Neuburg Siliceous Earth

for white solvent based

road marking paints

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1 Introduction

Benefits of using Neuburg Siliceous Earth have already been shown in water based road marking paints with respect to an increased hiding power and improved abrasion resistance.

The present report concerns the use of Neuburg Siliceous Earth in a white, solvent based road marking paint. The starting formulation contained calcium carbonate and talc as fillers and titanium dioxide as pigment. These products were partly or fully replaced by Sillitin Z 89 und Sillitin V 88.

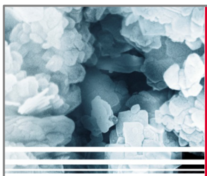
The objective of the project was to maintain or even improve the performance properties and to arrive cost savings by partially taken out the titanium dioxide.

2 Experimental

2.1 Base formulation

The guide formulation from the company DIC Performance Resins (formerly Reichhold) given in *Fig. 1* served as the starting point of the study. The coarse calcium carbonate (d_{50} 15 µm) was maintained in all batches, i.e. was not changed.

In the individual formulation variants, the solvent content was kept constant. The flow time in the DIN 6 cup was 20 ± 5 s.



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Base Formulation *

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		Parts by weight
Burnock AC 4010 (60 % in BA)	Binding agent (Styrene acrylate)	200.0
Shellsol A	Solvent	59.6
Luvogel 4	Thickening agent	7.3
Anti Terra U	Wetting- / Dispersing agent	5.8
Sojalecithine	Wetting- / Dispersing agent	2.7
Titanium dioxide	Pigment	90.9
Talc 6 µm	Filler	22.7
Calcium carbonate 5 µm (NCC fine)	Filler	181.8
Calcium carbonate 15 µm (NCC coarse)	Filler	277.3
Aerosil 200	Rheological additive	3.6
Isopropanole	Solvent	18.2
Acetone	Solvent	21.0
Heptane	Solvent	68.0
Total		958.9

* by DIC Performance Resins

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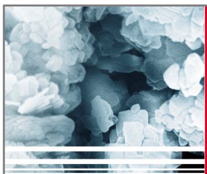
Fig. 1

2.2 Fillers used and their 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.

Fig. 2 gives a listing of the major filler characteristics. The two siliceous earth grades differ in particle size, where Sillitin Z 89 is somewhat finer. The natural calcium carbonate (NCC) offers lower oil absorption and a smaller specific surface area compared with the Sillitin grades. The specific values for Sillitin and talc are rather similar, where talc shows the higher average particle size.



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		Talc	Calcium carbonate fine	Neuburg Siliceous Earth	
				Sillitin V 88	Sillitin Z 89
Morphology		lamellar	corpuscular	corpuscular / lamellar	
Density	[g/cm³]	2.8	2.7	2.6	2.6
Particle size d_{50}	[µm]	6.4	5.7	3.6	2.0
Particle size d_{97}	[µm]	29	24	17	8
Oil absorption	[g/100g]	59	23	45	55
Specific surface area BET	[m²/g]	11.6	2.2	8.3	10.5

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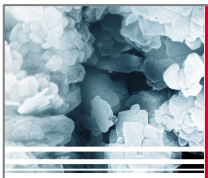
Fig. 2

The color values were determined with a spectral photometer measuring geometry d/8° and light D 65. The Sillitin grades and the talc give evidence of comparable brightness. As a result of the inherent color of Sillitin a slight yellow tinge will be remarked. This however can be totally avoided by using the Calcined Neuburg Siliceous Earth grade Silfit Z 91, which increases additionally the brightness.

Typically for this group of raw materials, the calcium carbonates are distinguished by high brightness (*Fig. 3*).



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Color	Talc	Calcium carbonate fine	Neuburg Siliceous Earth	
			Sillitin V 88	Sillitin Z 89
X	81	86	81	81
Y	85	91	85	85
Z	92	97	87	86

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Fig. 3

3. Formulation variations

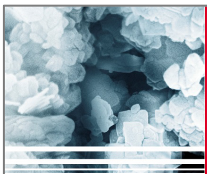
Fig. 4 summarizes the formulation variations. Starting from the guide formulation (control):

- In the first variant (full substitution of NCC) the 181.8 parts of the fine calcium carbonate were replaced at equal volume with the Neuburg Siliceous Earth grades Sillitin V 88 resp. Sillitin Z 89.

- In the second variant (partial substitution of NCC 50 % and full substitution of talc) half of the fine calcium carbonate, i.e. 90.9 parts and 22.7 parts of talc were replaced by Sillitin V 88 resp. Sillitin Z 89.

- In the third and last variant (full substitution of NCC and partial substitution of titanium dioxide) as in the first variant, the fine calcium carbonate (181.8 parts) and in addition 20.8 % of the titanium dioxide were replaced in case of using Sillitin V 88 and 23 % of the titanium dioxide in the event of Sillitin Z 89.

  This last variant specifically aimed highlighting the deliberate use of the expected improved hiding power of the Neuburg Siliceous Earth.



Formulation Variations

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	Control	Full substitution NCC	Partial substitution NCC (50 %) and full substitution Talc	Full substitution NCC and partial substitution TiO_2 (20.8 % / 23 %)
Titanium dioxide	90.9	90.9	90.9	72.0 / 70.0
Talc 6 µm	22.7	22.7	-	22.7
NCC fine, 5 µm	181.8	-	90.9	-
Sillitin V 88 / Z 89	-	175.1	108.6	187.1 / 188.3
NCC coarse, 15 µm	277.3	277.3	277.3	277.3
Binder, additives and solvents	386.2	386.2	386.2	386.2
Total	958.9	952.2	953.9	945.3 / 944.5

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Fig.4

4. Test methods and test results

4.1 Color values

For the determination of color values, the batches were drawn on contrast cardboards with the aid of an applicator with doctor blade. The wet film thickness came out at about 600 µm (corresponding to 250 µm dry film thickness). The films were dried for 24 hours at 23 °C and 50 % relative humidity before determining the color with the aid of a spectrophotometer with geometry 45°/0° and D 65 light.

Fig. 5 shows the brightness L*. The brightness results of the formulations with Neuburg Siliceous Earth generally tend somewhat lower.

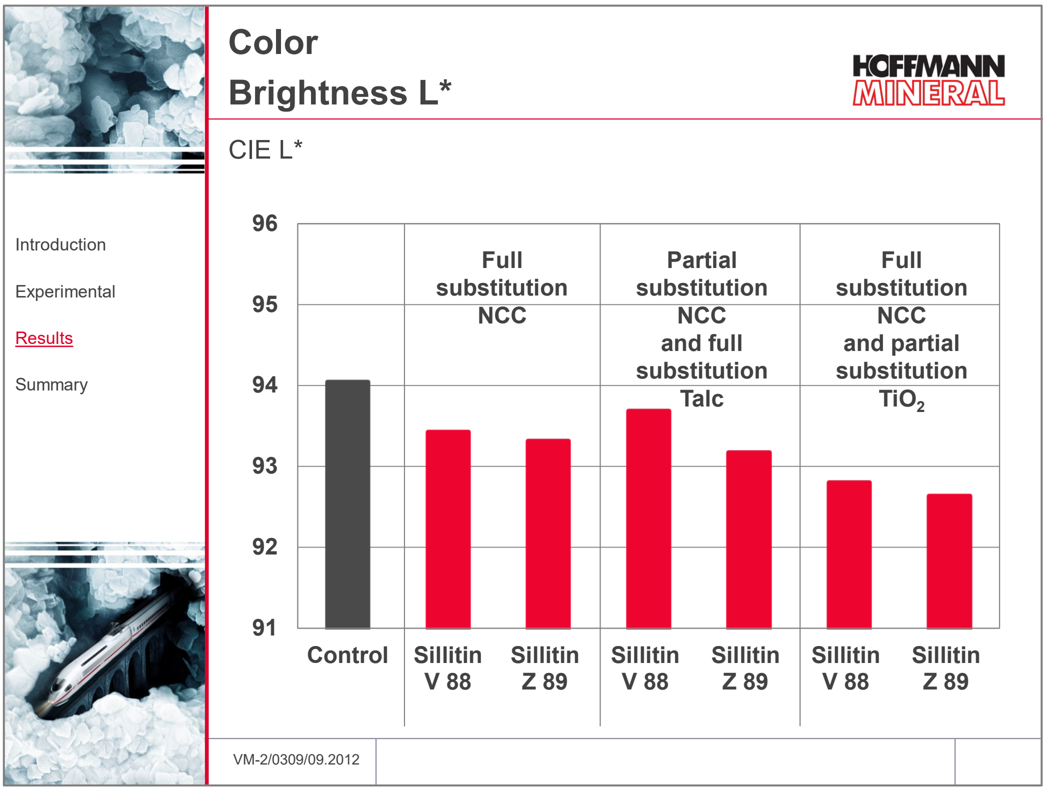

Fig. 5

The a* value of all formulations came out between -0.6 and –0.8.

The positive b* value, which reflects the yellowness, shows somewhat of an increase with Sillitin (*Fig. 6*). This can, however, be avoided by working with the calcined and white grade Silfit Z 91, which will also enhance the brightness L*.

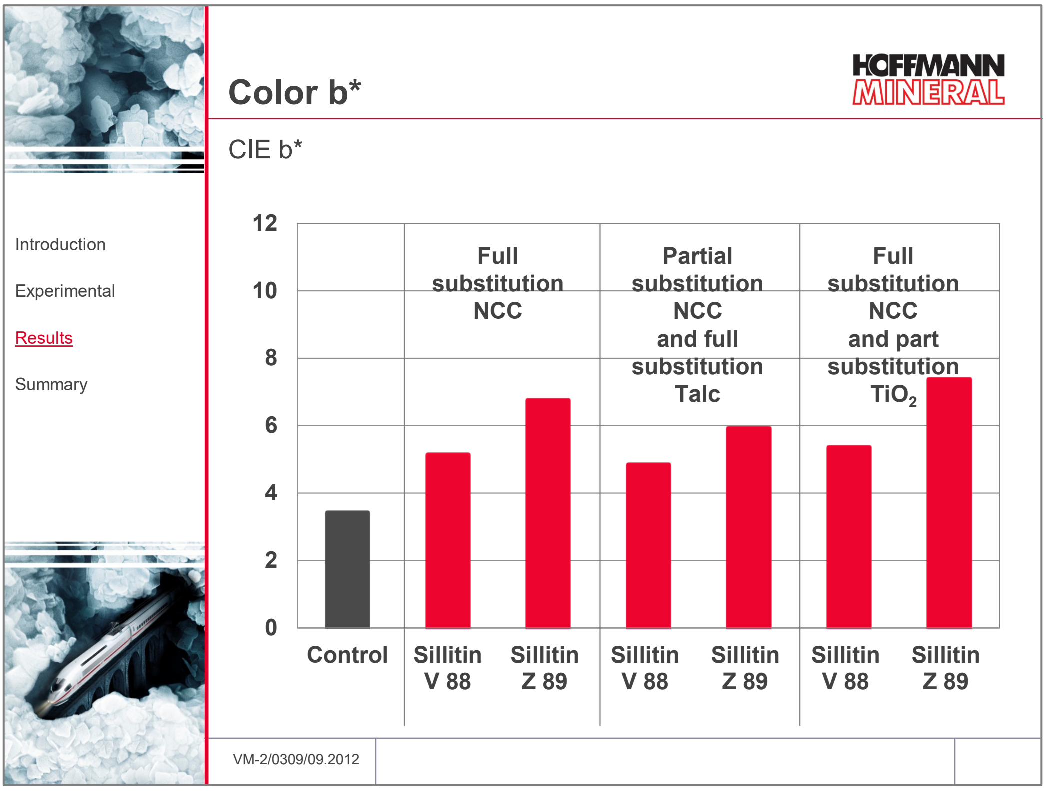

Fig. 6

From the obtained data for X, Y and Z, the standard chromaticity coordinates x and y can be calculated. The standard DIN EN 1436 specifies via four coordinates of x and y a color space for white road marking paints. All variants studied are situated in the center of this color space, with Sillitin V 88 closer to the control than Sillitin Z 89. The standard chromaticity coordinates with the partial replacement of titanium dioxide despite the heavily reduced pigment loading come out very close to the full substitution of calcium carbonate with the high titanium dioxide dosage (*Fig. 7*).

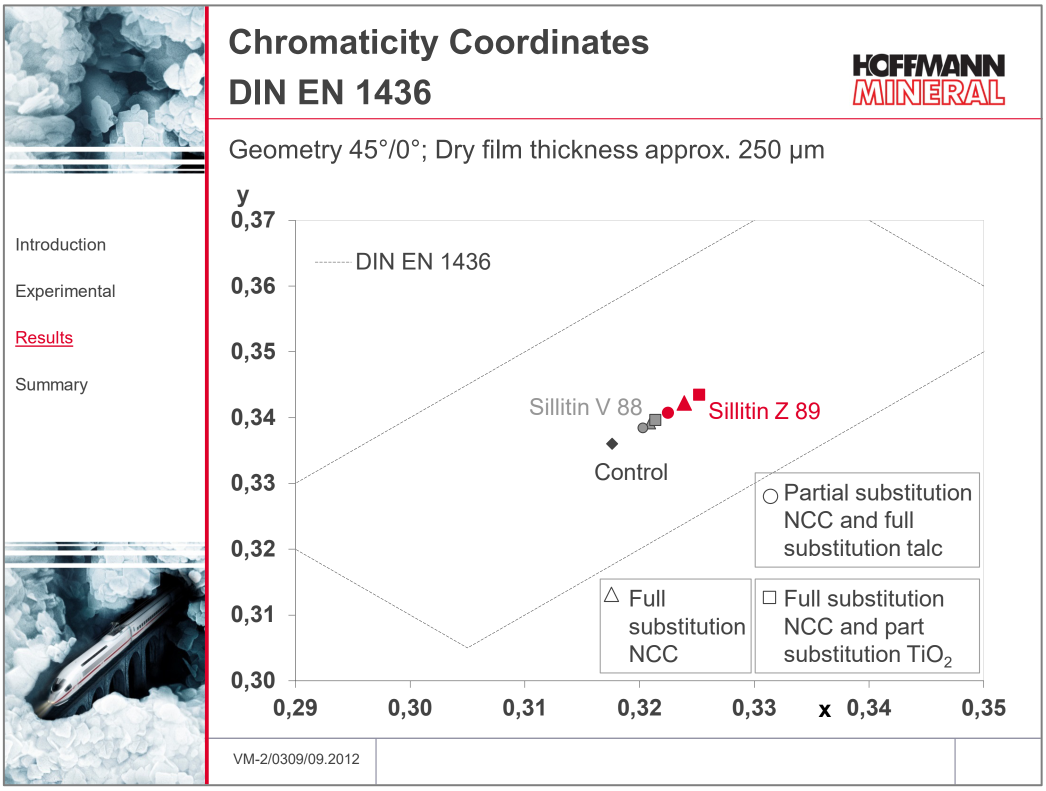

Fig. 7

4.2 Contrast ratio and hiding power

Different films with various wet thicknesses were applied onto black/white contrast cardboards with the aid of an applicator with doctor blade. After drying for 48 hours at 23 °C and 50 % relative humidity, the resulting dry film thicknesses were determined, and the color value Y measured over the black and the white underground. The quotient of Y black to Y white, multiplied by 100, gives the contrast ratio in percent. With a contrast ratio of >= 98 % a road marking paint is defined as covering.

Fig. 8 illustrates the hiding power via the contrast ratio at a wet film thickness at approx. 250 µm. Both Sillitin grades with full substitution of calcium carbonate give a better hiding power compared with the control.

When replacing part of the calcium carbonate and all the talc, no improvement can be obtained.

Although the control contains 20 % more pigment than the batches with the partial replacement of titanium dioxide, the hiding power of the formulations filled with Sillitin can be called at least comparable with the control

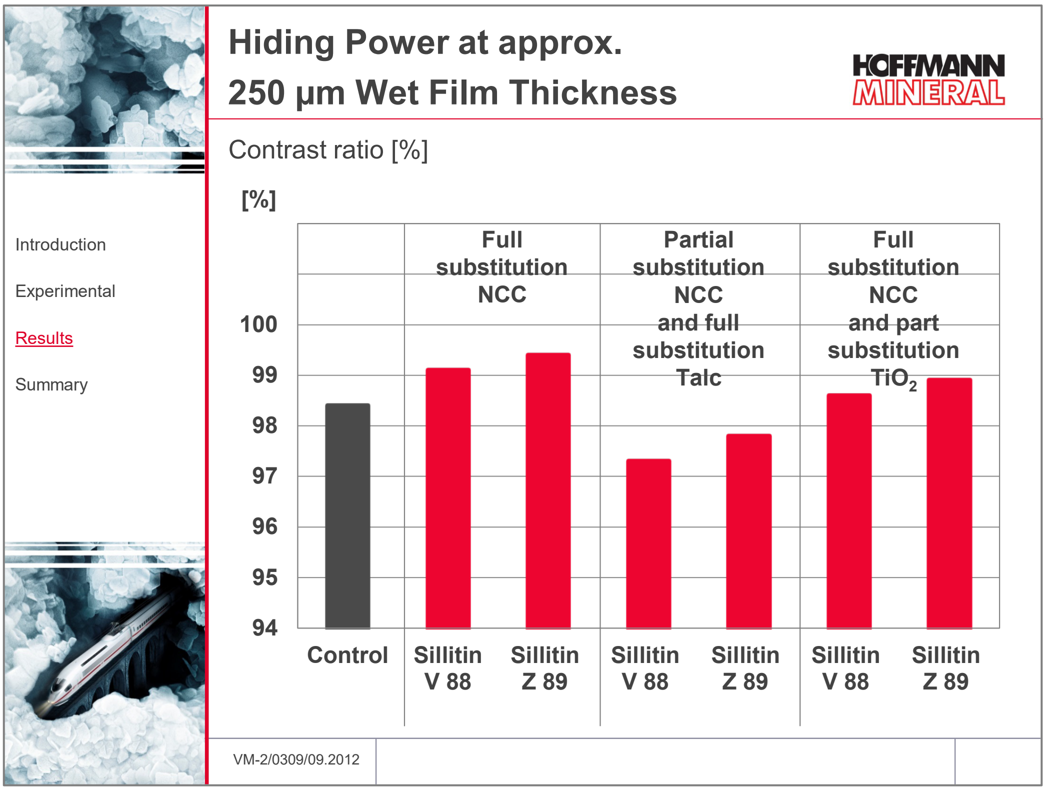

Fig. 8

Fig. 9 shows the necessary dry film thickness to reach 98 % covering. If only half of the calcium carbonate and the full portion of talc are replaced with Sillitin, the dry film thickness with 130 µm comes out comparable to the control. When replacing the whole calcium carbonate, the dry film thickness can be reduced considerably (up to 15 % when fully substituting the calcium carbonate and partially the titanium dioxide with Sillitin Z 89). These results confirm the better hiding power of the Sillitin containing formulations despite the titanium dioxide reduction by about 20 %.

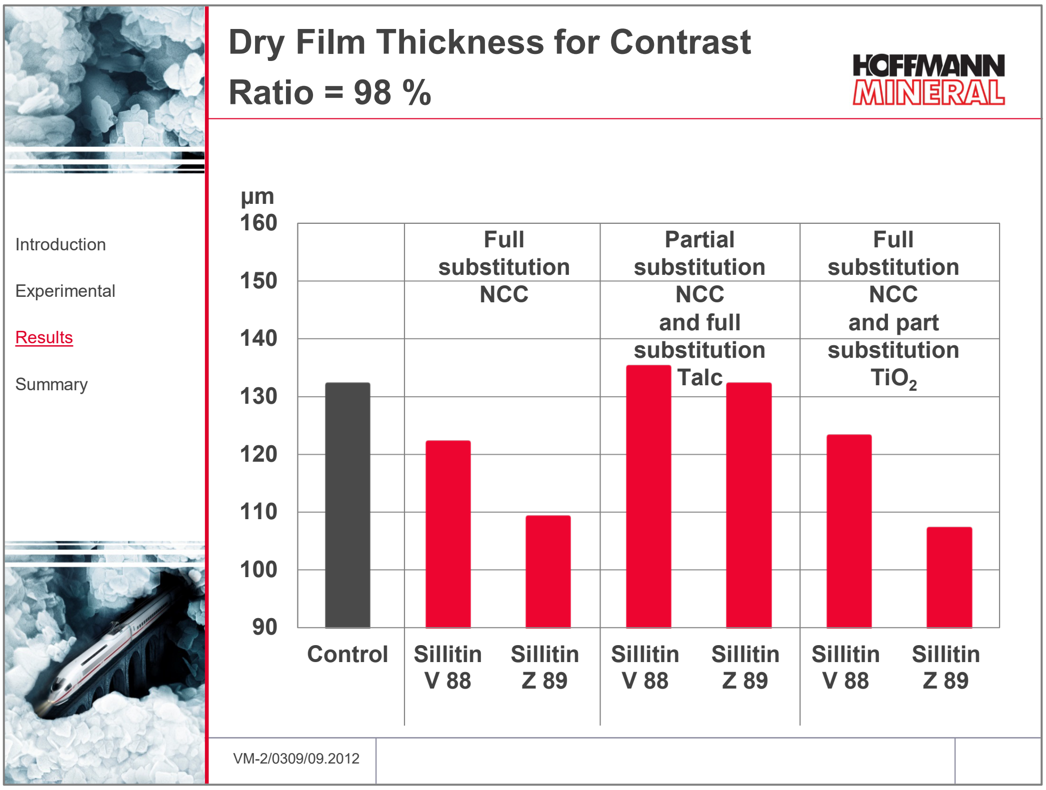

Fig. 9

4.3 Drying time (according to DIN 53150, drying stage 4)

The paint was applied on a metal sheet with 600 µm wet film thickness. After defined time intervals, a paper disc (diameter 26 mm, writing paper of 60-80 g/m²) was laid on the paint and loaded for 60 seconds with a rubber disc and a weight of 2 kg. After removing the rubber disc and the weight, the metal sheet was dropped vertically on a wood board. If the paper fell off, the drying stage 4 according to DIN 53150 is attained.

Fig. 10 indicates the drying time in minutes until obtaining stage 4. Both grades of Sillitin offer a markedly reduced time of drying compared with the control. When completely replacing the calcium carbonate with Sillitin, the drying time will be shortened by almost half an hour. This means the painted road can be faster re-opened for traffic because of the distinctly shorter drying time.

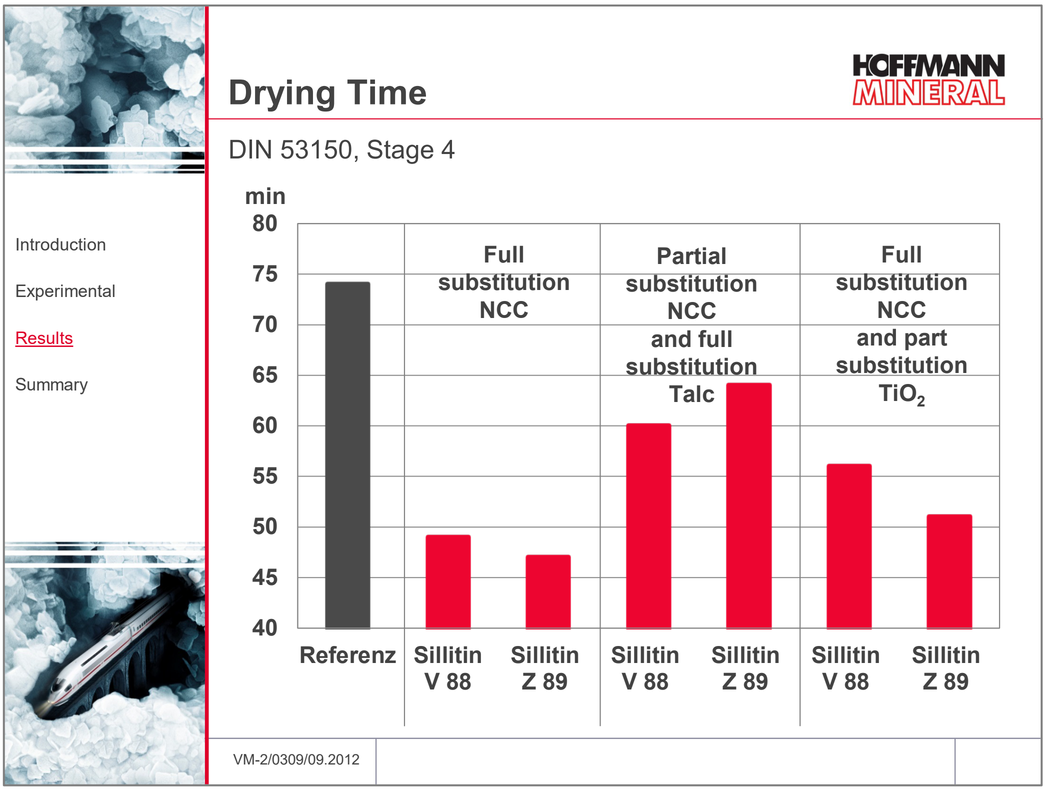

Fig. 10

4.4 Abrasion resistance

For the abrasion tests, Taber plates were coated and dried for 7 days at 23°C and 50 % relative humidity.

The abrasion loss was tested according to ASTM D4060 via the weight loss after 1000 revolutions with abrader wheels C17, which were cleaned and regenerated after each 500 revolutions with S11 abrasive sandpaper discs. *Fig. 11* shows the average abrasion loss after 1000 revolutions in milligrams, under a load of 1 kg onto the CS 17 wheels.

The use of Sillitin gives rise to reduced abrasion loss. When not only replacing calcium carbonate, but also talc, the abrasion resistance is improved even more dramatically.

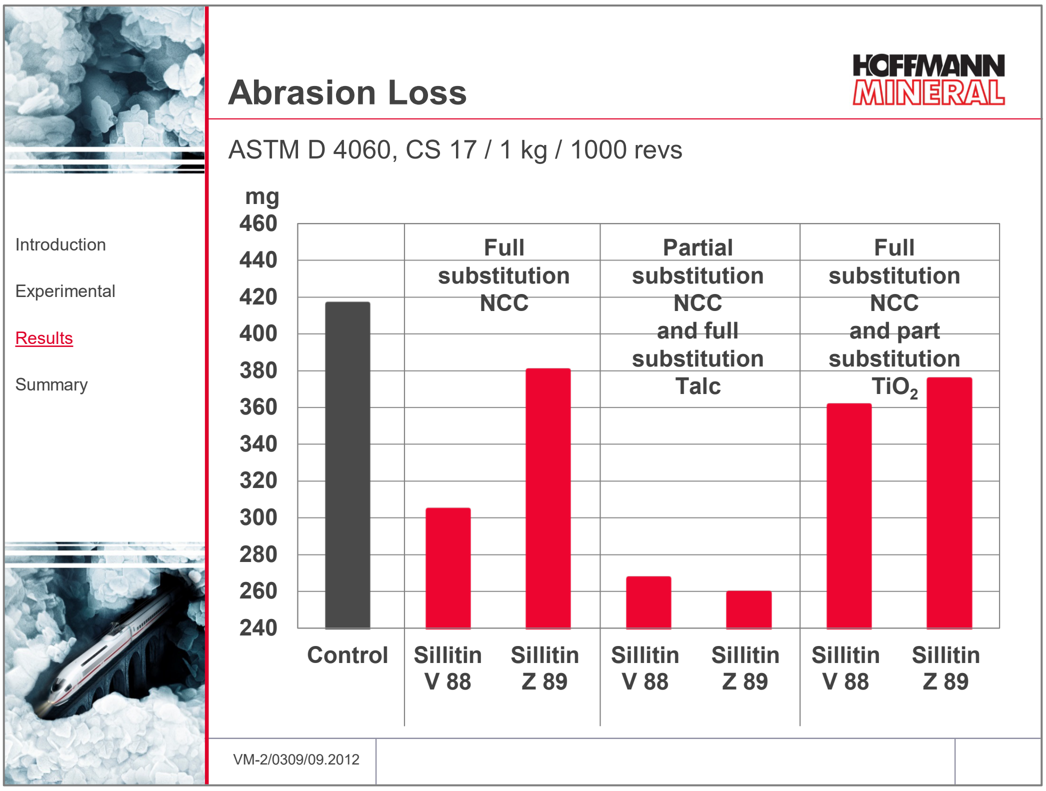

Fig. 11

5. Summary and outlook

The performance level of road marking paints can be markedly improved by working with Neuburg Siliceous Earth grades Sillitin V 88 or Sillitin Z 89:

- The color space as defined in DIN EN 1436 will be maintained, only the color values in the central area are minimally shifted.
- The hiding power will be improved, which means either lower film thicknesses can be applied or in the formulation the titanium dioxide content can be further reduced (cost savings).
- Even with titanium dioxide content by at least 20 %, the hiding power remains fully at level.
- The drying time will be shortened by 10 - 25 minutes, which means a painted road can be faster re-opened for traffic.
- The abrasion resistance (in particular when replacing talc) is improved thus the life time of the road marking paint comes out longer.

Sillitin V 88 is specifically recommended because of its more neutral color and, depending on the filler blend used, the better abrasion resistance. Sillitin Z 89 is distinguished by lower wear on the processing units and a better hiding power.

For high requirements to color neutrality, the new Neuburg Siliceous Earth grade Silfit Z 91 (not available at the time of conducting the study) is recommended, which through the calcination process offers a brighter color and a higher color neutrality than the Sillitins.

In a study of water based formulations up to 40 % titanium dioxide could be replaced with a parallel partial substitution of calcium carbonate with Silfit Z 91 without losing hiding power however with gaining cost advantages. The color space of the white road marking paint remained absolutely unchanged. In addition, also an improvement in abrasion resistance was obtained.

<u>Notes concerning an earlier publication:</u>

In the technical report „Filler Optimization for Road Marking Paints“ based on a similar binder, but with toluene and acetone as solvents and calcium carbonate, cristobalite and diatomaceous earth (kieselguhr) as fillers, further pertinent properties were examined, which should also be of relevance for the present study

The partial substitution of calcium carbonate with Neuburg Siliceous Earth resulted in marked improvements in the following areas:

- Drying time (complete drying)
- Night visibility
- Skid resistance (grip)