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Optimization of corrosion protection properties of waterborne 2C epoxy clear coats with Neuburg Siliceous Earth

Author: Susanne Reiter
Hubert Oggermüller

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HOFFMANN MINERAL GmbH • Muenchener Strasse 75 • D-86633 Neuburg (Donau) • Phone +49 (0) 8431 53-0
www.hoffmann-mineral.com • e-mail: info@hoffmann-mineral.com

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1 Introduction

Anti-corrosion paints with sufficient protection properties can only be prepared with the help of anti-corrosion pigments. When working with such pigments, however, an application as clear coats is not possible, as the refractive indices of the binder and the pigments are very different.

The fine sized Neuburg Siliceous Earth, on the other hand, is characterized by a refractive index close to that of the binder, which makes the filler in the coating appear transparent. As in earlier anti-corrosion studies found, Neuburg Siliceous Earth as a functional filler is able to decidedly improve the corrosion protection properties because of its unique mineralogical composition.

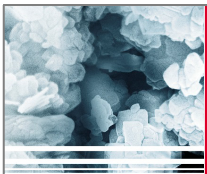
The objective of this study was to meet the following requirement profile of the clear coat by using Neuburg Siliceous Earth:

- sufficient flexibility and excellent adhesion on various substrates
- good transparency
- no milky blushing of the clear coat after exposure to humidity
- improved anti-corrosion properties

2 Experimental

2.1 Base formulation

The base formulation from the Allnex Austria GmbH Company given in *Fig. 1* served as the starting point of the study. The A-Component, the non-labeled amine hardener BECKOCURE™ EH 2260w/41WA, was crosslinked stoichiometrically to 60 % with the B-Component, which consisted of a mixture of the aqueous liquid resin BECKOPOX™ EP 147w and the flexible epoxide dispersion BECKOPOX™ EP 386w/52 WA.



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Base Formulation

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	Description	Parts by weight
A-Component: BECKOCURE™ EH 2260w/41WA [*1]	Amine hardener	61.1
B-Component: BECKOPOX™ EP 147w [*1] BECKOPOX™ EP 386w/52WA [*1]	Epoxy resin	12.5 37.5
Total		111.1
Solids content [%]		51.4

[*1] http://allnex.com/the-easy-cure-system

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Fig. 1

Without dilution, the solids content was 51.4 %.

2.2 Fillers used and characteristics

Neuburg Siliceous Earth, extracted in the surrounding of Neuburg (Danube), is a natural combination of corpuscular 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, which are covered by amorphous silica opal-like.

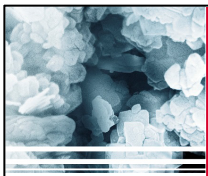
The calcination of the Neuburg Siliceous Earth helps to drive off the crystal water present in the kaolinite portion and to generate calcined kaolinite. The crypto-crystalline silica portion remains inert under the temperature chosen. Through an integrated air classifier process grain sizes > 15 µm are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

Fig. 2 to 4 summarize the typical properties of the fillers used. Sillitin Z 89 is a light-colored grade of Neuburg Siliceous Earth. Silfit Z 91 is calcined and in consequence the brightest and most color neutral grade. Aktisil AM is modified with an amino functional group based of the Neuburg Siliceous Earth material Sillitin Z 86, and therefore is characterized by the lowest brightness L* and the highest yellowish tint b*. The experimental test product TP 2008037 is an amino functional version of Sillitin Z 89, and as a result more color neutral than Aktisil AM.

The high degree of fineness of the Neuburg Siliceous Earth results in mean particle size diameter d_{50} of around 2 µm and a top cut of about 7 to 10 µm.

The oil absorption represents the binder requirement and is between 45 and 61 grams of linseed oil per 100 g of filler for the grades included in this study.

All samples tested are characterized by a specific surface area BET of 8 to 11 m²/g.



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Filler Characteristics

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Filler	Description	Surface Treatment
Sillitin Z 89	Neuburg Siliceous Earth d_{50}: 1.8 µm, d_{97}: 7.1 µm	none
Silfit Z 91	Calcined Neuburg Siliceous Earth d_{50}: 2.0 µm, d_{97}: 8.6 µm	none
Aktisil AM	Neuburg Siliceous Earth d_{50}: 2.2 µm, d_{97}: 10 µm	amino functionalized
TP 2008037	Neuburg Siliceous Earth (Experimental product similar to Aktisil AM, but more color neutral) d_{50}: 2.2 µm, d_{97}: 8.3 µm	amino functionalized

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Fig. 2

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Filler Characteristics

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Filler	Oil absorption [g/100g]	Specific surface area BET [m²/g]
Sillitin Z 89	55	11
Silfit Z 91	55	8
Aktisil AM	45	9
TP 2008037	61	9

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Fig. 3

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Filler Characteristics

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Filler	Color L*	Color a*	Color b*
Sillitin Z 89	94.7	-0.1	3.4
Silfit Z 91	95.3	-0.2	0.9
Aktisil AM	93.0	0.5	8.1
TP 2008037	94.8	-0.1	3.4

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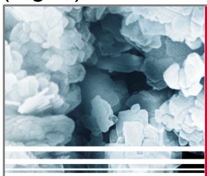
Fig. 4

2.3 Formulation variations

The unfilled base formulation served as control and as the starting point of the study. Sillitin Z 89, Silfit Z 91 and Aktisil AM were evaluated at a loading of 15 parts by weight (pbw), which led to a pigment volume concentration (PVC) of 9.9 %. Aktisil AM was also additionally tested at 25 pbw in order to obtain an improved corrosion protection via the increased solids content resp. PVC. The TP 2008037 was analogously used only in the higher loading of 25 pbw, in order to arrive at a more color neutral comparison version (*Fig. 5*).



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Formulations

Parts by weight

	Control	Sillitin Z 89 15 pbw	Silfit Z 91 15 pbw	Aktisil AM 15 pbw	Aktisil AM 25 pbw	TP 2008037 25 pbw
A-Component (Amine hardener)	61.1	61.1	61.1	61.1	61.1	61.1
+ Filler	0	15	15	15	25	25
B-Component	50	50	50	50	50	50
Total	111.1	126.1	126.1	126.1	136.1	136.1
Solids content [%]	51.4	57.1	57.1	57.1	60.3	60.3
PVC [%]	0	9.9	9.9	9.9	15.5	15.5

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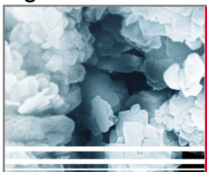
Fig. 5

Figure 6 shows the same composition of the formulations, but expressed in percent.



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Formulations

Parts per cent

	Control	Sillitin Z 89 15 pbw	Silfit Z 91 15 pbw	Aktisil AM 15 pbw	Aktisil AM 25 pbw	TP 2008037 25 pbw
A-Component (Amine hardener)	55	48.45	48.45	48.45	44.90	44.90
+ Filler	0	11.90	11.90	11.90	18.37	18.37
B-Component	45	39.65	39.65	39.65	36.73	36.73
Total	100	100	100	100	100	100
Solids content [%]	51.4	57.1	57.1	57.1	60.3	60.3
PVC [%]	0	9.9	9.9	9.9	15.5	15.5

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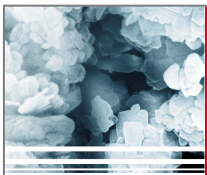
Fig. 6

2.4 Adjustment of application viscosity

As the control as well as the filled formulations were too viscous for application, they were diluted with water to a viscosity suitable for practical use. In doing so, at first the A- and the B-Component were mixed in the appropriate ratio and then immediately diluted with water.

The aimed application viscosity at a shear rate of 25 s^{-1} should be in the region of 1.8 to 2.0 Pas, but could not precisely be reached in all cases. For this reason, the dilution with water in percent is indicated with “setpoint” (meets the aimed viscosity) and the “real value” (reflecting the resulting viscosity), see *Fig. 7*. The measured values of the viscosity were taken from the corresponding upward curve.

The results shown for the solids content already include the indicated “real value dilution”.



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Adjustment of Application Viscosity

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Component A and B mixed, plus water for dilution

	Control	Sillitin Z 89 15 pbw	Silfit Z 91 15 pbw	Aktisil AM 15 pbw	Aktisil AM 25 pbw	TP 2008037 25 pbw
Water [%]	Setpoint ~ 3.0 Real value 3.8	4.7	5.0	Setpoint ~ 5.0 Real value 6.8	Setpoint ~ 7.5 Real value 5.6	Setpoint ~ 7.5 Real value 4.9
Resulting viscosity at 25 s^{-1} [Pa*s] *1	1.5	1.9	1.8	1.4	2.6	2.4
Solids content [%]	49.5	54.6	54.4	53.5	57.1	57.5

*1 Intended application viscosity at 25 s^{-1}: 1.8 – 2.0 Pa*s

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Fig. 7

2.5 Batch preparation, application and drying

The batches were prepared in a dissolver - mounted agitator bead mill (APS 1000) with the aid of glass beads (diameter 2 mm) and cooling with water. The batch size of the A-Component had a weight of about 350 g. The batches were dispersed for 10 minutes at 2000 rpm, which corresponds to a peripheral speed of 7.9 m/s.

Subsequently the A- and B-Components were mixed in the given ratio and diluted with deionized water.The application was carried out with a Walther Pilot spray gun with a nozzle diameter of 2 mm and a compressed air supply of about 1.7 bar.

For this study two different substrates, both without pre-treatment, were used:
- Aluminum: Gardobond F
- Steel: Gardobond OC

The drying of the coated panels took place for 30 minutes at 60 °C. They were then stored for further seven days at 23 °C and a relative humidity of 50 %, in order to achieve full cure. The dry film thickness came out between 60 and 80 µm, but for the same test always samples of similar thicknesses were used.

2.6 Test methods

Color values

The CIE color values L* and b* were determined with a spectrophotometer, test geometry d/8° and light quality D 65.

Gloss

The gloss was measured with a Micro-Tri-Gloss from the Byk Company.

Pendulum hardness (Koenig)

The pendulum hardness was determined according to DIN EN ISO 1522. The hardness of a coating is indicated by the time of damping, expressed by the time in seconds which the pendulum needs to go back from 6° to 3° deflection.

Flexibility (Cupping Test)

In the cupping test according to DIN 1520 a hemisphere was slowly pressed with constant speed from the backside into the coating. During the test, the formation of cracks in the coating is observed. The results are expressed as the maximum possible cupping in millimeters where no cracks are yet visible.

Adhesion (Cross Cut Test 1mm)

For the cross-cut test according to DIN EN ISO 2409 the coating was cut with the aid of a cross-cut knife under angles of 90°. Based on the degree of chipping caused by the crossing cuts, the cross-cut index was defined as indicated in the standard. At a cross-cut index of GT 0, the edges of the cuts are completely smooth and none of the lattice squares shows evidence of chipping; with an index of GT 5, more than 65 % of the coating surface suffer from chipping.

Humidity test

The humidity test was run for 240 hours according to DIN EN ISO 6270-2 CH on aluminum and steel substrates. After this time, the panels were evaluated for the remaining gloss, the degree of blistering according to DIN EN ISO 4628-8, the degree of rusting according to DIN EN ISO 4628-3, the cross-cut as an indicator for the adhesion, and the transparency resp. the milky blushing by measuring the color and determination of delta E.

Salt spray test

The neutral salt spray test was also carried out for 240 hours according to DIN EN ISO 9227. Prior to exposure, two coated panels of each substrate (steel, aluminum) were lengthwise scribed with a scratching tool according to van Laar. After exposure to salt spray, the remaining gloss and the delamination at scribe according to DIN EN ISO 4628-8 were evaluated.

3. Results

3.1 Color

As a result of the transparent nature of the coating film, the measured color represents mainly the color of the substrate. However, because of the use of fillers certain color changes can occur, which then are compared and judged versus the unfilled control.
The a* value which represents the red-green contributions, for all formulations was found at a comparable level of -0.1 to 0.2. This means changes through the use of fillers could not be detected.

The brightness L* gave the highest result for the control with 67.6. For the variants with filler the L* value still was found at a level of around 64 to almost 66 (*Fig. 8*), which confirms the ongoing good transparency of the clear coat despite of the filler addition.

The b* value, which describes the yellow-blue contributions, was the most neutral for the control with 1.1, followed by Sillitin Z 89 and Silfit Z 91 with 3.8 resp. 3.7. When working with the yellowish tinted Aktisil AM, the higher b* value of 7.5 was reached already with the low loading of 15 pbw. A higher filler portion of 25 pbw led to an increased b* value of 9.6. The experimental product TP 2008037 imparted an improved color neutrality. Even at the high loading of 25 pbw the product just caused a b* value of 5 (*Fig. 9*).

So in summary, a filler caused color change is only noticeable in the b* value, although the lower levels are hardly to distinguish by naked eye.

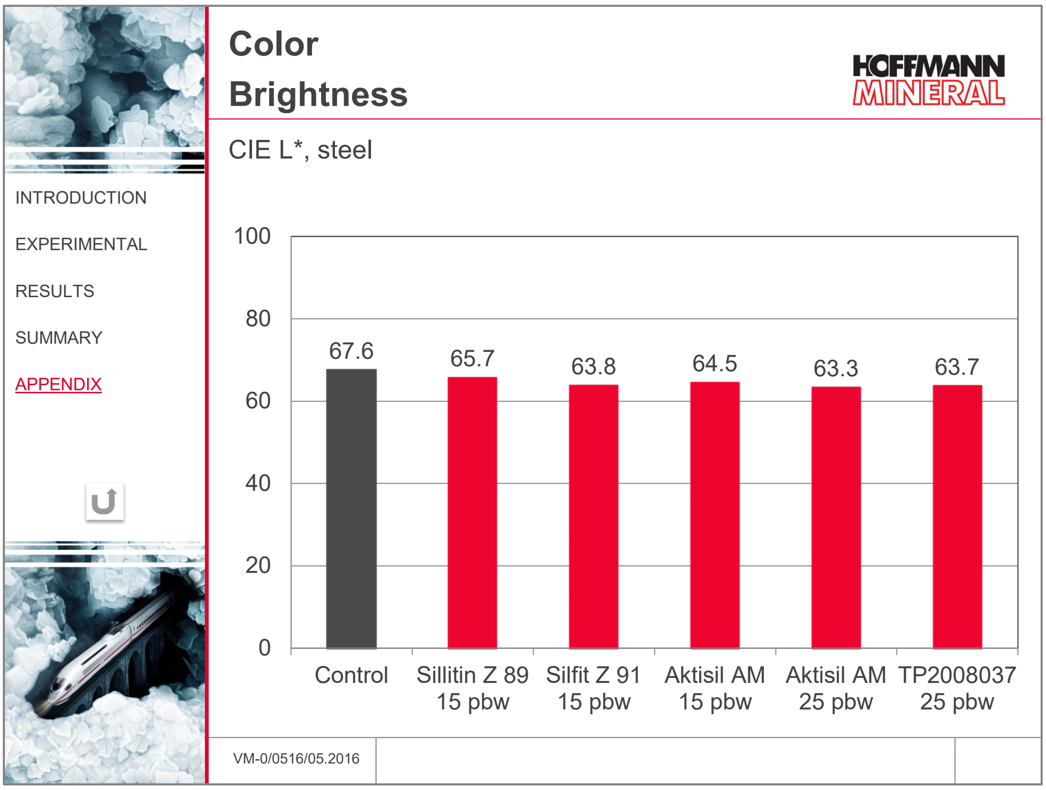
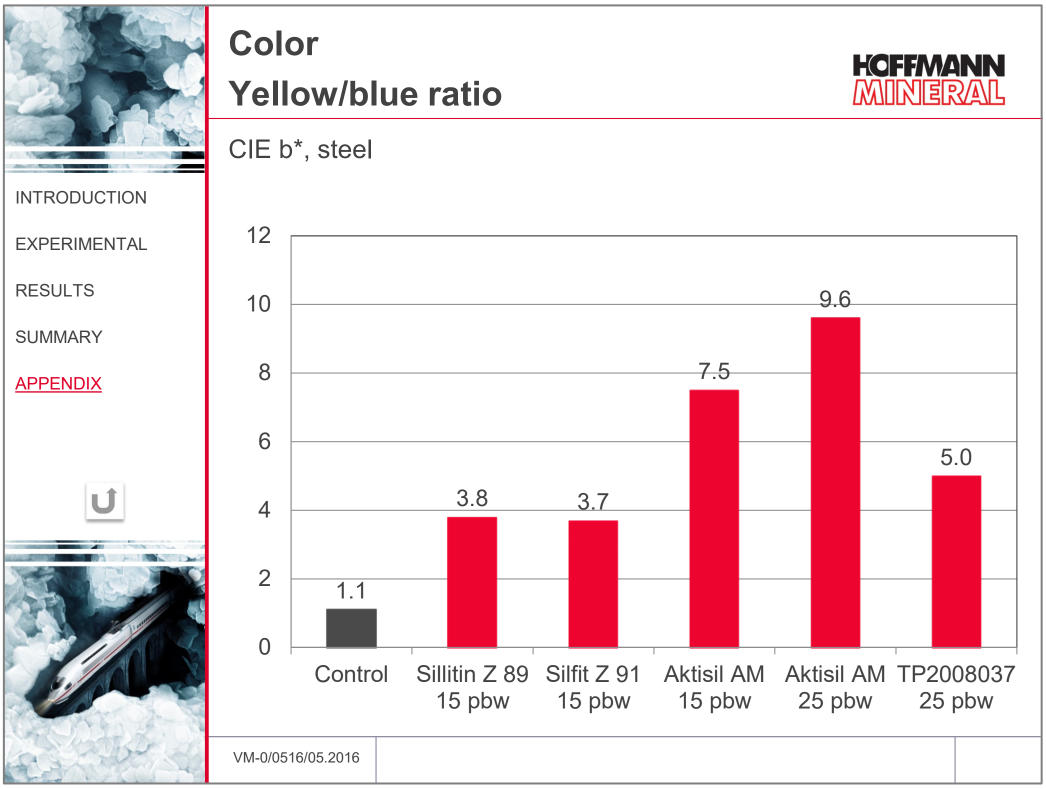


Fig. 8


Color
Yellow/blue ratio
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CIE b*, steel
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12
10
8
6
4
2
0
1.1
3.8
3.7
7.5
9.6
5.0
Control
Sillitin Z 89 15 pbw
Silfit Z 91 15 pbw
Aktisil AM 15 pbw
Aktisil AM 25 pbw
TP2008037 25 pbw
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Fig. 9

3.2 Gloss

Fig. 10 shows the gloss at 60°. The first bar in the graph refers to the gloss measured on steel substrate, the second one on aluminum. Quite evidently, as a result of the transparency of the clear coat, the substrate takes also part in the determination and the aluminum surface is characterized by a higher reflection. But this result can also be interpreted as a marked confirmation of the high-level transparency.

The unfilled control offered the highest gloss, but the coatings with the Neuburg Siliceous Earth grades are able, at least at the lower loading of 15 pbw, to retain the gloss at a very acceptable level.

When working with 25 pbw Neuburg Siliceous Earth, the gloss came out moderately reduced as a result of the higher pigment volume concentration.

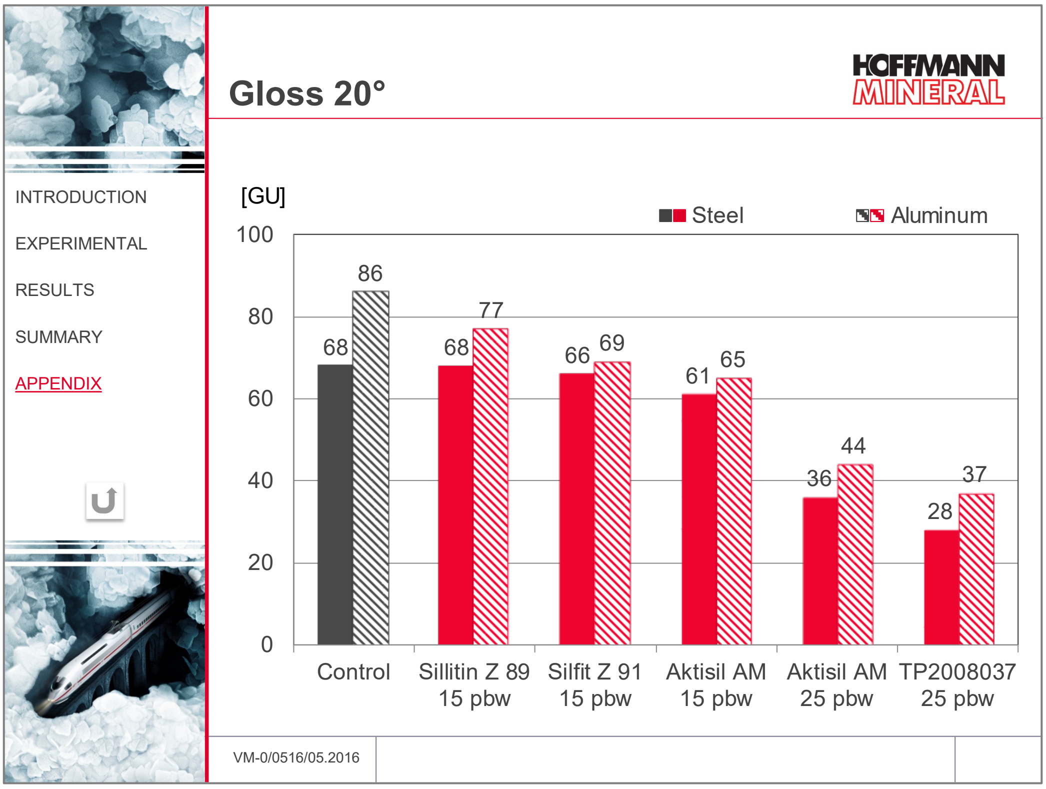


Fig. 10

3.3 Pendulum hardness

The pendulum hardness was determined on steel substrate after three resp. seven days of storage at 23 °C and 50 % relative humidity. The first bar in *Fig. 11* refers to the result after three days, the second one after seven days.

Apart from the time-related hardness increase no important effects of the fillers could be noticed, even so versus the unfilled control formulation.

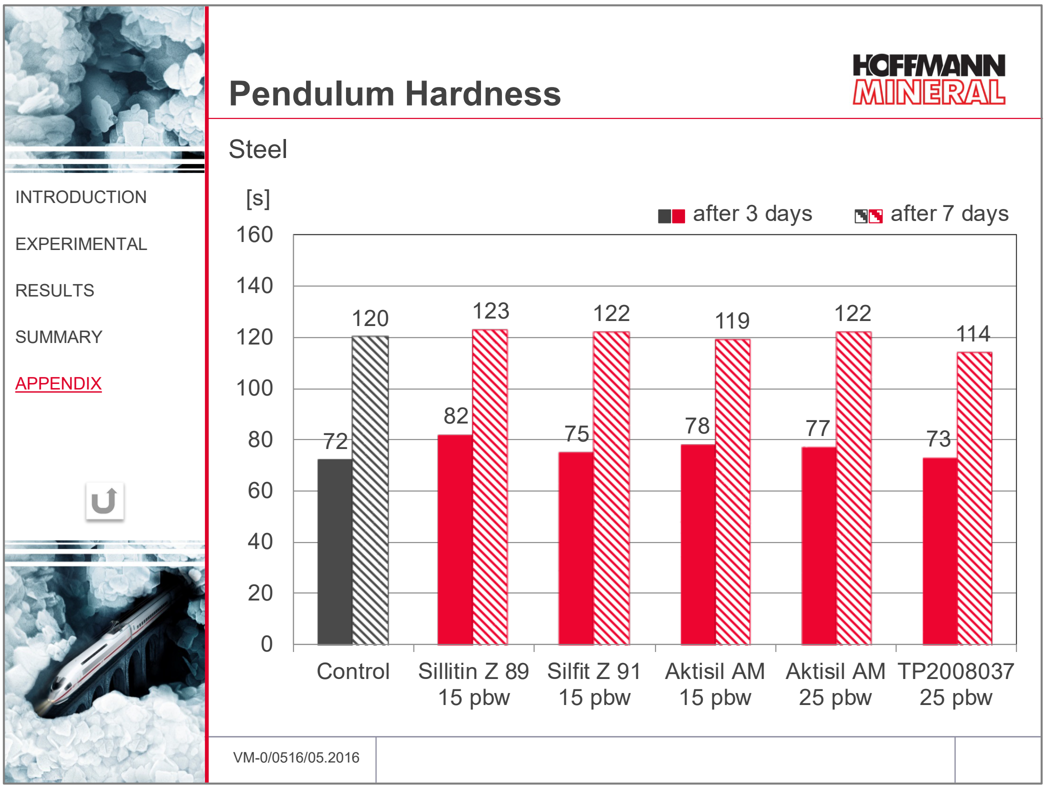


Fig. 11

3.4 Flexibility

The flexibility was determined after seven days of storage at room temperature by the Erichsen Cupping Test. The control impressed with an outstanding cupping result of 10 mm. The use of fillers leads to a marginal increase of the brittleness: at 15 pbw of filler the cupping value reaches about 8 mm, for the two PVC increased variants with 25 pbw, the result for Aktisil AM comes off somewhat higher than 6 mm, with TP 2008037 at 7.4 mm. In summary, it can be stated that the filler-loaded versions all offer a good flexibility with cupping levels of 6 to 8 mm (*Fig. 12*).

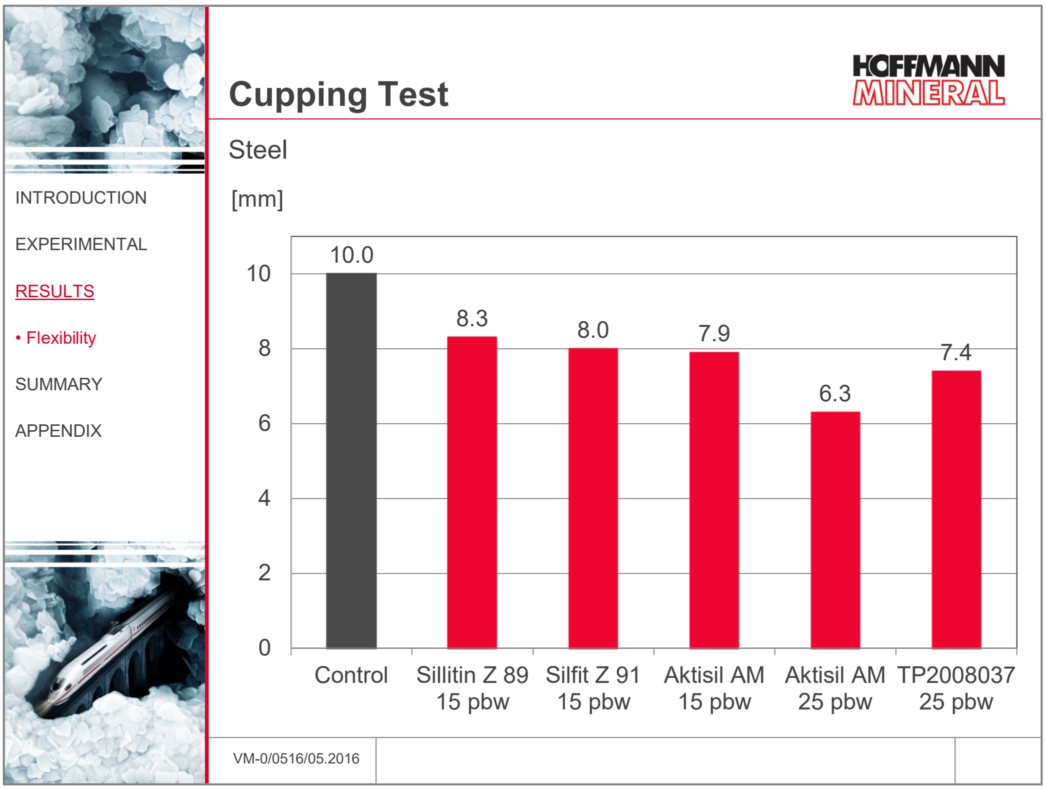


Fig. 12

3.5 Adhesion

The adhesion of the clear coat on untreated substrates (steel and aluminum) was evaluated via the cross cut test. The unfilled control and the formulations loaded with filler on both substrates showed outstanding adhesion with a cross cut rating of GT 0 (*Fig. 13*).

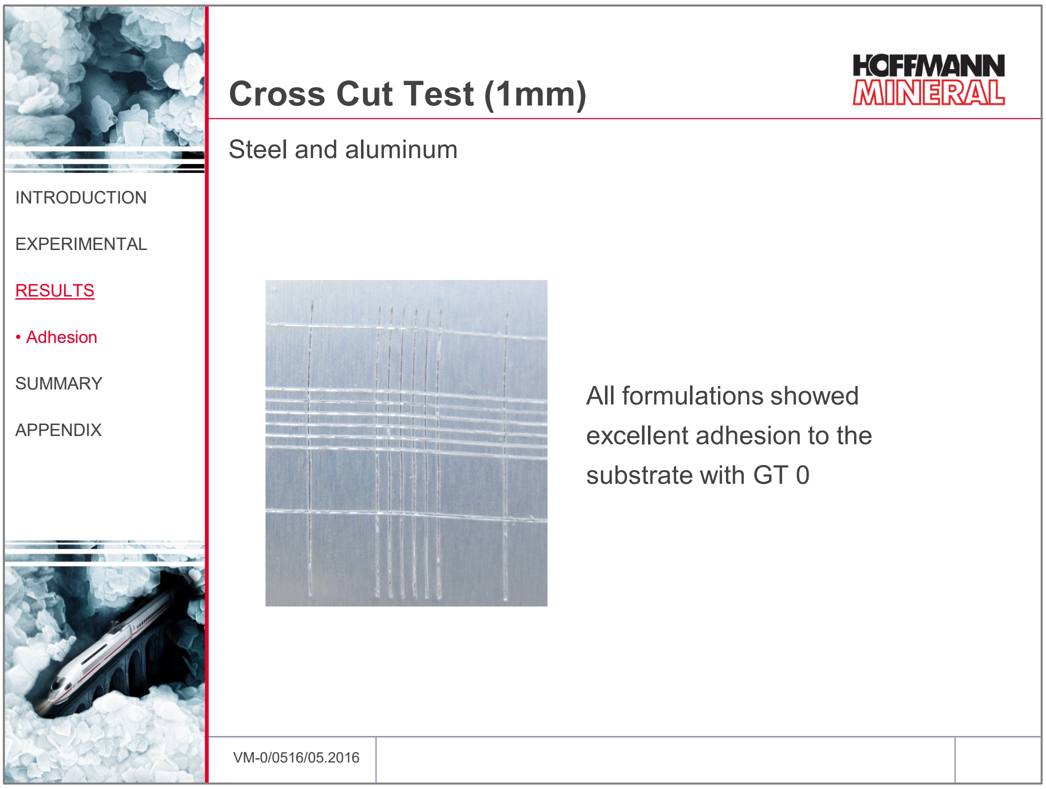


Fig. 13

3.6 Humidity test

The humidity test was run for 240 hours. After this time, the remaining gloss, the degree of blistering as well as rusting, the transparency resp. the white blushing were evaluated via color measurement, the determination of delta E and the cross cut test as an indicator for the adhesion.

Fig. 14 illustrates the 60° gloss. The first bar refers to the gloss result, the second bar indicates the remaining gloss in percent of the initial level. The higher the last result comes out, the better the gloss is retained over the exposure time. Evidently the control came off poorest with only 86 % of remaining gloss. Sillitin Z 89 was already able to improve the remaining gloss to 92 %. When working with Silfit Z 91 or Aktisil AM the gloss after the 240 hours humidity test was almost the same as prior to the test. TP 2008037 showed the very best gloss retention during the exposure chosen. In summary, it is virtually possible to distinctly improve the gloss retention via the addition of fillers.

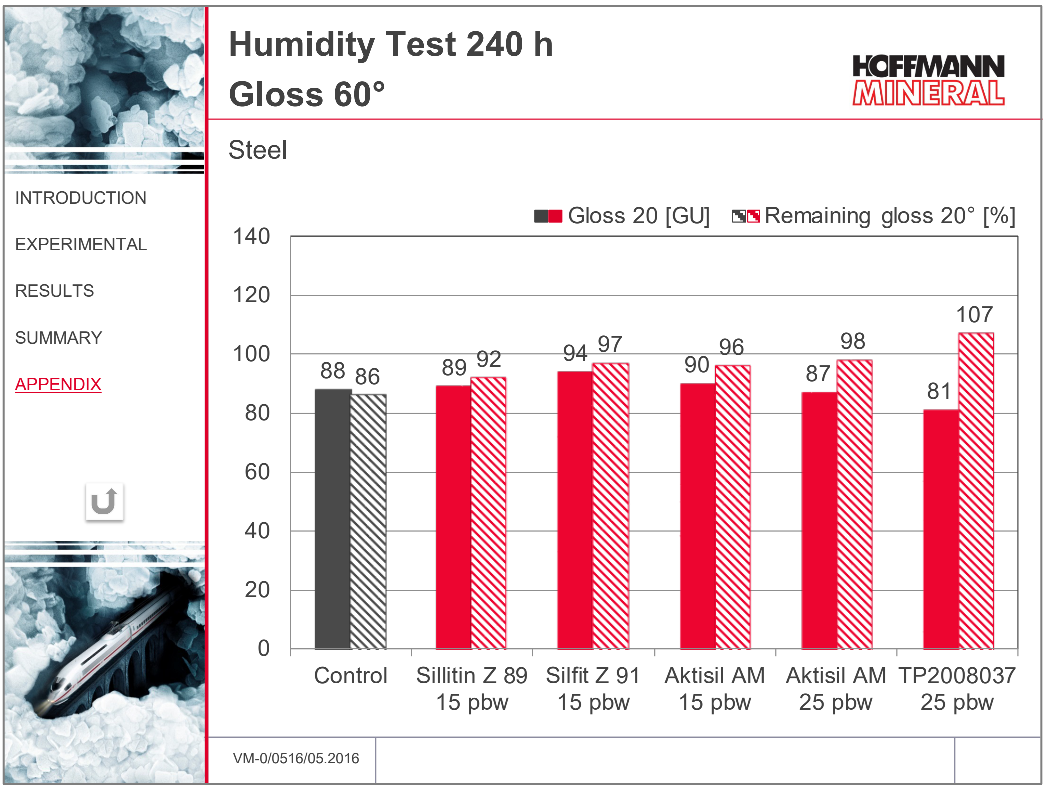


Fig. 14

Fig. 15 visualizes a panel after 240 hours humidity test. The image serves as reference for all tested substrates and formulation variants, there was no blistering or rust formation. Hence all results were rated at Ri 0 according to the standard.

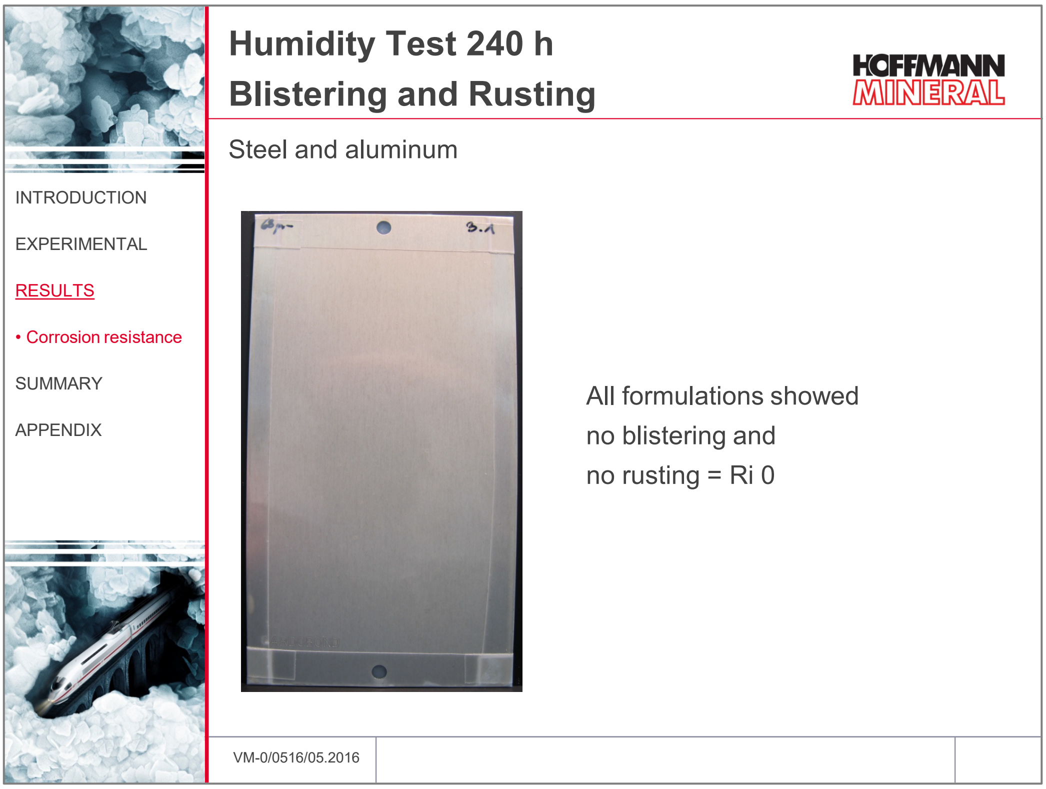


Fig. 15

Fig. 16 gives evidence of the transparency after 240 hours humidity test, measured as delta E. A higher delta E level indicates a higher opacity (corresponding to milky-white blushing) after exposure.
The control came off with the highest delta E result of 6.6, and thus showed the strongest milky-white blushing. The use of Sillitin Z 89 or Aktisil AM at 15 pbw improved the clear coat quality with bringing down delta E to 4.7 resp. 4.2. When adding 25 pbw of Aktisil AM or TP 2008037, the transparency could still further be optimized (delta E 3.1 resp. 3.6). The obviously best result could be obtained with Silfit Z 91, where almost the full original transparency could be retained over the total time of exposure. This is also distinctly visible in *Fig. 17.*

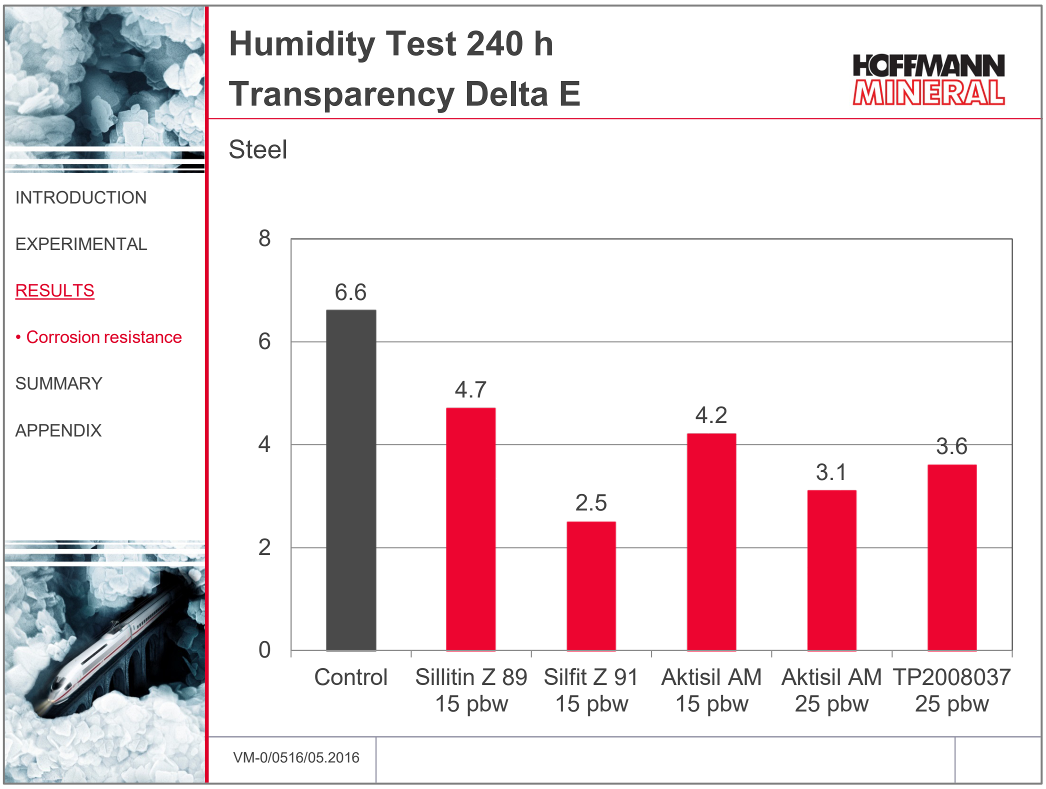


Fig. 16

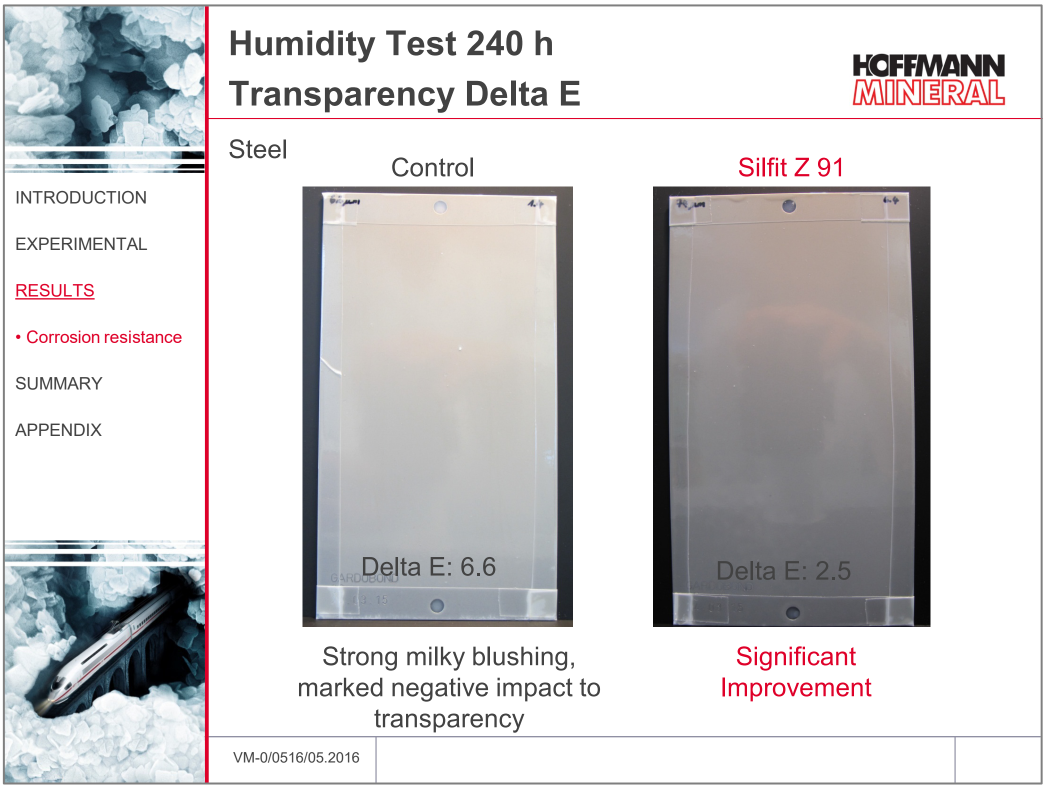


Fig. 17

In order to determine the adhesion of the clear coat on steel substrate, the cross cut test was done immediately after 240 hours humidity test (first bar in *Fig. 18*). After one hour of regeneration at room temperature, a second test was run, see the second bar in the graph. The cross cut test for all formulations was found between 0 and 1, and this is why a medium level of 0.5 is indicated. Such a result corresponds to an excellent adhesion of the clear coat.

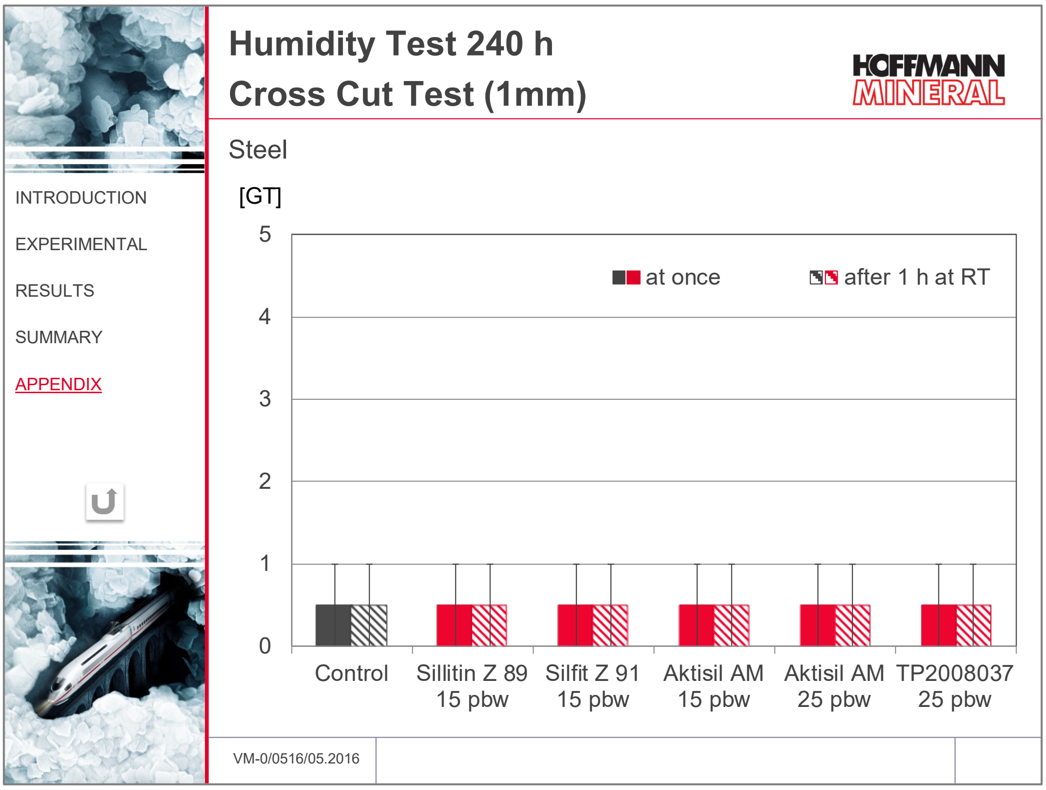


Fig. 18

On aluminum substrate, this result could be fully confirmed. The cross cut test result for all formulations came out at 0.

3.7 Salt Spray Test

After 240 hours of exposure to a neutral salt spray, the remaining gloss and the delamination at scribe were evaluated.

Fig. 19 illustrates the 60° gloss after exposure. The first bar refers to the measured gloss result, the second bar to the remaining gloss in percent of the original level. The higher this result comes out, the better is the retention of gloss during the time of exposure. The control with only 95 % remaining gloss was positioned in the last place. The addition of Neuburg Siliceous Earth led to a retention of 100 % of the gloss. The functionalized grades Aktisil AM and TP 2008037 gave the very best results with a loading of 25 pbw, and therefore take the top position of the assessment.

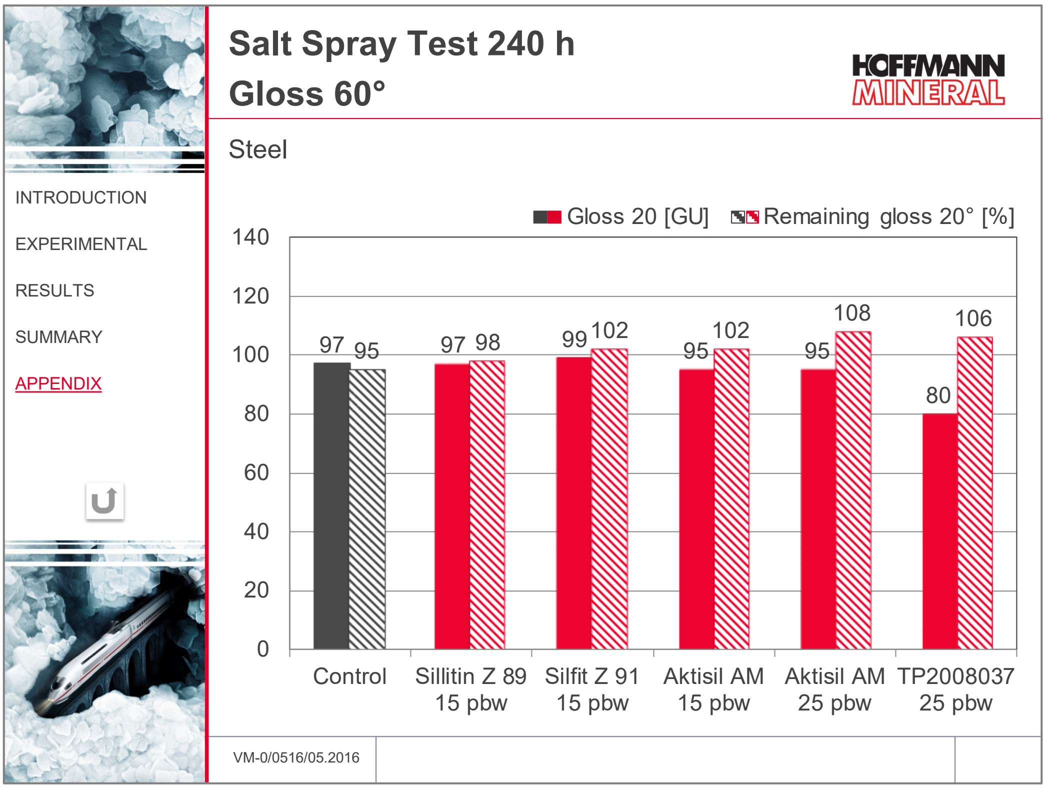


Fig. 19

The delamination was determined according to the standard by trying to remove the non-adhering coating with a cutter knife, starting at the scribe. As evident from *Fig. 20,* in case of the aluminum substrate it was not possible to detach the coating. This way, the delamination for all formulations remains at 0 mm.

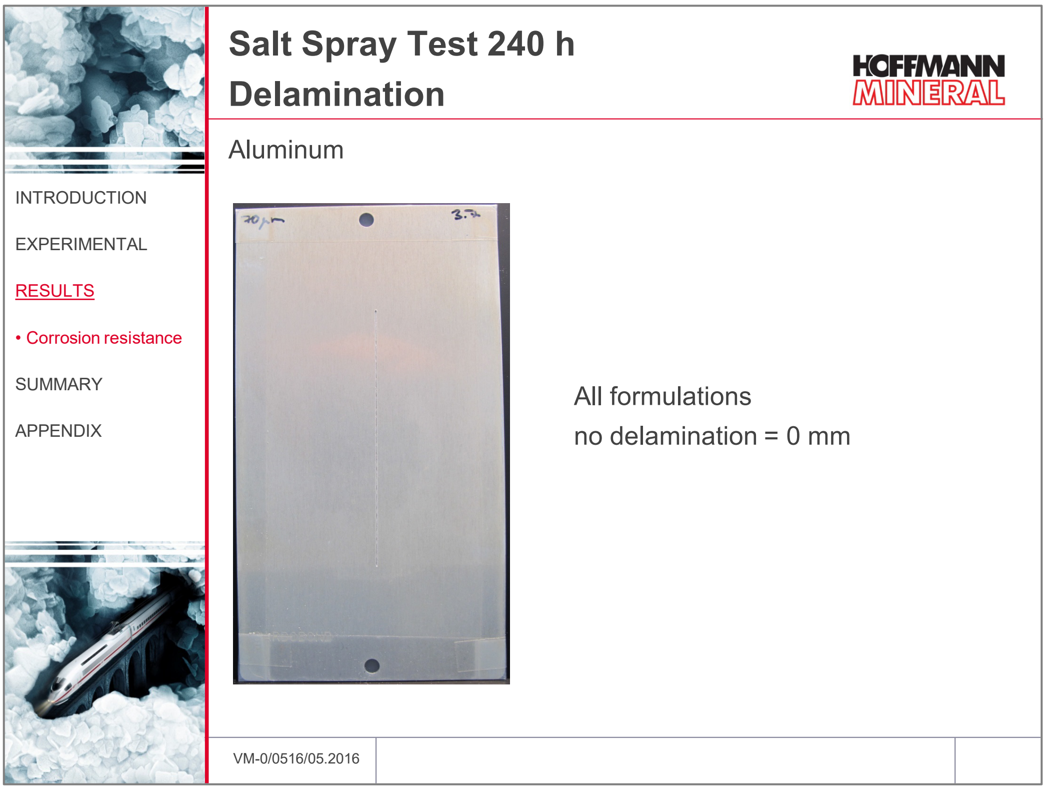
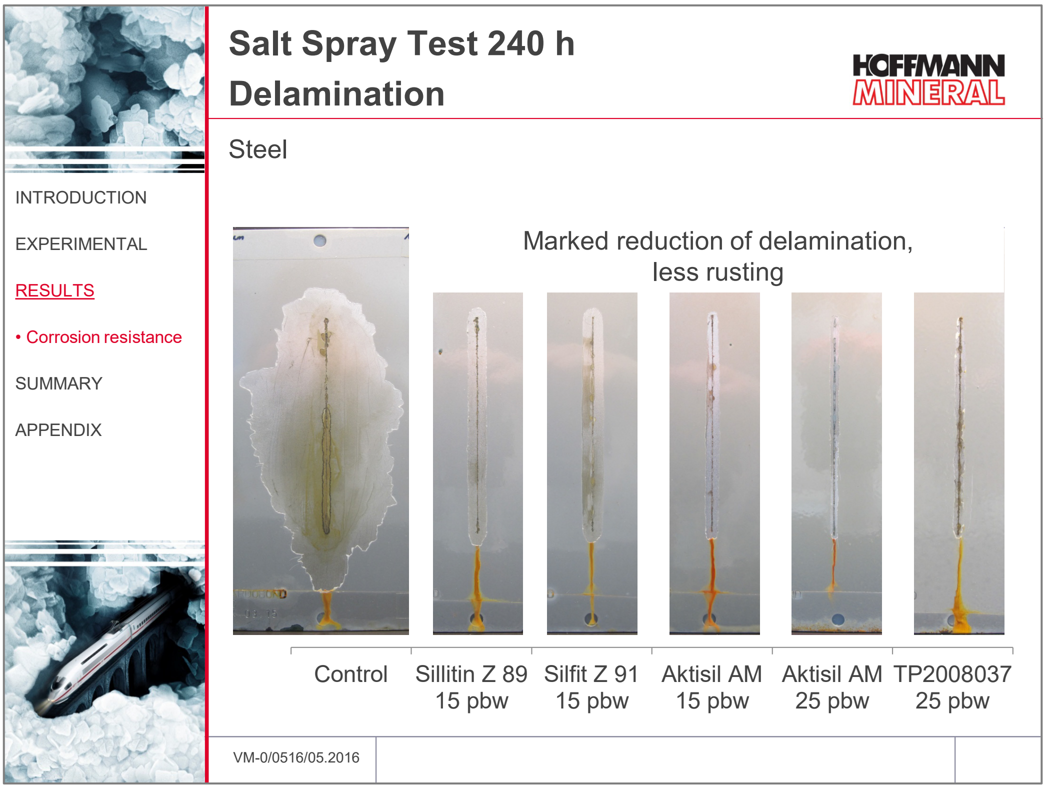


Fig. 20

On steel substrate, by contrast, marked differences can be observed between the unfilled control and the filler loaded clear coats. *Fig. 21* indicates the delaminated areas of the individual formulations. The control had very poor adhesion, the coating could be removed from the scribe almost to the edge of the panel. Working with 15 pbw Sillitin Z 89 clearly reduced the area of delamination, the coating could be detached just over some millimeters. Similar results were achieved with the color neutral Silfit Z 91. However, with a functional filler such as Aktisil AM, an improvement could be obtained already with 15 pbw in comparison with the untreated Sillitin Z 89 or Silfit Z 91. With the next step of filler loading at 25 pbw, a further progress came within reach, resulting in an even more optimized situation with a delamination tending to go down towards zero. The experimental product TP 2008037, which has been subjected to the same amino functional group as Aktisil AM (only starting from a more color neutral base material), was comparable with Aktisil AM.

In *Fig. 22*, the delamination figures according to the standard are illustrated. The two bars refer to the double determination using two panels. Apart from the control, no bigger variations between the results of the two panels were noticeable. This means the conclusion is justified and confirmed that the delamination can be reduced to a minimum by using Neuburg Siliceous Earth as functional filler.

Moreover, also the rust formation on the metal surface within the delaminated area comes off reduced, and thus distinctly improved.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Sillitin Z 89 15 pbw
Silfit Z 91 15 pbw
Aktisil AM 15 pbw
Aktisil AM 25 pbw
TP2008037 25 pbw
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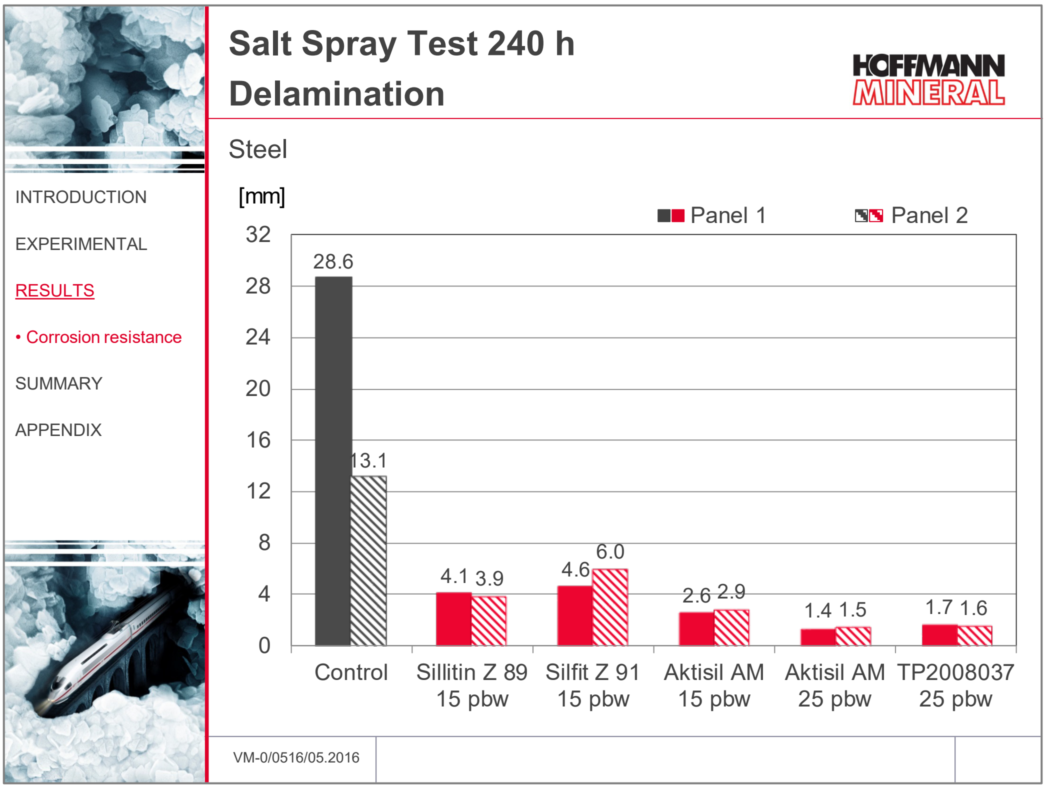
Fig. 21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[mm]
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Panel 2
32
28
24
20
16
12
8
4
0
28.6
13.1
4.1 3.9
4.6 6.0
2.6 2.9
1.4 1.5
1.7 1.6
Control
Sillitin Z 89 15 pbw
Silfit Z 91 15 pbw
Aktisil AM 15 pbw
Aktisil AM 25 pbw
TP2008037 25 pbw
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Fig. 22

4 Summary

A waterborne two-component epoxy clear coat, modified with Neuburg Siliceous Earth offers the following quality profile:

- ✓ transparency and color neutrality, especially by using Silfit Z 91
- ✓ high gloss (60° angle: >80 GU)
- ✓ excellent adhesion to the substrate (Cross Cut Test result 0 to 1)
- ✓ good flexibility (Cupping Test result 6 to 8 mm)
- ✓ best price-performance ratio, especially by using Sillitin Z 89
- ✓ no white blushing of the clear coat after exposure to humidity test, complete retention of transparency and color neutrality over exposure time, especially by using Silfit Z 91 at a loading of 15 pbw
- ✓ significant improvement of corrosion resistance:
    - working with Aktisil AM or the more color neutral TP 2008037 minimizes the delamination at scribe. This optimization is particularly evident in the higher PVC version with 25 pbw
    - reduced rust formation