Partial replacement of titanium dioxide by Neuburg Siliceous Earth in a white polyester based coil coating top coat

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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 an excellent adhesion of the individual layers.

The primer coat will protect the metal against corrosion and offers good adhesion to the substrate. In particular the topcoat has to respond to decorative requirements and offer the following functional properties:

- ✓ high flexibility
- ✓ easy cleaning
- ✓ high scratch resistance
- ✓ good adhesion to the primer
- ✓ long term resistance against UV light and outdoor weathering

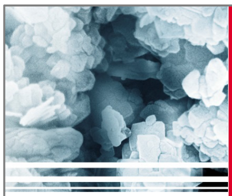
The present report will answer the question whether in a white, exclusively, titanium dioxide pigmented top coat, a functional high quality filler such as the Neuburg Siliceous Earth is able to compensate a partial replacement of the titanium dioxide and still maintain the optical properties, especially color and hiding power, as well as the mechanical properties.

The starting point of the study was a polyester-based white topcoat formulation with a titanium dioxide content of 28 % without any filler.

2 Experimental

2.1 Base formulation and variations

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



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Base Formulation *

HOFFMANN MINERAL

Top Coat			%
A	Dynapol LH 538-02	Binding agent (Polyester)	43.2
	Aerosil 200	Rheological additive (Fumed silica)	0.2
	Kronos 2310	Pigment (Titanium dioxide)	28.1
	Solvesso 150	Solvent	6.0
B	Cymel 303	Melamine resin	7.0
	Cymel 327	Melamine resin	1.5
	Nacure 2500	Catalyst	0.7
	Resiflow FL 2	Leveling agent	0.5
	Byk 057	Defoaming agent	0.5
	Butyldiglycol acetate	Solvent	12.3
Total			100.0

Solids content w/w	[%]	65
Solids content v/v	[%]	53.7
Pigment volume concentration (PVC)	[%]	17.5

* by Evonik

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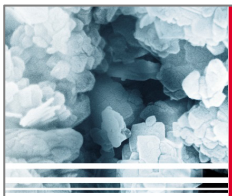
Fig. 1

Starting from this base formulation, 20 % of the titanium dioxide pigment were replaced by two different grades of Neuburg Siliceous Earth, Sillitin Z 89 and Aktifit AM. This replacement was done at equal volume (3.7 parts) and respectively at equal weight (5.6 parts).

Fig. 2 lists the corresponding formulation variations. With the replacement at equal volume, the pigment volume concentration (PVC) of the reference formulation (17.5 %) is being maintained. The replacement at equal weight results in an increase of the PVC to 19.1 % due to the different densities of titanium dioxide and Neuburg Siliceous Earth (*Fig. 3*).



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Formulations

HOFFMANN MINERAL

		by equal volume 3.7 pbw		by equal weight 5.6 pbw	
	Control	Sillitin Z 89	Aktifit AM	Sillitin Z 89	Aktifit AM
Dynapol LH 538-02	43.2	43.2	43.2	43.2	43.2
Aerosil 200	0.2	0.2	0.2	0.2	0.2
Kronos 2310	28.1	22.5	22.5	22.5	22.5
Sillitin Z 89		3.7		5.6	
Aktifit AM			3.7		5.6
Solvesso 150	6.0	6.0	6.0	6.0	6.0
Cymel 303	7.0	7.0	7.0	7.0	7.0
Cymel 327	1.5	1.5	1.5	1.5	1.5
Nacure 2500	0.7	0.7	0.7	0.7	0.7
Resiflow FL 2	0.5	0.5	0.5	0.5	0.5
Byk 057	0.5	0.5	0.5	0.5	0.5
Butyldiglycol acetate	12.3	12.3	12.3	12.3	12.3
Total	100.0	98.1	98.1	100.0	100.0
PVC [%]	17.5	17.5	17.5	19.1	19.1

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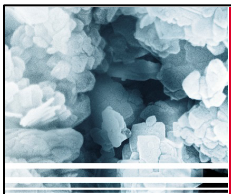
Fig. 2

2.2 Fillers used and their typical properties

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 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.

Typical properties of the titanium dioxide and the Neuburg Siliceous Earth grades included in the study, i.e. Sillitin Z 89 and the calcined, amino functional Aktifit AM, are summarized in *Fig. 3*. The titanium dioxide has a smaller particle size, a lower oil absorption and a somewhat higher specific surface area compared with the siliceous earth grades.



Filler Characteristics

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		Titanium dioxide	Neuburg Siliceous Earth Sillitin Z 89	Calcined Neuburg Siliceous Earth Aktifit AM
Morphology		corpuscular	corpuscular / lamellar	
Density	[g/cm³]	4.0	2.6	2.6
Particle size d_{50}	[µm]	0.3	2.0	2.0
Particle size d_{97}	[µm]	2.0	8.5	10
Oil absorption	[g/100g]	21	55	60
Specific surface area BET	[m²/g]	17	10	7.5
Functionalization		Al-, Si- and Zr compounds	---	Amino

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Fig. 3

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. After adding the B component, the mix was homogenized for 1 minute at 6 m/s.

The formulations were applied with a wire-wound bar onto zinc plated steel sheets 0.55 mm thick with a chromate-free pre-treatment, Bonder 1303, with a standard PU primer layer thickness of 5 µm.

The coatings were stoved in a continuous furnace heated to 320 °C with a residence time of 38 s and resulting peak metal temperature PMT of 241°C.
The dry film thickness came out at about 16 µm.

3 Results

3.1 Color

The color results were determined with a spectral photometer (measuring geometry d/8°). With all formulations, the a* value was found at a level of -1.3. Also the brightness L* with Sillitin Z 89 and Aktifit AM came out similar to the control (*Fig. 4*). This way, the hiding power of the filler containing coatings, despite the reduction of titanium dioxide loading by 20 %, positions itself at a comparable level with the reference coating with full titanium dioxide content, as otherwise the grey primer layer would shine through, and the brightness L* would result markedly lower.

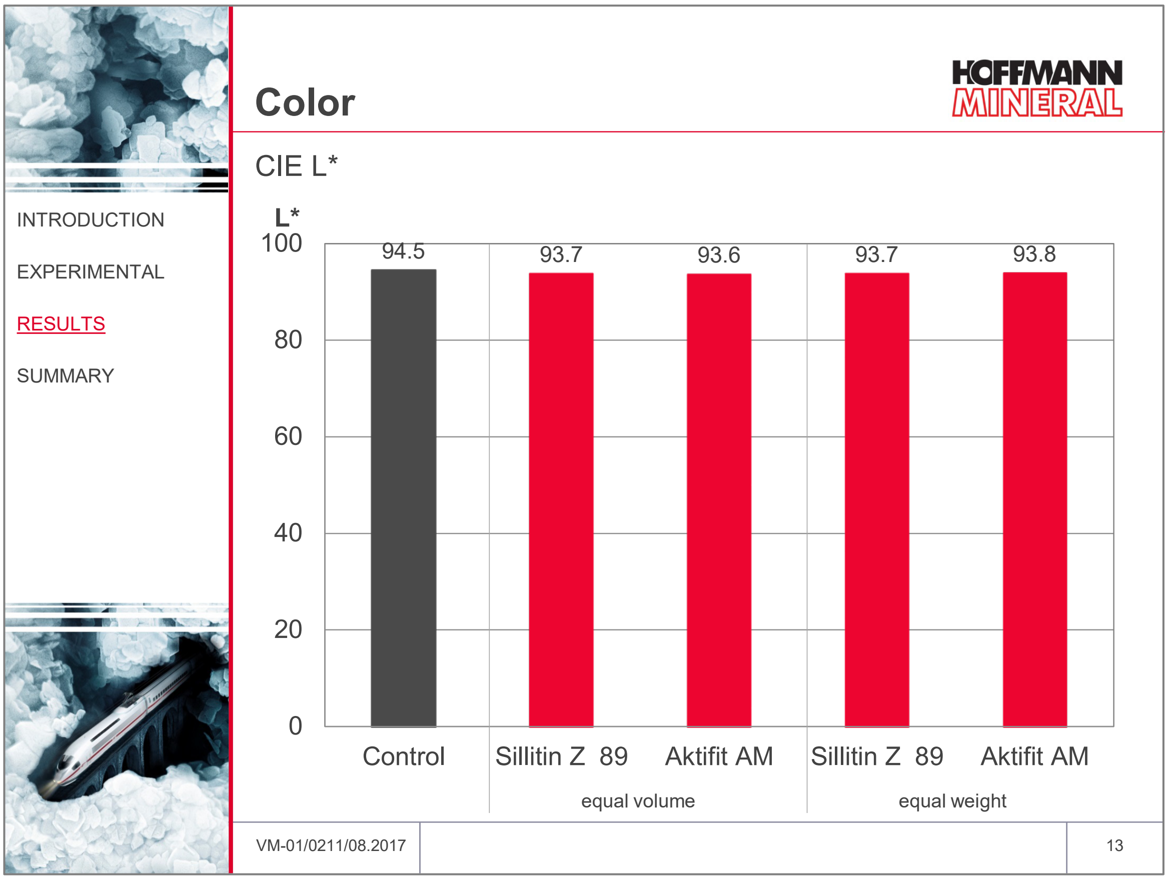


Fig. 4

With Sillitin Z 89, the color value b* comes off somewhat higher due to the slightly yellowish tint of the product. By contrast, the color-neutral Aktifit AM gives results similar to the control with full titanium dioxide content (*Fig. 5*). The same effect can also be realized with Silfit Z 91 which is the untreated version of Aktifit AM (not demonstrated here).

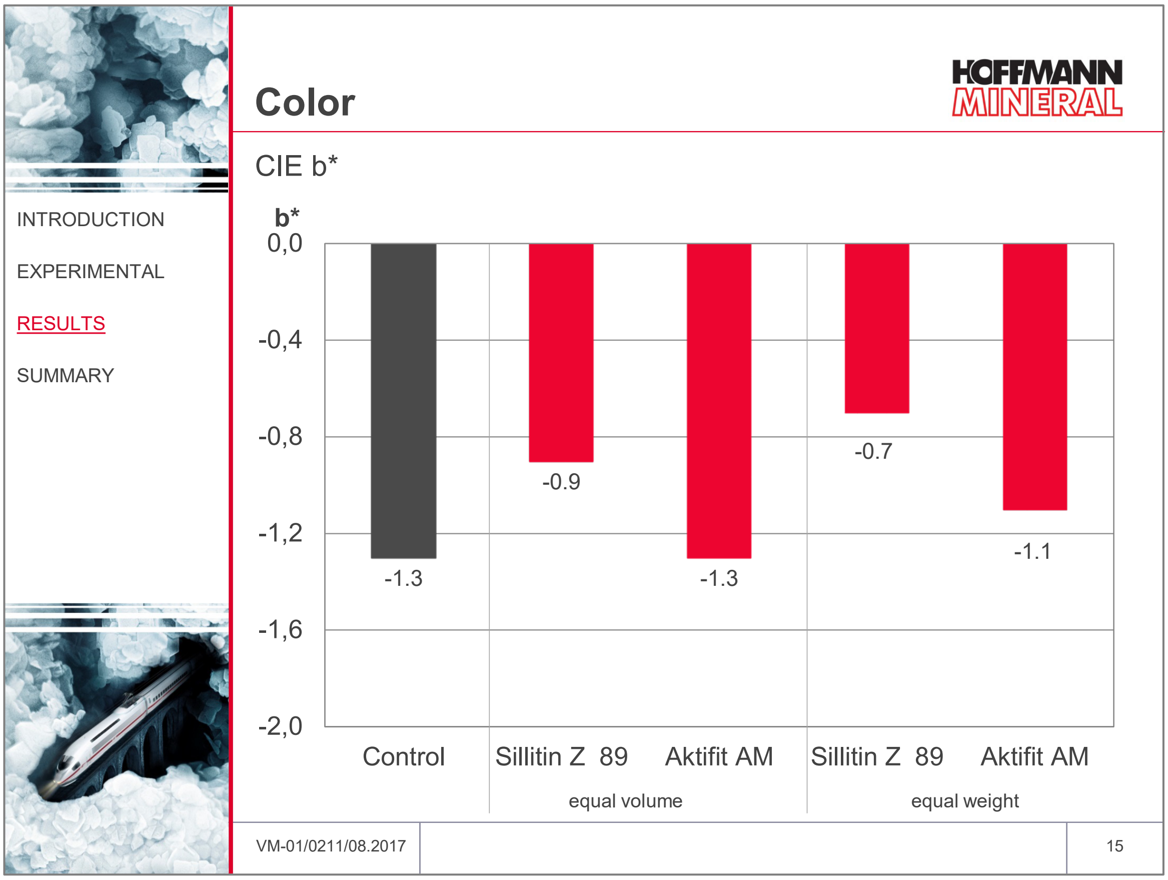


Fig. 5

3.2 Gloss and haze

The use of the mineral fillers marginally tends to reduce the gloss values, an effect enhanced by the higher PVC when replacing with equal weight. Sillitin Z 89 offers slightly higher gloss than Aktifit AM (*Fig. 6)*.

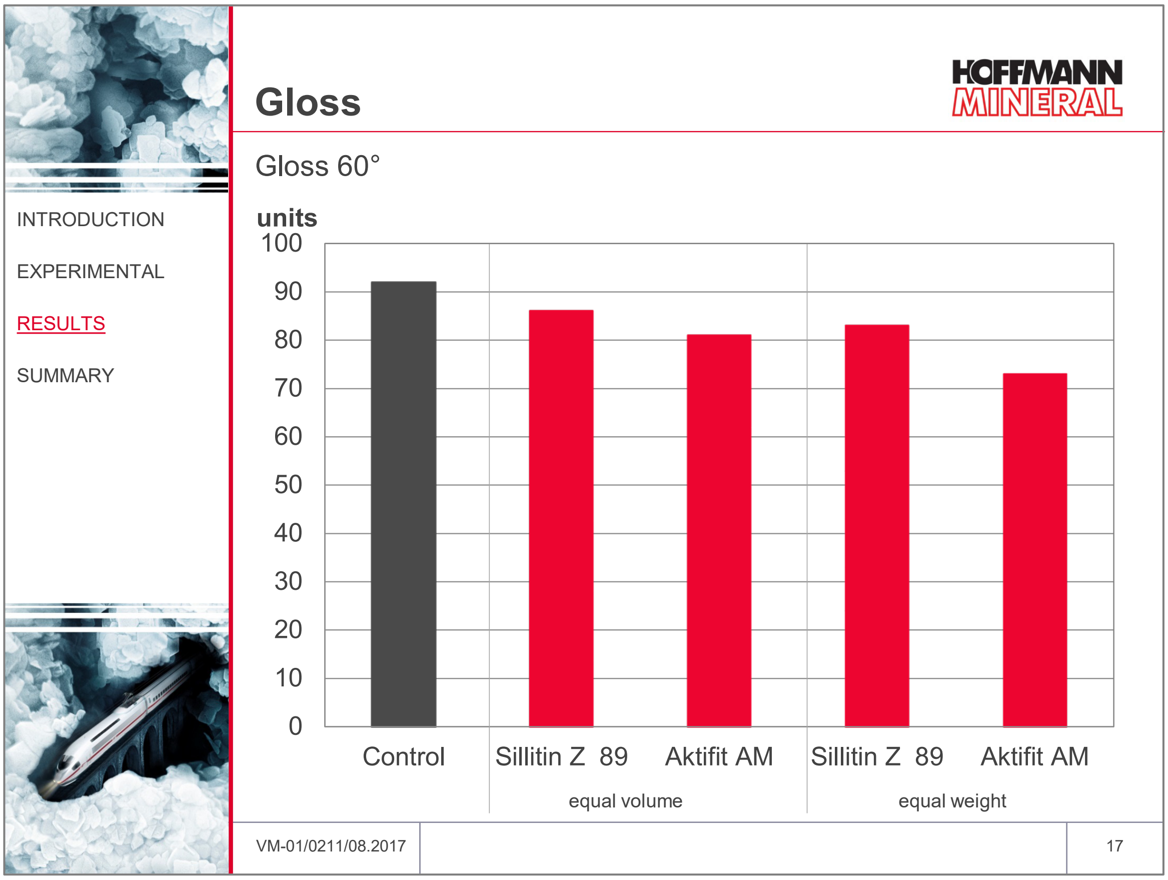


Fig. 6

This result remains true also with the measuring angle of 20° corresponding to high gloss *(Fig. 7)*. The effects are useful to know for applications where certain matting is desired, as for instance façade elements, where glare should be avoided.

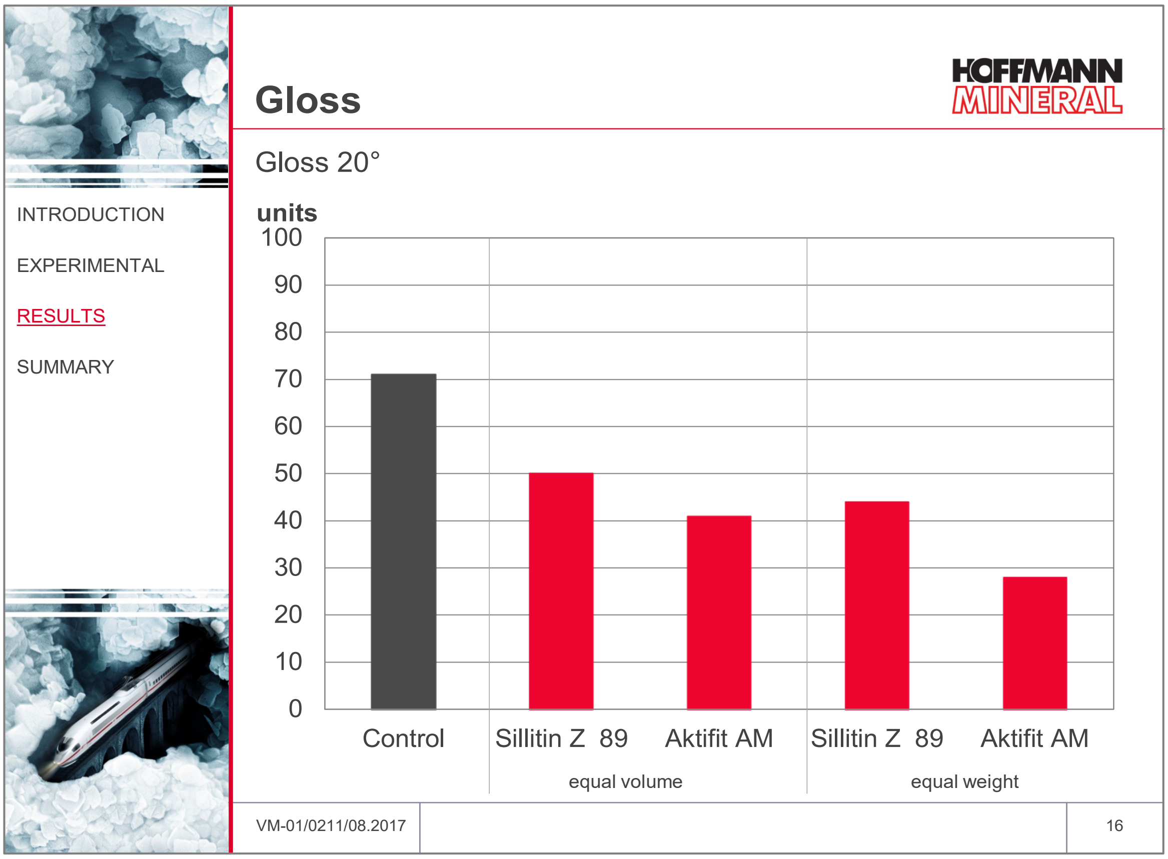


Fig. 7

The results give rise to expectations about a stronger haze. *Fig. 8* presents haze data which increase somewhat along with the titanium dioxide substitution, and come out inversely proportional to the 20° gloss.

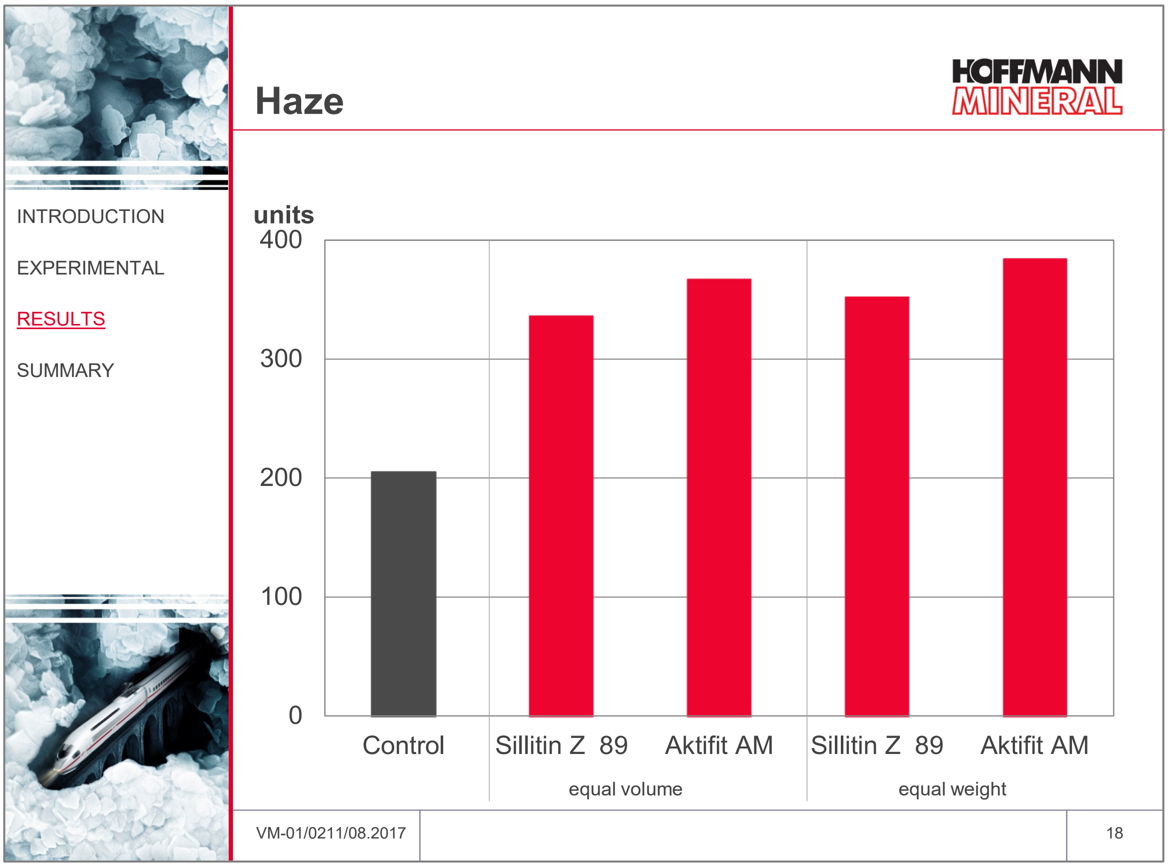


Fig. 8

3.3 Degree of cure / crosslinking

In order to check the cure respectively the degree of crosslinking, the resistance of the coating against methyl ethyl ketone (MEK) was determined. In this test, a cotton pad soaked with MEK will be rubbed over the coated surface until the substrate becomes visible. The number of passes required represents an index for the resistance and for the degree of crosslinking of the coating (*Fig. 9*). All coatings tested arrived more than 200 double strokes, which suggests a very high degree of crosslinking, and implies therefore no negative influence of Sillitin Z 89 or Aktifit AM.

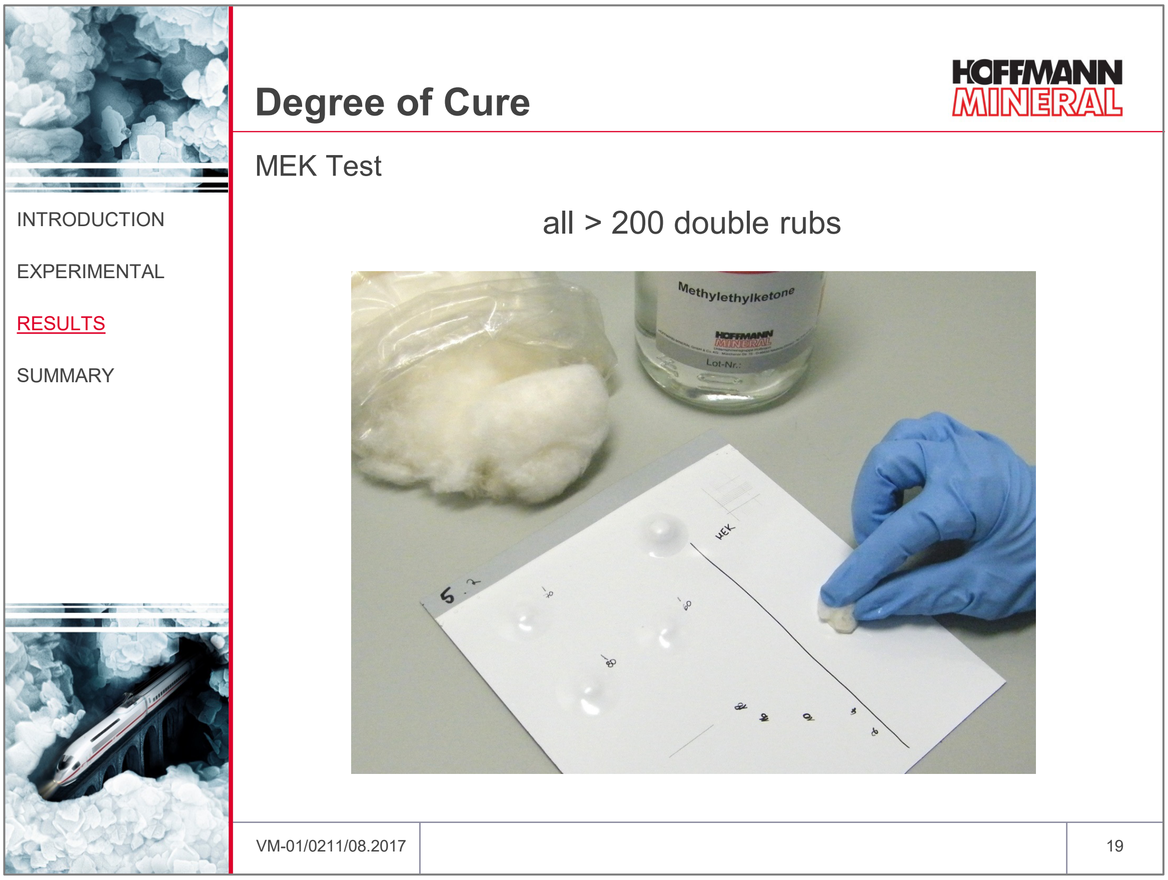


Fig. 9

3.4 Hardness

The hardness of the coating was determined via pendulum damping test according to Koenig (DIN EN ISO 1522). The partial replacement of titanium dioxide by the Neuburg Siliceous Earth grades tends to lead to higher hardness results, in particular with Aktifit AM (*Fig. 10*).

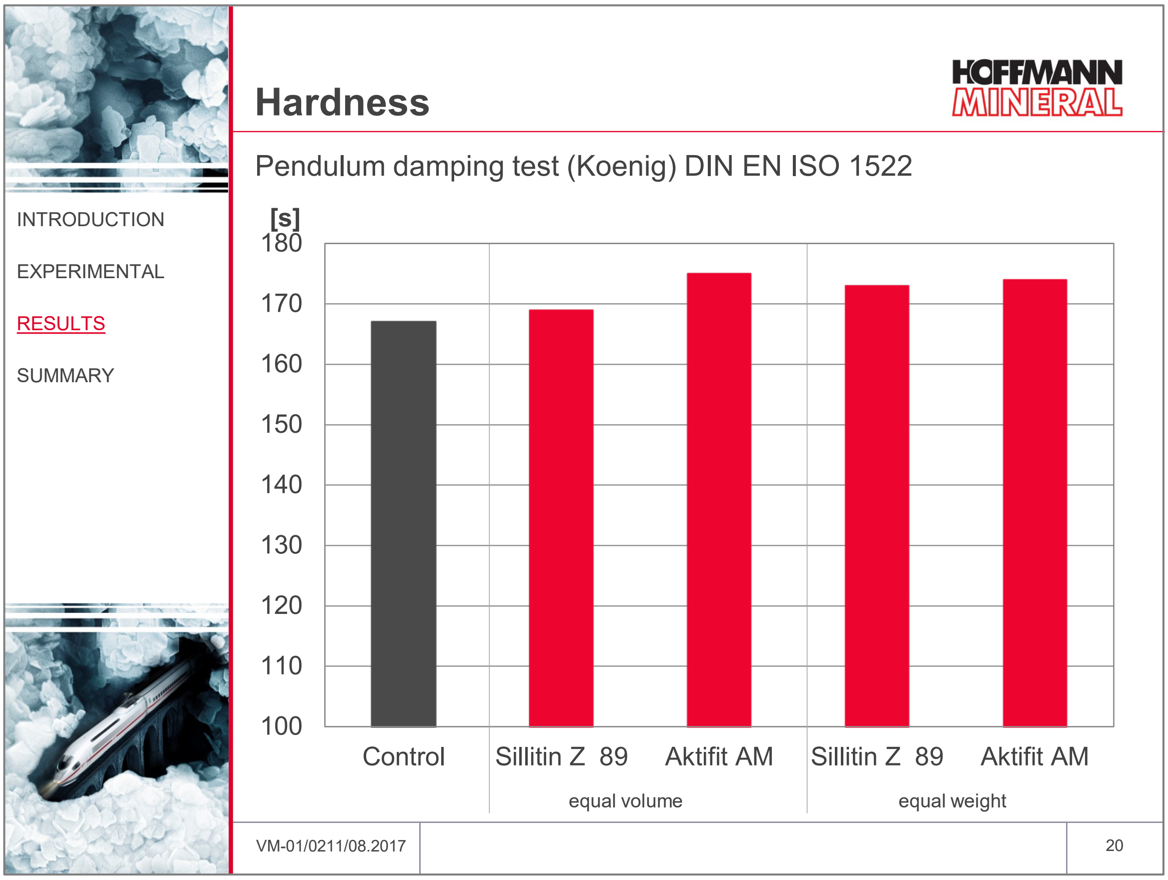


Fig. 10

3.5 Adhesion

Adhesion was tested with the cross-cut test according to DIN EN ISO 2409 with a blade distance of 1 mm. All formulations, with cross-cut results of Gt 0, showed very good adhesion (*Fig. 11*).

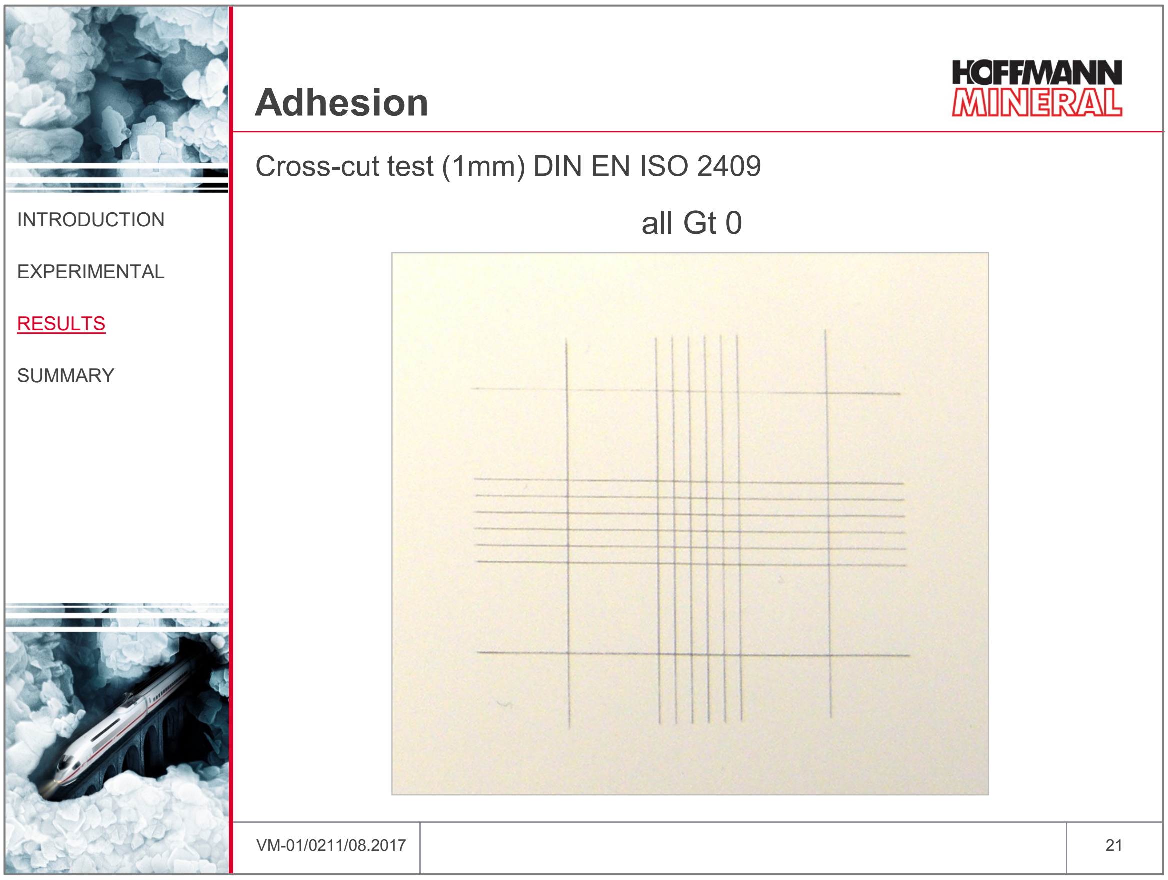


Fig. 11

3.6 Mechanical resistance

The mechanical resistance was tested by scratching the coating with a weight-loaded metal tip until the substrate became visible. The test equipment as shown in *Fig. 12* is a Corrocutter from the Erichsen company (Model 639). The round hard metal tip according to van Laar, which has a diameter of 0.5 mm, will be pulled over the coated surface with a defined force gradually increased from 2 to 20 Newton. The result of the test is expressed as the force necessary to scratch the coating down to the substrate. Aktifit AM gave a very favorable result, with a higher resistance against scratches than found for the reference coating (*Fig. 13*).

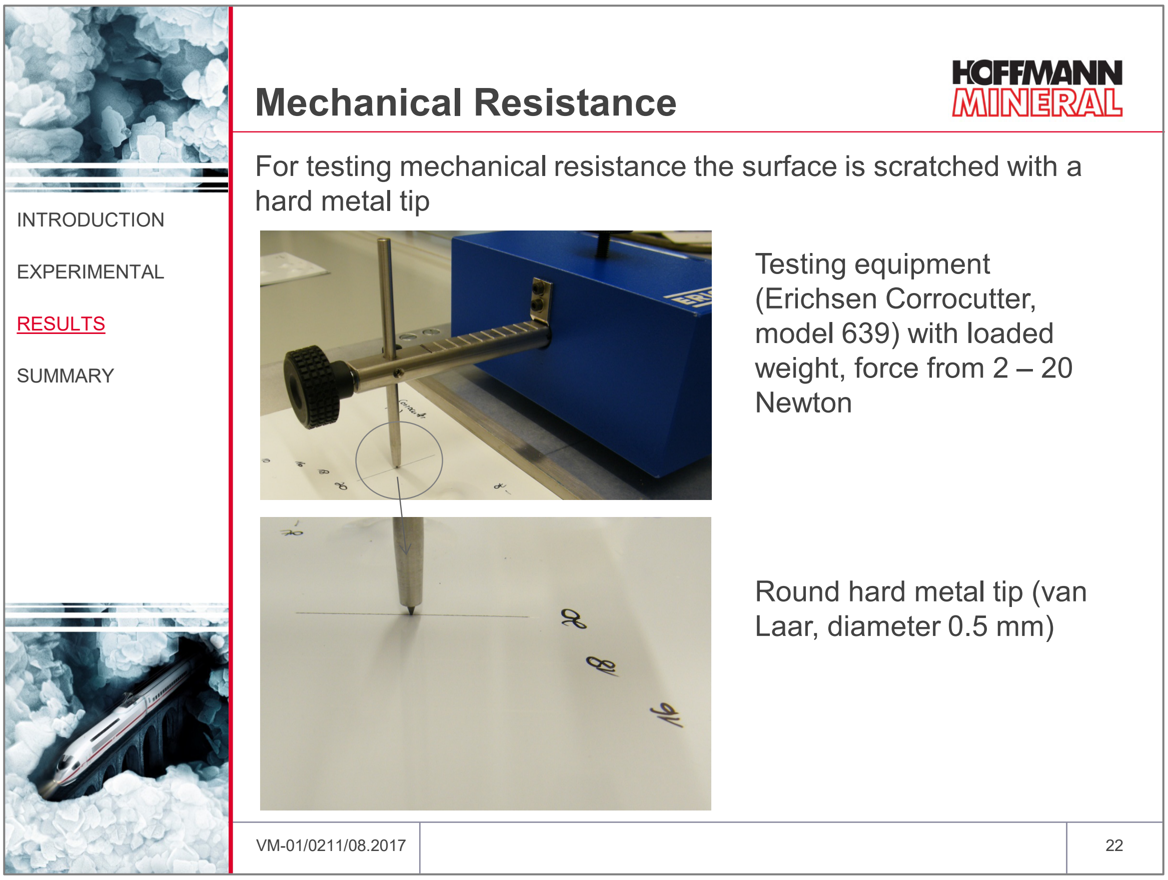
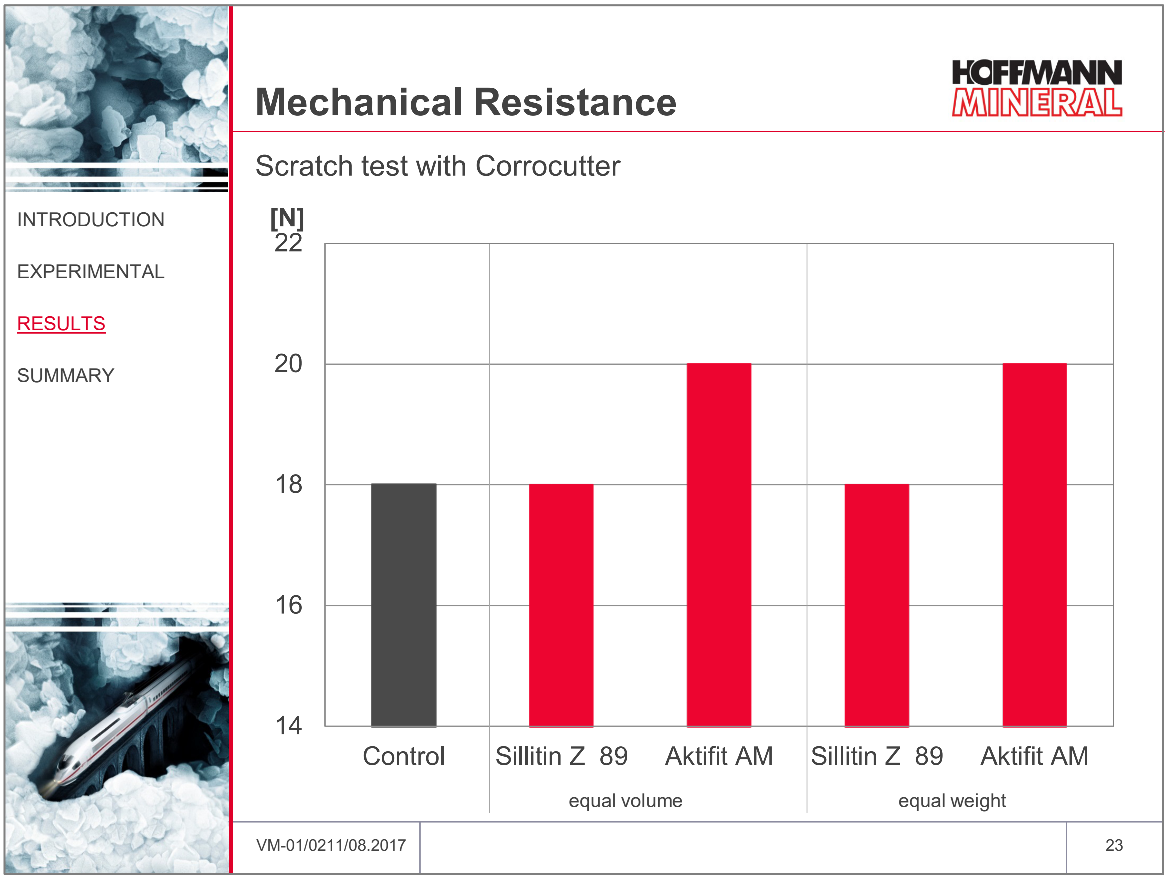


Fig. 12



Mechanical Resistance
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Scratch test with Corrocutter
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Control
Sillitin Z 89
Aktifit AM
Sillitin Z 89
Aktifit AM
equal volume
equal weight
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Fig. 13

3.7 Flexibility

The flexibility of the coatings under slow deformation was determined via cupping test according to DIN ISO 1520. No filler effects could be observed, as all formulations came out with results close to 8 mm (*Fig. 14*).

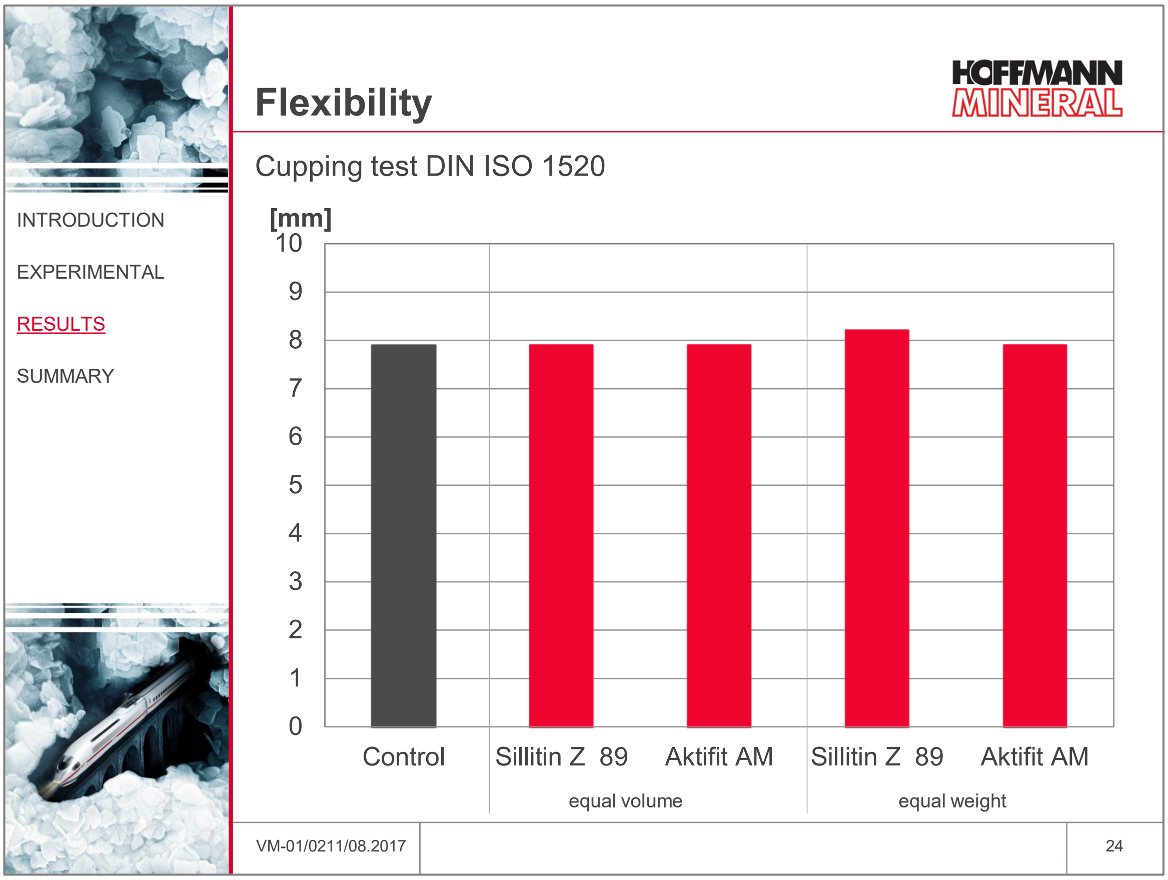

Fig. 14

For checking the flexibility under a fast, impact-like deformation, the Reverse Impact Test according to DIN EN ISO 6272-1 was used. Here the weight will fall onto the uncoated backside and the deformation caused on the coated front side will be assessed for cracks. The record gives the level at which just no more cracks are visible.

With the fillers added at equal volume, the results are on level with the reference. Replacement at equal weight leads to slightly lower results (*Fig. 15*).

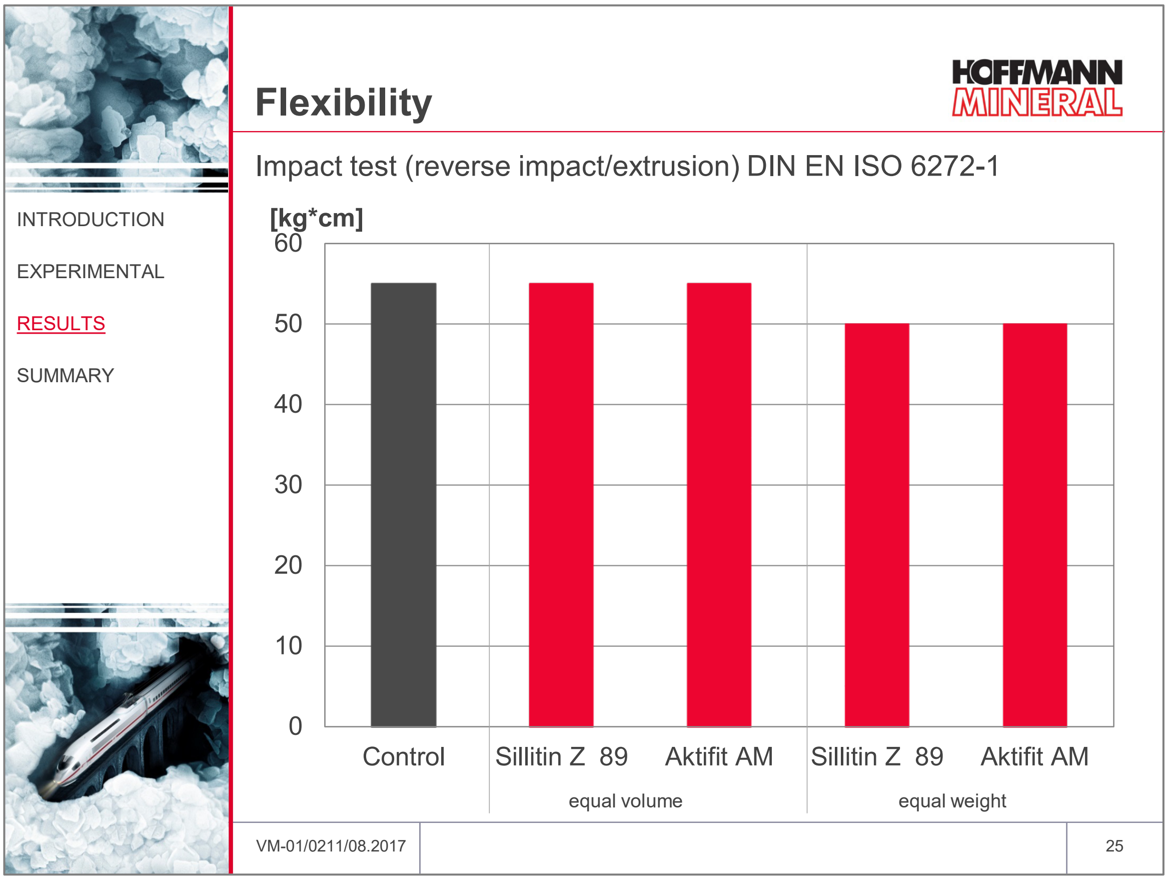

Fig. 15

3.8 Weathering resistance

The accelerated artificial weathering test with short-wave UV light and moisture creates damages which can be measured by changes of color and gloss as well as by chalking. The results are used for the assessment of the weathering resistance.
The QUV-B test with maximum irradiation intensity at 313 nm was carried out 400 hours, in cycles of 4 hours UV exposure at 60° followed by 4 hours condensation at 50°C.

The color difference delta E, with figures between 0.7 and 0.9, for all formulations comes out comparably low, which means that no negative effect can be attributed to the partial replacement of titanium dioxide.

When looking at the gloss results, Aktifit AM results in some cases even better than the control regarding gloss retention. The remaining gloss at 60° as shown in *Fig. 16* relative to the original level, Aktifit AM still comes off equal to the reference, and this way above the uncalcined and untreated grade Sillitin Z 89.

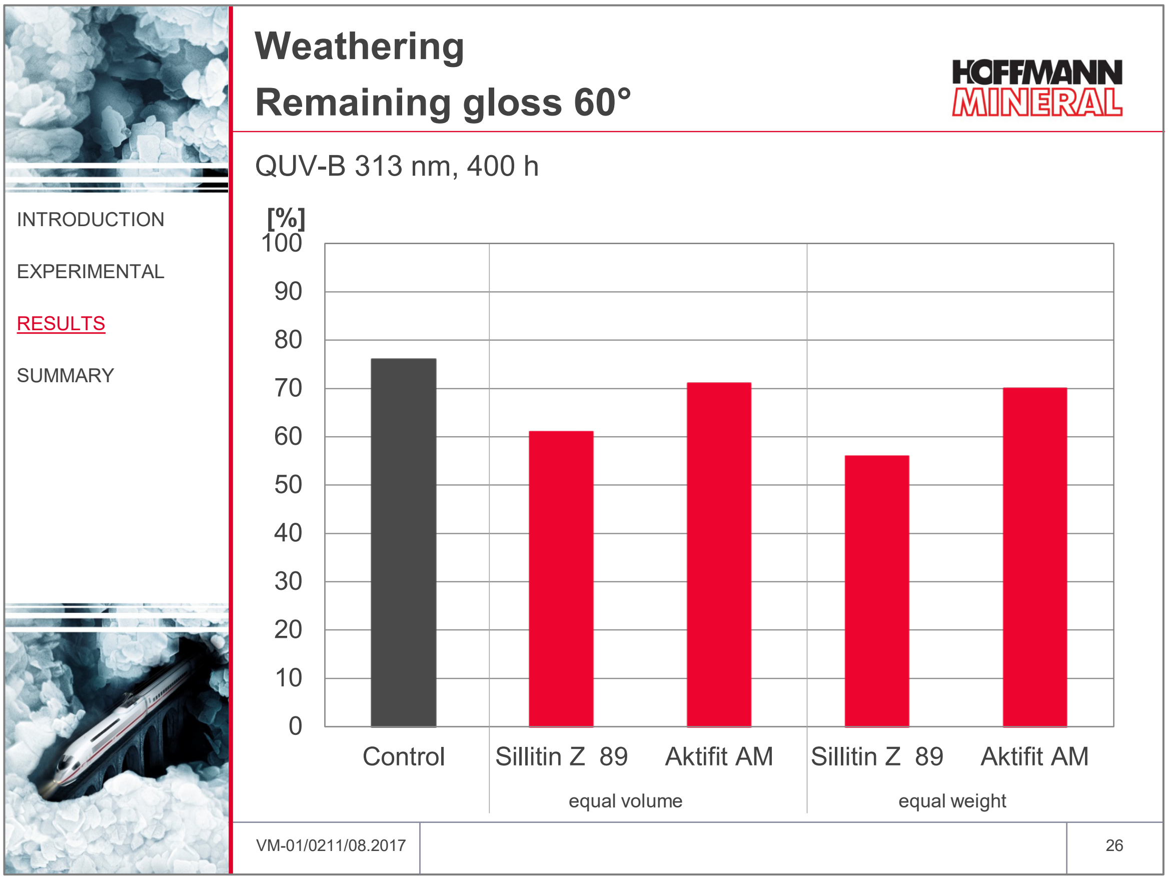

Fig. 16

In the more sensitive determination at 20° Aktifit AM even offers somewhat higher results in comparison with the control with full titanium dioxide addition, and is therefore markedly superior to Sillitin Z 89 *(Fig. 17)*.

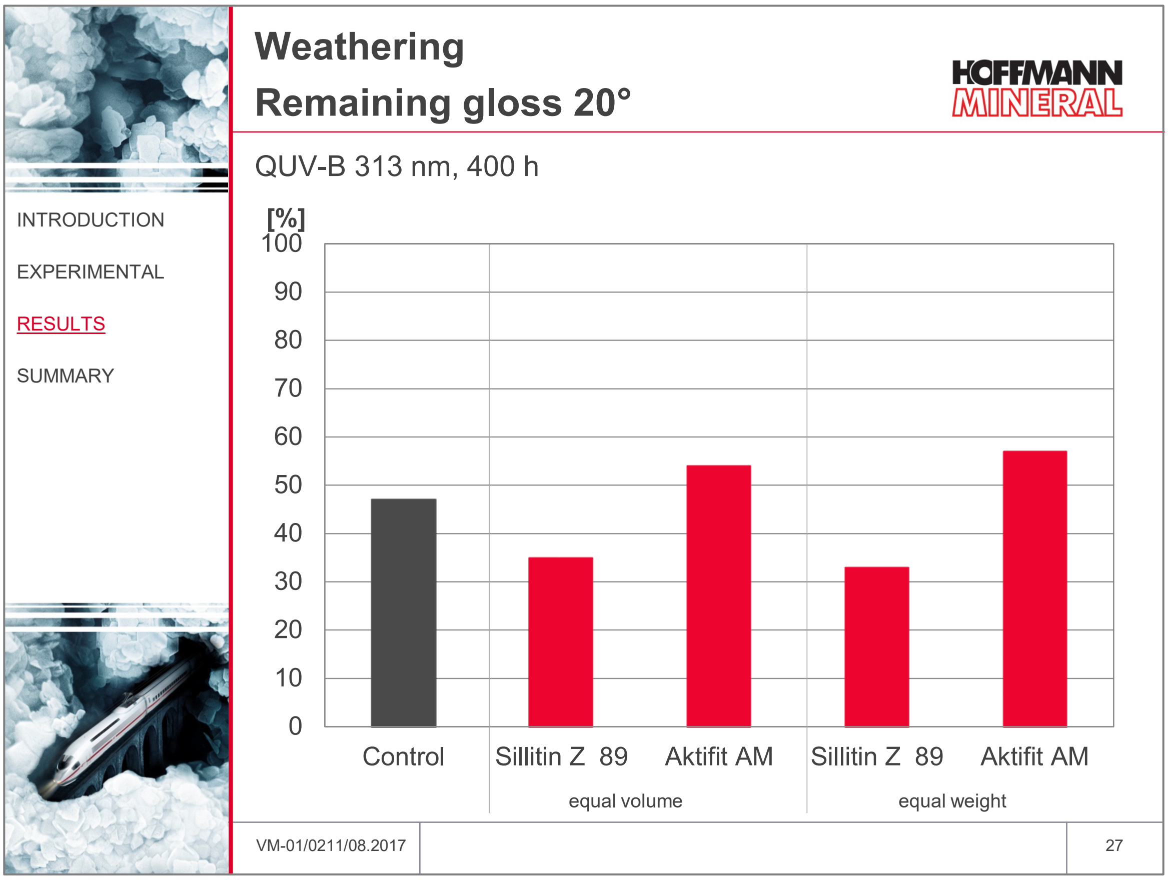

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Fig. 17

The pigment and filler particles removable by adhesive tape pull-off from the surface are considered as chalking insofar as the reduction of the light transmission of the scotch tape is measured.

All coatings show only insignificant opacity of the scotch tape, well below 5 %, which can be judged as no chalking. Chalking would be acknowledged only from 10 % upwards.

Nonetheless here too Sillitin Z 89 brings about a somewhat higher change than Aktifit AM which comes out at a very low level and comparable with the reference (*Fig. 18).*

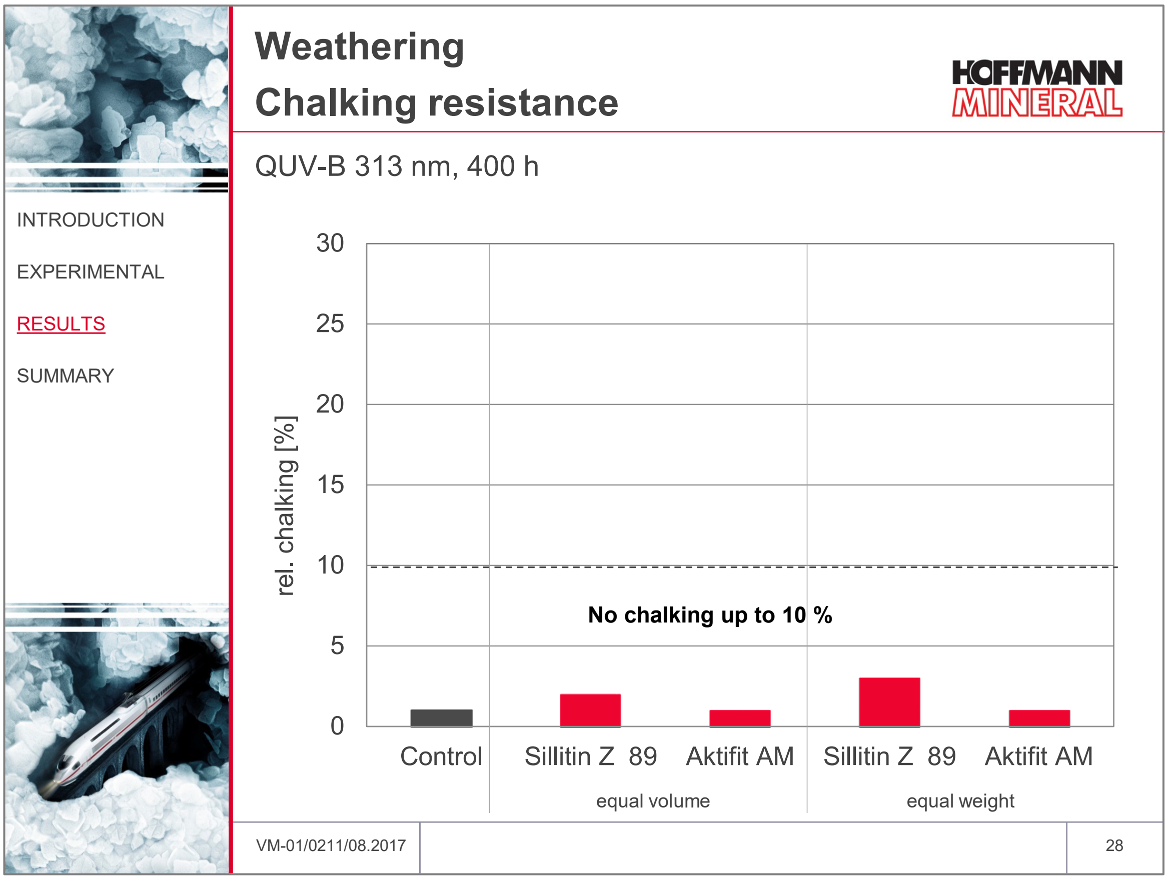

Fig. 18

4 Summary and outlook

Based on the experience accumulated in other application areas of Neuburg Siliceous Earth, and looking at the results of the present study, a partial replacement of 20 % titanium dioxide can be definitely recommended. The optical and mechanical properties will be at least maintained, and some of them even improved by the addition of the Neuburg Siliceous Earth grades.

Replacing 20 % of titanium dioxide and using

Sillitin Z 89 results in:

- a very slight reduction of gloss
- slight yellowish tinge (avoidable with Silfit Z 91)
- similar brightness L* and thus comparable hiding power

+ **trend towards slightly higher hardness**
+ **a very cost efficient formulation**

Aktifit AM results in:

- a slight reduction of gloss
- similar brightness L* and thus comparable hiding power
- maintained color neutrality
- very good weathering resistance

+ **slightly higher hardness**
+ **improved scratch resistance**
+ **a cost efficient formulation**