Reduced titanium dioxide content:

Neuburg Siliceous Earth

in road marking paints

(water based, white,

wet film thickness 600 µm)

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1 Introduction

Benefits of Neuburg Siliceous Earth have shown up already in earlier studies on solvent and also water based road marking paints with regard to an increased hiding power and improved abrasion resistance.

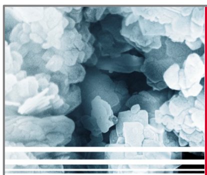
The present work with a white water based road marking paint will evaluate the partial replacement of titanium dioxide and calcium carbonate with Neuburg Siliceous Earth under constant pigment volume concentration.

The objective of the study was to maintain or rather improve the performance properties at a wet film thickness of 600 µm along with reducing the costs through the replacement of titanium dioxide with Neuburg Siliceous Earth.

2 Experimental

2.1 Base formulation

The starting point of the study was a base formulation as received from the Dow Chemical Company (formerly Rohm & Haas) as given in *Fig. 1*.



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Base Formulation *

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		Parts per weight
Fastrack 53	Binding agent (Acrylate dispersion)	366.0
Foamaster 8034	Defoaming agent	2.4
Triton X 405	Wetting-/ Dispersing agent	2.9
AS 238	Wetting-/ Dispersing agent	8.2
Titanium dioxide (TiO_2)	Pigment	96.0
Natural calcium Carbonate (NCC)	Filler	456.0
Ethanol	Solvent	11.8
Foamaster 8034	Defoaming agent	0.3
Texanol	Coalescence agent	38.0
Water		18.1
Total		1000

* by Dow Chemical Company (Rohm & Haas)

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Fig. 1

Starting from the base formulation with 96 parts by weight (pbw) titanium dioxide and 456 pbw natural calcium carbonate, 40 % of the titanium dioxide and 12.5 pbw calcium carbonate were replaced at equal volume with the calcined Neuburg Siliceous Earth grade Silfit Z 91 *(Fig.2)*.

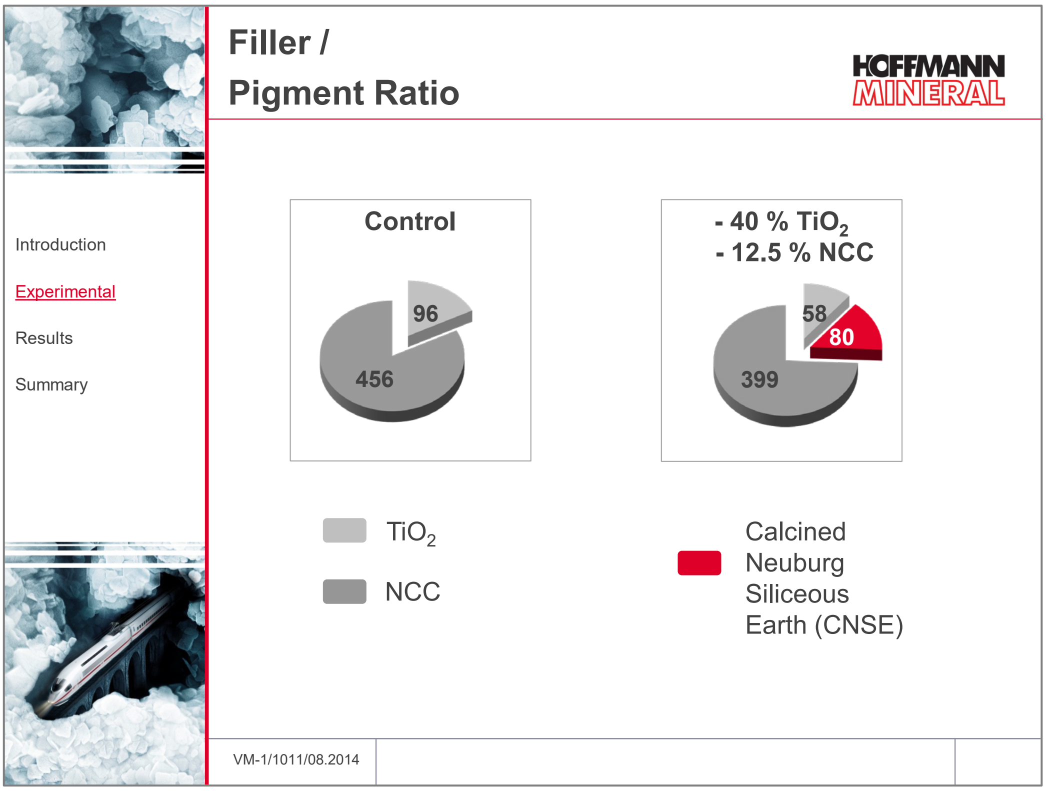

Fig. 2

The individual formulation variations are given in *Fig. 3*. The aminopropyl-triethoxysilane was added in order to further improve the abrasion resistance of the marking paint. Silanes give the best effect with a silicate-type reaction partner, which is the case for Silfit Z 91, whereas there is no interaction with calcium carbonate.

Formulation Variations

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	Control	- 40 % TiO_2	
Fastrack 53	366	366	366
Foamaster 8034	2.4	2.4	2.4
Triton X 405	2.9	2.9	2.9
AS 238	8.2	8.2	8.2
Titanium dioxide (TiO_2)	96	58	58
Natural calcium carbonate (NCC)	456	399	399
Silfit Z 91		80	80
Amino silane			0.8
Ethanol	11.8	11.8	11.8
Foamaster 8034	0.3	0.3	0.3
Texanol	38	38	38
Water	18.1	18.1	18.1
Total (parts by weight)	1000	985	986
PVC [%]	51		

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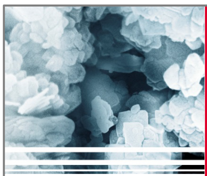
Fig. 3

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 crypto-crystalline silica portion remains inert under the temperature chosen. Through an integrated air classifier process grain sizes > 15 µm are being removed.

Fig. 4 summarizes the typical properties of the natural calcium carbonate (NCC) and the Calcined Neuburg Siliceous Earth grade Silfit Z 91. Compared with the natural calcium carbonate used in the base formulation, Silfit Z 91 is distinguished by a higher oil absorption, a higher specific surface area and a smaller particle size.



Filler Characteristics

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		NCC	Calcined Neuburg Siliceous Earth
			Silfit Z 91
Morphology		corpuscular	corpuscular / lamellar
Density	[g/cm³]	2.7	2.6
Particle size d_{50}	[µm]	7.3	2.0
Particle size d_{97}	[µm]	28	10
Oil absorption	[g/100g]	30	60
Specific surface area BET	[m²/g]	1.3	7.5

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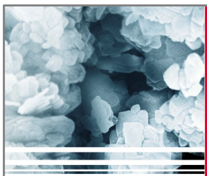
Fig. 4

The color values were determined with a spectral photometer measuring geometry d/8° and light D 65. Typically for this group of materials, the calcium carbonate impresses by particularly higher brightness results. Through the calcination process, Silfit Z 91 shows higher brightness and color neutrality than conventional Neuburg Siliceous Earth grades, as evident from the high L* and low b* values (*Fig. 5*).



Filler Characteristics

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Color	NCC	Calcined Neuburg Siliceous Earth
		Silfit Z 91
X	87	84
Y	91	89
Z	94	93
L*	97	95.4
a*	0.1	-0.2
b*	2.8	1.2

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Fig. 5

2.3 Preparation of batches

The test batches were prepared in a cooled vessel at a dissolver with a peripheral speed of 3 m/s. After a dispersion time of 10 min, the grain fineness as measured on the grindometer was between 15 and 20 µm.

3 Test methods and results

3.1 Hiding power (contrast ratio)

Different wet film 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 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 %. With a contrast ratio of >= 98 % a road marking paint is defined as covering.

Fig. 6 shows the contrast ratio at a wet film thickness of 600 µm (corresponding to 250-270 µm dry film thickness). For the formulations only filled with calcium carbonate, the hiding power becomes poorer with increasing titanium dioxide replacement. With Silfit Z 91, the hiding power remains at a high level. The more Silfit Z 91 is used and calcium carbonate is reduced, the better will come out the hiding power. Even with a 40 % reduction of titanium dioxide, the hiding power is at least as high as with the reference formulation with full titanium dioxide content (see the grey-circled points in *Fig. 6*). These two formulations will be taken into focus in the following, as here the best results with respect to raw material cost reduction and abrasion resistance could be obtained.

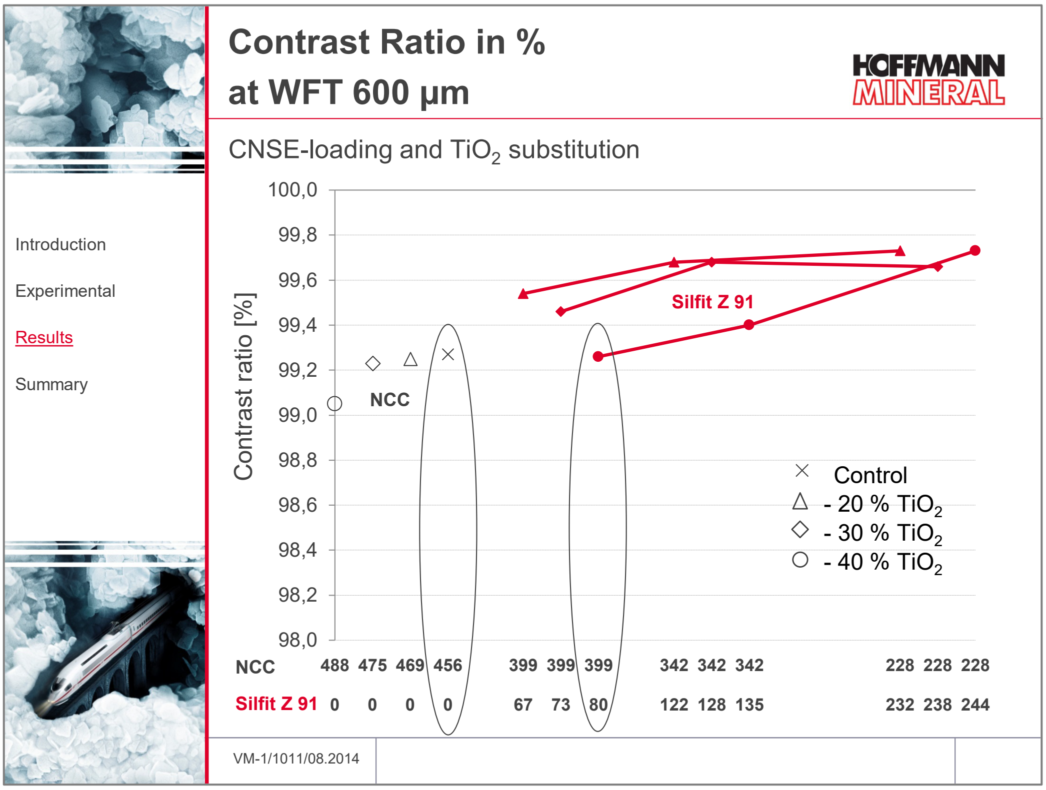

Fig. 6

3.2 Viscosity

Viscosity prior to dilution was determined in a Rheometer (plate/plate) at a shear rate of 100 s^{-1} .The results in Pa*s are given in *Fig. 7*. When working with Calcined Neuburg Siliceous Earth as filler, the marking paint will come out slightly thicker.

Therefore, the batches containing Silfit Z 91 were diluted with deionized water to the same flow time in the 6 mm DIN cup as the reference.

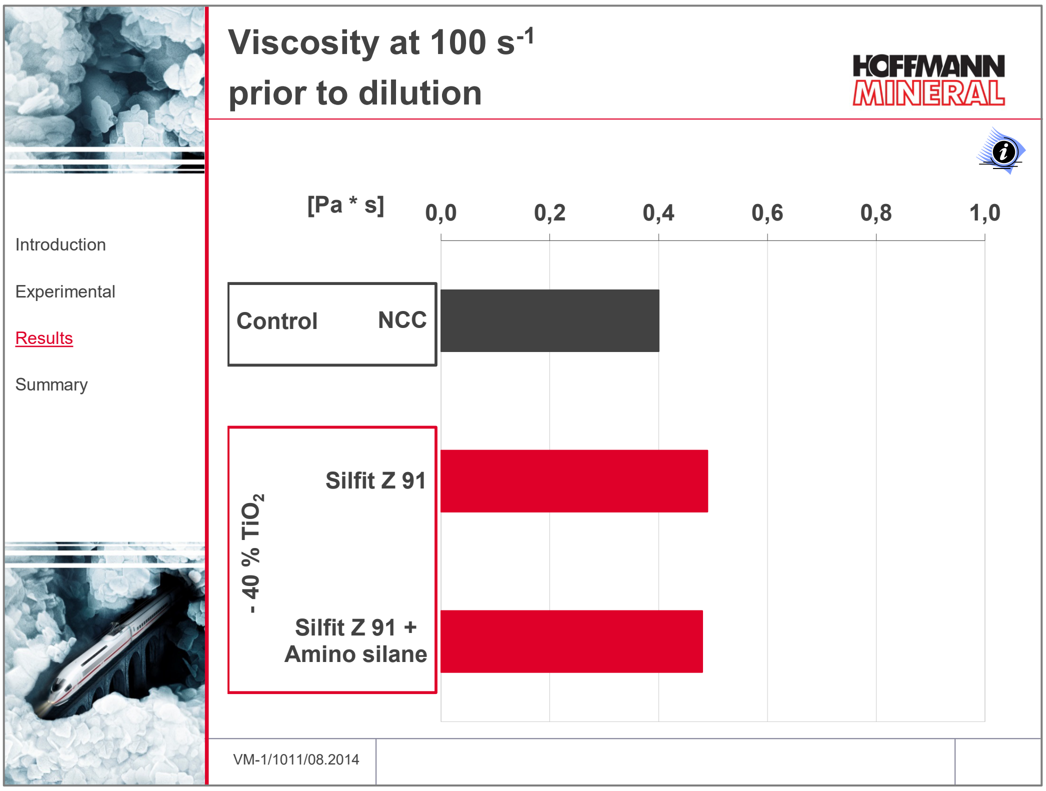

Fig. 7

Fig. 8 illustrates the dilution with deionized water in percent. The base formulation with calcium carbonate does not require any additional water for offering the processing viscosity of about 15 s in the 6 mm DIN cup. Silfit Z 91 needs about 1 % water for the viscosity adjustment, in the formulations with aminosilane about 1.5 %
The viscosity of the diluted batches in the Rheometer was about 0.4 Pa*s.

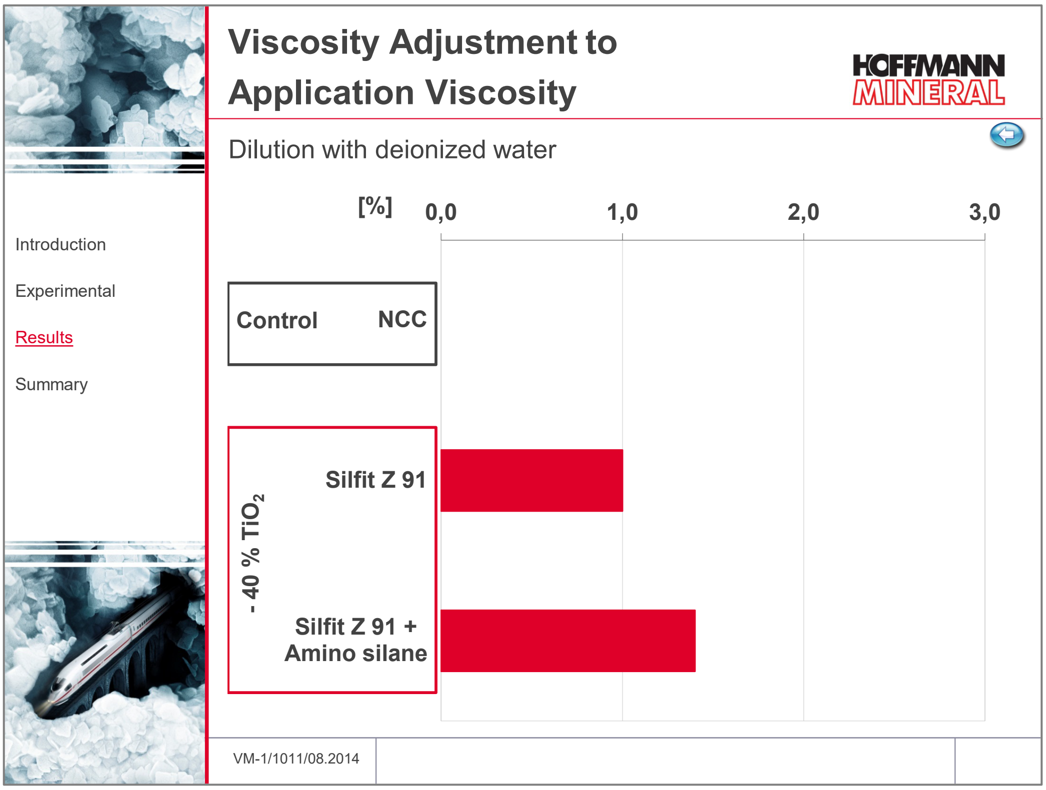

Fig. 8

The solids content by volume is given in *Fig. 9*. After diluting with deionized water the Silfit Z 91 formulations show slight lower solids content compared with the undiluted calcium carbonate filled reference formulation.

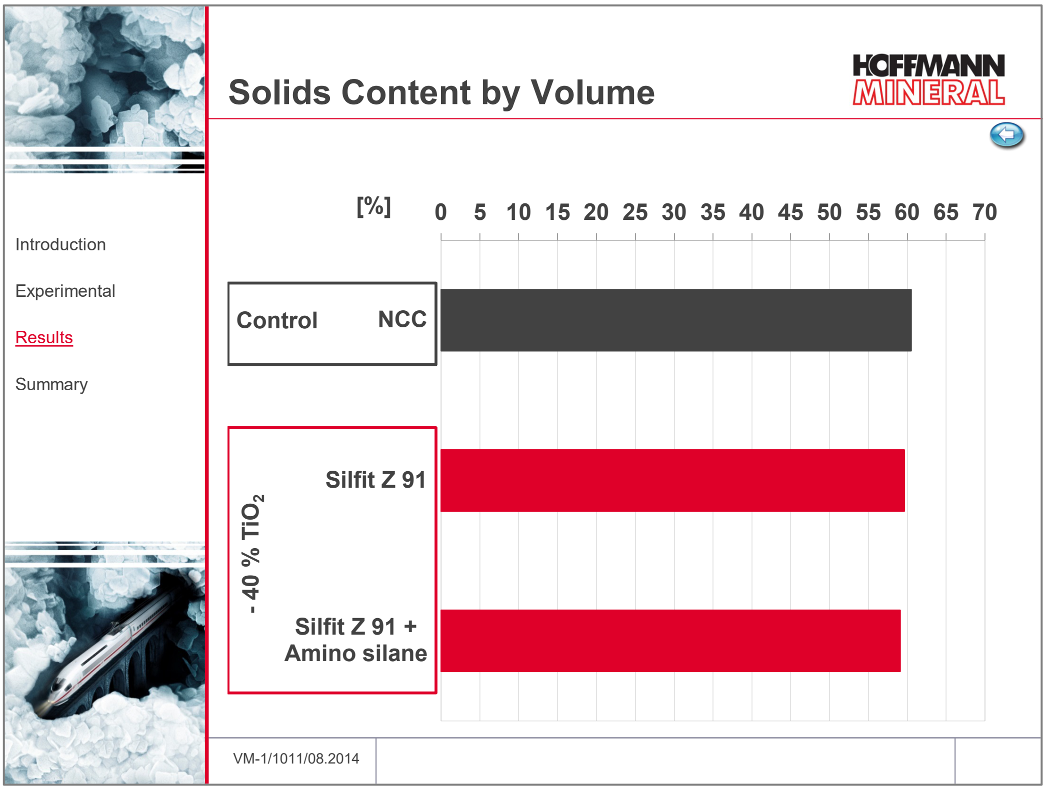

Fig. 9

3.3 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 to 280 µm dry film thickness). The films were dried for 24 h at 23 °C and 50 % relative humidity. The color was then determined with a spectrophotometer with a geometry of 45°/0° using D 65 light.

Fig. 10 illustrates the color values. If 40 % titanium dioxide are taken out of the formulation and replaced with Silfit Z 91, brightness will decrease marginally. The yellow/blue contribution b* as well as the red/green contribution a* remain practically unchanged.

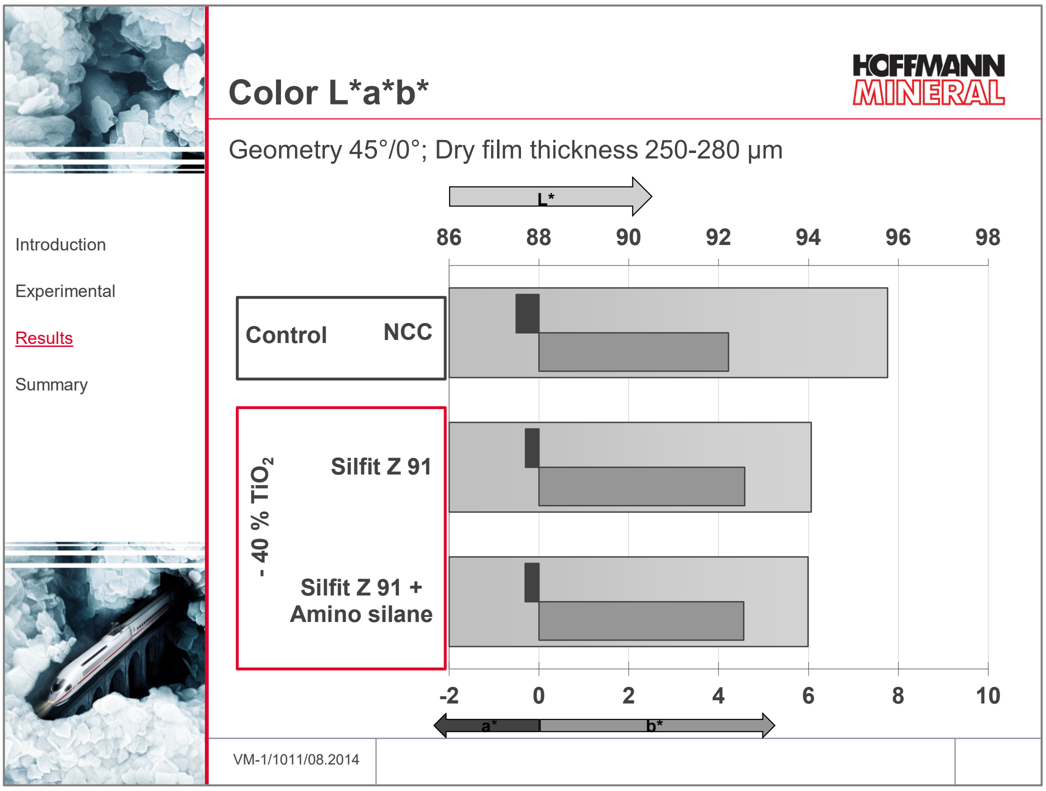

Fig. 10

From the resulting X, Y and Z values, it is possible to calculate the chromaticity coordinates x and y. The standard DIN EN 1436 (edition 2009-01) specifies for white road marking paints a colorimetric range via four coordinates for x and y. All batches tested are situated in the center of this color space. Evidently a reduction of titanium dioxide by 40 % compensated by Silfit Z 91 is possible without problems, as the color chromaticity coordinates required in the standard are exactly maintained (*Fig. 11).*

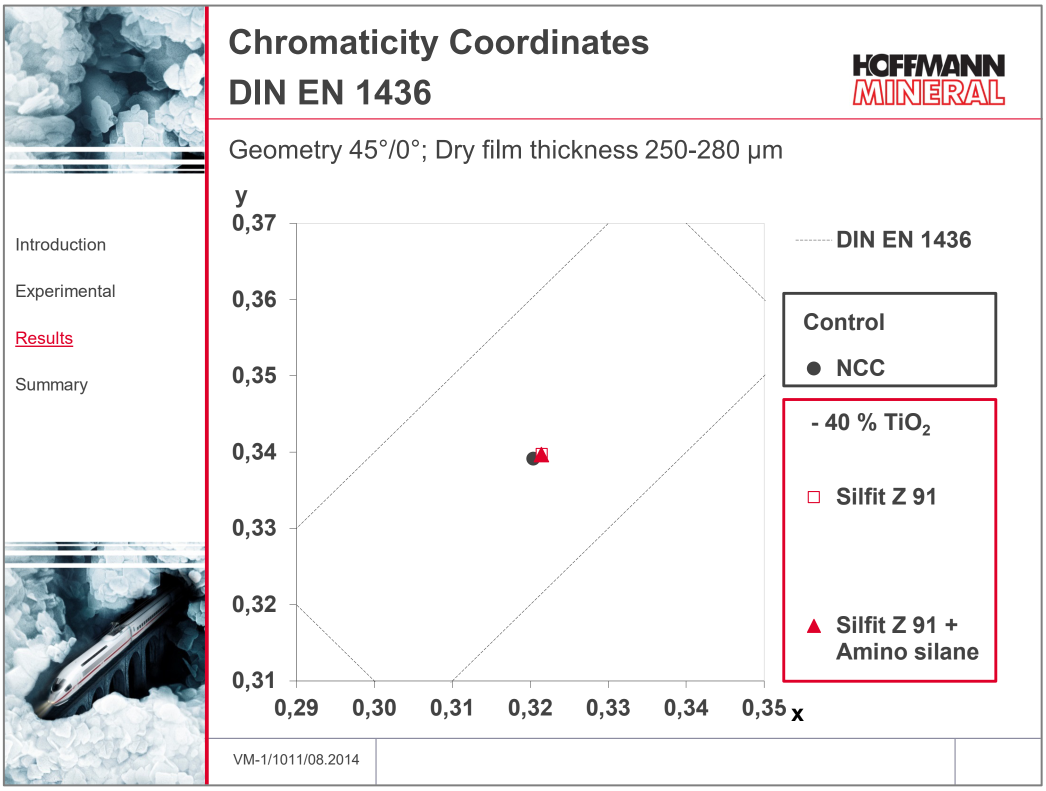

Fig. 11

3.4 Drying time

A metal sheet was covered 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 s with a rubber disc and a 2 kg weight. 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. 12 shows the drying time in minutes required to reach stage 4. As the drying time is highly dependent on the rate of air currents, attention was paid for air movements to remain practically inexistent, i.e. close to 0 m/s. The drying times reported are laboratory results which can differ according to weather conditions, the film thickness and the substrate; this is why the results should only be valued as indicative (at 23 °C and 50 % relative humidity) for a potential differentiation of the formulations.

The drying times come out very close to each other, all formulations position themselves just over 100 minutes, and Silfit Z 91 despite the higher water content also approaches the reference formulation. In view of the conditions and factors discussed above, a further differentiation does not appear possible, so all drying times can be regarded as equal.

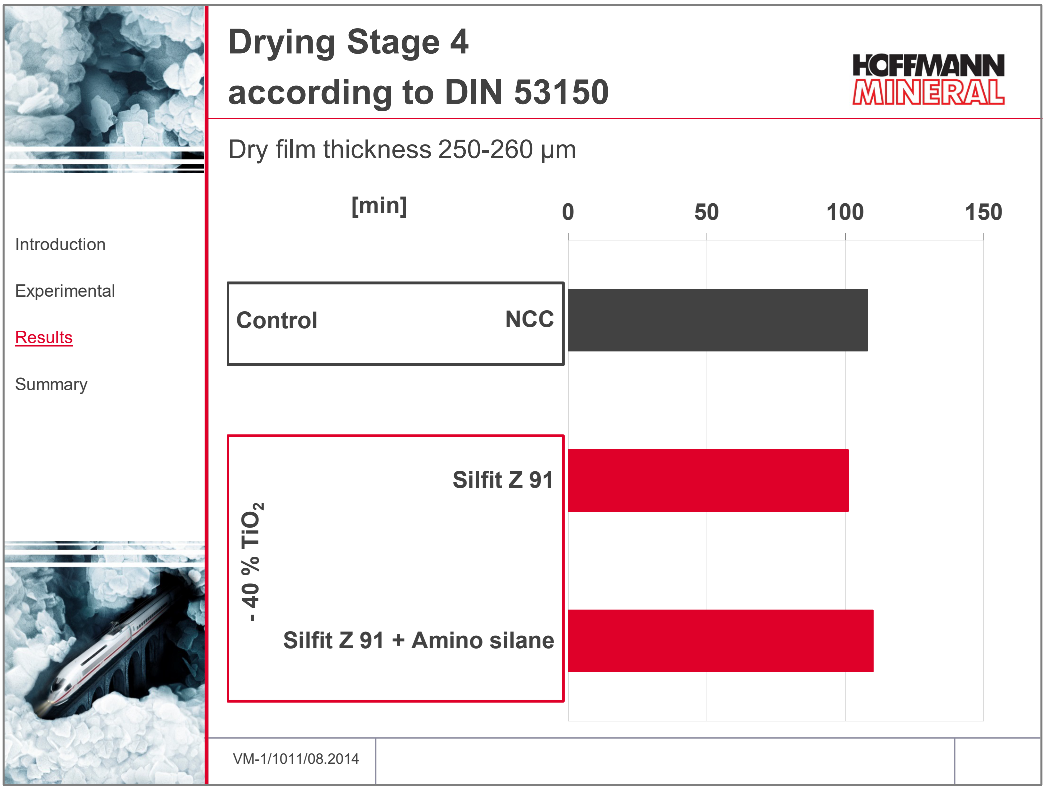

Fig. 12

3.5 Water wash-off resistance (early rain resistance)

In their drying behavior, road marking paints are dependent on the surrounding temperature, the humidity of the air and the applied film thickness. The lower the temperature, the higher the relative humidity and the bigger the applied quantity of marking color, the more time will take the drying. This can lead to problems during critical seasons with high amounts of precipitations. If a marking paint which has not yet dried completely, is exposed to rainfall, it will frequently run off, as it has not yet attained the required water resistance, i.e. is not yet “rain proof”.

The expression “Early Rain Resistance” was chosen to indicate the drying behavior of road marking paints, which ideally even under unfavorable weather conditions should rapidly become “rain proof”.

The test was carried out based on ASTM D7538. With the aid of a doctor blade (gap height 500 µm, film width 6 cm), the road marking paint was applied to a Leneta film. After drying for 5 minutes in horizontal position at 23 °C and 50 % relative air humidity, the Leneta film was attached vertically to a wall (*Fig. 13*). Using a Trigger Sprayer, the marking paint was sprayed on from a distance of 30 cm within 5 seconds with 6 shots of tab water (this corresponds to 0.086 l/min or 0.84 l/m^2). The Leneta film was then taken off the wall immediately, and dried in a horizontal position at room temperature.

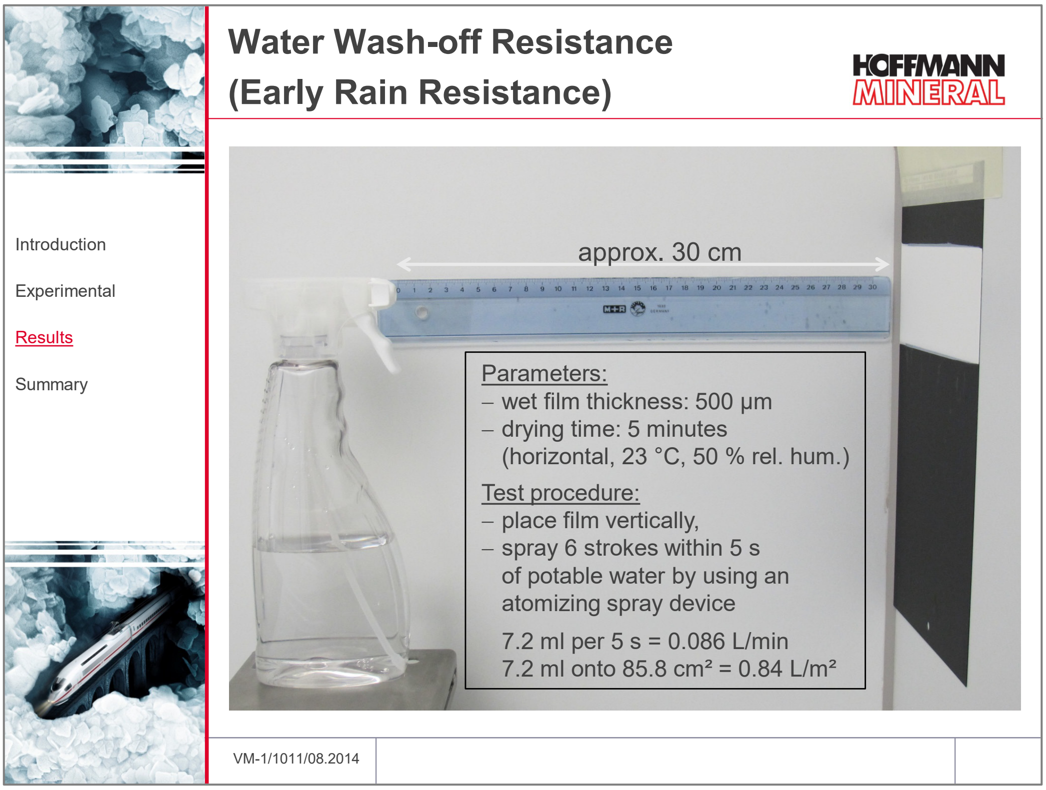

Fig. 13

The assessment of the “Early Rain Resistance” was done on the dry film.
The ranking scale is given in *Fig. 14*; only the film surface was assessed optically, and not the amount of washed-out particles. From 5 to 3 points the film surface was judged acceptable, from 2 to 0 points as insufficient.

Water Wash-off Resistance (Early Rain Resistance)

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Rating scale

	Points	Classification	Description
OK	5	no change	– no visible change of the surface
OK	4	nominal change	– surface is a little bit blurry
OK	3	slight change	– surface is blurry – slight sagging (within film width)
not OK	2	marked change	– considerable sagging (within film width)
not OK	1	intense change	– strong sagging (within film width)
not OK	0	destruction	– complete sagging, substrate becomes visible

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Fig. 14

The formulations with Silfit Z 91 visibly run off less strongly compared with the reference. Modifications of the film surface are not observed by using Silfit Z 91. This way, a road marking paint with Silfit Z 91 will rapidly become resistant against rain, even under unfavorable weather conditions.
An additional note for optimum use of the silane: during the process, the aminopropyl-triethoxysilane should be added without exception directly after the fillers, as otherwise a good early rain resistance cannot be ensured.
The assessment according to the ranking scale is illustrated by way of a bar graph in *Fig. 15*. Photographs of the dried film surface after the exposure to "simulated" rain are shown in *Fig. 16*.

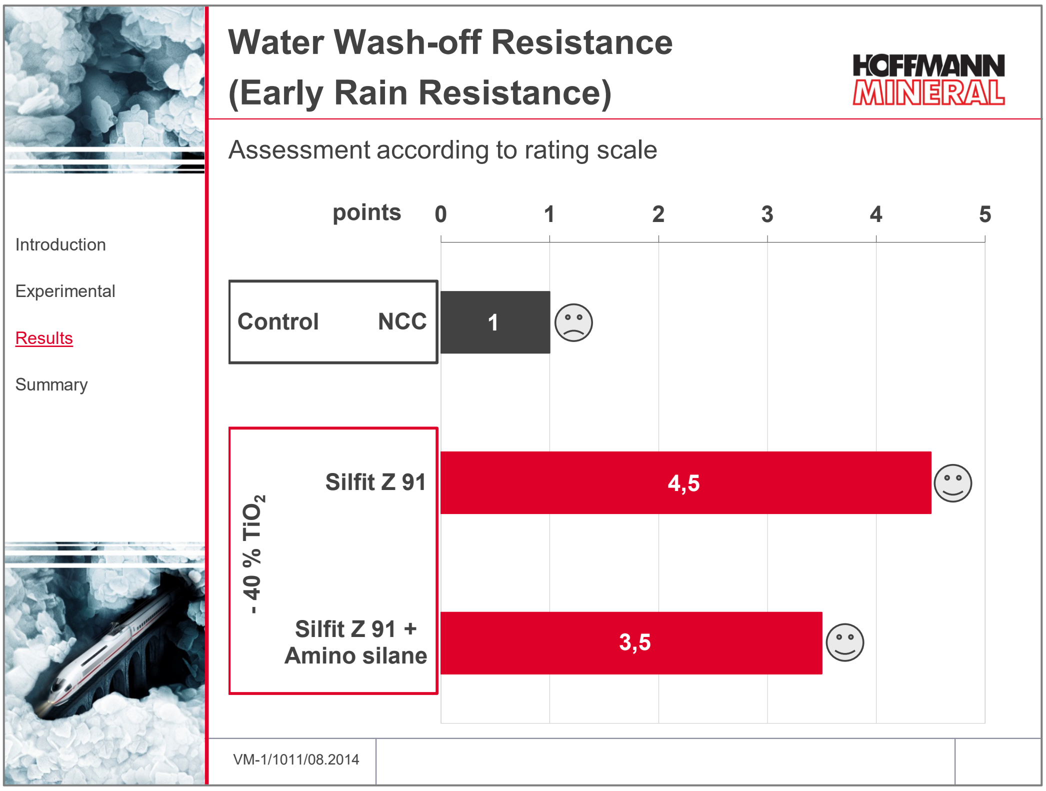
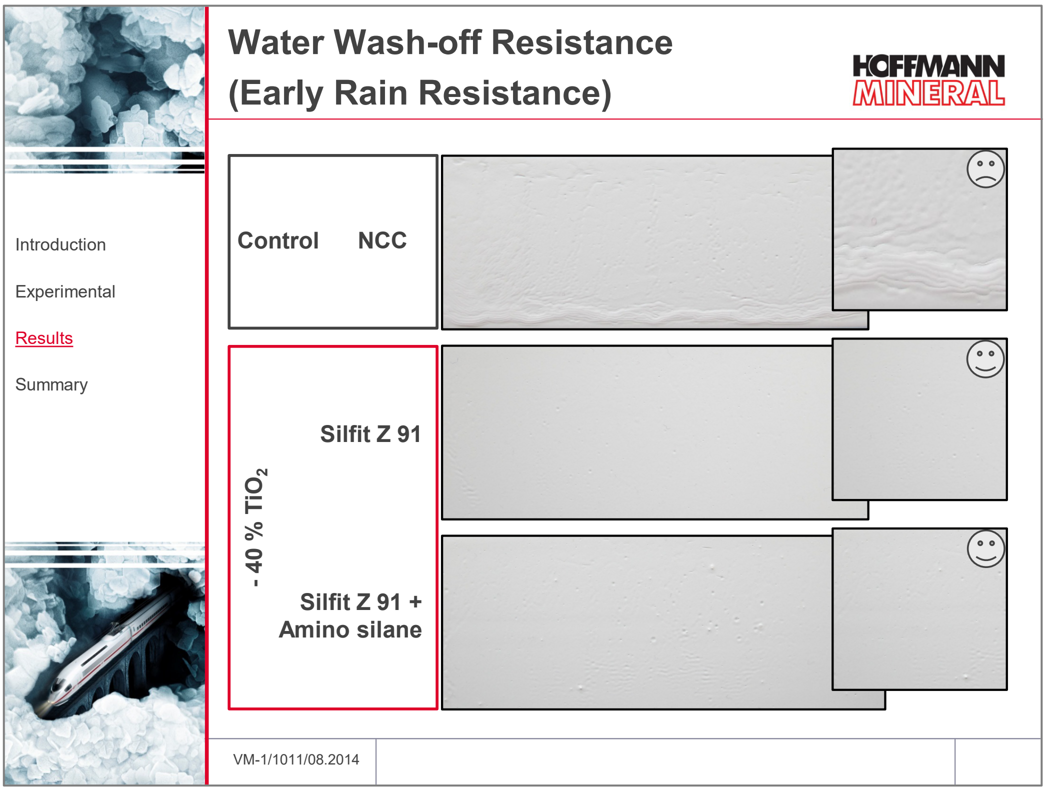


Fig. 15


Water Wash-off Resistance
(Early Rain Resistance)
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Control NCC
- 40 % TiO2
Silfit Z 91
Silfit Z 91 +
Amino silane
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Fig. 16

3.6 Abrasion resistance

For the abrasion tests, metal sheets 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. 17* shows the average abrasion loss after 1000 revolutions in milligrams, under a load of 1 kg onto the CS 17 wheels.

The replacement of 40 % titanium dioxide and 12.5 % natural calcium carbonate with Silfit Z 91 leads to an improvement of the abrasion resistance by 15 %. The additional use of the aminosilane gives another plus of 10 %. This means, Silfit Z 91 and aminosilane together give rise to a total improvement of 25 % in comparison with the results for the control formulation with full titanium dioxide and natural calcium carbonate content.

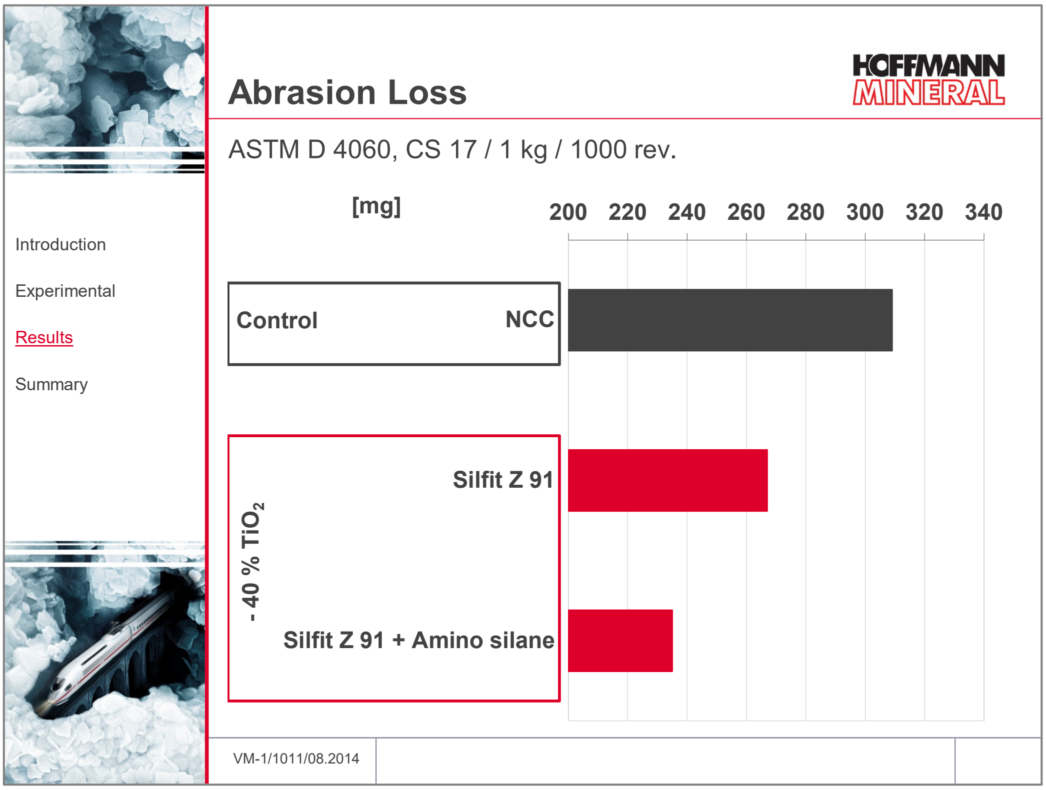

Fig. 17

3.7 Raw material costs

Fig. 18 shows the volume related raw material costs of the batches diluted to application viscosity.

Aside from the marginal water addition, in particular through the replacement of the markedly higher-priced titanium dioxide (input: € 2.40/kg) with Silfit Z 91 the formulations come out more favorable by 6 % than the reference.

This way, the costs can be lowered substantially through working with Silfit Z 91 in replacement of 40 % titanium dioxide and 12.5 % calcium carbonate.

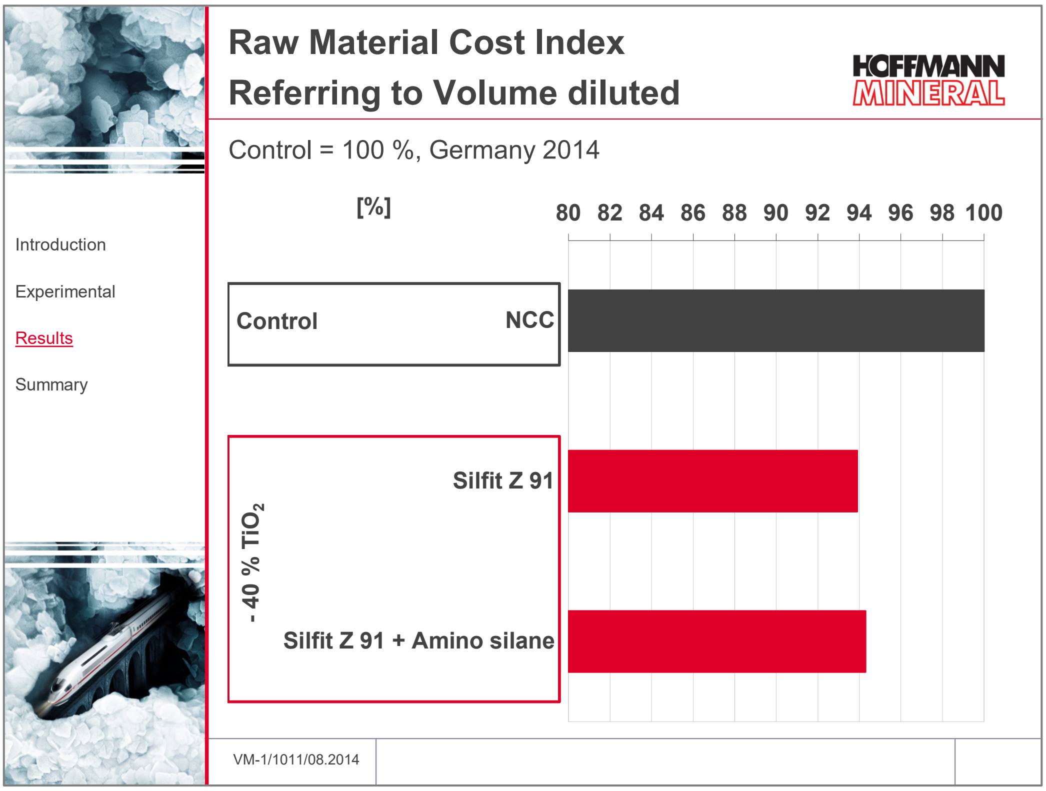

Fig. 18

Fig. 19 shows the weight based raw material costs of the formulations diluted to application viscosity. Even with this weight-related calculation, the replacement of 40 % titanium dioxide and 12.5 % calcium carbonate, via working with Silfit Z 91, the costs can be reduced by 4 %.

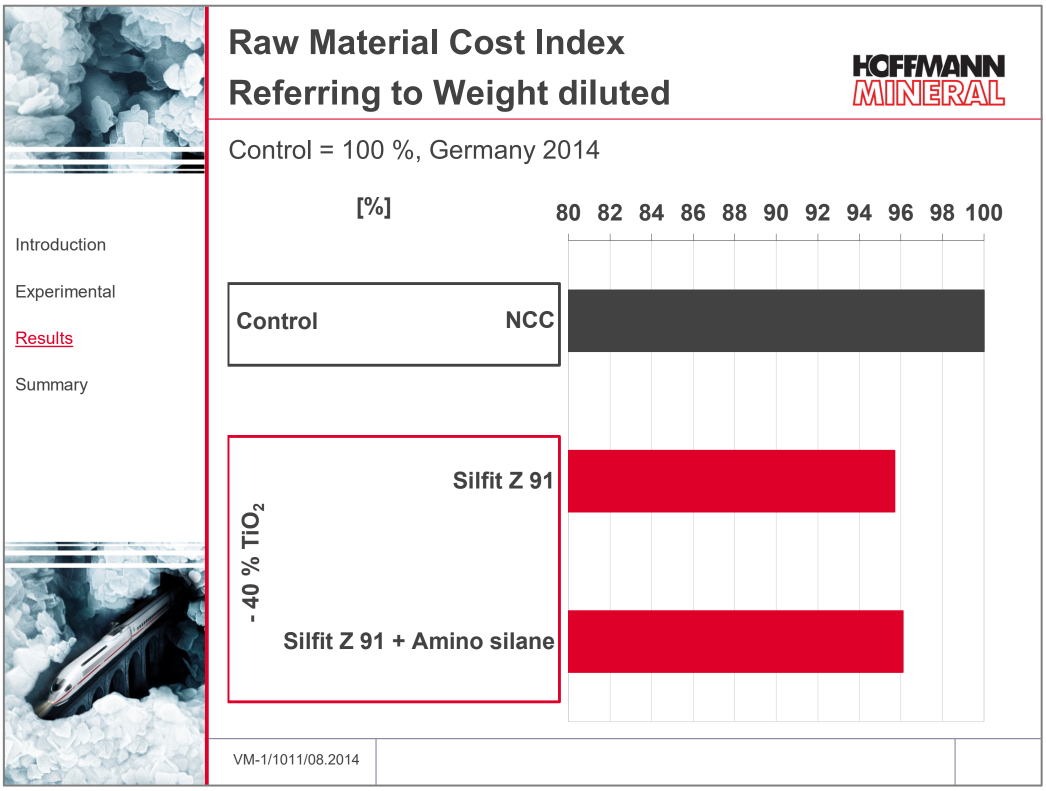

Fig. 19

4 Summary and outlook

Suggestions for white road marking paints:

The replacement of 40 % titanium dioxide and 12.5 % natural calcium carbonate with **Silfit Z 91** allows:

- to maintain the color space and the color neutrality in the center. The color location of the white marking paint will remain unchanged
- to increase the Early Rain Resistance so that no changes of the film surface can be observed after precipitations. A “swimming” of the coating on the road will be avoided, and the property profile of the marking paint remains unchanged
- to improve the abrasion resistance, in particular with an addition of aminopropyl-triethoxysilane
- to save on 40 % titanium dioxide without losing hiding power
- to realize a cost saving potential

Suggestions for thin film applications of road marking paints:

If wet film thickness lower than 600 µm can be applied, specific information is available. The technical report „Neuburg Siliceous Earth in Road Marking Paints (water based, white, low film thickness)“ indicates how through the use of Neuburg Siliceous Earth up to 30 % titanium dioxide can be replaced.

Suggestions for yellow road marking paints:

Especially for yellow road marking paints, aside from **Sillitin Z 89** in particular, the grade **Sillitin Z 86** has proved suitable as this product is characterized by an inherent yellowish tint, and offers a further price advantage. Yellow road marking paints, however, are formulated with a markedly lower addition of titanium dioxide, so that the limits of replacing the pigment and filler have to be established by individual tests.