Silfit Z 91

vs. precipitated $CaCO_3$ and TiO_2 in

high-quality, solvent-free VAE paint

Author: Bodo Essen
Hubert Oggermüller

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HOFFMANN MINERAL GmbH • Muenchener Strasse 75 • D-86633 Neuburg (Donau) • Phone +49 (0) 8431 53-0
www.hoffmann-mineral.com • e-mail: info@hoffmann-mineral.com

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1 Introduction

An outstanding optical property profile, excellent mechanical properties and freedom from emissions and solvents are essential characteristics of modern high quality interior emulsion paints. As decorative coating systems they contain a high portion of titanium dioxide, which as energy and cost intensive raw material is more and more subjected to variations in price and demand, and therefore decidedly affects the cost structure of the formulations.

As a result, lately a partial replacement of the white pigment with suitable mineral TiO_2 extenders is desired. Representatives of this class often are very fine, bright-colored calcium carbonates, silicates or also calcined clays.

The objective of the present study is an evaluation of calcined Neuburg Siliceous Earth Silfit Z 91 as a TiO_2 extender in comparison with precipitated calcium carbonate in such an interior emulsion paint.

The focus in particular lays on optical criteria such as brightness and color neutrality as well as hiding power and formulation costs as a measure for the efficiency and economic aspects. Further relevant characteristics such as processing properties and wet-scrub resistance will be judged via accompanying tests.

2 Experimental

2.1 Base formulation

The starting point according to *Fig. 1* is a European market approved formulation for a solvent-free matted interior emulsion paint based on a vinyl acetate / ethylene dispersion from Celanese Emulsions. Along with a classical filler combination of primarily carbonate portions and a natural quartz / mica / chlorite intergrowth, the pigmentation comprises 185 pbw of a surface treated rutil type TiO_2. In the function of a TiO_2 extender, a precipitated calcium carbonate is included.

Base Formulation

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		Parts by weight
Water deionized	-	291
Tylose MH 30000 YG8	Thickener	4
Calgon N, 10 % in water	Wetting / Dispersing	5
Lopon 895	Dispersing additive	3
Agitan 315	Defoamer	2
Parmetol MBX	Can preservation	1
Sachtleben RDDI	TiO_2 Pigment	**185**
Prec. Calcium Carbonate (PCC)	TiO_2 Extender	**70**
Omyacarb 2 GU	Filler	125
Omyacarb 5 GU	Filler	90
Omyacarb 10 GU	Filler	30
Plastorit 00	Filler	40
Agitan 315	Defoamer	2
Sodium hydroxide, 10 % in water	Neutralising agent	2
Mowilith LDM 1871 (VAE)	Emulsion binder	150
Total		**1000**

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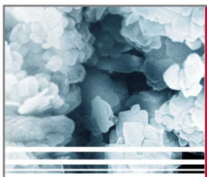
Fig. 1

2.2 Formulation variations

Starting from the control formulation with high titanium dioxide content, as seen in *Fig. 2*, at first only the part of the precipitated calcium carbonate is replaced by calcined Neuburg Siliceous Earth Silfit Z 91 at equal mass (1:1). For comparison, two analogous variants with equally high extender loading but reduced TiO_2 content are included (without TiO_2 compensation). In order to counteract the expected loss in hiding power, the TiO_2 reduction in the further test batches is done with compensating the white pigment portion with Silfit Z 91 in a 1:2 or 1:3 ratio. These formulation variants with a combined use of the two TiO_2 extenders, at their reduced white pigment content should offer a higher potential for raw material savings.



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Formulation Variations

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Variation of the Pigment / TiO_2-Extender package
All other formulation ingredients remain unchanged

	Full TiO_2		- 10 %				- 20 %
	185		166				148
			Without compensation for reduced TiO_2 content		With compensation for reduced TiO_2 content		
Control	PCC	Silfit	PCC	Silfit	Silfit 1 : 2	Silfit 1 : 3	Silfit 1 : 2
Precipitated Calcium Carbonate	70	---	70	---	70	70	70
Silfit Z 91	---	70	---	70	38	57	74
Solids content w/w [%]	63.0	63.0	62.3	62.3	63.6	64.3	64.3
PVC [%]	70.7	70.8	70.1	70.3	71.7	72.5	72.7

TiO_2-Extender

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Fig. 2

As shown by the data illustrated, the relevant characteristics of the formulation remain approximately unchanged.

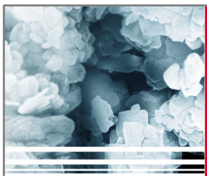
2.3 Characteristics of TiO_2 Extenders

Neuburg Siliceous Earth, as exploited near Neuburg-on-the-Danube, is a naturally formed mixture of corpuscular Neuburg silica and lamellar kaolinite: a loose conglomerate which cannot be separated by physical means. The silica portion, because of its natural formation, is characterized by a rounded grain shape, and consists of aggregated, crypto-crystalline primary particles about 200 nm.

The calcination of the Neuburg Siliceous Earth into Silfit Z 91 eliminates the crystal water of the kaolinite portion under formation of new, largely amorphous mineral phases. The silica portion at the applied temperature remains unchanged. Via an integrated air classifier process grain sizes > 15 µm are eliminated.

As shown in *Fig. 3*, the precipitated calcium carbonate used as a TiO_2 extender along with fine grain size shows a relatively low oil absorption. Silfit Z 91 is characterized by a moderately higher oil absorption, while density and specific surface area of the two TiO_2 extenders are comparable.

Both TiO_2 extenders in powder form along with very good color neutrality show high brightness numbers, still the exceptionally high L* value of the precipitated carbonate is not quite attained by Silfit Z 91.



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TiO2-Extender

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	Particle size		Oil absorption	Density	Specific Surface BET	Color		
	d_{50} [µm]	d_{97} [µm]	[g/100g]	[g/cm³]	[m²/g]	L*	a *	b*
Precipitated Calcium Carbonate	0.3	10	26	2.7	8	97.9	0.0	0.6
Silfit Z 91	2.0	10	55	2.6	8	95.5	- 0.1	0.7

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Fig. 3

2.4 Preparation of batches, application and testing

The preparation of the compounds followed the sequence of the raw materials indicated in the pertinent formulation, and was carried out in a laboratory dissolver under cooling with water.

Pigment, TiO_2 extender and fillers were pre-mixed and, after adding to the mixer, dispersed for 20 min with a peripheral speed of the toothed disc of 15 m/s. After adding the binder and the other additives, a maturing time of 12 h was observed.

The coatings were applied un-diluted and usually per doctor blade with an automated applicator. The drying and conditioning of the color films as well as the tests after 7 days of storage (28 days for wet-scrub resistance) were done in an air-conditioned laboratory at 23 °C and 50 % relative humidity. Detailed indications are given in *Figs. 4* and *5*.

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Preparation

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Mixing and dispersing	Mixing with dissolver, in sequence of mentioning in the formulation Peripheral speed of toothed disc (Cowles blade) 15 m/s for 20 min, water cooling with T max. = 60°C
Let Down	With Binder and further additives
Maturation	Over night
Application	Undiluted with doctor blade on automated film applicator or as indicated
Substrate	As indicated, depending on testing
Conditioning	Drying conditions before / during tests: 23 °C / 50 % relative humidity (RH) Drying time before testing: 28 days for wet-scrub resistance, otherwise 7 d

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Fig. 4

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Testing

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Paint Preparation	
Incorporation, Foam formation	Subjective assessment
Wet Paint	
Fineness of grind	Grindometer 0 – 50 µm
Viscosity	1d after preparation, Rheometer 23°C, Searle system
Storage stability	Undiluted in 1l-metal can, 6 months 23°C
Application with doctor blade gap 300 µm on Leneta film, DFT* ~ 170 µm	
Wet-scrub resistance	200 Cycles on automated wet-scrub resistance tester according to ISO 11998. Classification along with DIN EN 13300
Application: gap 100 - 400 µm gradually with doctor blade on cardboard	
Color / Gloss	L*, a*, b* over white, 85°-Gloss (Sheen) at full hiding film with DFT 120 µm
Hiding Power	Contrast ratio over black/white depending on dry film thickness. Calculation of minimum dry film thickness to comply with DIN EN 13300 classifications and resulting spreading rates, contrast ratio at given spreading rate respectively

* Dry film thickness

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Fig. 5

3 Results

3.1 Processing properties and storage stability

As a result of the generally very good dispersion characteristics of Neuburg Siliceous Earth especially in aqueous media, Silfit Z 91 comes out with similarly rapid and good incorporation during the batch preparation as the comparative variants with precipitated calcium carbonate. The grain size of the completed interior emulsion paints via grindometer tests is situated uniformly at 35 µm, a figure which mainly goes back to the use of the relatively coarse Plastorit 00.

The resulting rheology profile gives evidence of the strong shear thinning of interior emulsion paints. The markedly lower viscosity of 0.36 to 0.45 Pas under high shear loading (1000 s^{-1}) reflects the easy processing and spreadability. High viscosity numbers of 102 to 136 Pas under low shear (0.1 s^{-1}) indicate low run-off tendency after application and make the film layer thicknesses possible which are required for good hiding power.

All formulations after 6 months show excellent storage stability without phase separation or signs of sedimentation.

3.2 Wet-scrub resistance

The use of Silfit Z 91 maintains the excellent wet-scrub resistance of the coatings with the best classification (wet abrasion loss < 5 µm dry film thickness after 200 scrub cycles). Even at high loadings and in combination with precipitated calcium carbonate, the stringent requirements of Class 1 are met (*Fig. 6*).

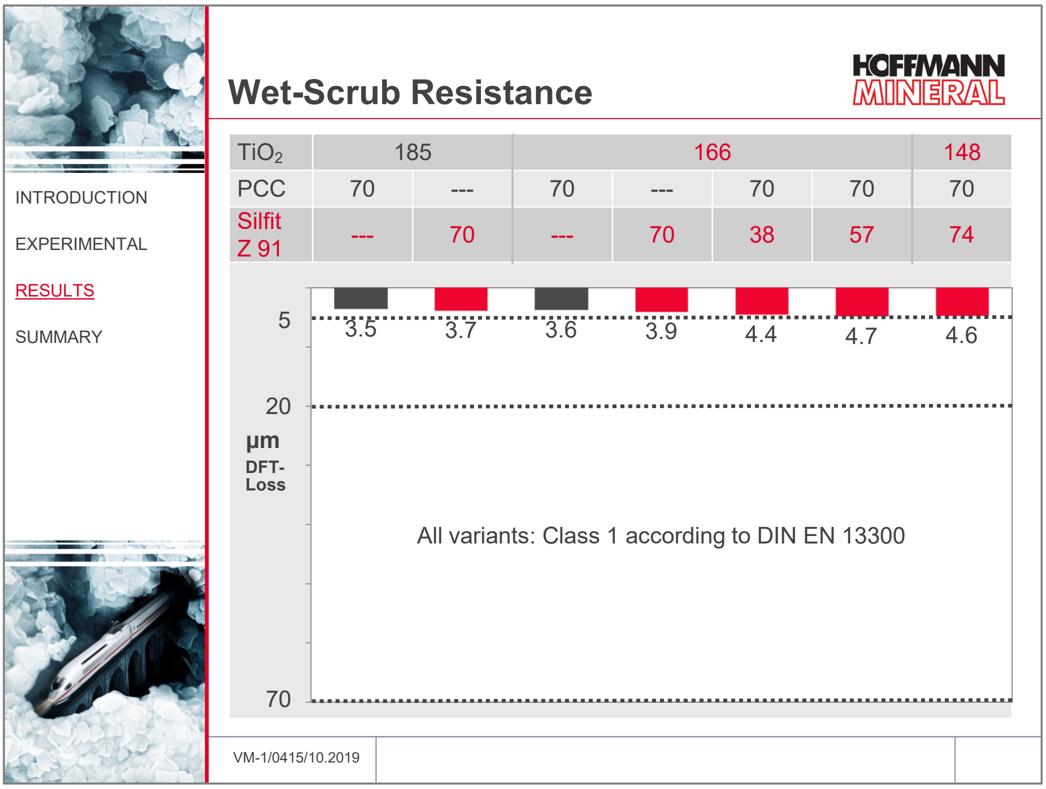


Fig. 6

3.3 Gloss

All versions with a degree of gloss at 85° of < 10 units according to DIN EN 13000 show a “mat” appearance.

3.4 Color

Despite the brightness differences of the extenders in powder form, Silfit Z 91 offers approximately a brightness in the coating comparable with the precipitated calcium carbonate (*Fig. 7*).

A further reduction of the TiO_2 addition practically does not affect the color values of the interior emulsion paints; the color neutrality of the control formulation with a regular TiO_2 loading remains unchanged with the use of Silfit Z 91.

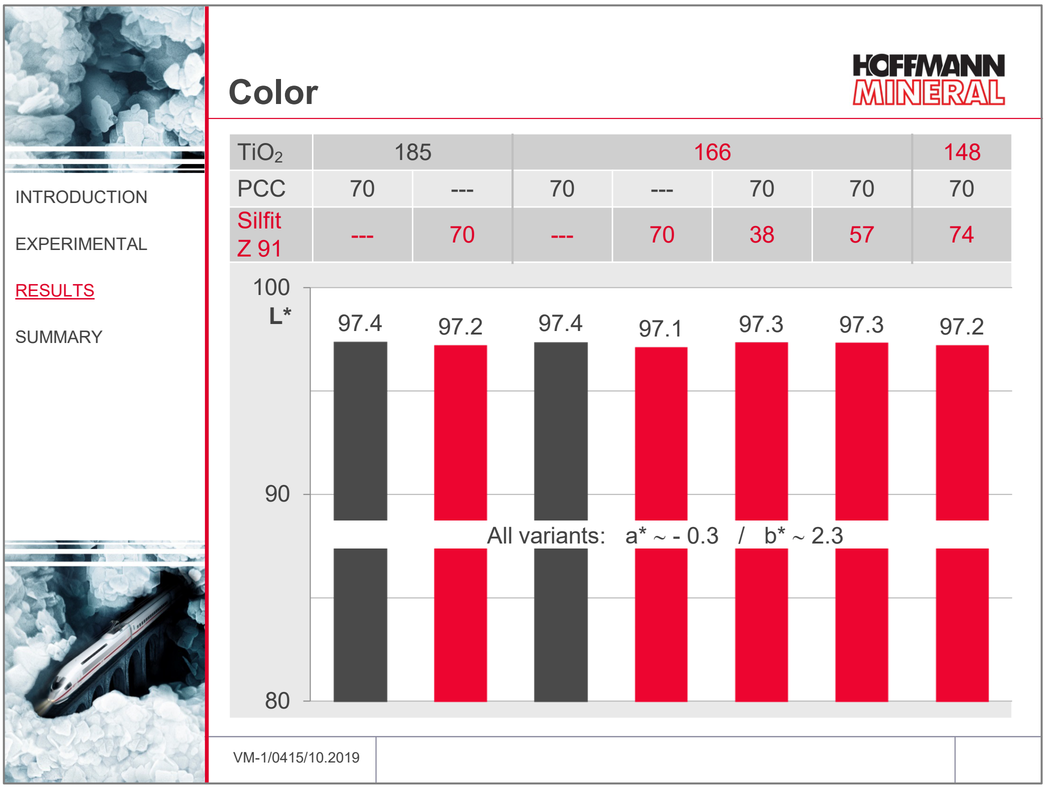


Fig. 7

3.5 Hiding power

For the definition of the hiding power, the EU Ecolabel offers a good starting point. As a help for the user, it distinguishes and honors products which help serve the high quality requirements of the market, and in particular offer as high as possible an environment and health preserving contribution during production and application. The objective of the recognized voluntary environment sign is to sensibilize for an improved environmental protection by working with correspondingly labeled products.

The reduction of the white pigment titanium dioxide, which is ecologically precarious during its production, represents a step in this direction, and is already considered and quantified by the Ecolabel for interior emulsions paints:

- Spreading rate ≥ **8 m² / liter** at a hiding power with contrast ratio of 98 %
- Content of white pigments (refractive index ≥ 1.8) ≤ **40 g / m²** of dried film at a hiding power with contrast ratio of 98 % and a wet-scrub resistance Class 1

The Ecolabel requirement is met by all formulations in *Fig. 8*. Silfit Z 91 impresses by overall better spreading rates. In the versions with Silfit alone or in combination with the precipitated calcium carbonate the loading of TiO_2 can, therefore, be reduced by up to 20 % without sacrifices in the performance vs. the control.

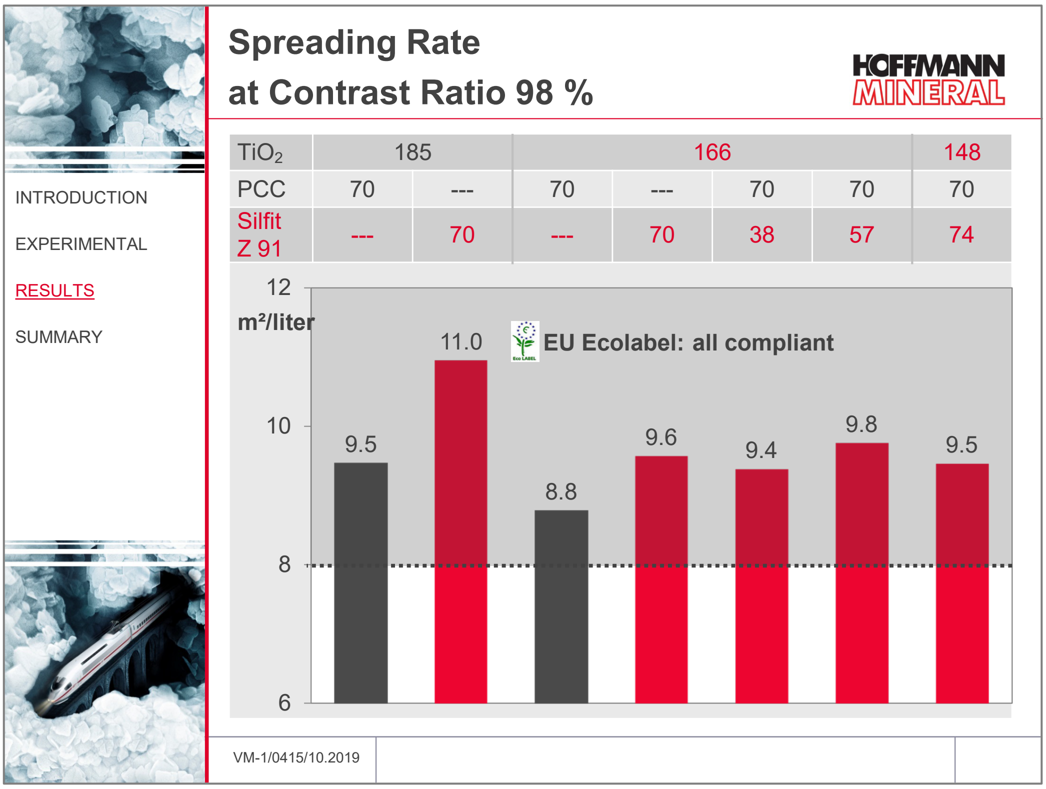


Fig. 8

This situation is of advantage with respect to the surface related consumption of titanium dioxide (*Fig. 9*).

The titanium dioxide concentrations per square meter of coated surface for all formulation variants are clearly within the compliant region below the limit of 40 g/m² (*Fig. 9*).

However, the higher spreading rates of the formulations with Silfit Z 91 compared to the precipitated calcium carbonate provide an application in lower film layer thickness.

The effectively reduced paint consumption with material savings is last not least reflected in a diminished surface related TiO_2 content.

If the white pigment content of a formulation is already reduced, this will cause additionally and particularly beneficial effects as shown in *Fig. 9* on the right-hand side.

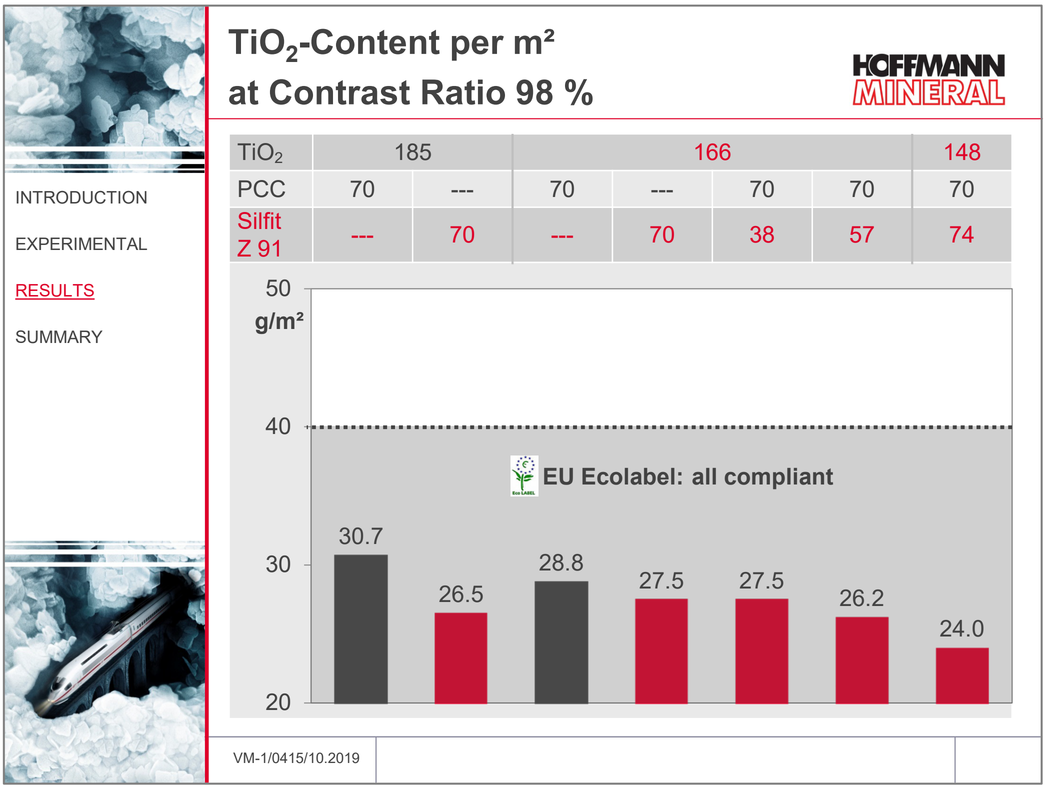


Fig. 9

Compared with precipitated calcium carbonate, Silfit Z 91, therefore, offers a distinct contribution towards reducing the white pigment content and to better preserve the environment. At the same time, Silfit Z 91 makes further cost savings possible, as discussed in the following paragraph.

3.6 Cost / Performance calculations

The base of the relations illustrated in *Fig. 10* are the volume related raw material costs in Germany 2019 (upper graph, left-hand column) as well as the volume related spreading rate resulting from the hiding power (upper graph, right-hand column). The results are expressed as the relative change with respect to the control formulation with an index of 100.

The lower part of the graph summarizes per addition the changes in costs and spreading rate as an index for the effective performance capability.

In the 1:1 comparison the better spreading rate of Silfit Z 91 markedly over-compensates the slightly higher raw material costs vs. precipitated calcium carbonate. While a partial replacement of TiO_2 with Silfit Z 91 looks possible without optical drawbacks, the evident loss of performance with the precipitated calcium carbonate despite the favorable formulation approach will not be compensated in the total balance. Only the combination with Silfit Z 91 is able to offer TiO_2 and cost savings without losses in performance.

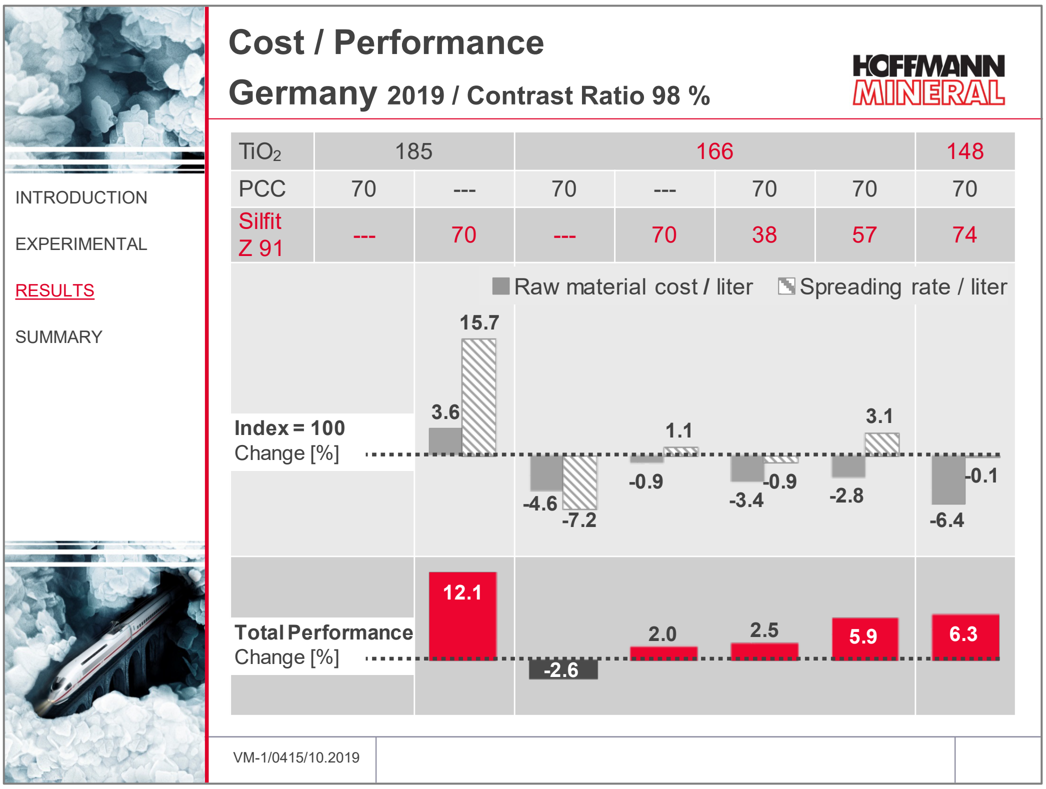


Fig. 10

4 Summary

Silfit Z 91 in the present study has shown the following performance in comparison with precipitated calcium carbonate:

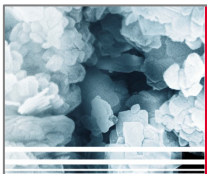
- Practicable comparable properties with respect to processing, storage stability, color, gloss and wet-scrub resistance
- Significant improvement of hiding power, so any loss of hiding power through partial TiO_2 reduction will be easily compensated

The results with using Silfit Z 91 in high quality interior emulsion paints compared with precipitated calcium carbonate are as follows:

- Excellent optical color values and wear resistance of the coatings
- Markedly higher spreading rate which allow to decrease thickness of layers and surface related material consumption under cost savings
- Along with improved hiding power possibility to reduce TiO_2 with real savings in white pigment and raw material costs without loss of performance
- Further reduction of the TiO_2 content per surface unit which already conforms to the Ecolabel requirements (white pigment limitation)

With this property profile, Silfit Z 91 offers a distinct contribution towards the formulation of still more environmentally friendly coating systems and underlines in an essential way its suitability as an effective TiO_2 extender for modern interior dispersion-based emulsion paints.

Recommended formulations including Silfit Z 91 can be found in *Fig. 11*.



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Starting Formulations

<table>
<tr><th colspan="2">[1] Very high hiding power / spreading rate
[2] TiO_2-reduction + good hiding power
[3] High cost savings</th><th>[1]</th><th>[2]</th><th>[3]</th></tr>
<tr><td colspan="2">Water deionized</td><td colspan="3">291</td></tr>
<tr><td colspan="2">Tylose MH 30000 YG8</td><td colspan="3">4</td></tr>
<tr><td colspan="2">Calgon N, 10 % in water</td><td colspan="3">5</td></tr>
<tr><td colspan="2">Lopon 895</td><td colspan="3">3</td></tr>
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<tr><td colspan="2">Parmetol MBX</td><td colspan="3">1</td></tr>
<tr><td colspan="2">Sachtleben RDDI</td><td>185</td><td>166</td><td>148</td></tr>
<tr><td colspan="2">Socal P2</td><td>---</td><td>70</td><td>70</td></tr>
<tr><td colspan="2">Omyacarb 2 GU</td><td colspan="3">125</td></tr>
<tr><td colspan="2">Omyacarb 5 GU</td><td colspan="3">90</td></tr>
<tr><td colspan="2">Omyacarb 10 GU</td><td colspan="3">30</td></tr>
<tr><td colspan="2">Plastorit 00</td><td colspan="3">40</td></tr>
<tr><td colspan="2">Agitan 315</td><td colspan="3">2</td></tr>
<tr><td colspan="2">Silfit Z 91</td><td>70</td><td>(38 to) 57</td><td>74</td></tr>
<tr><td colspan="2">Sodium hydroxide, 10 % in water</td><td colspan="3">2</td></tr>
<tr><td colspan="2">Mowilith LDM 1871 (VAE)</td><td colspan="3">150</td></tr>
<tr><td colspan="2"></td><td></td><td></td><td></td></tr>
<tr><td>Solids content w/w</td><td>[%]</td><td>70.8</td><td>72.5</td><td>72.7</td></tr>
<tr><td>PVC</td><td>[%]</td><td>63.0</td><td>64.3</td><td>64.3</td></tr>
</table>

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Fig. 11

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