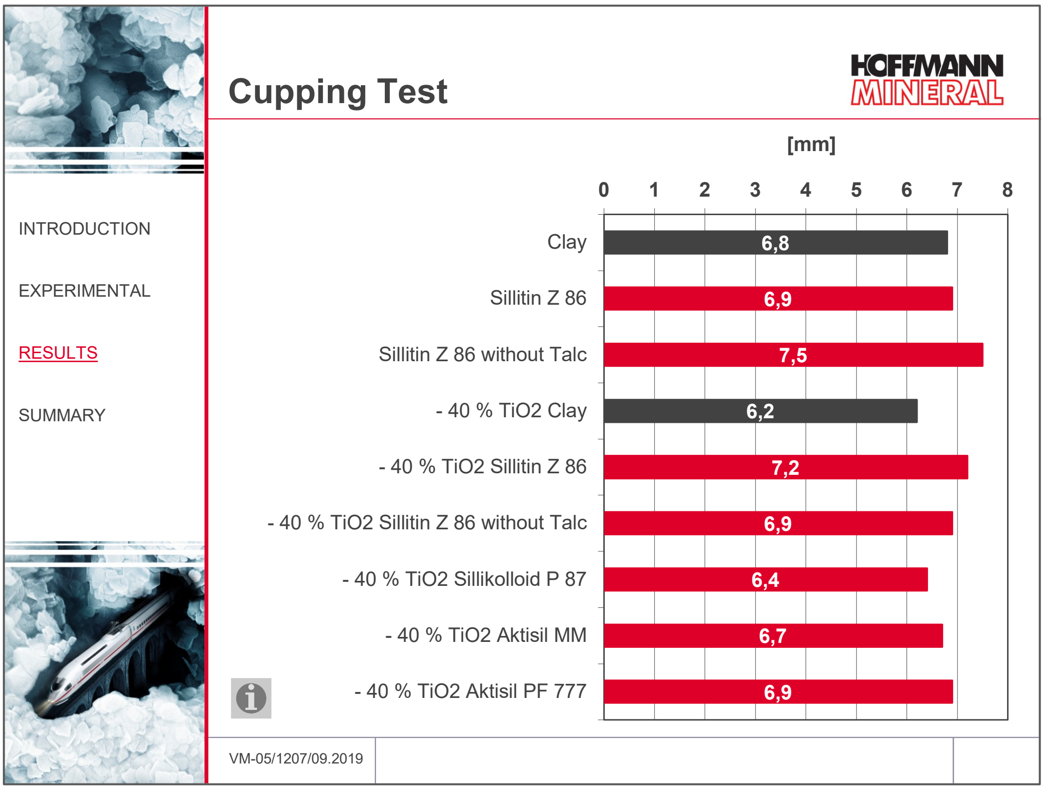


Fig. 13

3.7 Impact test

For testing the ductility at high speed with a dropping weight of 1 kg, the impact resp. the reverse impact test at -20°C were run on different substrates (DIN EN ISO 6272). *Fig. 14* illustrates the impact test on phosphatized steel panels. The different formulations attained values between 52 and 65 inch·pound, only the batches containing Sillitin Z 86 without talc as well as Aktisil PF 777 distinguished themselves from the other fillers with 69 to 78 inch·pound.

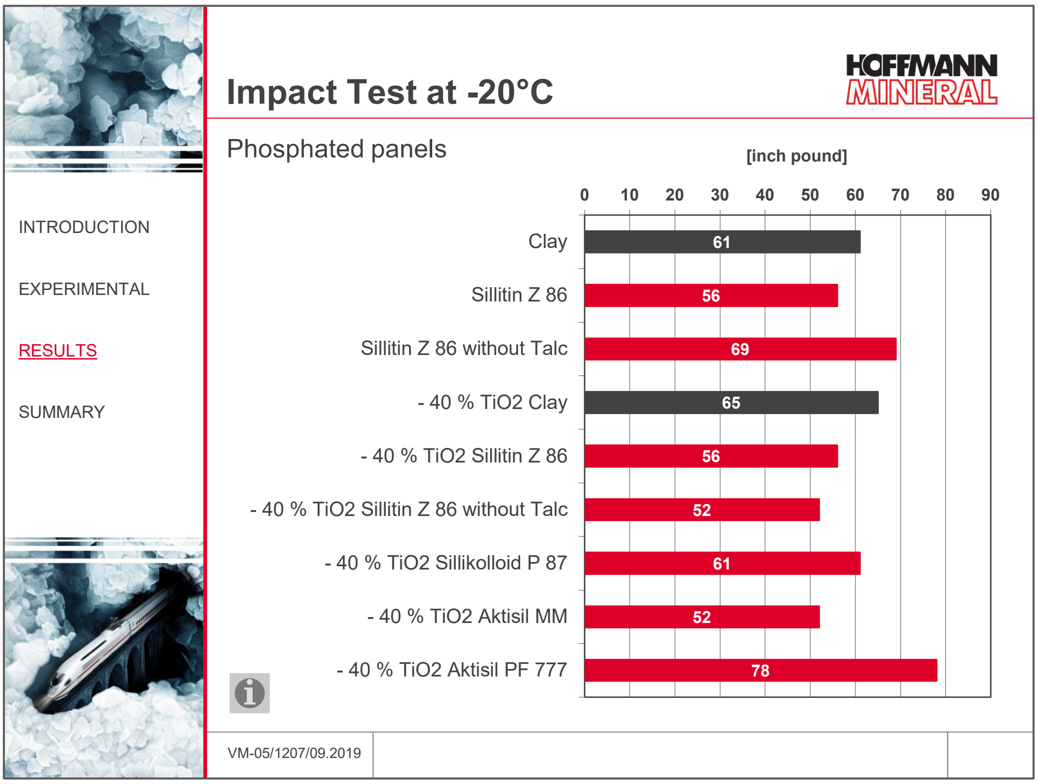


Fig. 14

Fig. 15 shows the impact test on electrolytically zinc plated and phosphatized panels. Here Sillitin Z 86, in particular the formulation without titanium dioxide substitution and without talc, offered very good results with 87 inch·pound. But also when the titanium dioxide content is reduced, independent of the presence of talc, this Neuburg Siliceous Earth grade came up to high values between 74 and 78 inch·pound.

In comparison, the result for the clay with reduced titanium dioxide content came off markedly poorer.

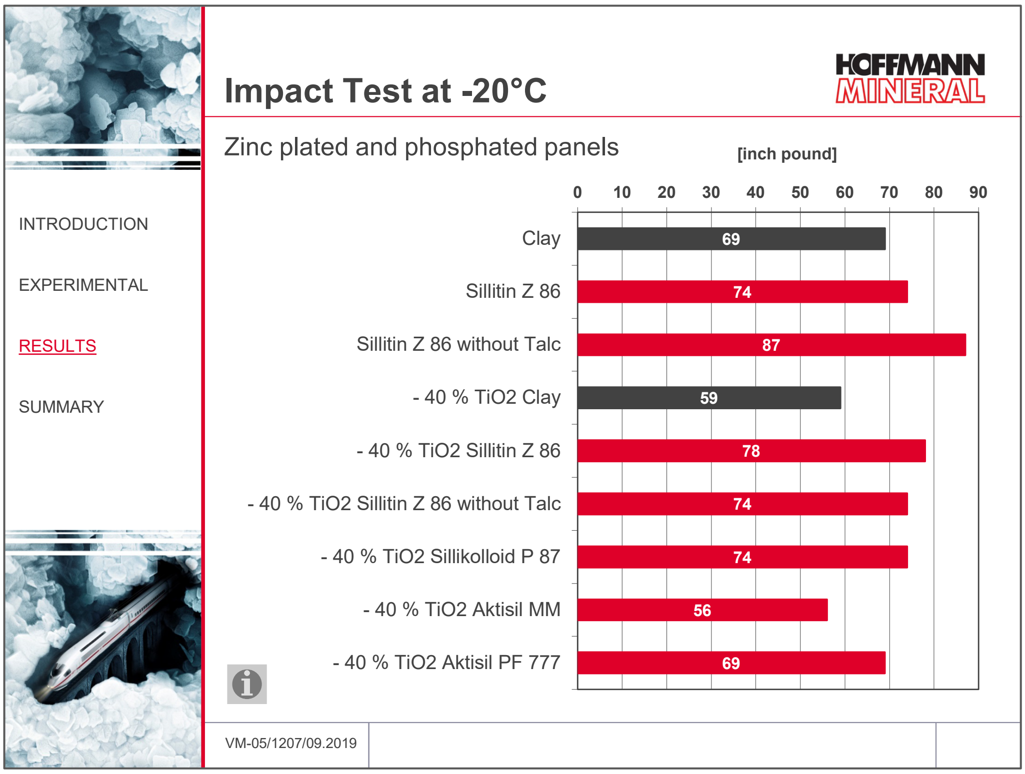


Fig. 15

Fig. 16 illustrates the reverse impact test on the phosphatized rear side of the steel panels. In this test, no differentiation was found between the fillers, as all results were lower or equal than 8.7 inch·pound.

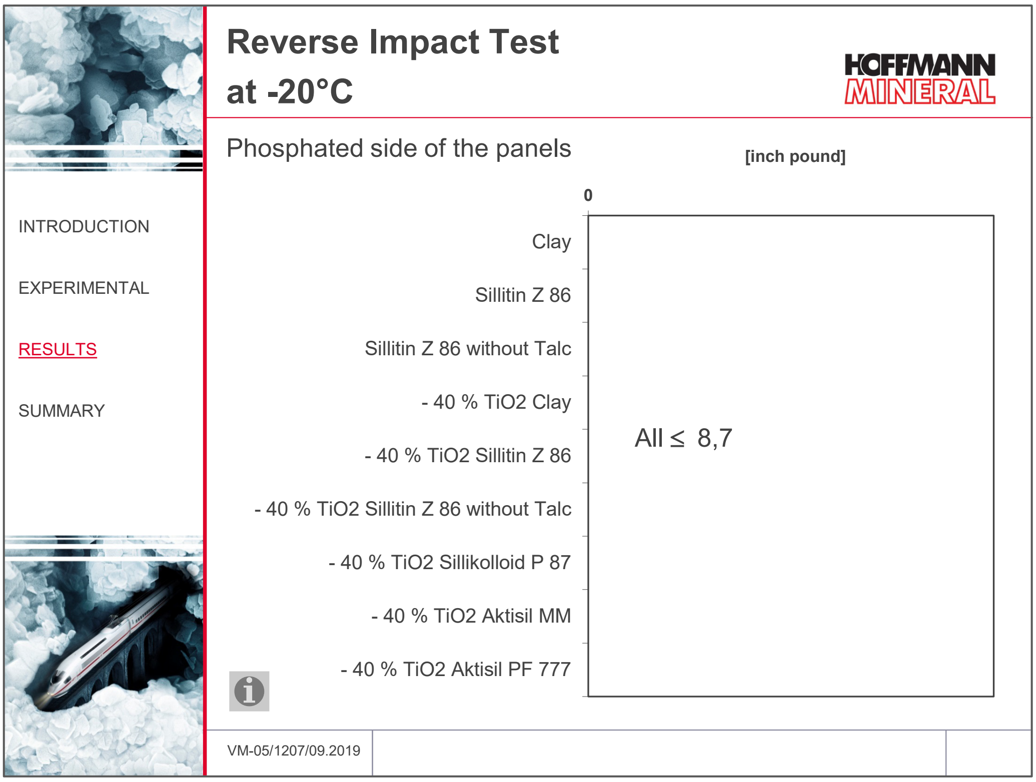


Fig. 16

3.8 Adhesion (cross cut test)

The cross cut test (DIN ISO 2409) was carried out for testing adhesion of the coatings. All results came out between 0 and 1, so no differentiation between the fillers was possible (*Fig.* 17).

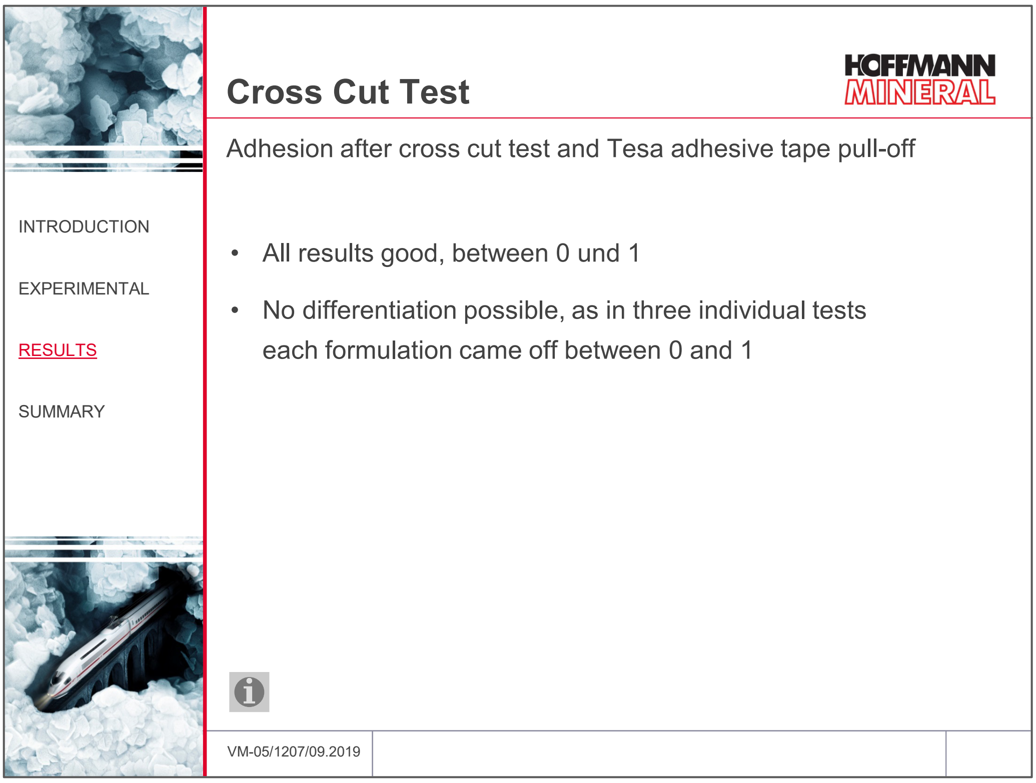


Fig. 17

3.9 Cyclic corrosion test according to VDA 621-415

In order to evaluate the corrosion protection under cyclic exposure, the alternating weathering test according to VDA 621-415 was run over a period of 20 cycles. One cycle takes 7 days and includes 24 hours of salt spray test (DIN EN ISO 9227), 4 days condensation climate with alternating humidity and air temperature AHT (DIN EN ISO 6270-2), and 48 hours of standard climatic conditions 23°C 50 % rel. humidity (DIN 50014).

This cyclic exposure test is considered to offer the best correlation to outside weathering, in particular also in case of zinc plated substrates. Subsurface corrosion (delamination) indicates the corrosion starting from a defined damage (scribe) in the interface between coating and substrate. The width of the delamination is regarded as a measure for the degree of corrosion protection of car paints under alternating exposure. *Fig. 18* shows the average delamination after 20 VDA test cycles. The delamination attains for all formulations 0.7 to 0.9 mm without significant differences. Likewise, with respect to the degree of blistering 1 to 3 and the blister size 2, no conclusive differentiation was possible between the fillers tested.

The adhesion of the coatings after the VDA test was determined by cross cut test (DIN EN ISO 2409). All results came out equal to those prior exposition between 0 and 1, thus no differentiation could be established.

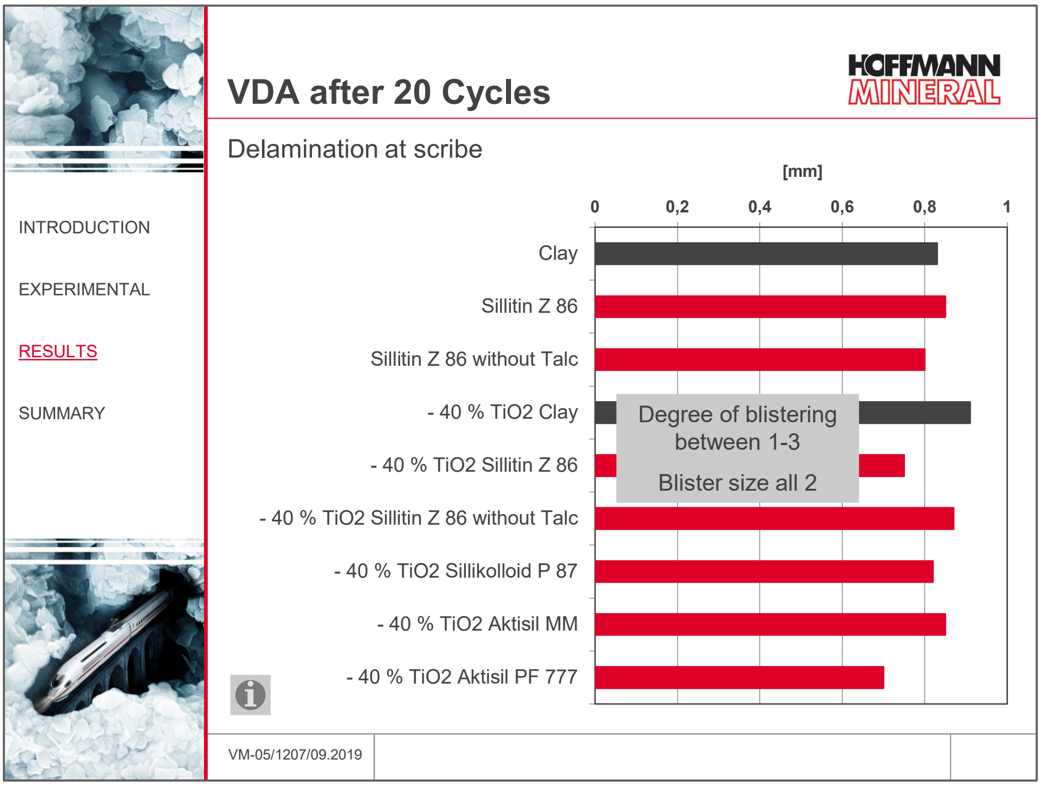
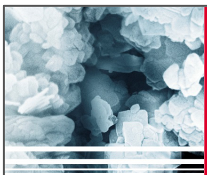


Fig. 18

4 Summary and outlook

Fig. 19 summarizes the filler effects and their advantages and disadvantages in the tests as discussed, reported versus the reference formulation with clay, talc and full titanium dioxide content.



Summary

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Summary of the results "at a glance" Specimen Reference: Standard formulation (with Clay)	L effect, area 2 (gloss 60°)	Throwing powder (corrosion protection limit)	Perforated panels (edge covering)	Cutter knives (edge covering)	Cupping Test	Impact Test -20°C (phosphated panels)	Impact Test -20°C (zinc plated and phosphated panels)	Adhesion (Cross Cut Test)	VDA Test (after20 Cykles) Delamination at scribe
Sillitin Z 86	0	0	+	0	0	0	0	0	0
Sillitin Z 86 without Talc	++	0	+	not tested	+	+	++	0	0
- 40 % TiO2 Clay	0	0	0	-	-	0	-	0	0
- 40 % TiO2 Sillitin Z 86	-	0	0	-	+	0	+	0	0
- 40 % TiO2 Sillitin Z 86 without Talc	+	0	0	not tested	0	0	0	0	0
- 40 % TiO2 Sillikolloid P 87	0	0	0	not tested	-	0	0	0	0
- 40 % TiO2 Aktisil MM	0	0	0	-	0	0	-	0	0
- 40 % TiO2 Aktisil PF 777	-	0	0	0	0	++	0	0	0

Compared to the standard Clay:

- \+ Advantage
- \+ \+ Significant advantage
- \- Disadvantage
- \- \- Significant Disadvantage
- 0 Without any remarkable difference to the standard

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Fig. 19

Sillitin Z 86 without talc shows benefits in the L effect, in particular with respect to a more glossy surface at the critical horizontal area. Furthermore, Sillitin Z 86 offers superior edge covering and high ductility in both tests (cupping test and impact test at -20°C).

Sillitin Z 86 is recommended because of its favorable price / performance ratio.

Substituting 40 % titanium dioxide, Sillitin P 87 and Aktisil MM show benefits in the L effect. They are not as sentitive to the presence of talc as Sillitin Z 86 at the critical horizontal area. Aktisil PF 777 with substitution of 40 % titanium dioxide shows comparable results to the clay, but better impact test at -20°C on phosphatized panels.

5 Appendix

Property	Unit	Titanium dioxide	American clay	Sillitin Z 86 (Neuburg Siliceous Earth)	Sillikolloid P 87 (Neuburg Siliceous Earth)	Aktisil PF 777 (Neuburg Siliceous Earth)	Aktisil MM (Neuburg Siliceous Earth)	Talc
Composition		Titanium dioxide	Clay	Silica / kaolinite	Silica / kaolinite	Sillitin Z 86 alkyl functionalized	Sillitin Z 86 mercapto funcionalized	Talc
Particle size distribution d10	µm	0.1	0.3	0.6	0.5	0.8	0.7	1.8
d50	µm	0.3	1.9	1.9	1.5	2.2	2.2	5.2
d97	µm	0.9	8	9	6	10	10	17
Residue 40µm	ppm	23	3	3	4	6	7	5
Loss on ignition	%	1.2	14.4	4.5	5.4	5.4	5.4	3.7
Volatile matter at 105°C	%	0.5	1.0	0.5	0.4	0.2	0.4	0.2
Electrical conductivity	µS / cm	57	154	78	49	-	37	78
Oil absorption	g / 100g	26	56	50	50	35	49	55
pH value		7.4	4.7	8.1	7.3	7.1	7.2	9.2
Brightness Y			82.7	81.8	81.9	79.6	80.9	89.0
Z			82.5	74.5	74.9	74.6	74.7	93.3