Reduced titanium dioxide content:

Neuburg Siliceous Earth

in road marking paints

(water based, white, low film thickness)

Author: Susanne Reiter
Hubert Oggermüller

VM-1/1010/10.2014

Contents

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.

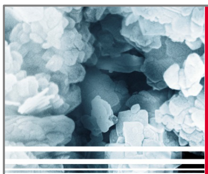
The present work with a white water based road marking paint will evaluate the partial replacement of titanium dioxide and calcium carbonate with Neuburg Siliceous Earth under constant pigment volume concentration.

The objective of the study was to maintain or even improve the performance properties of thin layer applications while reducing the costs through the titanium dioxide replacement 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*.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

Base Formulation *

HOFFMANN MINERAL

		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)

VM-3/1011/09.2014

Fig. 1

Starting from the reference formulation containing 96 parts by weight (pbw) titanium dioxide (TiO_2) and 456 pbw natural calcium carbonate (NCC), 20 resp. 30 % of the titanium dioxide were replaced in a first step at equal volume by calcium carbonate. This means the replacement of 20 % titanium dioxide led to 469 pbw natural calcium carbonate and 77 pbw titanium dioxide, while the replacement of 30 % titanium dioxide required 475 pbw natural calcium carbonate besides 67 pbw titanium dioxide.
In the formulations with Neuburg Siliceous Earth, the reduced parts of titanium dioxide are the same as in the comparable formulations with calcium carbonate. In addition, another 25 % of the original natural calcium carbonate were replaced at equal volume by two grades of Neuburg Siliceous Earth. This led at 20 % titanium dioxide replacement to 342 pbw calcium carbonate, 77 pbw titanium dioxide and 122 pbw Neuburg Siliceous Earth, and at 30 % titanium dioxide replacement to 342 pbw calcium carbonate, 67 pbw titanium dioxide and 128 pbw Neuburg Siliceous Earth (*Fig. 2*). The individual formulation variations are summarized in *Fig. 3*.

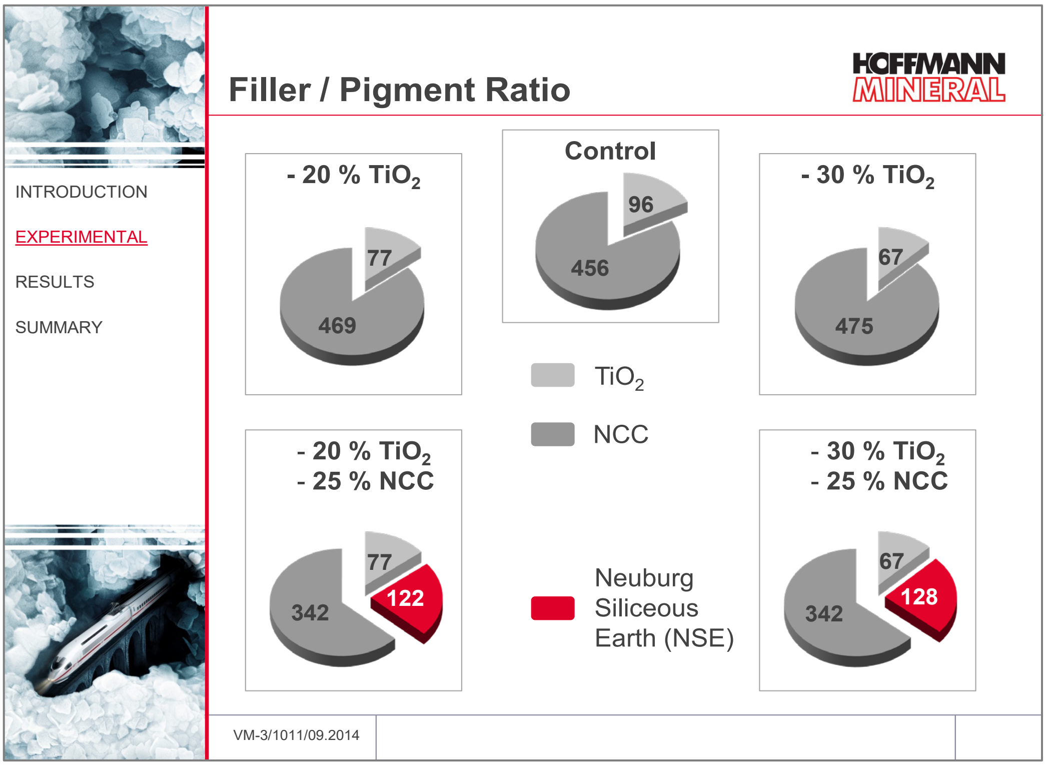


Fig. 2

Formulation Variations

HOFFMANN MINERAL

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY

	Control	- 20 % TiO_2			- 30 % TiO_2		
Fastrack 53	366	366	366	366	366	366	366
Foamaster 8034	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Triton X 405	2.9	2.9	2.9	2.9	2.9	2.9	2.9
AS 238	8.2	8.2	8.2	8.2	8.2	8.2	8.2
Titanium dioxide	96	77	77	77	67	67	67
Natural calcium carbonate	456	469	342	342	475	342	342
Sillitin Z 89			122			128	
Silfit Z 91				122			128
Ethanol	11.8	11.8	11.8	11.8	11.8	11.8	11.8
Foamaster 8034	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Texanol	38	38	38	38	38	38	38
Water	18.1	18.1	18.1	18.1	18.1	18.1	18.1
Total (parts by weight)	1000	994	989	989	990	985	985
PVC [%]	51						

VM-3/1011/09.2014

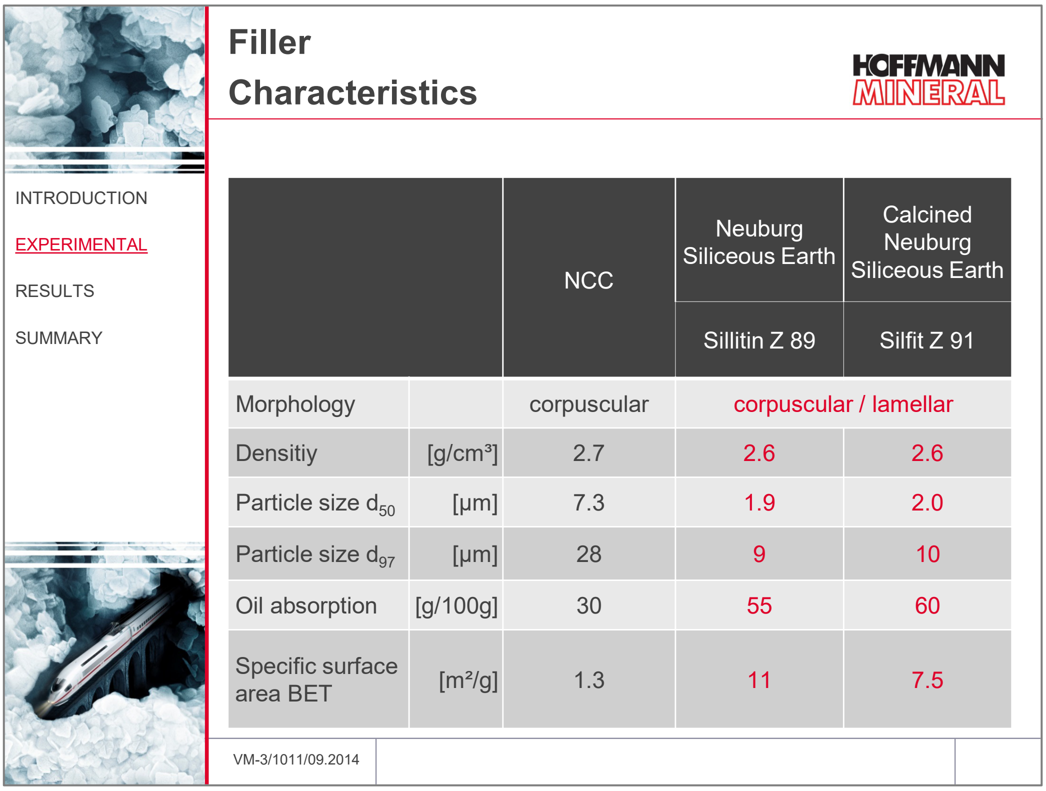
Fig. 3

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.

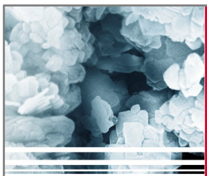
Fig. 4 indicates the typical properties of the natural calcium carbonate and the two Neuburg Siliceous Earth grades included in the study, i.e. Sillitin Z 89 and the calcined grade Silfit Z 91. Compared with the natural calcium carbonate used in the control formulation, Sillitin Z 89 and Silfit Z 91 are characterized by higher oil absorption, a higher specific surface area and a lower particle size.



		NCC	Neuburg Siliceous Earth Sillitin Z 89	Calcined Neuburg Siliceous Earth Silfit Z 91
Morphology		corpuscular	corpuscular / lamellar	
Densitiy	[g/cm³]	2.7	2.6	2.6
Particle size d_{50}	[µm]	7.3	1.9	2.0
Particle size d_{97}	[µm]	28	9	10
Oil absorption	[g/100g]	30	55	60
Specific surface area BET	[m²/g]	1.3	11	7.5

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. The slight yellow tinge of Sillitin Z 89 is evident from the higher b* value. Through the calcination process Silfit Z 91 gives higher brightness and color neutrality, as evident from the high L* and low b* results (*Fig. 5*).



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

Filler Characteristics

HOFFMANN MINERAL

Color	NCC	Neuburg Siliceous Earth	Calcined Neuburg SiliceousEarth
		Sillitin Z 89	Silfit Z 91
X	87	81	84
Y	91	86	89
Z	94	86	93
L*	97	94	95.4
a*	0.1	0.1	-0.2
b*	2.8	4.1	1.2

VM-3/1011/09.2014

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 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. 6*. When working with Neuburg Siliceous Earth as filler, the road marking paint will come out thicker, and this more so with Sillitin Z 89 than with Silfit Z 91.

For this reason, the batches with Neuburg Siliceous Earth grades were diluted with deionized water to the same level of flow time in the 6 mm DIN cup as was found for the reference formulation.

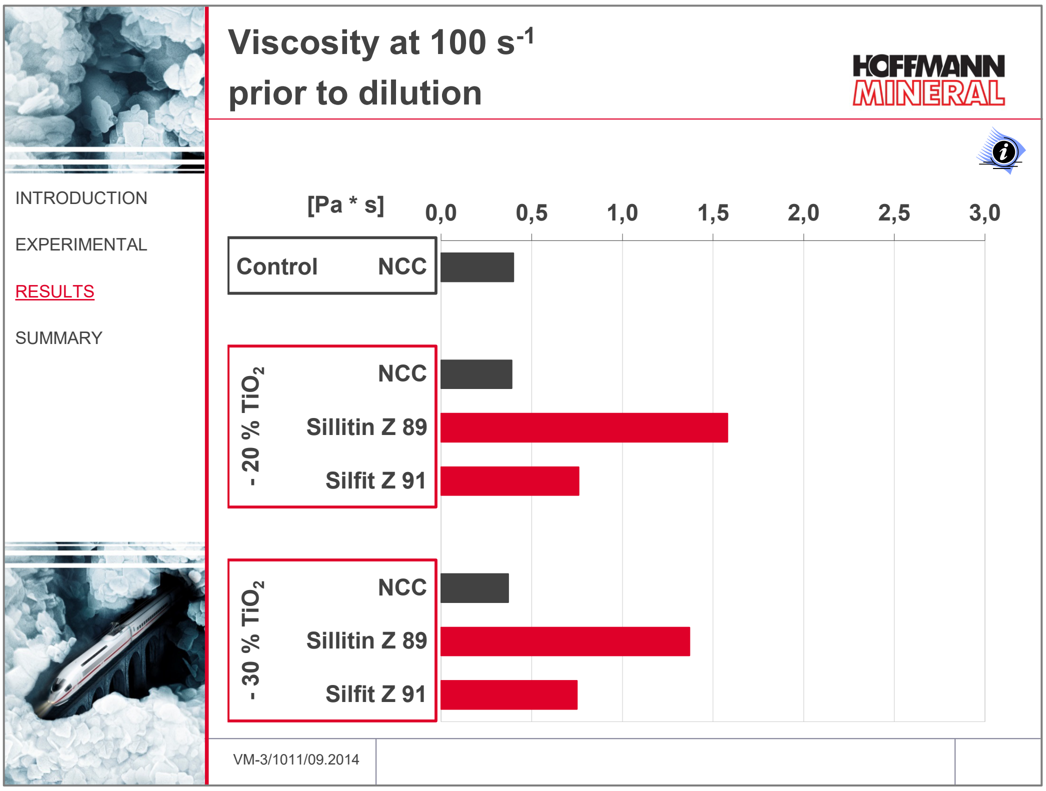


Fig. 6

Fig. 7 illustrates the degree of dilution with deionized water in percent. The formulations with only calcium carbonate do not need water additions for obtaining a processing viscosity of about 15 s in the 6 mm cup. Sillitin Z 89 requires about 4 % water for this adjustment, Silfit Z 91 just half of that amount. In the rheometer, the viscosity of the diluted batches was 0.4 ± 0.1 Pa*s.

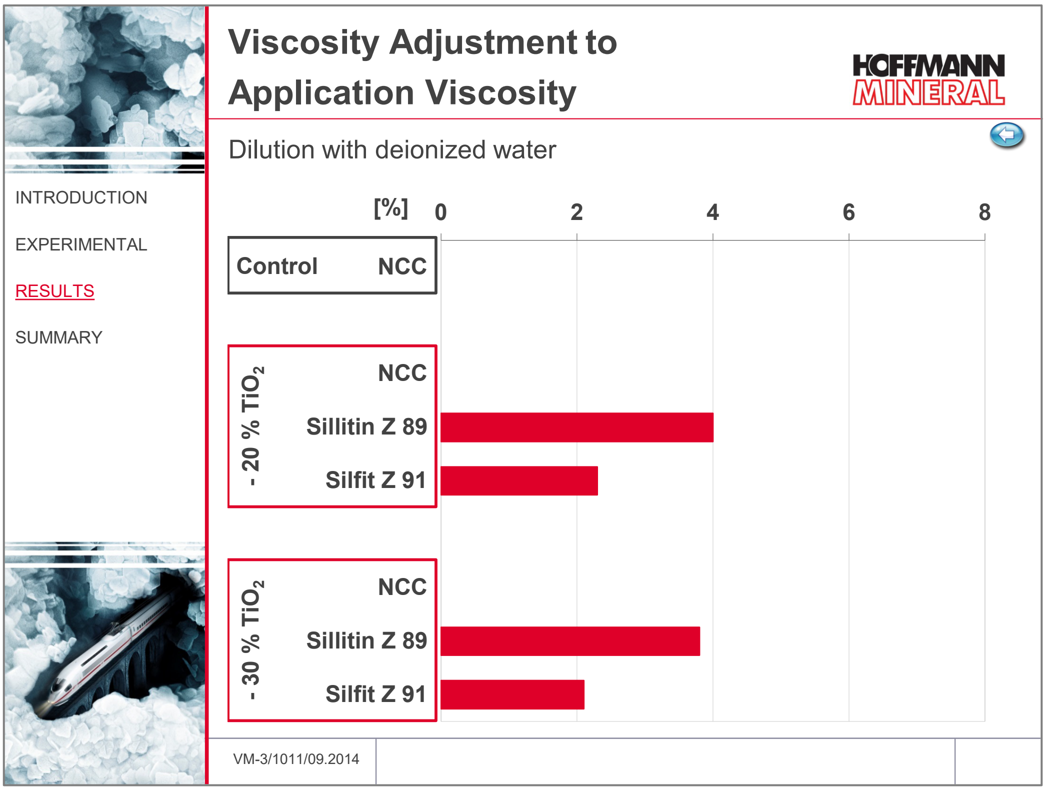


Fig. 7

The solids content of the batches is illustrated in *Fig. 8*. As a result of the dilution with deionized water, the batches compounded with Neuburg Siliceous Earth have lower solids content by volume than the undiluted calcium carbonate reference formulations.

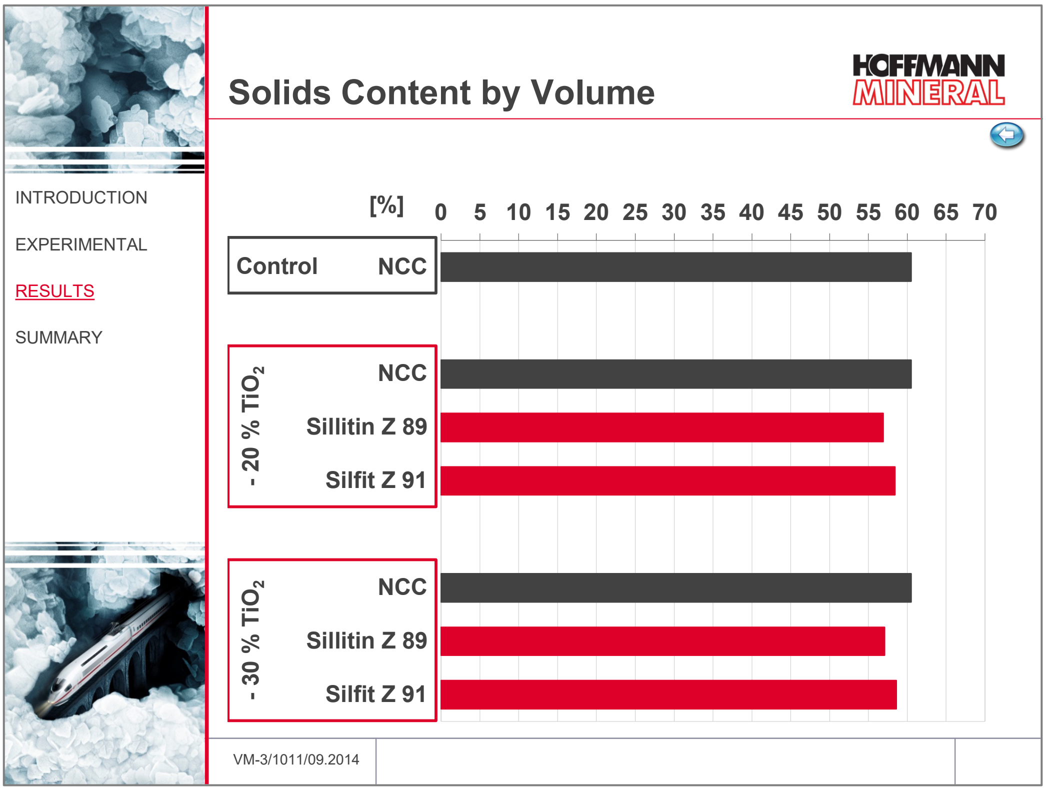


Fig. 8

3.2 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 270 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. 9 gives the color results obtained. The more titanium dioxide is taken out of the formulation, the more the brightness is decreased. In view of the inherent color of Sillitin Z 89, the trend towards a lower L* and an increasing b* becomes evident, while a* remains almost unchanged. When working with the color-neutral Silfit Z 91, no change of the color results can be recorded, only the brightness is slightly reduced.

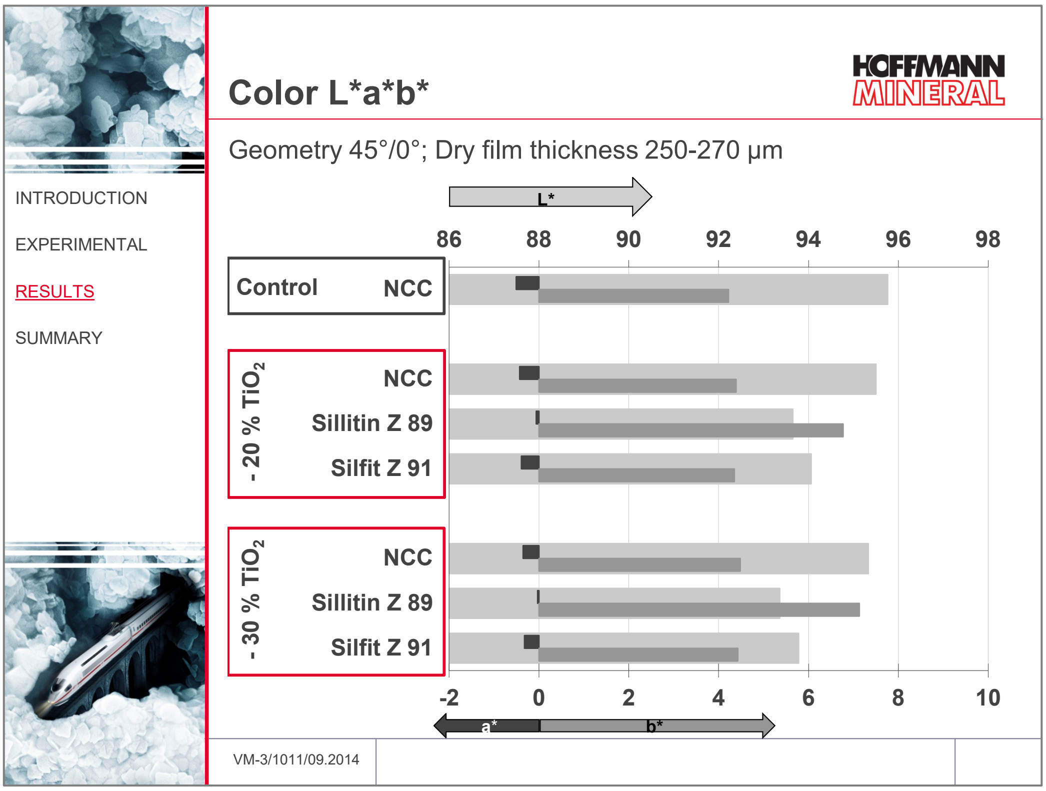


Fig. 9

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. Because of the inherent color of Sillitin Z 89, the chromaticity coordinates of these coatings are found somewhat shifted away from the reference. The batches with the color-neutral Silfit Z 91 as well as those with calcium carbonate give almost identical results with the control formulation (*Fig. 10*).

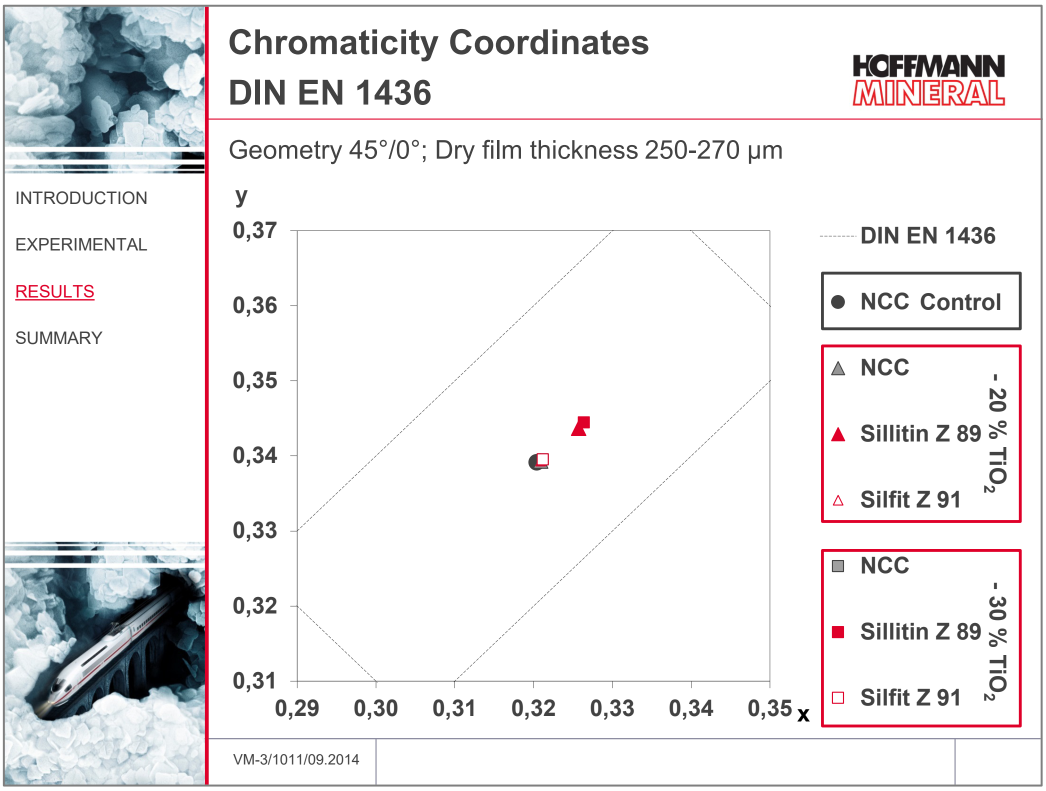


Fig. 10

3.3 Drying time

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 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. 11 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 are well comparable within each other, all formulations come out just above 100 minutes. An explication for the marginally longer drying time with Neuburg Siliceous Earth may be the higher water content. In view of the conditions and influence factors discussed above, a further differentiation does not look possible, which means the drying times should be regarded as equal throughout.

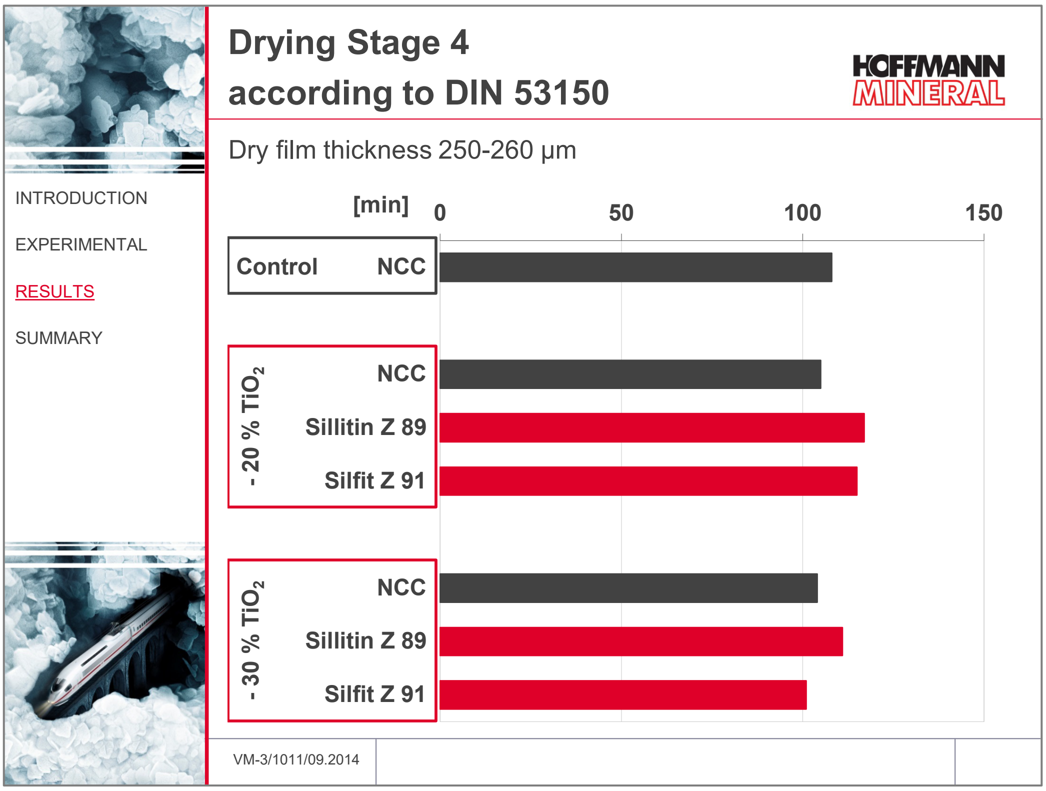


Fig. 11

3.4 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. 12*). 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.

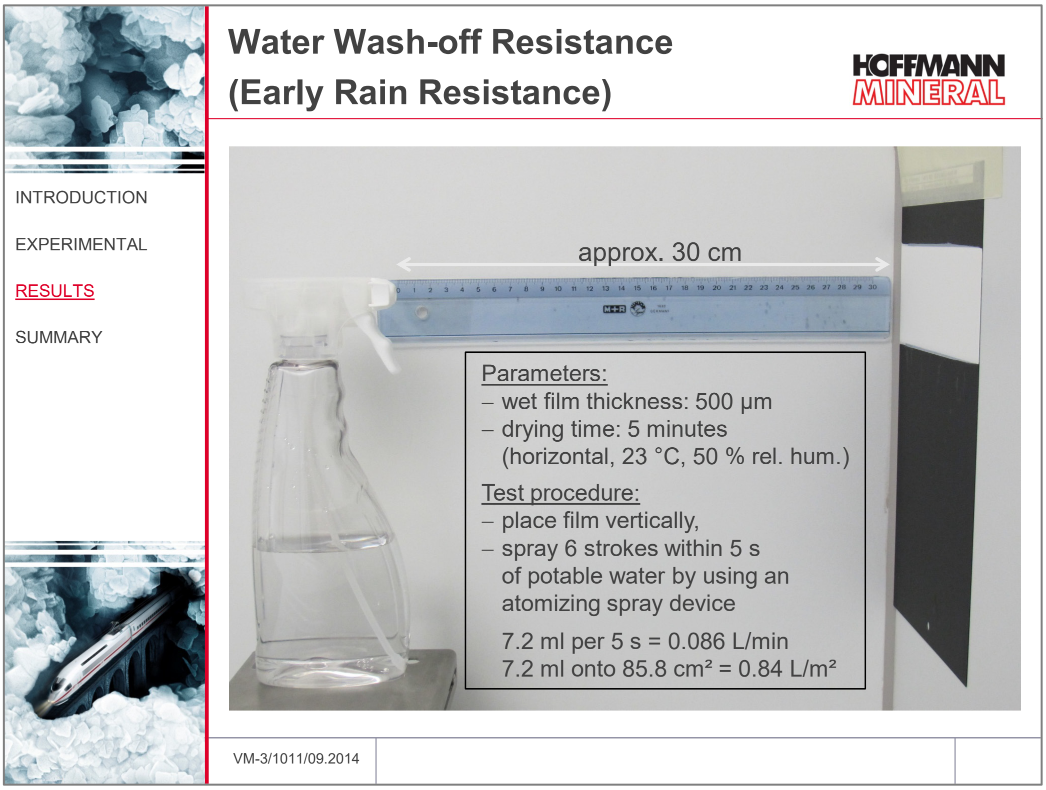
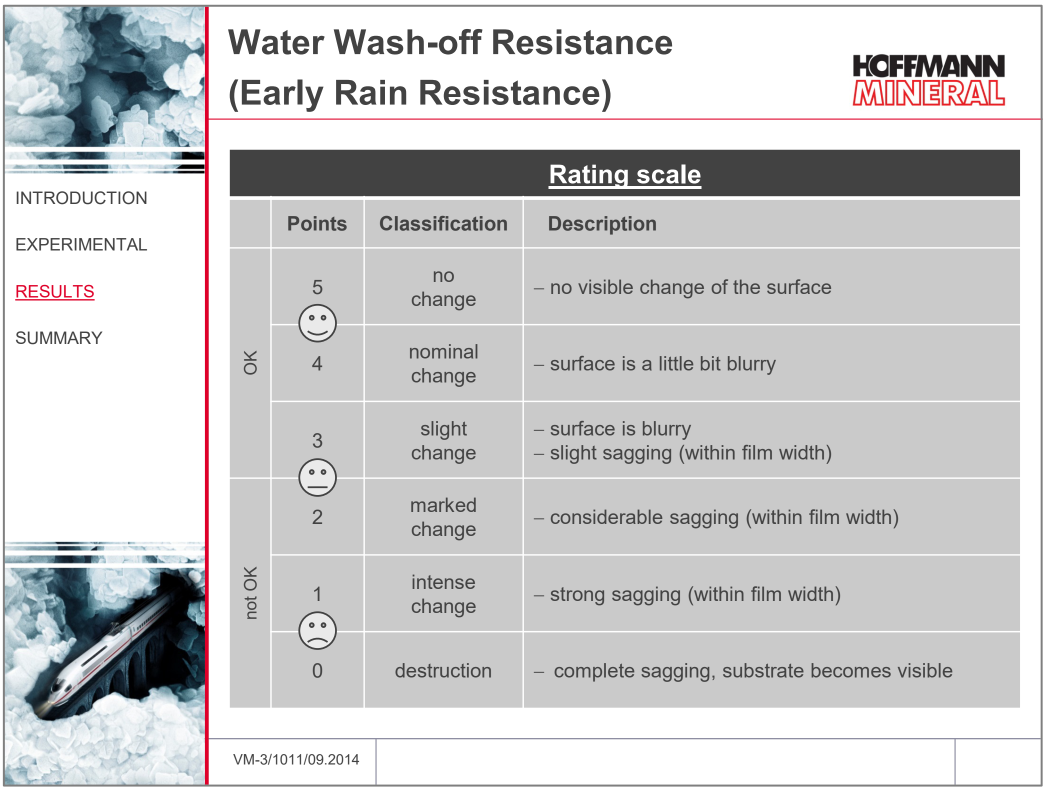


Fig. 12

The assessment of the “Early Rain Resistance” was done on the dry film.
The ranking scale is given in *Fig. 13*; 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.



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

Fig. 13

Note: The Early Rain Resistance was tested only for the formulations with 20 % replacement of titanium dioxide, the results, however, should also be valid for 30 % substitution. The formulation with Sillitin Z 89 visibly runs off less strongly compared with the reference. With Silfit Z 91, the coating does not run off any more at all. Modifications of the film surface are not observed. This way, a road marking paint with Silfit Z 91 will rapidly become resistant against rain, even under unfavorable weather conditions.

The assessment according to the ranking scale is illustrated by way of a bar graph in *Fig. 14*. Photographs of the dried film surface after the exposure to “simulated” rain are shown in *Fig. 15*.

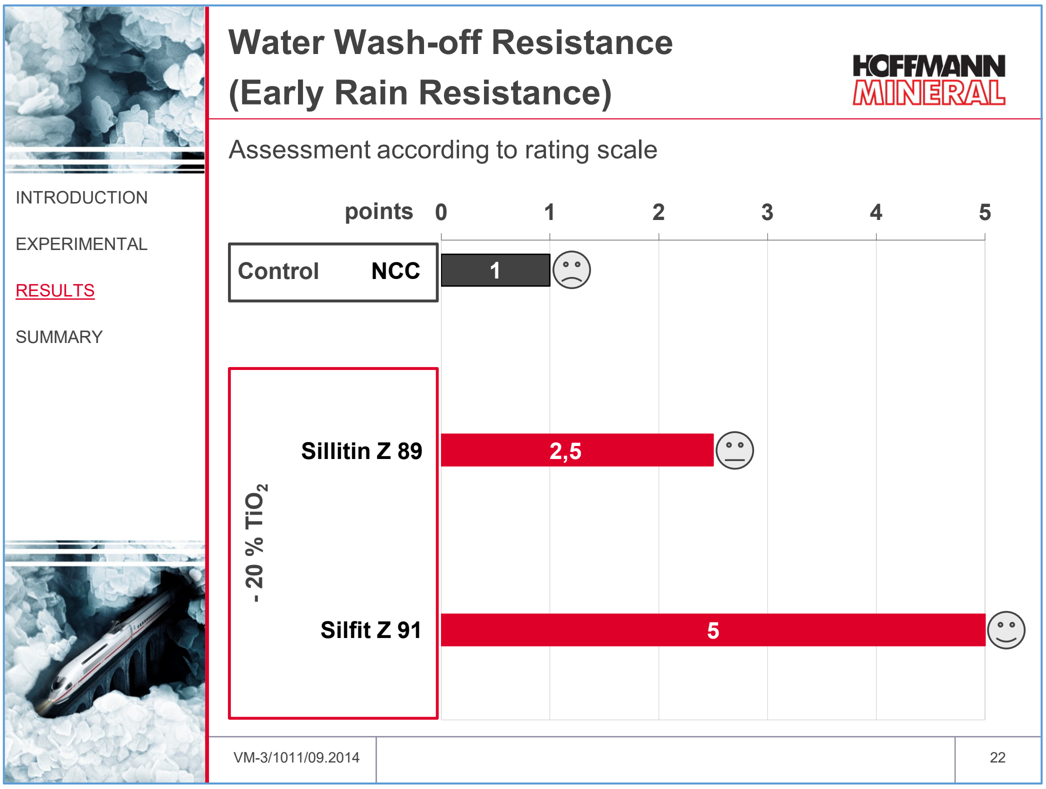


Fig. 14

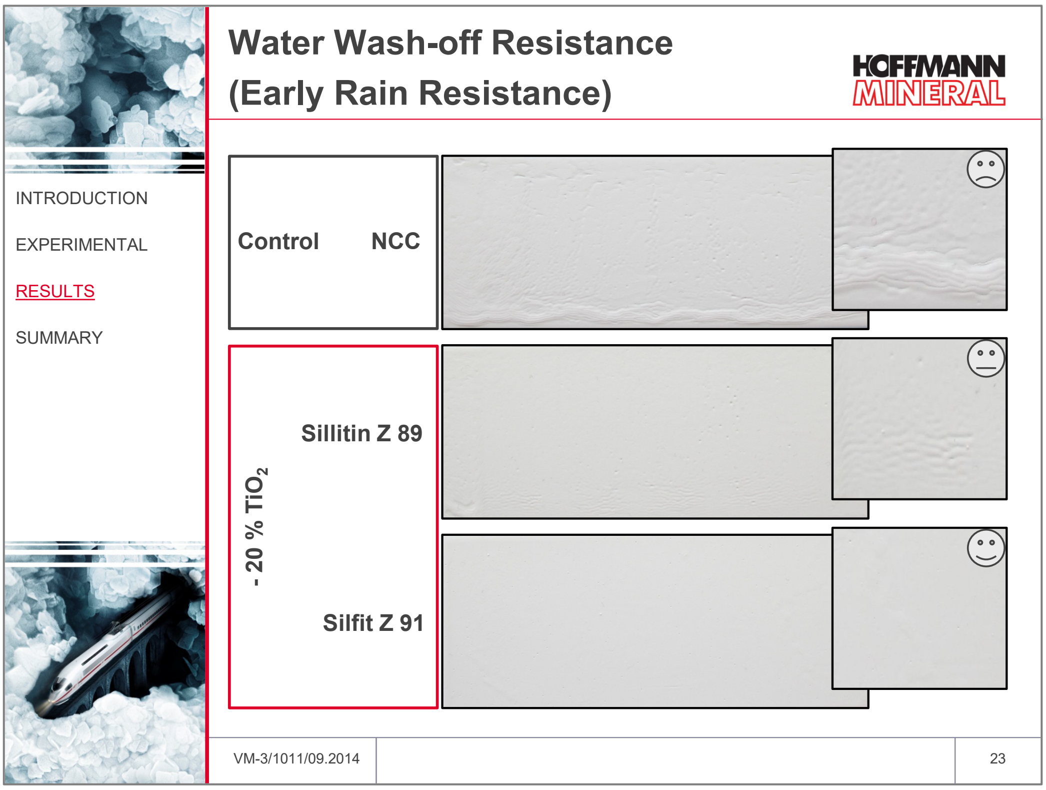


Fig. 15

3.5 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 D 4060 via the weight loss after 1000 revolutions with abrader wheels C 17, which were cleaned and regenerated after each 500 revolutions with S 11 abrasive sandpaper discs. *Fig. 16* shows the average abrasion loss after 1000 revolutions in milligrams, under a load of 1 kg onto the CS 17 wheels. When titanium dioxide and calcium carbonate are replaced by Neuburg Siliceous Earth, the abrasion loss comes out reduced. The use of Sillitin Z 89 or Silfit Z 91 helps to markedly improve the abrasion resistance.

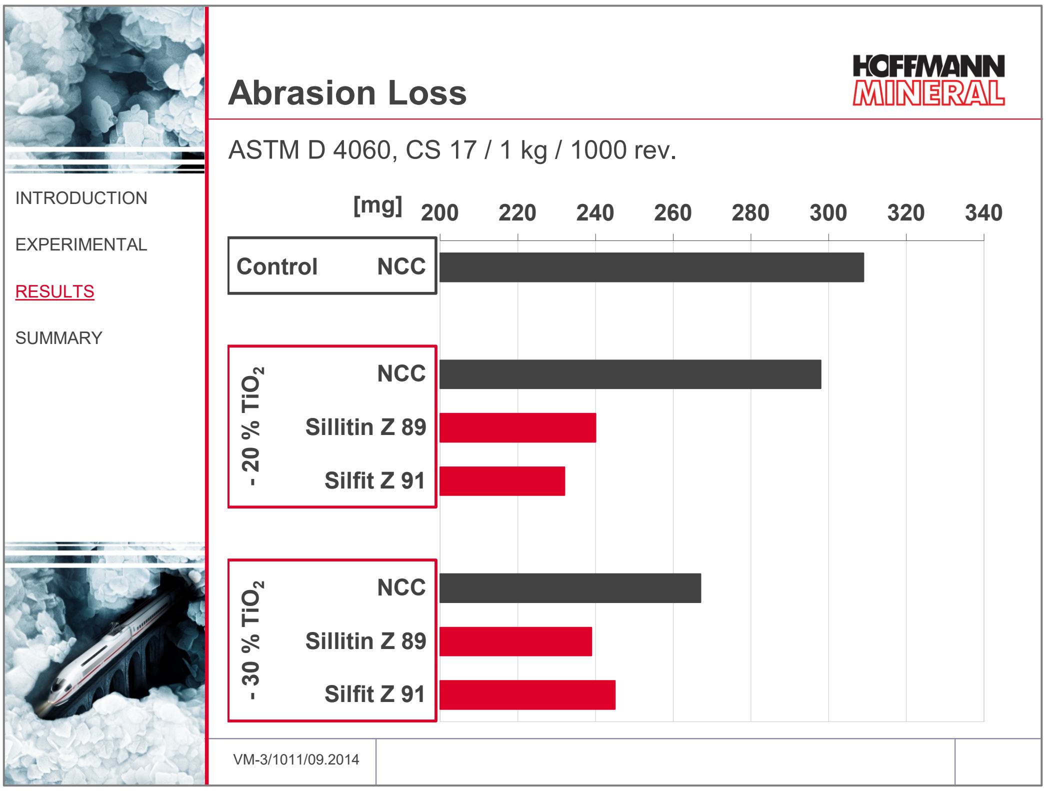


Fig. 16

3.5 Hiding power (contrast ratio)

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 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. 17 shows the necessary dry film thickness to reach 98 % covering. The formulations which just contain calcium carbonate require markedly higher film thicknesses in order to become covering. As more titanium dioxide is replaced with calcium carbonate, the hiding power will come out poorer.

If on the other side Sillitin Z 89 or Silfit Z 91 is used, the dry film thickness for a covering coating can clearly be decreased despite the reduced titanium dioxide addition. The example of 20 % titanium dioxide reduction and replacement with Sillitin Z 89 shows this effect most clearly. Compared with the reference formulation, the required film thickness is lowered by 24 µm or 15 %.

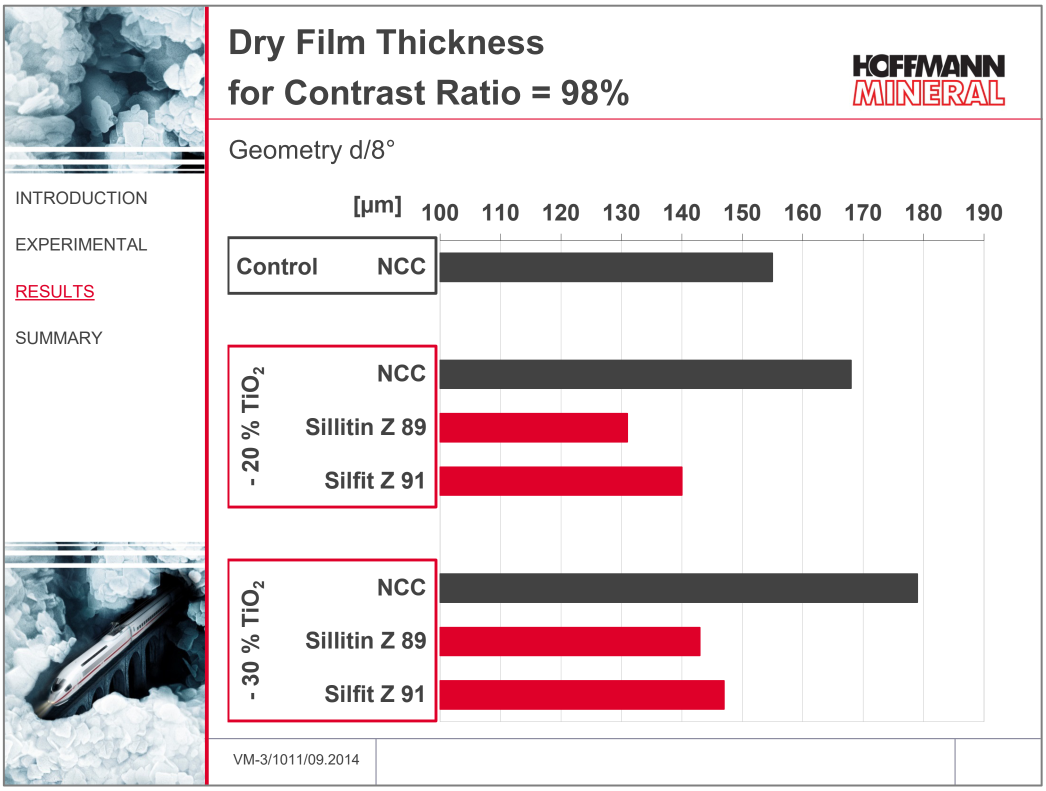


Fig. 17

From the dry film thickness results, the corresponding wet film thicknesses were calculated. The theoretical wet film thickness which at least has to be applied in order to come off with a covering coating is shown in *Fig. 18*. A lower wet film thickness indicates a lower material consumption, and thus also a lower cost of the painting. If 20 % titanium dioxide is replaced with calcium carbonate, more material has to be spread, as the wet film thickness is higher than for the reference formulation. In the case of Sillitin Z 89 or Silfit Z 91, less material is required to arrive a covering coating, which means Neuburg Siliceous Earth allows to lower the costs. Even with 30 % titanium dioxide is replaced, the formulations with Neuburg Siliceous Earth are slightly superior to the reference with full titanium dioxide content, although the volume solids content (see *Fig. 8*) is lower because of the water addition.

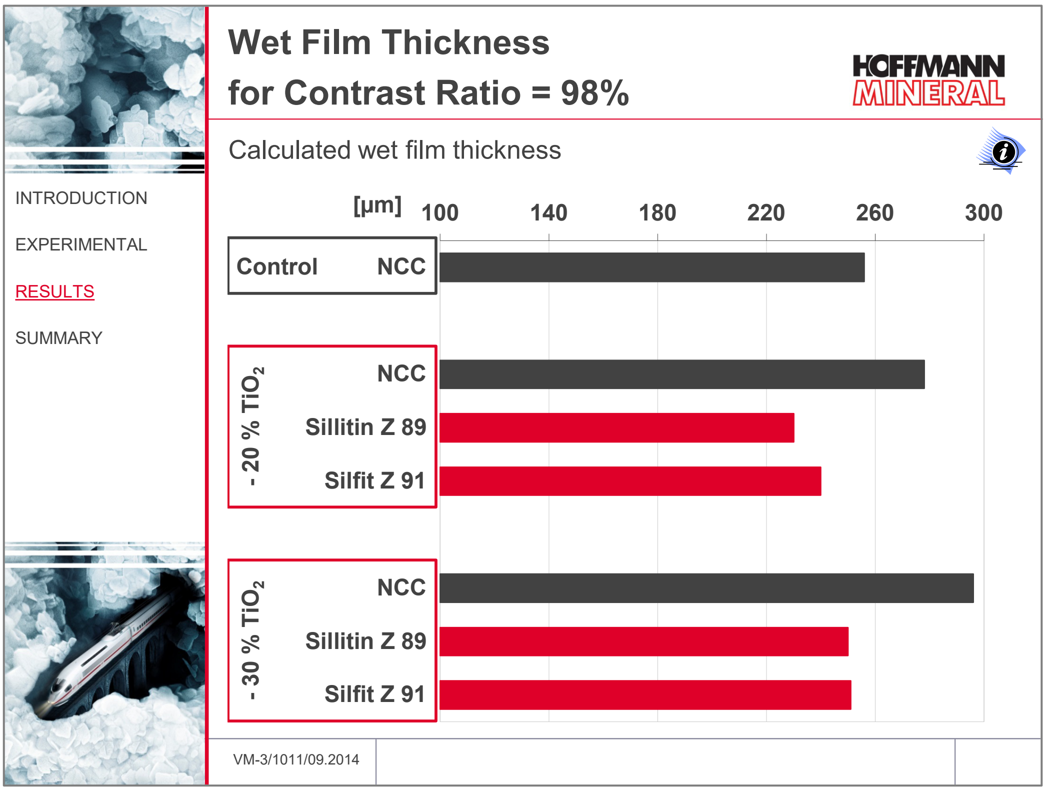


Fig. 18

3.6 Spreading rate and costs

If one calculates the theoretical spreading rate/efficiency in m²/L, a markedly higher result is found for 20 % titanium dioxide replacement with Neuburg Siliceous Earth (*Fig. 19*). Even 30 % titanium dioxide replacement with Sillitin Z 89 or Silfit Z 91 gives almost the same spreading rate as obtained with the reference formulation with full titanium dioxide content. The corresponding formulations with calcium carbonate only offer a markedly lower spreading rate than the reference.

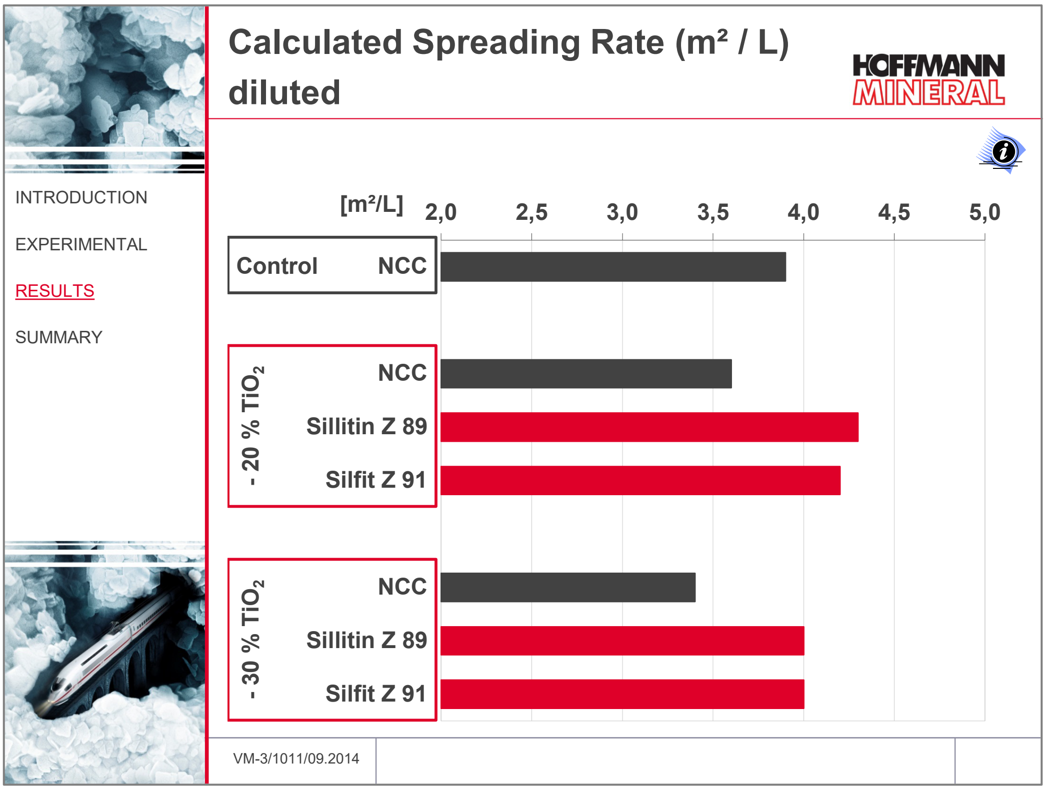


Fig. 19

These statements are also true for the spreading rate related to mass (m²/kg) (*Fig. 20*).

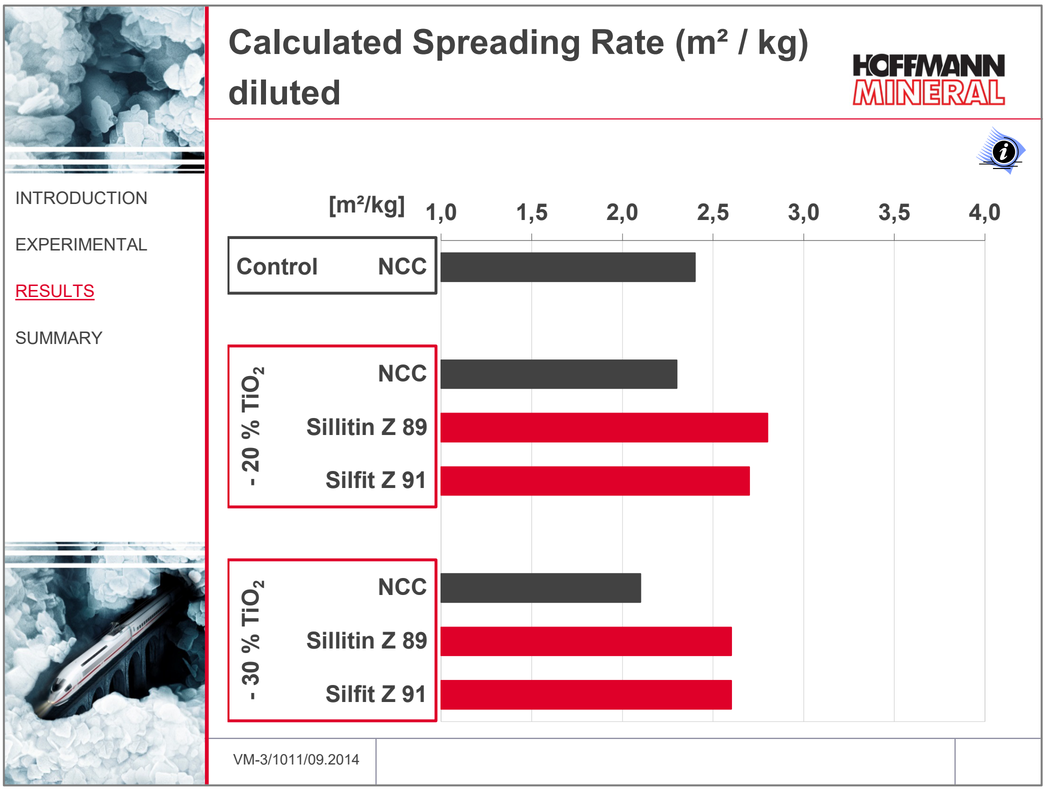


Fig. 20

Fig. 21 illustrates the volume related raw material costs of the formulations diluted to application viscosity. Aside from the unsignificant addition of water, in particular through the replacement of the distinctly higher-priced titanium dioxide (input: € 2.40/kg) with the Neuburg Siliceous Earth grades, the formulations come out at lower cost by 2 to 5 % compared with the reference.

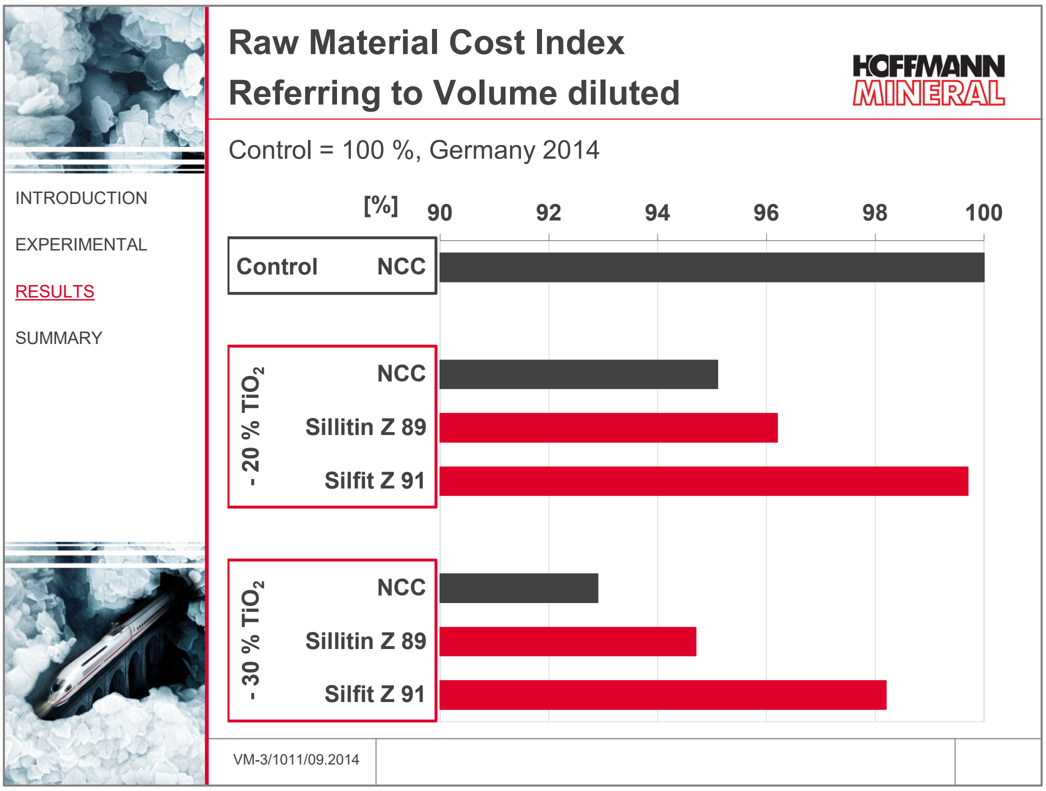


Fig. 21

Looking in *Fig. 22* at the total system costs (spreading rate resp. hiding power and raw material costs) it becomes clearly evident that the formulations containing only calcium carbonate come out higher and thus more costly than the reference. The formulations filled with Neuburg Siliceous Earth present all a more favorable picture than the reference. At 20 % titanium dioxide replacement, with Sillitin Z 89 even a cost reduction for the total system of 14 % can be realized. With the very color-neutral Silfit Z 91 the savings potential can come up to 7 %.

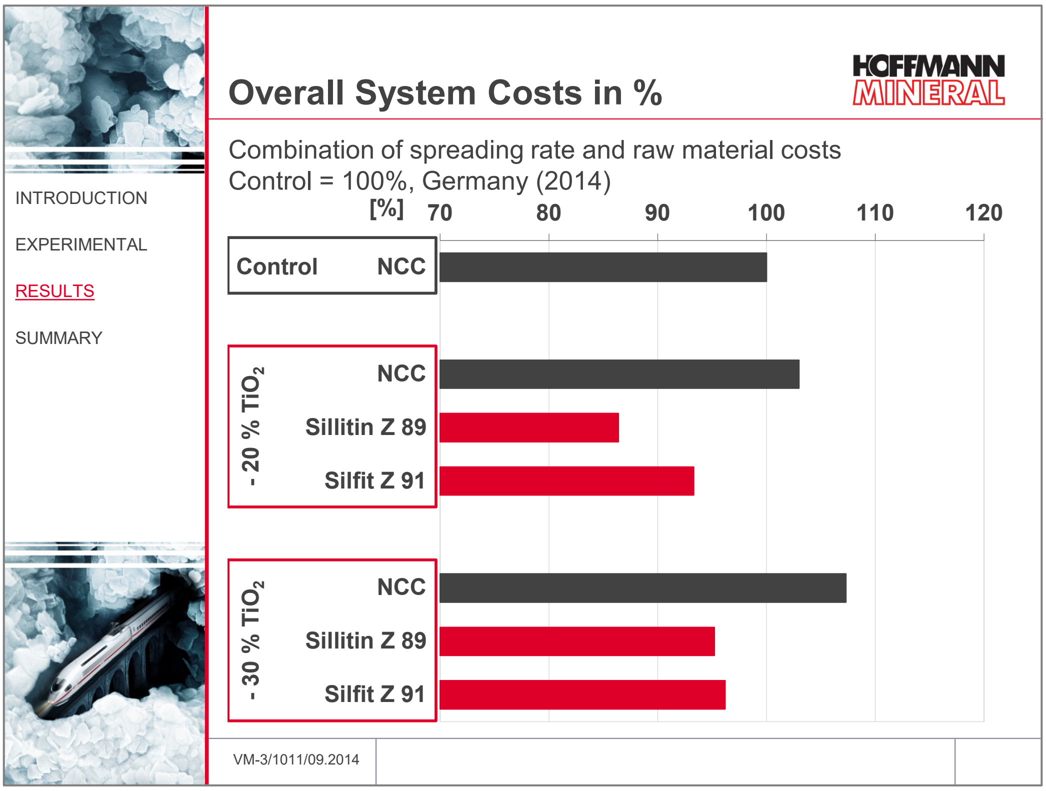


Fig. 22

4. Summary and outlook

The use of Neuburg Siliceous Earth in road marking paints allows:

- to maintain the color space. The formulations with Sillitin Z 89 will come out somewhat darker and slightly yellowish, but this leads only to a small parallel shift in the central region of the standard. The use of Silfit Z 91 maintains the color neutrality in the center, as evident from a higher brightness and a markedly lower yellowish tinge

- the use of Neuburg Siliceous Earth helps to increase the Early Rain Resistance. With Sillitin Z 89, the marking paint is washed out by precipitations to a markedly lower extent compared with calcium carbonate. With Silfit Z 91, no changes of the film surface can be observed after the exposure. A "swimming" of the coating on the road will be avoided, and the property profile of the marking paint remains unchanged

- to markedly increase the abrasion resistance

- to strongly improve the hiding power, thus utilizing a notable reduction of the titanium dioxide content

- to offer a potential for cost savings

Recommendation for thin film white road marking paints:

A marked improvement of the hiding power as well as potential cost savings can be realized by replacing up to 20 % titanium dioxide and 25 % calcium carbonate with **Sillitin Z 89**.

When using **Silfit Z 91**, it is possible to replace up to 30 % titanium dioxide and 25 % calcium carbonate without losing hiding power, and still arrive at a cost advantage. The color neutrality of the white road marking paint remains fully unchanged and the Early Rain Resistance can be improved significantly.

Recommendation for requirement of fixed 600 µm wet film thickness:

In case that no use can be made of the improved hiding power with Neuburg Siliceous Earth in view of required wet film thicknesses of 600 µm, further information is available. The Technical Report „Neuburg Siliceous Earth in Road Marking Paints (water based, white, wet film thickness 600 µm" explains how 40 % titanium dioxide and 12.5 % calcium carbonate can be replaced with **Silfit Z 91**. This way, marked cost savings can be realized without losing hiding power.
Furthermore, the Early Rain Resistance is considerably increased and the abrasion resistance can be enhanced by up to 25 %.

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.