# Calcined Neuburg Siliceous Earth

# as partial titanium dioxide substitute

# in 2C PU top coat white

Authorship: Barbara Mayer
Hubert Oggermüller

VM-0/0620/06.2020

## Contents

# 1 Introduction

Titanium dioxide is probably the most discussed white pigment. This is a matter of availability and supply bottlenecks or the pricing of pigment manufacturers, which is difficult for processors to calculate. The obligation to label the pigment and the resulting difficulty in handling it in production are a further challenge for paint and coatings manufacturers. Nevertheless, its high opacity, which no other white pigment achieves with the same application quantity and which is particularly necessary for light-colored, decorative applications, makes it indispensable for paint producers.

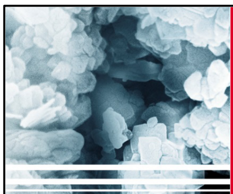
The aim of every producer is therefore to disperse titanium dioxide as well as possible in order to use as little of it as possible. Alternatives are also being sought to keep the titanium dioxide concentration in paints and coatings as low as possible. One possibility is to replace part of the pigment with a suitable spacer filler.

The report presented here follows this objective and is intended to show how Calcined Neuburg Siliceous Earth (CNSE) can be used to replace part of the titanium dioxide while maintaining the properties of the paint.

# 2 Experimental

## 2.1 Base Formulation

The test was carried out in a solvent-based two-component polyurethane varnish. Fig. 1 shows the components A and B of the control formulation. The formulation is based on a recommendation from Covestro, but Disperbyk 118 was selected as the dispersant and Desmophen 680 BA as the polyester polyol. The formulation contains 29.6 % titanium dioxide without any additional filler, just 0.18 % of a hydrophobic, fumed silica to support the rheological additive Bentone. The stoichiometric ratio of polyol to isocyanate is 1.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

**Base Formulation**

HOFFMANN MINERAL

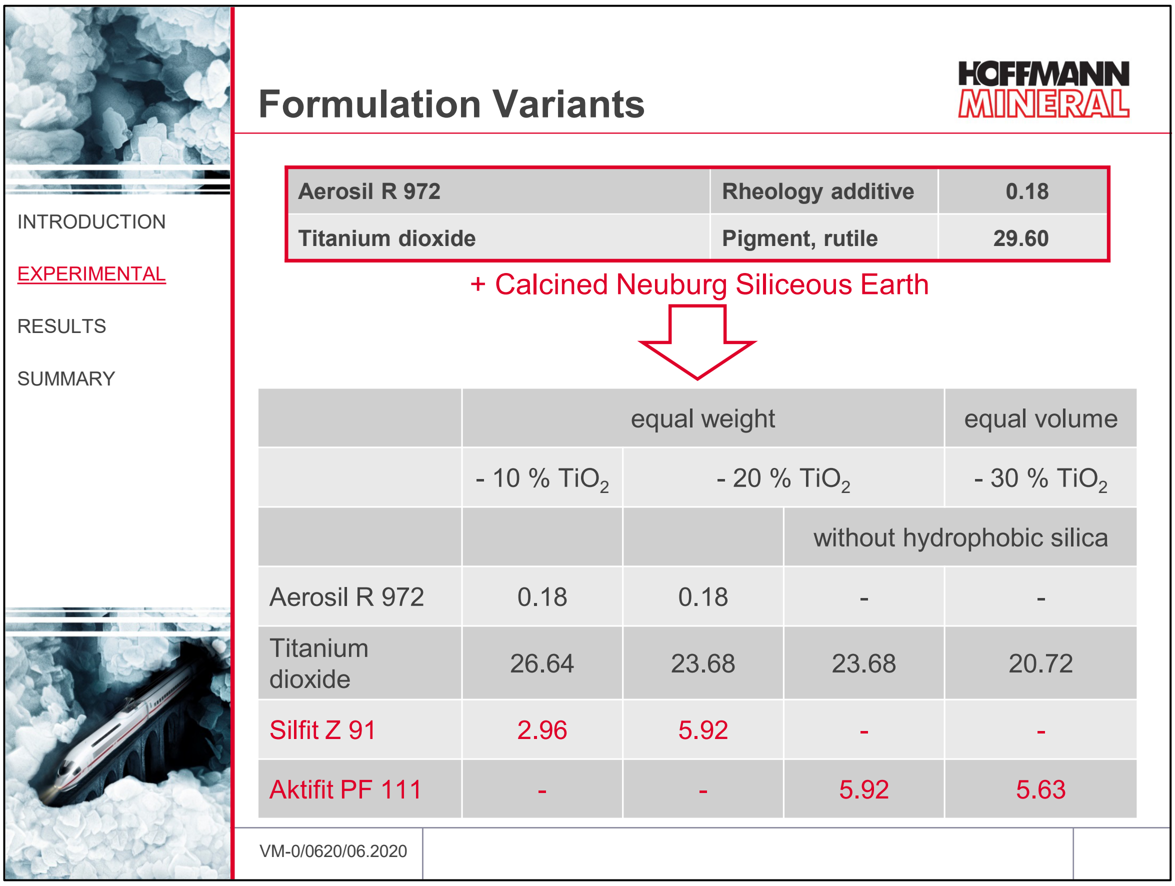
| | | | Control |
|---|---|---|---|
| Component A | Desmophen 680 BA | Polyesterpolyol | 35.38 |
| | Borchi Gol OL 31 | Surface additive | 0.73 |
| | Byk 141 | Defoamer | 0.37 |
| | Tinuvin 292 (50% in Xylene) | Light stabilizer | 0.73 |
| | Dabco 33-LV (10% in Butyl acetate) | Catalyst | 3.71 |
| | Bentone 38 (10% in Solvent Naphta 100 : Anti Terra U = 85:5) | Rheology additive | 2.60 |
| | Disperbyk 118 | Dispersing agent | 0.74 |
| | **Aerosil R 972** | **Rheology additive, hydrophobic, fumed silica** | **0.18** |
| | **Titanium dioxide** | **Pigment, rutile** | **29.60** |
| | Methoxypropylacetate / Butyl acetate 1:1 | Solvent | 14.39 |
| Comp. B | Desmodur ultra N 3390 BA | Polyisocyanate | 9.83 |
| | Methoxypropylacetate | Solvent | 1.74 |
| **Total** | | | **100.00 %** |

VM-0/0620/06.2020

*Fig. 1*

## 2.2 Formulation Variants

The scheme for the introduction of Neuburg Siliceous Earth as a substitute for titanium dioxide and rheological additive of hydrophobic silica is shown in *Fig. 2*. The initial titanium dioxide concentration of the control formulation was reduced relatively by 10 % and 20 % by weight, resulting in a content of 26.64 % and 23.68 % respectively and was compensated by Silfit Z 91. With Aktifit PF 111, also 20 % of the titanium dioxide were replaced by the same weight.
In another approach, 30 % titanium dioxide was replaced by the same volume, thus 20.72 parts of titanium dioxide remain in the formulation. Due to the concept of the same volume and difference in density, the Aktifit PF 111 content is only 5.63 parts. In both variants, the hydrophobic silica has been completely omitted, and the Aktifit PF 111 is to take over this task.

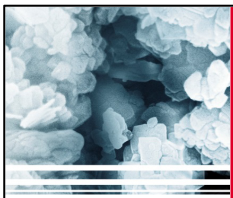



| | | |
|---|---|---|
| **Aerosil R 972** | **Rheology additive** | **0.18** |
| **Titanium dioxide** | **Pigment, rutile** | **29.60** |

| | equal weight | | | equal volume |
|---|---|---|---|---|
| | - 10 % $TiO_2$ | - 20 % $TiO_2$ | | - 30 % $TiO_2$ |
| | | | without hydrophobic silica | |
| Aerosil R 972 | 0.18 | 0.18 | - | - |
| Titanium dioxide | 26.64 | 23.68 | 23.68 | 20.72 |
| Silfit Z 91 | 2.96 | 5.92 | - | - |
| Aktifit PF 111 | - | - | 5.92 | 5.63 |

*Fig. 2*

*Fig. 3* shows the parts by weight for the individual formulations. With Silfit Z 91, a weight-equal replacement takes place, and thus the total is 100 % again.
By saving the silica with Aktifit PF 111, the sum is reduced by this part. Another cause of total weight parts reduction is the equal-volume replacement considering the difference in density between pigment and Aktifit PF 111. In terms of particulate solids (titanium dioxide and filler), 2.5 % dispersing agent Disperbyk 118 was used. In the last formulation, the equal-volume replacement of titanium dioxide results in a smaller particulate solid quantity and therefore in a reduction of the dispersing agent concentration to 0.66 parts by weight.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

## Formulation Variants Parts by weight

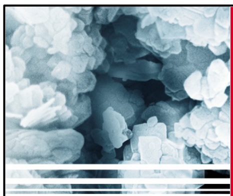
HOFFMANN MINERAL

| | | - 10 % $TiO_2$ equal weight Silfit Z 91 | - 20 % $TiO_2$ equal weight Silfit Z 91 | - 20 % $TiO_2$ equal weight Aktifit PF 111 | - 30 % $TiO_2$ equal volume Aktifit PF 111 |
|---|---|---|---|---|---|
| Component A | Desmophen 680 BA | 35.38 | 35.38 | 35.38 | 35.38 |
| | Borchi Gol OL 31 | 0.73 | 0.73 | 0.73 | 0.73 |
| | Byk 141 | 0.37 | 0.37 | 0.37 | 0.37 |
| | Tinuvin 292 (50% in Xylene) | 0.73 | 0.73 | 0.73 | 0.73 |
| | Dabco 33-LV (10% in Butyl acetate) | 3.71 | 3.71 | 3.71 | 3.71 |
| | Bentone 38 (10% in Solvent Naphta 100 / Anti Terra U = 85:5) | 2.60 | 2.60 | 2.60 | 2.60 |
| | Disperbyk 118 | 0.74 | 0.74 | 0.74 | 0.66 |
| | Aerosil R 972 | 0.18 | 0.18 | | |
| | Titanium dioxide | 26.64 | 23.68 | 23.68 | 20.72 |
| | Silfit Z 91 | 2.96 | 5.92 | | |
| | Aktifit PF 111 | | | 5.92 | 5.63 |
| | Methoxypropylacetate / Butyl acetate 1:1 | 14.39 | 14.39 | 14.39 | 14.39 |
| Comp. B | Desmodur ultra N 3390 BA | 9.83 | 9.83 | 9.83 | 9.83 |
| | Methoxypropylacetate | 1.74 | 1.74 | 1.74 | 1.74 |
| **Total** | | **100** | **100** | **99.82** | **96.49** |

VM-0/0620/06.2020

*Fig. 3*

In *Fig. 4* all formulations are recalculated to 100 % for a better overview.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

## Formulation Variants to 100 %

HOFFMANN MINERAL

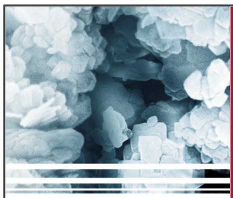
| | | - 10 % $TiO_2$ equal weight Silfit Z 91 | - 20 % $TiO_2$ equal weight Silfit Z 91 | - 20 % $TiO_2$ equal weight Aktifit PF 111 | - 30 % $TiO_2$ equal volume Aktifit PF 111 |
|---|---|---|---|---|---|
| Component A | Desmophen 680 BA | 35.38 | 35.38 | 35.45 | 36.67 |
| | Borchi Gol OL 31 | 0.73 | 0.73 | 0.73 | 0.76 |
| | Byk 141 | 0.37 | 0.37 | 0.37 | 0.38 |
| | Tinuvin 292 (50% in Xylene) | 0.73 | 0.73 | 0.73 | 0.76 |
| | Dabco 33-LV (10% in Butyl acetate) | 3.71 | 3.71 | 3.72 | 3.85 |
| | Bentone 38 (10% in Solvent Naphta 100 / Anti Terra U = 85:5) | 2.60 | 2.60 | 2.60 | 2.69 |
| | Disperbyk 118 | 0.74 | 0.74 | 0.74 | 0.68 |
| | Aerosil R 972 | 0.18 | 0.18 | | |
| | Titanium dioxide | 26.64 | 23.68 | 23.72 | 21.47 |
| | Silfit Z 91 | 2.96 | 5.92 | | |
| | Aktifit PF 111 | | | 5.93 | 5.84 |
| | Methoxypropylacetate / Butyl acetate 1:1 | 14.39 | 14.39 | 14.42 | 14.91 |
| Comp. B | Desmodur ultra N 3390 BA | 9.83 | 9.83 | 9.85 | 10.19 |
| | Methoxypropylacetate | 1.74 | 1.74 | 1.74 | 1.80 |
| **Total** | | **100.00 %** | **100.00 %** | **100.00 %** | **100.00 %** |

VM-0/0620/06.2020

*Fig. 4*

## 2.3 Filler Characteristics

Fig. 5 shows the typical powder characteristics of titanium dioxide and fillers. Titanium dioxide is the rutile crystal form, which is aftertreated with aluminum, silicon and zirconium oxide. The average particle size $d_{50}$ of 0.2 µm is in the typical range for pigments with high hiding power. It is very bright with 98 in the L* value, but is relatively high in the yellow range, indicated by a b* value of 2.6.
Calcined Neuburg Siliceous Earth is produced by a thermal process, which is connected to the classic Neuburg Siliceous Earth. The resulting product Silfit Z 91 shows a high brightness with an L* value of 95. High color neutrality is given with a b* value of only 1. The mean particle diameter $d_{50}$ is 2 µm. The hydrophobic grade Aktifit PF 111 is obtained by surface treatment with an alkyl functional group and provides largely the same color and particle size distribution as its base product Silfit Z 91, and can be used additionally for rheology control. The density of titanium dioxide is relatively high at 4.1 g/cm³, while that of the Neuburg Siliceous Earth products is significantly lower at 2.6 g/cm³, which means a reduction in the weight of the solids package in the case of an equal-volume pigment substitute.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

### Filler Characteristics

HOFFMANN MINERAL

| | Titanium dioxide | Silfit Z 91 | Aktifit PF 111 |
|---|---|---|---|
| Color L* | 98.1 | 95 | 94 |
| Color a* | -0.3 | -0.1 | -0.2 |
| Color b* | 2.6 | 1 | 1 |
| Particle size $d_{50}$ [µm] | 0.2 | 2 | 2 |
| Particle size $d_{97}$ [µm] | 0.8 | 10 | 10 |
| Density [g/cm³] | 4.1 | 2.6 | 2.6 |
| Surface treatment | $Al_2O_3$, $SiO_2$, $ZrO_2$ treatment | --- | alkyl functionalized, hydrophobic |

VM-0/0620/06.2020

*Fig. 5*

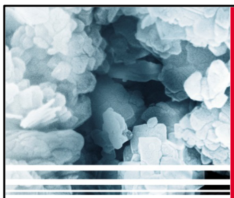
## 2.4 Preparative Methods

The conditions for the production and application of the paints and conditioning of the plates before the tests are shown in *Fig. 6*.

The varnishes were prepared on a dissolver with an adapted bead mill under grinding with glass beads at 4.7 m/s for 10 minutes. The volume of glass beads of the type "Diamond-Pearls polished" with 2 mm diameter corresponded to the preparation volume. The grinding process contained all raw materials of component A except the solvent. The lacquers were stored in uncoated cans at room temperature. Component B was freshly prepared by mixing before application.

After 14 days of storage, the application was carried out with a doctor blade at a gap height of 360 µm on cold rolled steel of the type Q-Panel R 48. For this purpose, the components were homogeneously mixed in the appropriate ratio. The resulting dry film thickness was approx. 120 µm or as indicated.

The optical properties were determined after 2 days conditioning at 23°C and 50% relative humidity.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

### Preparative Methods

HOFFMANN MINERAL

| | |
|---|---|
| Mixing | Grinding with glass beads at the dissolver with adapted bead mill: 10 min at 4,7 m/s |
| Application | After 14 days of maturing<br>Substrate: cold rolled steel, Q-Panel Typ R 48<br>Doctor blade: gap 360 µm<br>Dry film thickness: ~ 120 µm, or as indicated |
| Conditioning | Drying conditions<br>2 days at 23 °C / 50 % relative humidity |

VM-0/0620/06.2020

*Fig. 6*

# 3 Results

## 3.1 Viscosity

The viscosity was measured with a rheometer MCR 300 from Anton Paar and cylinder system CC27 after 28 days of storage. As shown in *Fig. 7*, low and high shear rates of 0.1 $s^{-1}$ and 100 $^{s-1}$ were evaluated. The replacement of titanium dioxide by Silfit Z 91 has no influence on the viscosity. If Aktifit PF 111 is used as a titanium dioxide replacement and the rheology supporting silica is omitted, the structure build-up is taken over by the filler, as can be seen from the values of the viscosity at low shear rate.

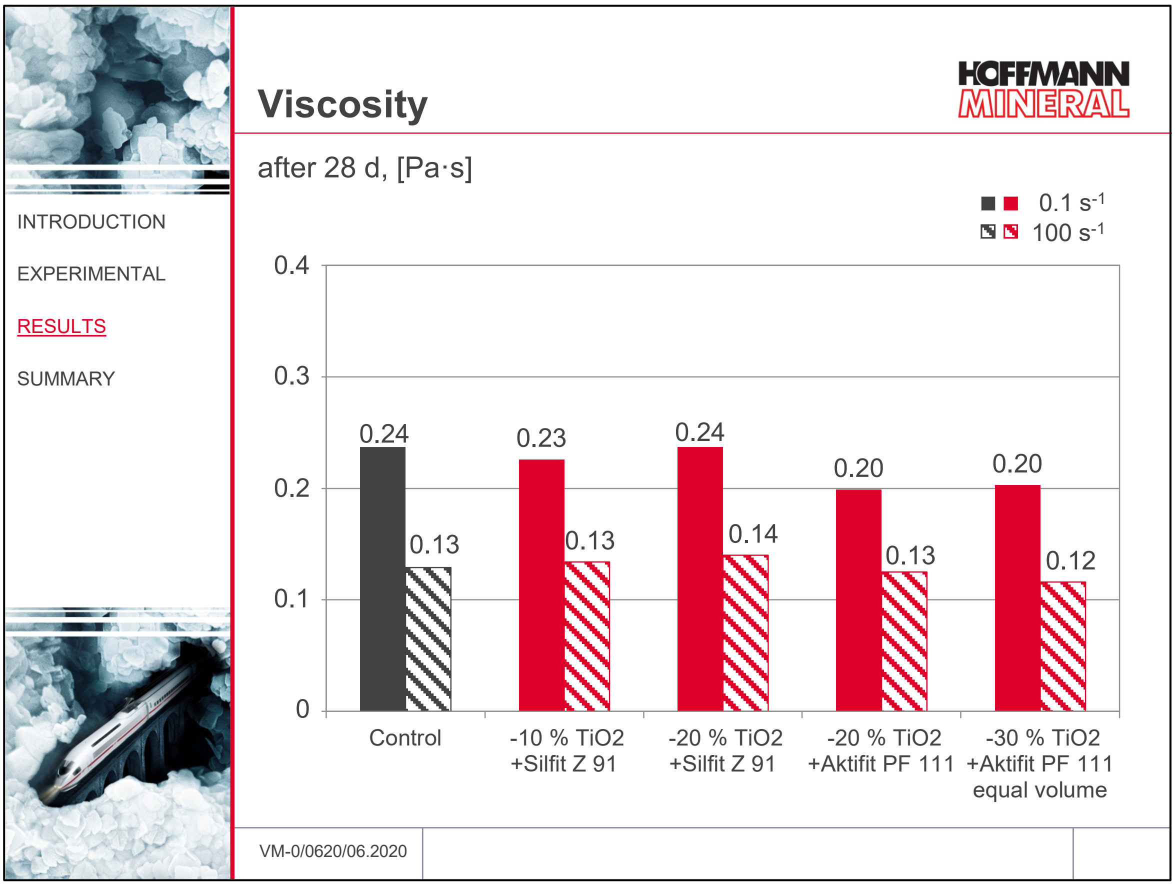



*Fig. 7*

## 3.2 Color

The colour, see *Fig.8*, was measured with geometry d/8° and standard illuminant D65. By replacing titanium dioxide, the brightness L* decreases slightly, but not below 97. The a* - value, representing the red / green portion, remains unchanged. The b* value, representing the yellow / blue component, is slightly reduced with Silfit Z 91 and Aktifit PF 111. The lower the b* value, i.e. the blue portion increases in color, the whiter a surface is perceived. At visual evaluation the slightly lower brightness L* with Silfit Z 91 and Aktifit PF 111 can be compensated by the lower b* value resulting in a more blueish white.

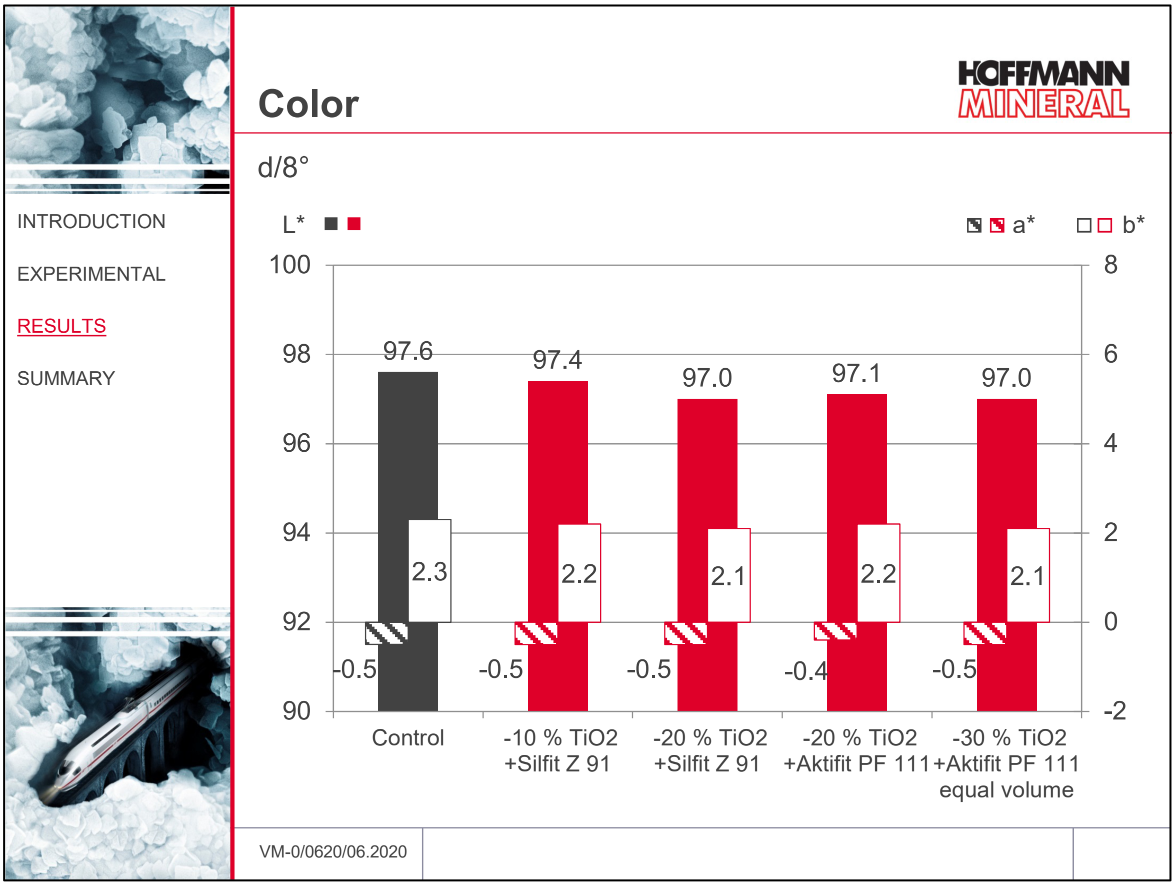



*Fig. 8*

## 3.3 Contrast Ratio

The contrast ratio is determined by measuring the coating´s standard color value Y with a spectrophotometer on the black and white areas of a contrast carton. For this purpose, the quotient of Y black to Y white, multiplied by 100, is calculated. This value indicates the contrast ratio in percent. If the contrast ratio is greater than 98%, a coating is considered opaque. All formulations shown in *Fig. 9* achieve a contrast ratio greater than 98 % at a dry film thickness of 70 µm, indicating similar hiding power. Only the variant with 30 % titanium dioxide replacement is slightly lower by about half a percentage point, all other formulations achieve very similar values in the accuracy range of the method.

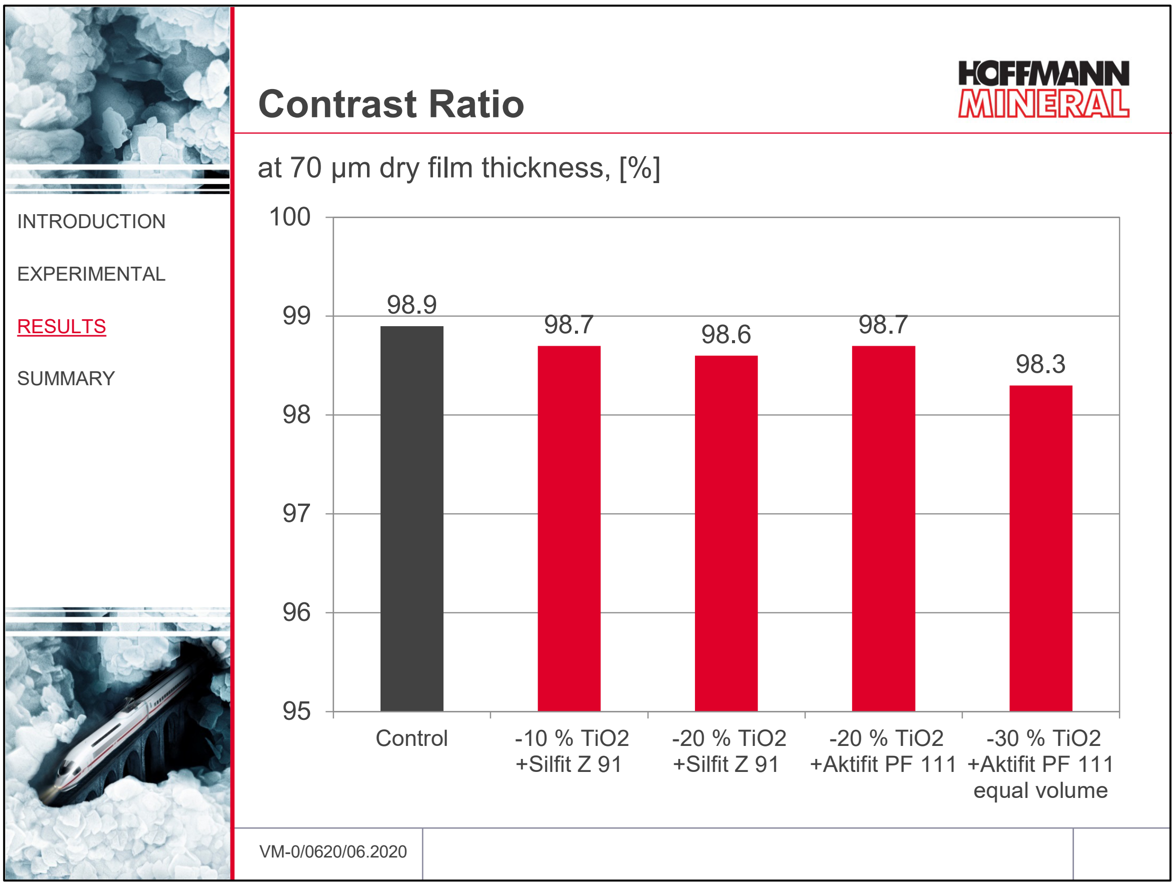



*Fig. 9*

## 3.4 Gloss

The gloss shown in *Fig. 10* was determined with a micro-TRI-gloss instrument from BYK. High gloss coatings are usually evaluated at 20° measuring angle. All formulations are high in gloss with more than 90 gloss units. The 93 gloss units at 20 % titanium dioxide replacement by Silfit Z 91 compared to the control with 95 GU can be measured, but cannot be distinguished by the human eye. All formulations containing Aktifit PF 111 show exactly the same high gloss value as the control formulation with full titanium dioxide content. The absence of the silica should also have a positive effect on the gloss.

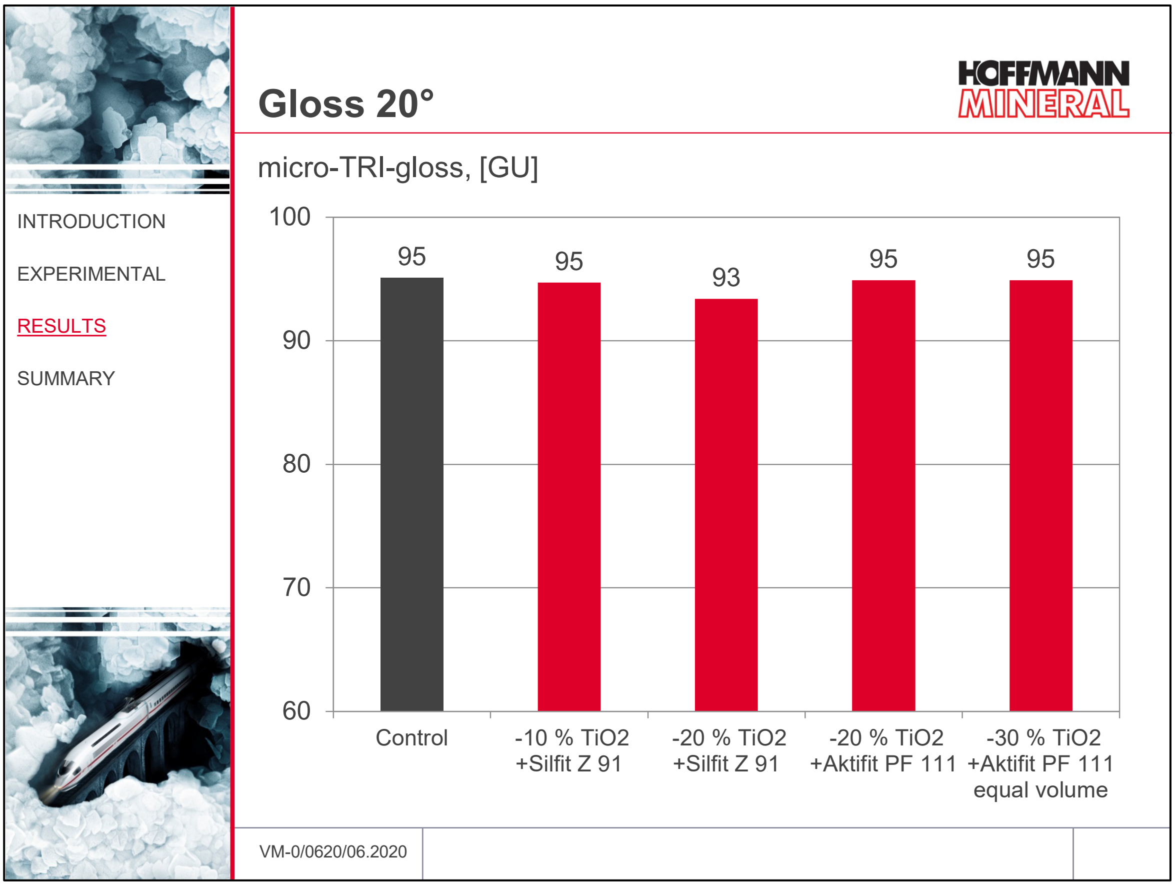



*Fig. 10*

## 3.5 Haze

Diffuse scattered light next to the directed reflection of the 20° gloss is called haze. Haze can cloud the clear reflection of a surface. Therefore, to assess the surface quality of the topcoat, the haze was measured with a micro-haze device from BYK. The results are shown in *Fig. 11*. The values obtained can be considered very good for all formulations. A difference is, as with gloss 20°, only measurable, but cannot be distinguished by eye. Here too, a clearer surface is achieved by omitting the silica and using Aktifit PF 111. Thus the tendency of the rheology agent silica to influence gloss and haze negatively can be largely confirmed.

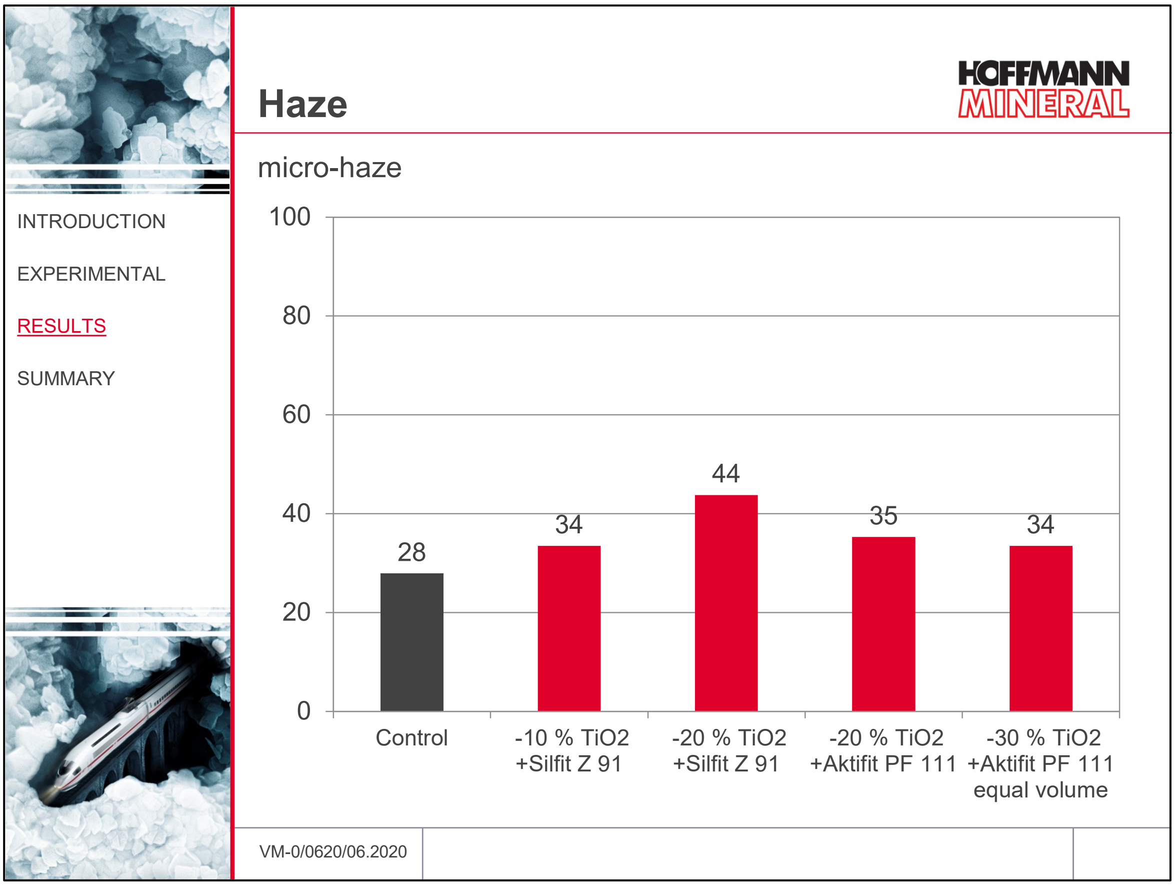


*Fig. 11*

### 3.6 Cost Reduction Potential

Formulation costs can be reduced by reducing titanium dioxide. The values shown in *Fig. 12* were calculated on the basis of raw material costs in Germany for 2020. The control formulation was set as the reference value. If titanium dioxide is reduced, a saving of up to 1.8 %, based on volume, can be achieved with a 10 % replacement by Silfit Z 91. With 20 % replacement, the saving increases to 3.5 %. In the formulations with Aktifit PF 111 and without the fumed silica, 3.1 % savings are achieved with a 20 % replacement, with a 30 % equivalent volume replacement even 4.1 % savings compared to the control formulation.

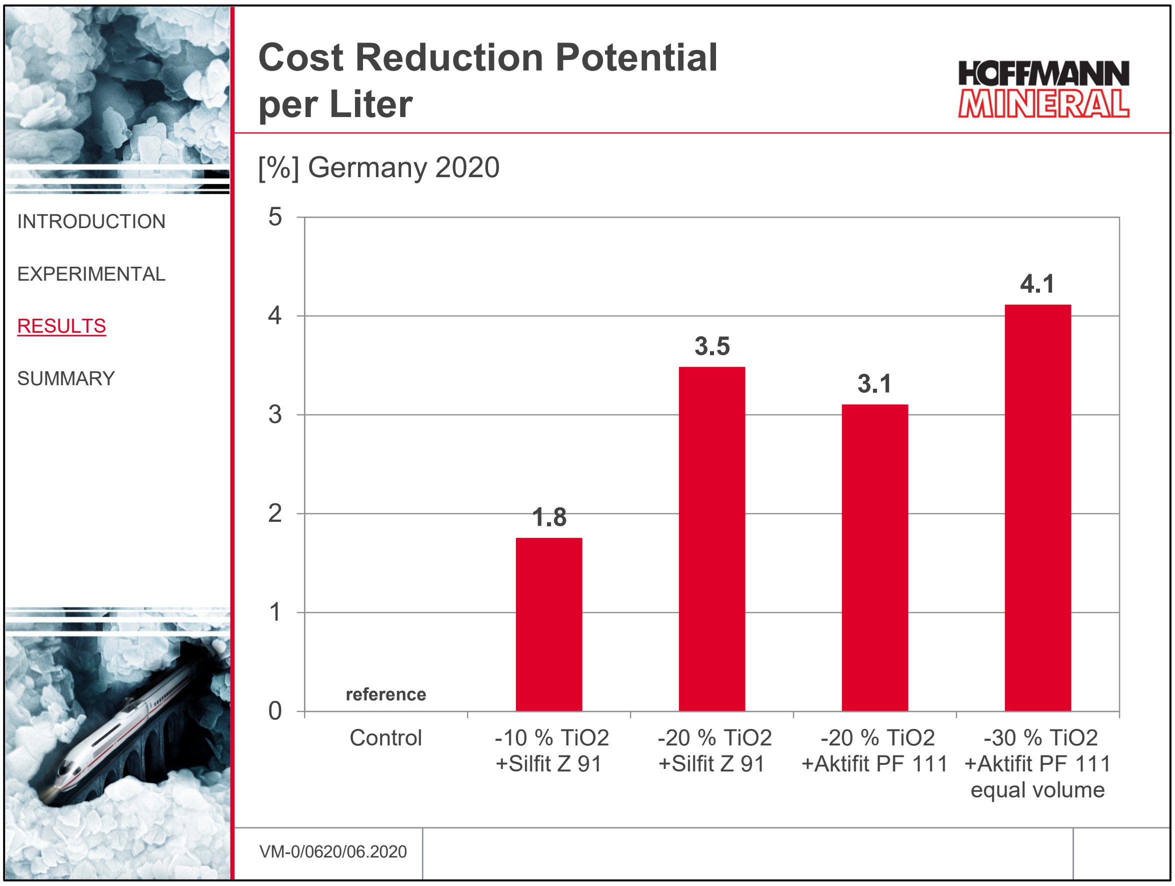



*Fig. 12*

# 4 Summary

As shown in this study using the example of a 2K PU topcoat, by Calcined Neuburg Siliceous Earth a part of the titanium dioxide can be successfully replaced. The optically brilliant appearance of decorative applications is completely preserved. Further properties can be positively influenced by a targeted filler selection.

The advantages of Calcined Neuburg Siliceous Earth in detail:

Silfit Z 91 & Aktifit PF 111

- Very high brightness and colour neutrality
- High contrast capacity
- Very high gloss
- Very low haze
- Savings potential Formulation costs

When using Aktifit PF 111, the use of hydrophobic, fumed silica for rheology control can be dispensed with, thus avoiding its negative effect on gloss and haze and simplifying handling.