Silfit Z 91

in grey-colored

washing machine gaskets

Author: Nicole Holzmayr
Hubert Oggermüller

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HOFFMANN MINERAL GmbH • Muenchener Strasse 75 • D-86633 Neuburg (Donau) • Phone (+49-84 31) 53-0
www.hoffmann-mineral.com • e-mail: info@hoffmann-mineral.com

Contents

1 Introduction

Neuburg Siliceous Earth is being used in washing machine gaskets as it leads to long flow times along with short cure times, a welcome combination for the manufacture of molded rubber parts.

In addition, the filler offers a balanced ratio between tensile strength, tear resistance and compression set, plus good resistance against washing suds.

Until now, only non-calcined Siliceous Earth fillers have found application in this field. As Hoffmannn Mineral constantly endeavors to enlarge its product portfolio in order to offer customers an increased variety of applications, there has been launched now also a calcined version of Neuburg Siliceous Earth - Silfit Z 91.

Silfit Z 91 is a naturally occurring conglomerate of amorphous and cryptocrystalline silica with lamellar kaolinite, which has been subjected to a heat treatment. The components and the thermal process lead to a product that offers special performance benefits as a functional filler.

In the present work, the effect of this calcined Silfit Z 91 in a grey-colored washing machine gasket was studied in comparison with Sillitin, Sillikolloid and a calcined clay.

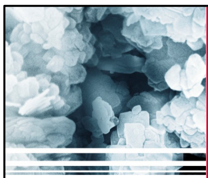
Particular attention is given to the properties of compounds with and without addition of precipitated silica, which is traditionally used in this application because of its reinforcing action.

Another aspect of this study is the possibility to avoid the yellowish tint which is clearly seen in light-colored compounds filled with Sillitin or Sillikolloid. In the manufacturing process of Silfit Z 91, the color of the powder can be deliberately adjusted, which is also reflected in the color of (light-colored) rubber compounds.

Furthermore, the effect of the calcined Silfit Z 91 on filler-induced mold fouling (plating) will be evaluated. The occurrence of plating tends to negatively affect the surface quality of extruded or molded articles, leading to scrap and the need to stop the production units for cleaning purposes. The corresponding costs could be saved if the plating would be reduced or even totally avoided by the selection of a more suitable filler in the compound.

2 Experimental

2.1 Base formulation



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

Base Formulation
Washing Machine Gasket

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	with silica	without silica
Vistalon 3666	175.00	175.00
Stearic Acid	1.00	1.00
Zinkoxyd aktiv	5.00	5.00
Mineral Filler	**100.00**	**150.00**
Silica (pptd., BET appr. 130 m²/g)	**25.00**	**-----**
Kronos 2222	9.00	9.00
Corax N 550/30	0.35	0.35
Aflux S	3.00	3.00
DEG	3.00	3.00
Silanogran PV	4.80	4.80
Sunpar 2280	25.00	25.00
Sulfur	0.70	0.70
Rhenogran MBT-80	2.40	2.40
Rhenogran CLD-80	1.20	1.20
Rhenocure TP/S	3.60	3.60
Total	**359.05**	**384.05**

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Vistalon 3666:	EPDM, crystalline, oil-extended (paraffinic oil, 75 phr)
Stearic acid:	processing aid
Zinkoxyd aktiv:	zinc oxide active
Silica :	precipitated, surface area approx. 130 m²/g
Kronos 2222:	titanium dioxide
Corax N 550/30:	carbon black
Aflux S:	dispersion aid and lubricant (no longer available, it was included just for comparison reasons)
DEG:	diethylene glycol
Silanogran PV:	polybutadiene, silanized (50 %)
Sunpar 2280:	paraffinic oil, plasticiser
Rhenogran MBT-80:	mercaptobenzthiazole (80 %)
Sulfur:	ground sulfur
Rhenogran CLD-80:	caprolactamdisulfide (80 %)
Rhenocure TP/S:	zinc dialkyldithiophosphate
Mineral filler :	see 2.2 "Mineral fillers and compound preparation"

The mineral fillers were tested in combination with silica and also without silica.
In order to adjust equal hardness levels and thus comparable cured rubber properties, the filler loading in the compounds without silica was proportionately increased.

Mineral fillers and compound preparation

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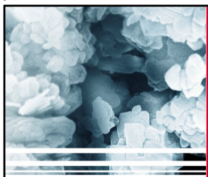

INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

Fillers, Characteristics

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		Calcined Clay	Neuburg Siliceous Earth		
		Polestar 200 R	Sillitin N 85	Sillikolloid P 87	Silfit Z 91
Particle Size d_{50}	[µm]	3.6	2.3	1.1	2.0
Particle Size d_{97}	[µm]	19	12	4.3	10
Oil Absorption	[g/100g]	60	47	53	59
Specific Surface Area BET	[m²/g]	6.5	10	12	7.6
Calcination		yes	none	none	yes

VM-2/0610/02.2011

Silfit Z 91 was evaluated in comparison with two standard grades of Neuburg Siliceous Earth as well as against calcined clay.

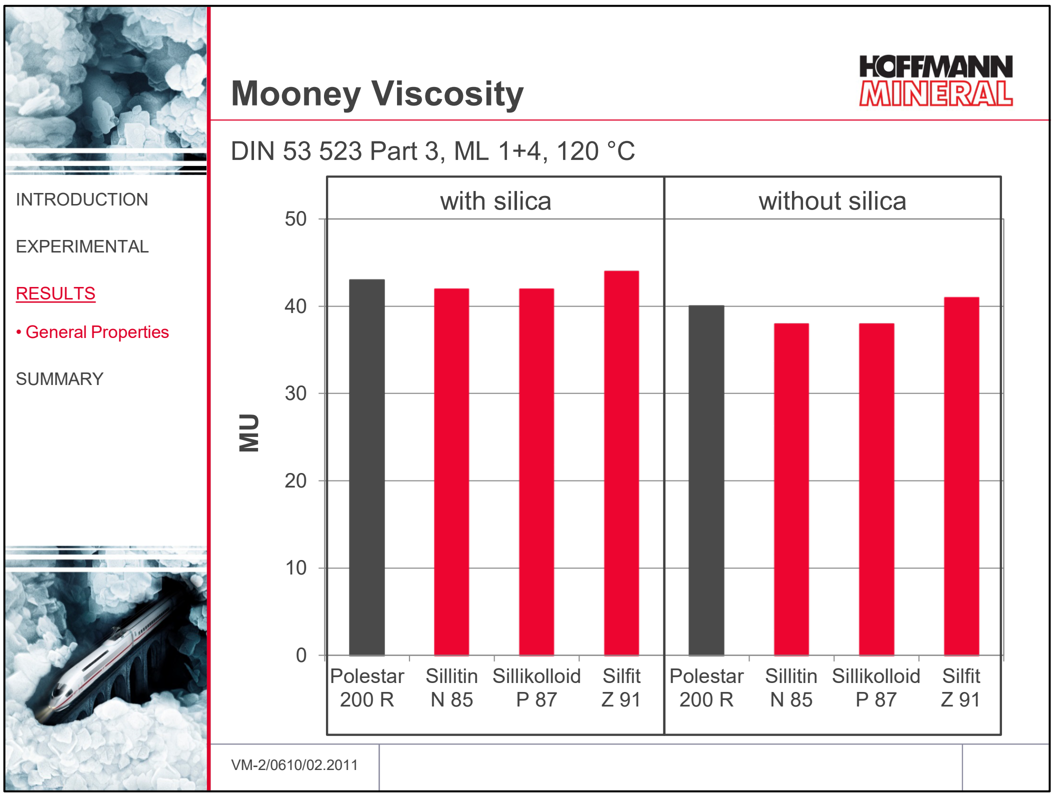
The calcined clay is somewhat coarser than the Neuburg Siliceous Earth products. The oil absorption and the specific surface area are in a range comparable with Silfit Z 91

The specific surface areas of the two Siliceous Earth standard grades are somewhat higher compared with the two fillers mentioned above. Sillitin N 85 has a somewhat higher grain size than Silfit Z 91. Sillikolloid P 87 shows the lowest grain size of all fillers considered here, and thus offers the highest fineness. The oil absorption of Sillitin N 85 and Sillikolloid P 87 are at a somewhat lower level than Silfit Z 91.

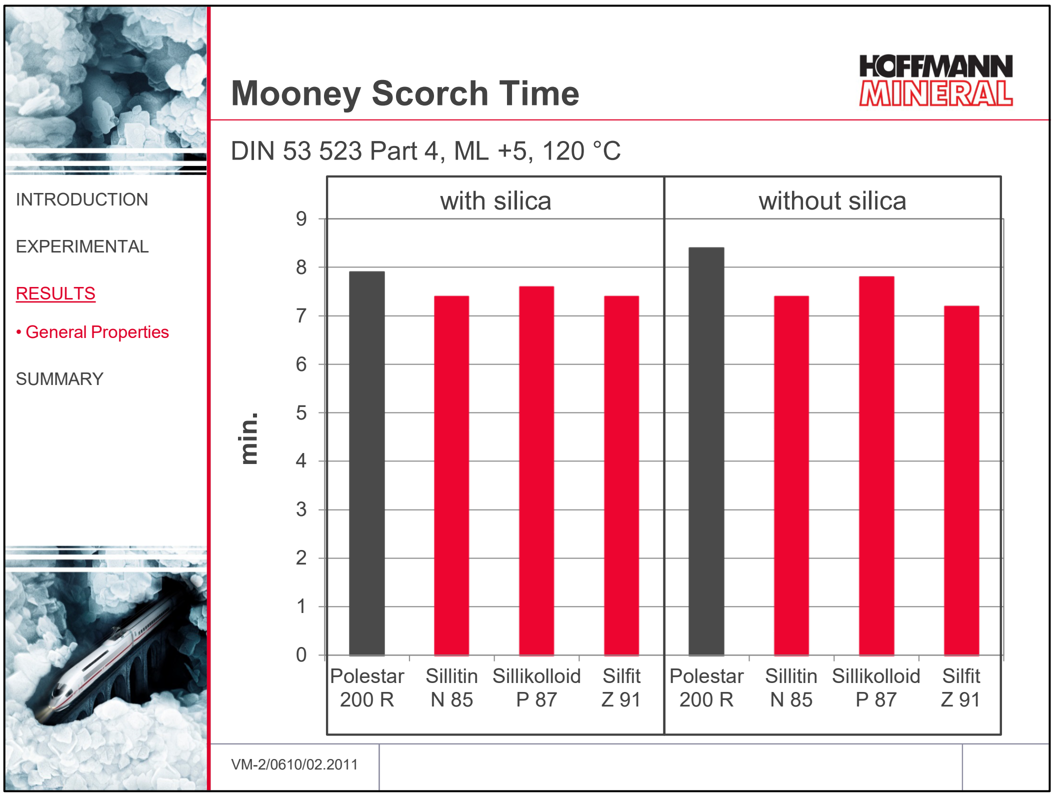
The compounding was done on a laboratory mill (Schwabenthan Polymix 150 L). The rubber was fed onto the mill at 50 °C, and subsequently all the other ingredients were added at constant mill temperature in the sequence given in the formulation table.

3 Results

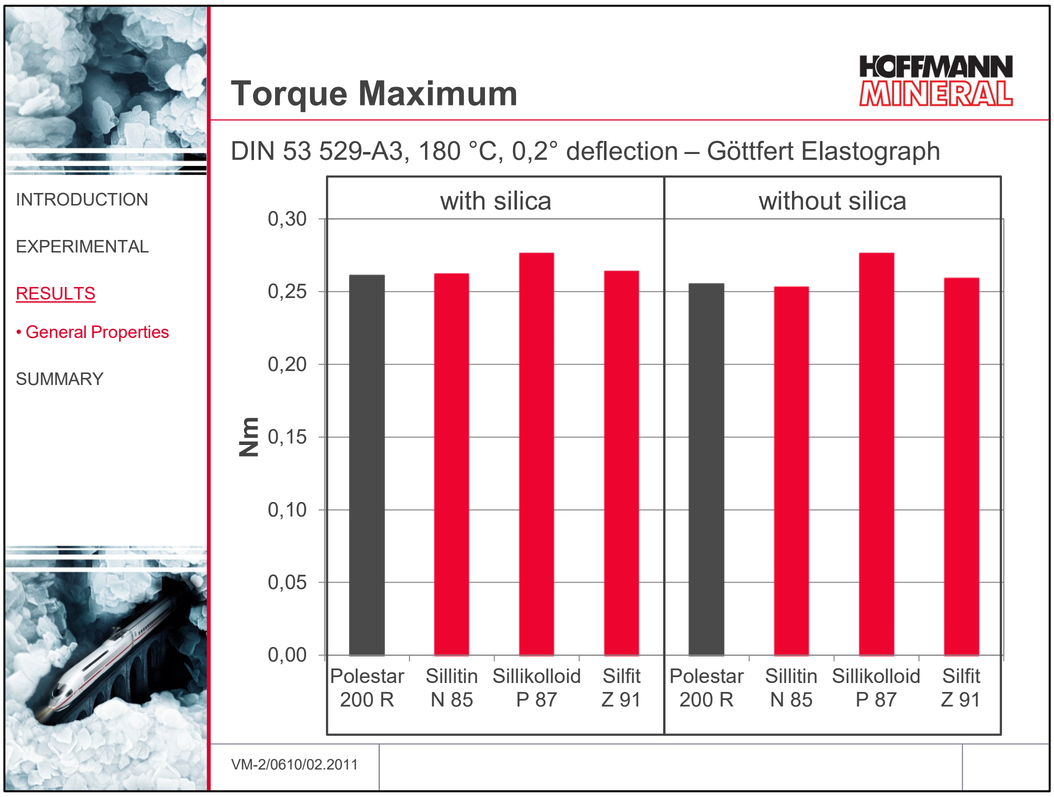
3.1 Viscosity, scorch and cure characteristics



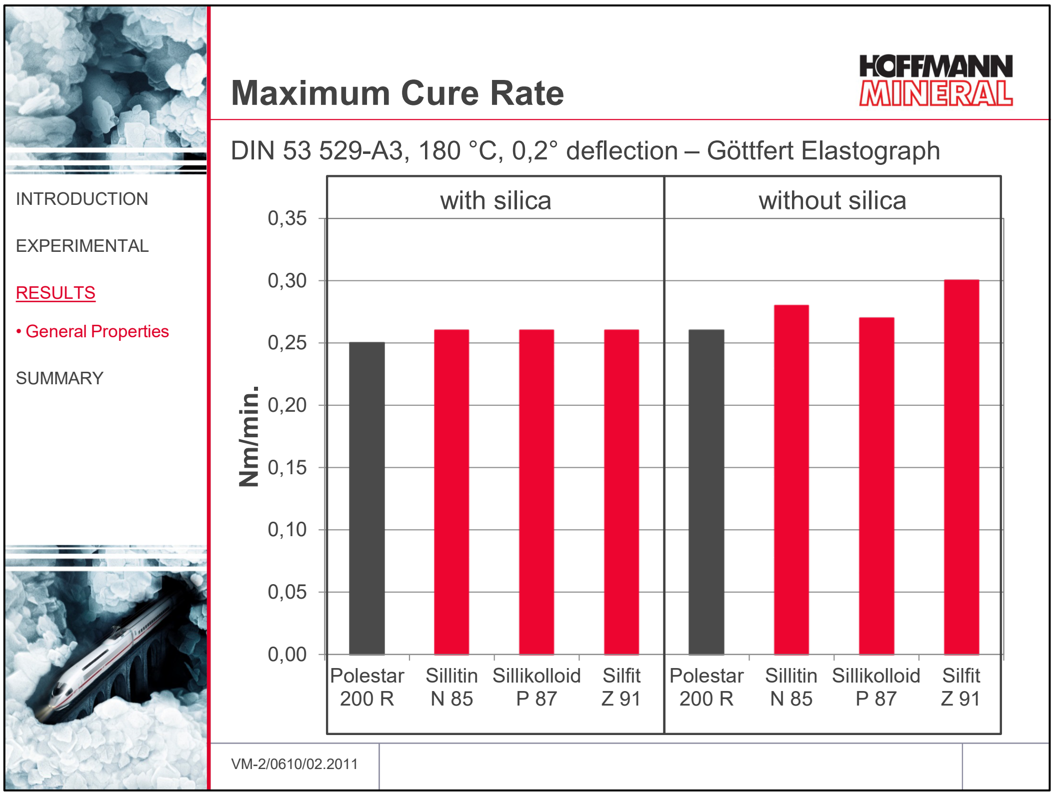
The graph shows that Silfit Z 91 does not give any significant viscosity differences versus the standard Siliceous Earth grades and the calcined clay.
Replacing the silica with a mineral filler in all cases leads to a marginal decrease of the viscosity.



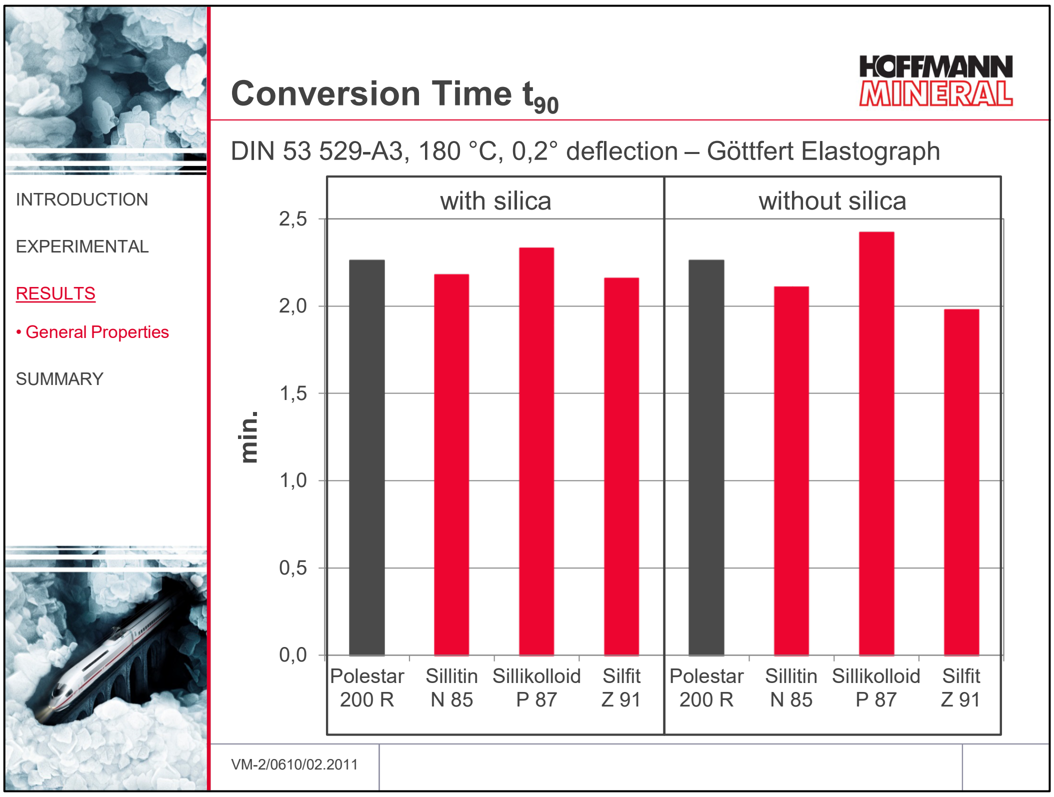
The increase of viscosity from the minimum value by 5 Mooney units takes sufficiently long time with all fillers tested, generally 7 to 8 minutes, and this with or without the presence of silica.



The Vulcameter torque maxima with Sillitin N 85, Silfit Z 91 and the calcined clay are all on a comparable level. Only Sillikolloid P 87 leads to a somewhat higher figure.
Replacing the silica hardly has any effect on the torque results.



Between the compounds with silica, there is no difference with respect to the cure rate. The cure rate goes up, however, when the silica is replaced. With the calcined clay, Sillitin N 85 and Sillikolloid P 87 the increase is just moderate. A significant increase of the cure rate is seen with Silfit Z 91.



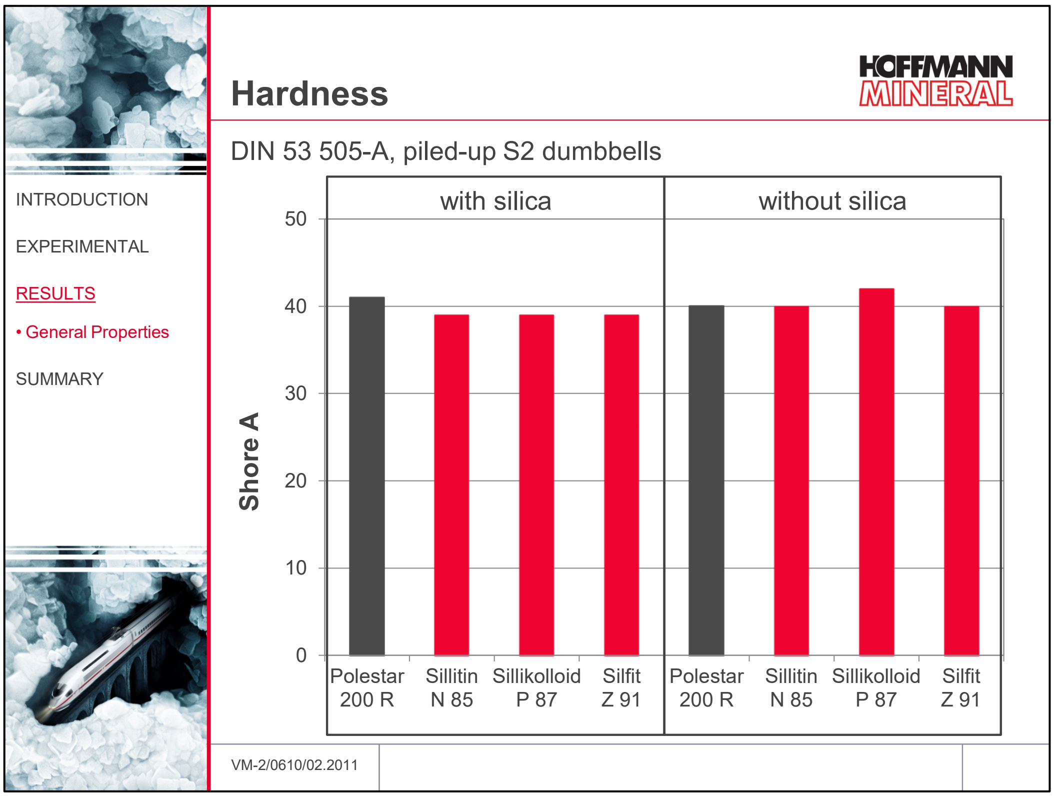
The cure time t_{90} is fairly short for all compounds, which presents an advantage for the formulation under test. Washing machine gaskets are manufactured as molded parts. In order to produce high amounts in the shortest time possible, short curing times are desirable.

The graph indicates that in compounds with silica the calcined clay and Sillikolloid P 87 give similar conversion times, while the compounds with Sillitin N 85 and Silfit Z 91 come out marginally shorter. The replacement of the silica does practically not change the time to full cure for the calcined clay, Sillitin N 85 and Sillikolloid P 87, whereas a further reduction is observed with Silfit Z 91.

3.2 Mechanical properties

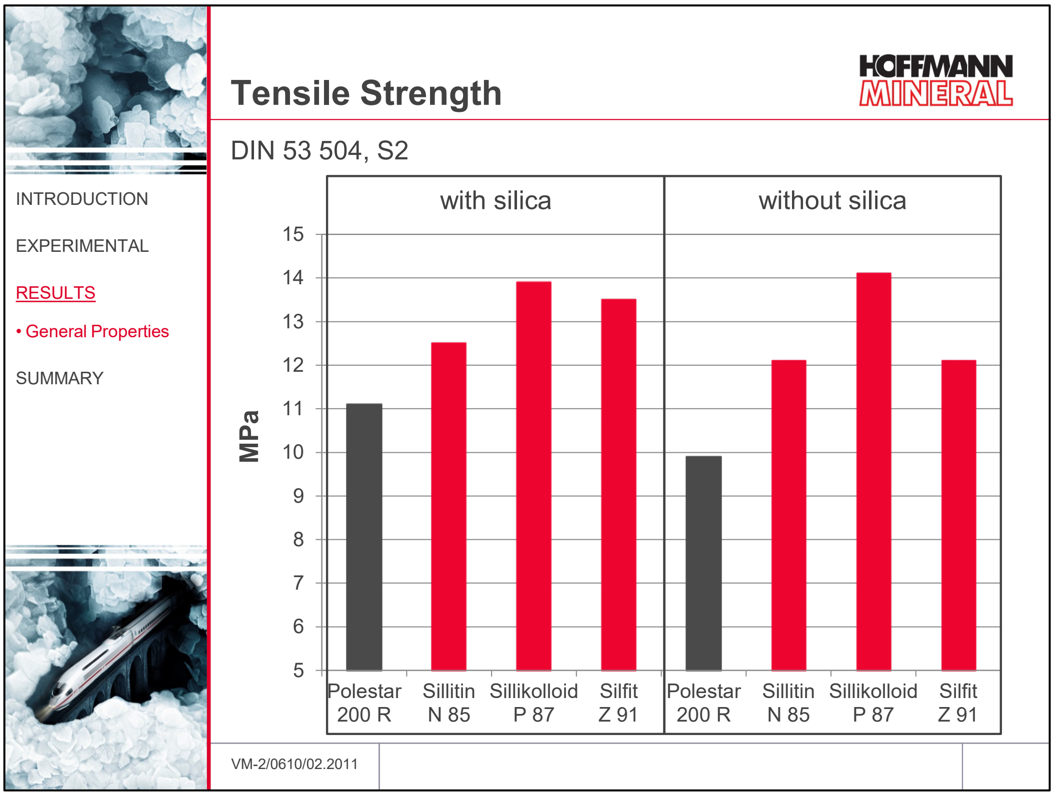
The compounds were cured in a laboratory press at 180 °C.

As the conversion time t_{90} was shorter than 5 minutes throughout, all compounds and the different test specimens were cured for a fixed time of 5 minutes.



The Shore hardness was determined on three piled-up S2 dumbbells.

No significant difference was found between the individual compounds. The replacement of the silica with a mineral filler in a ratio of 1:2 in all cases resulted in the desired identical hardness, which means that also all other cured rubber properties should allow a direct comparison.

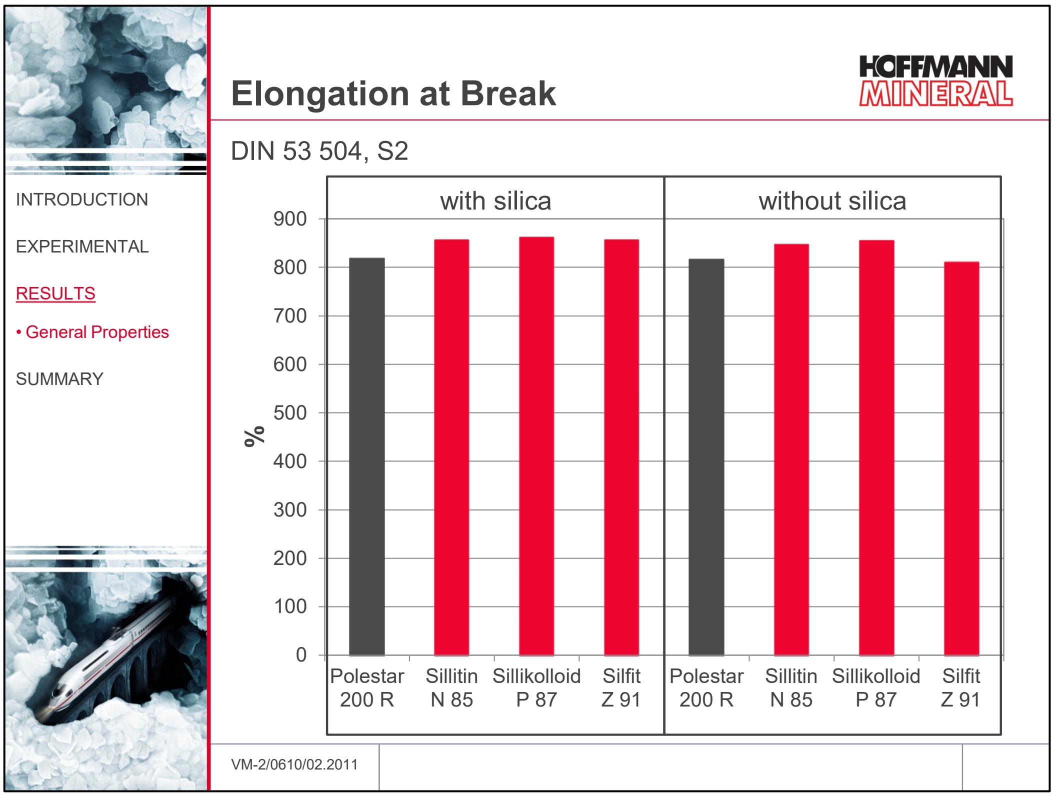


All Siliceous Earth grades are able to surpass the tensile strength of the calcined clay, and this with or without the presence of silica.

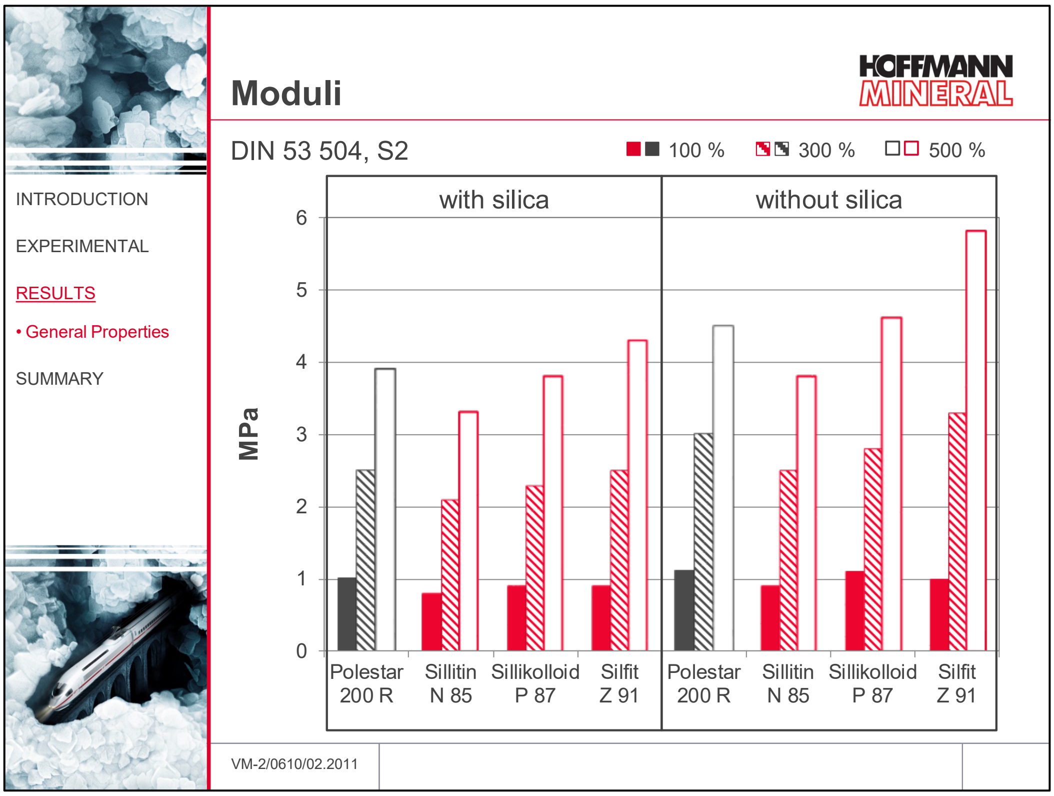
In the compounds containing silica, Silfit Z 91 gives a similar tensile strength to Sillikolloid P 87, and this at a level higher than with Sillitin N 85.

After replacing the silica, the highest tensile strength of the three Siliceous Earth grades is obtained with Sillikolloid P 87, followed by Sillitin N 85 and Silfit Z 91 at a level somewhat lower.

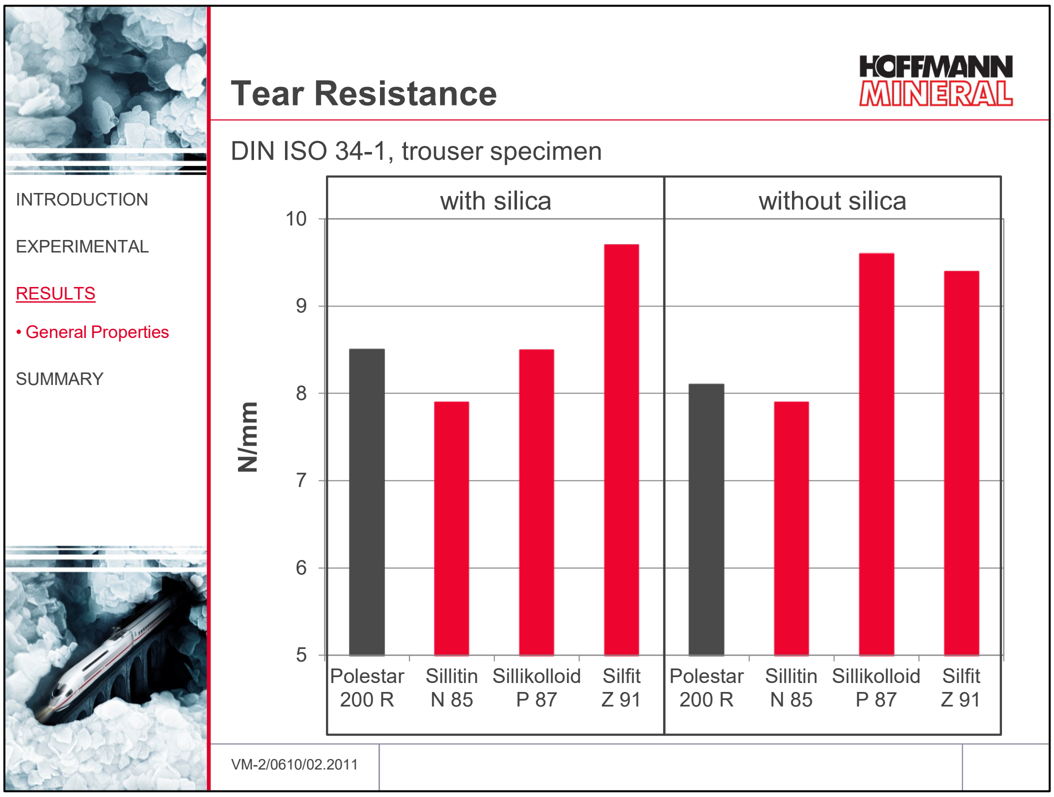
Silfit Z 91 even without silica imparts a higher tensile strength compared with calcined clay plus silica.



The elongation at break does not give evidence of a difference between the fillers tested. Likewise, the replacement of the silica does not affect the elongation.

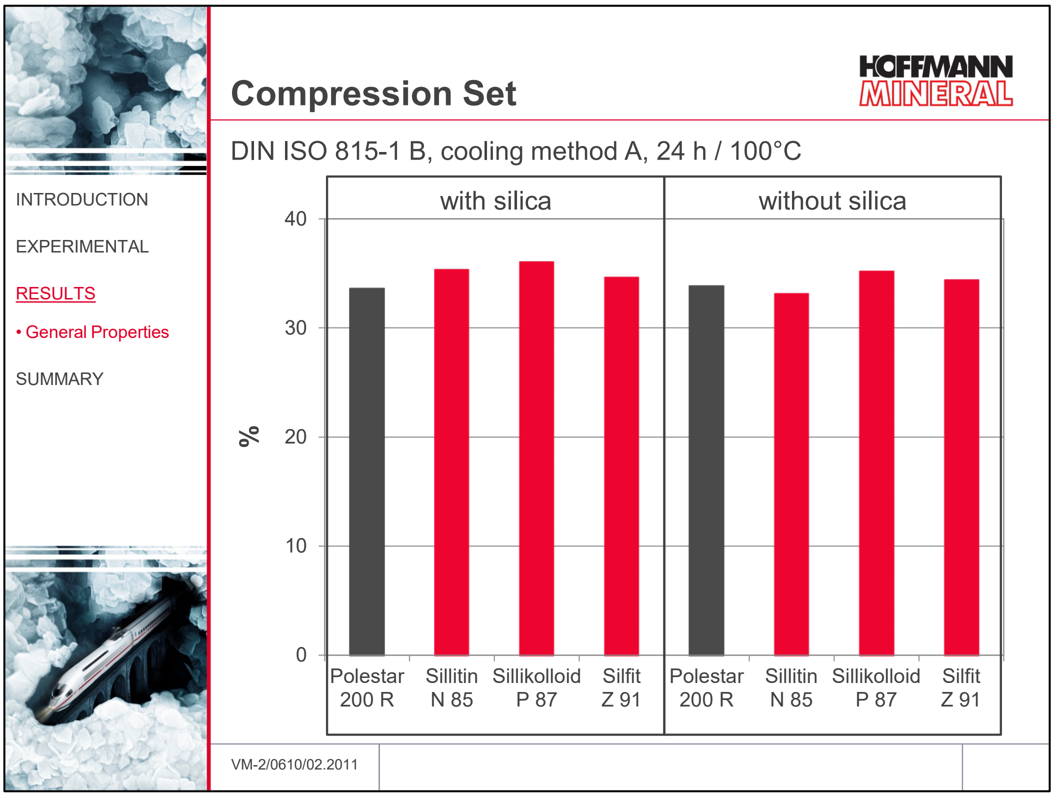


With or without silica, Sillikolloid P 87 gives tensile moduli comparable with calcined clay, with Sillitin N 85 slightly lower. The highest moduli are obtained with Silfit Z 91. Without silica the increase vs. the other fillers is even more significant than in the presence of silica. Similar to what was found for the tensile strength, Silfit Z 91 without silica results in markedly higher moduli compared with the calcined clay plus silica.



In the silica loaded compounds the tear resistance with Sillikolloid P 87 comes out at level with calcined clay, i.e. somewhat higher than with Sillitin N 85. Silfit Z 91 allows to obtain the highest tear resistance of the series.

The replacement of silica with Sillikolloid P 87 results in a higher tear resistance. By contrast, with calcined clay, Sillitin N 85 and Silfit Z 91 no effects of the silica replacement can be observed. Rather it is evident that with Silfit Z 91 no silica is required to arrive at a higher tear resistance than the calcined clay with or without silica.

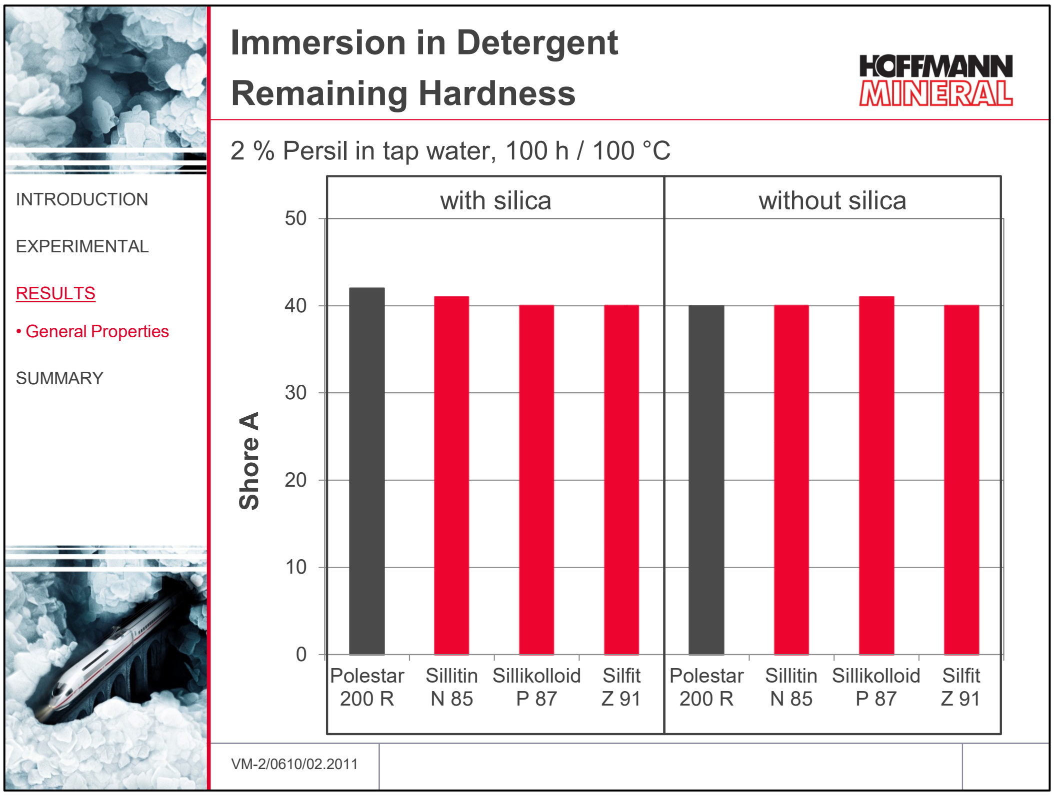


The selection of the filler has no noticeable effect on the compression set. All tested fillers give comparable figures.

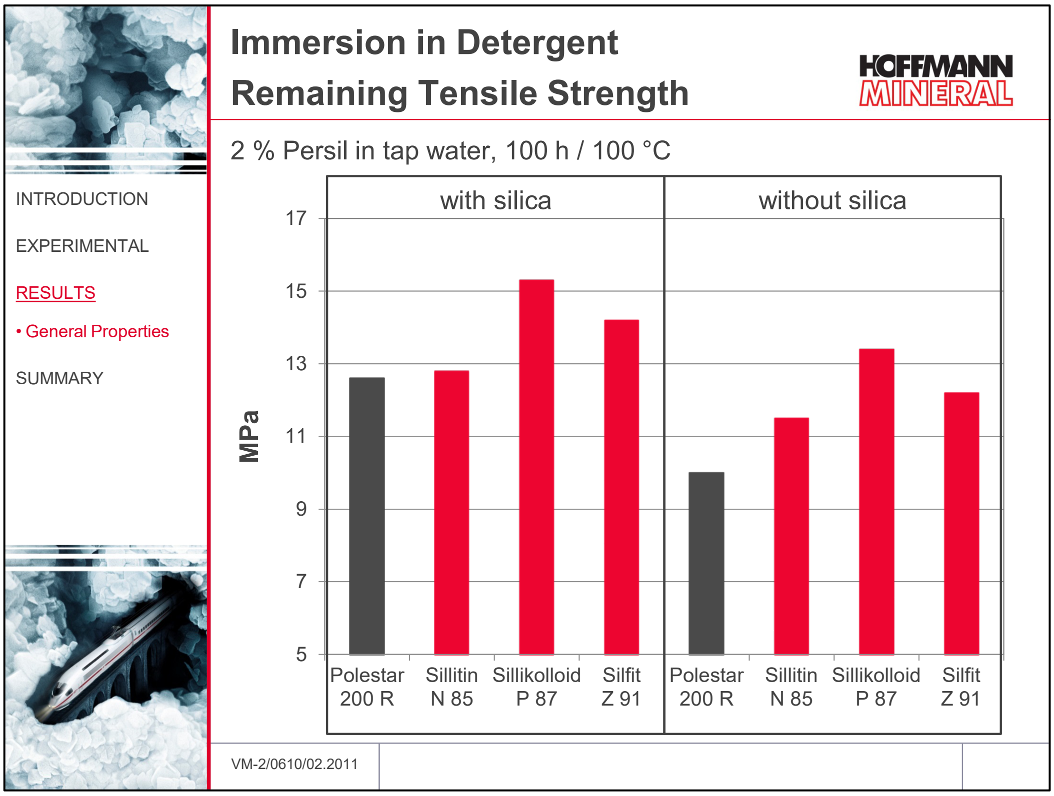
Likewise, the replacement of the silica does not change the compression set.

3.3 Immersion in detergent

The immersion in detergent was carried out on S2-dumbbells for 100 hours at 100 °C in a 2% Persil in tap water sud. The sud temperature at the beginning of the immersion of the dumbbells was 95 °C, then the temperature was increased up to 100 °C. This way of proceeding corresponds with the Gorenje-standard GOS 420.

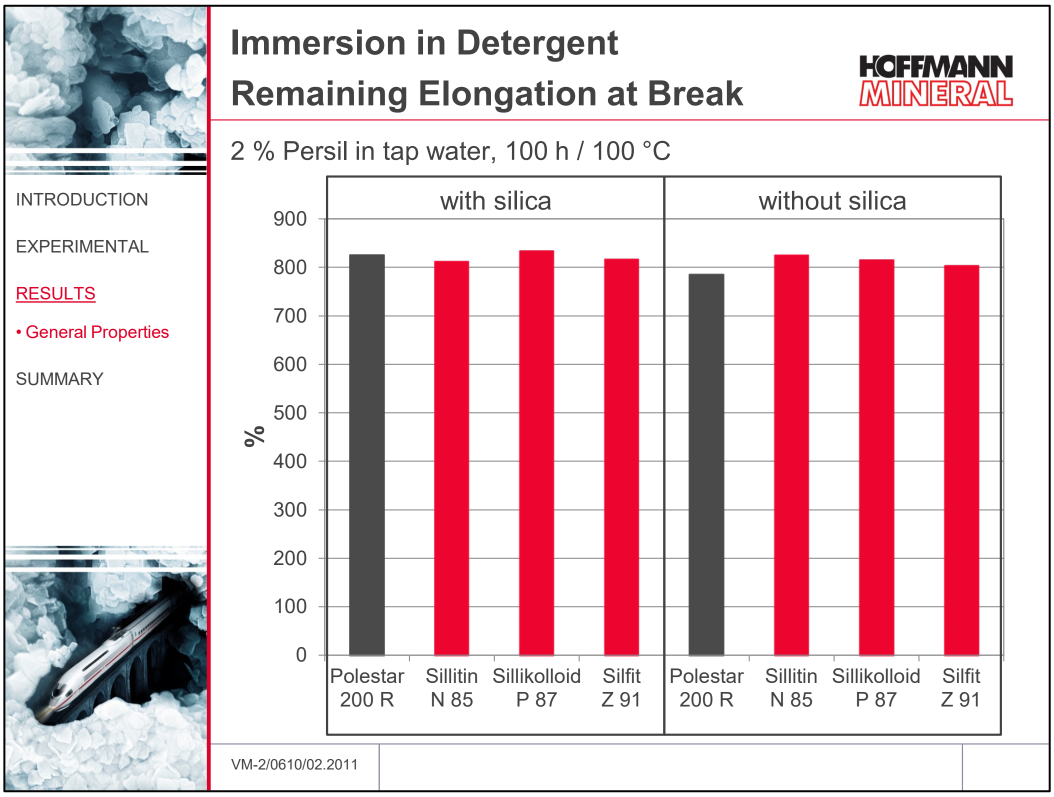


The Shore hardness was determined on three piled-up S2 dumbbells.
After the immersion in detergent no differnences between the compounds can be observed.
The replacement of the silica has no effect on the hardness after immersion in detergent.

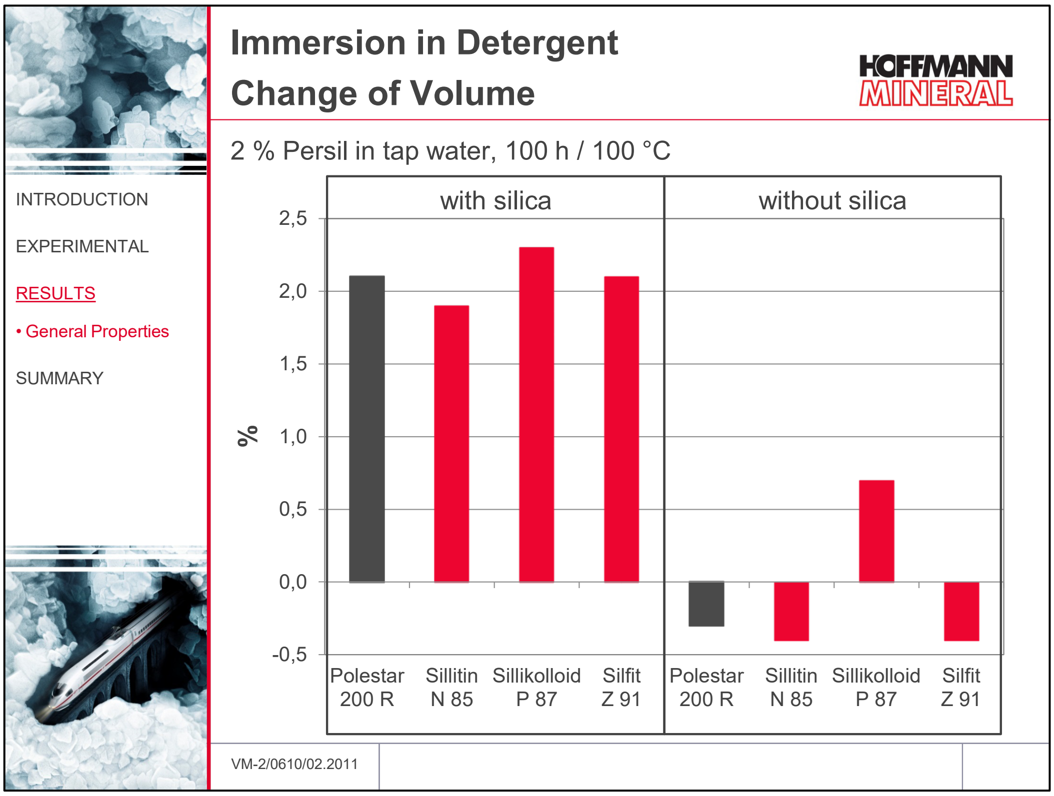


After the immersion in detergent, the compounds with silica containing Sillikolloid P 87 and Silfit Z 91 obtain the highest tensile strength levels. The value reached with Sillitin N 85 is similar to the one with Polestar 200 R.

By replacing the silica - as already stated for the initial values - with the Neuburg Siliceous Earth grades, higher tensile strength levels can be realized than with Polestar 200 R. The results with Silfit Z 91 and Sillitin N 85 are comparable and are somewhat lower than with Sillikolloid P 87. It is noticeable, that after the immersion in detergent, with Silfit Z 91 without any silica a tensile strength can be obtained which is on the same level as the Polestar 200 R/silica-combination.



After the immersion in detergent no differences between the fillers can be observed regarding the elongation at break.
Even the replacement of the silica has no effect on the elongation at break after immersion in detergent.



Neither the compounds with nor the compounds without silica show significant differences between the fillers regarding the changes of volume.
A decrease of the change of volume can be observed for the compounds with replacement of the silica.

3.4 Hot air aging

Hot air aging (according to DIN 53 508) was carried out on S2 dumbbells and tear resistance specimen for 168 hours at 120 °C.

In each case, tensile strength, moduli, elongation at break, tear resistance and hardness were determined, and the changes vs. the original figures (directly after cure) calculated.

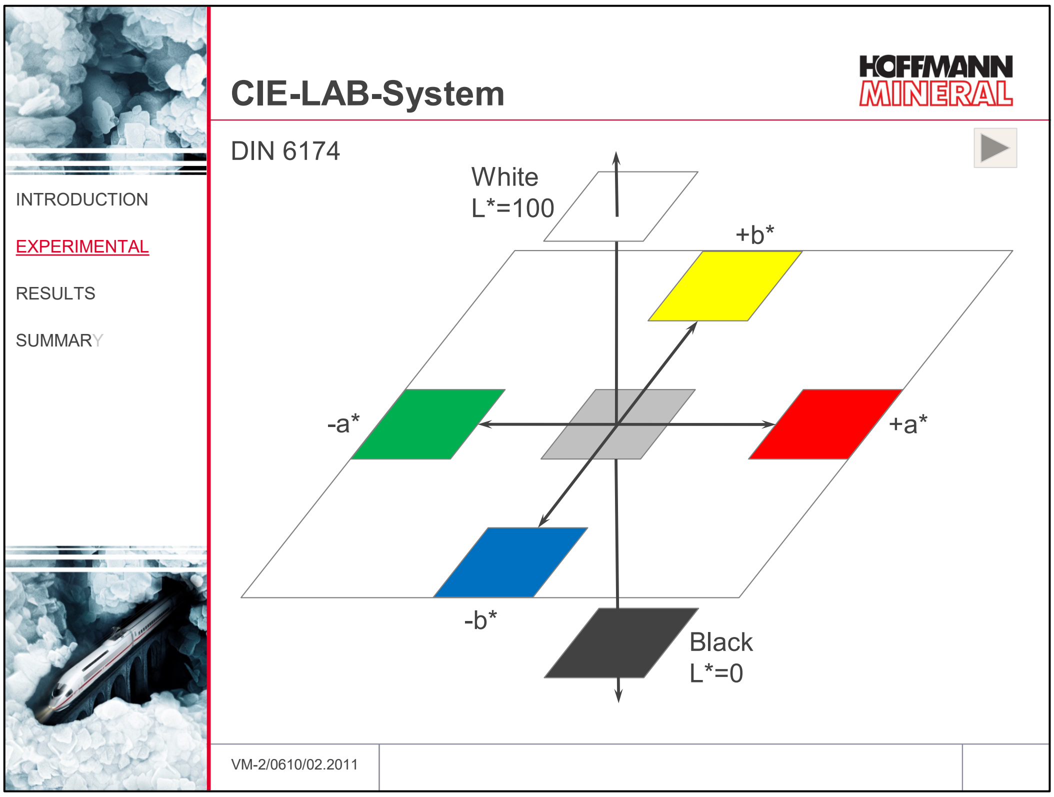
It became clear that there were no significant differences between the individual fillers as well as between the compounds with and without silica. The changes e.g. for tensile strength and elongation at break are in the range of -40 %, hardness increased by about 9 Shore A. As all the compounds behaved in the same manner, the results will not further be discussed here.

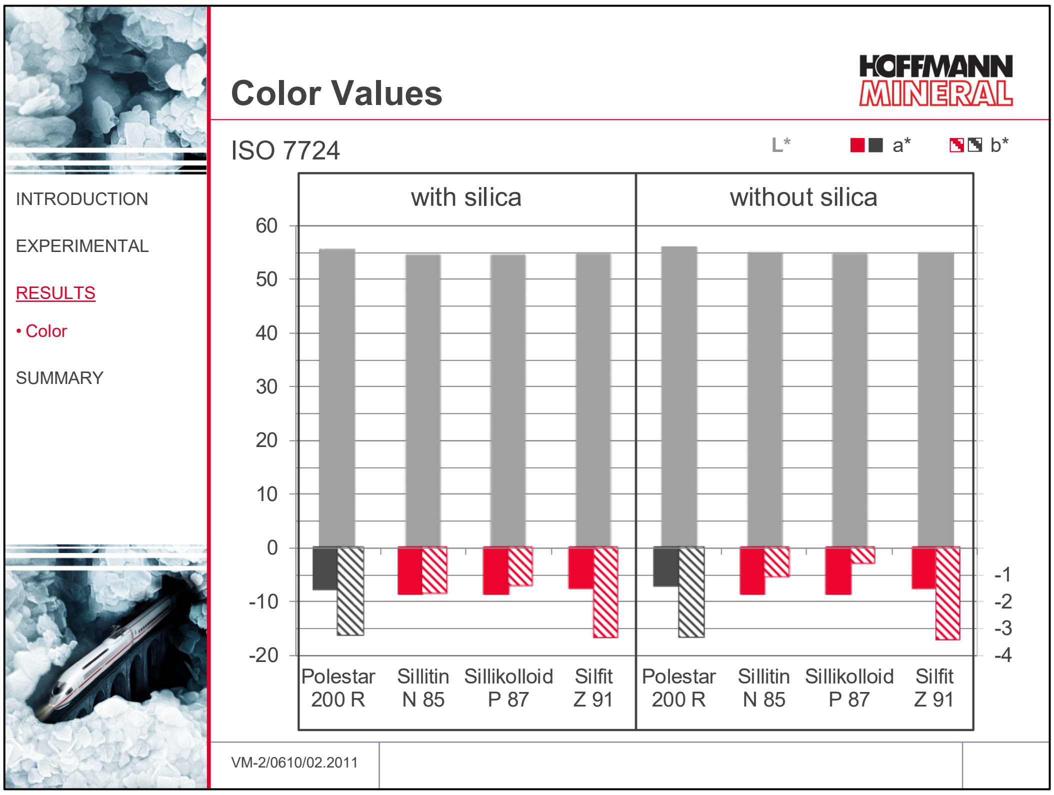
3.5 Color

Light colored compounds loaded with Sillitin or Sillikolloid often are characterized by a visible yellowish tint. In the present study – a grey washing machine gasket – the color adjustment is made with a combination of titanium dioxide and carbon black.

In the production of Silfit Z 91 it is possible to arrive at a desired color by adjusting the process parameters. As the tests confirmed, this has positive effects with respect to the color quality of the cured articles.

The color tests were run with a Spectral Photometer Luci 100 from the Dr. Lange company, with light D65, a test geometry d/8° (without gloss trap) and the normal observation angle of 10°. The determinations included the L*, a* and b* levels.





The vertical axis on the left indicates the L* value, the vertical axis on the right the a* and b* results.

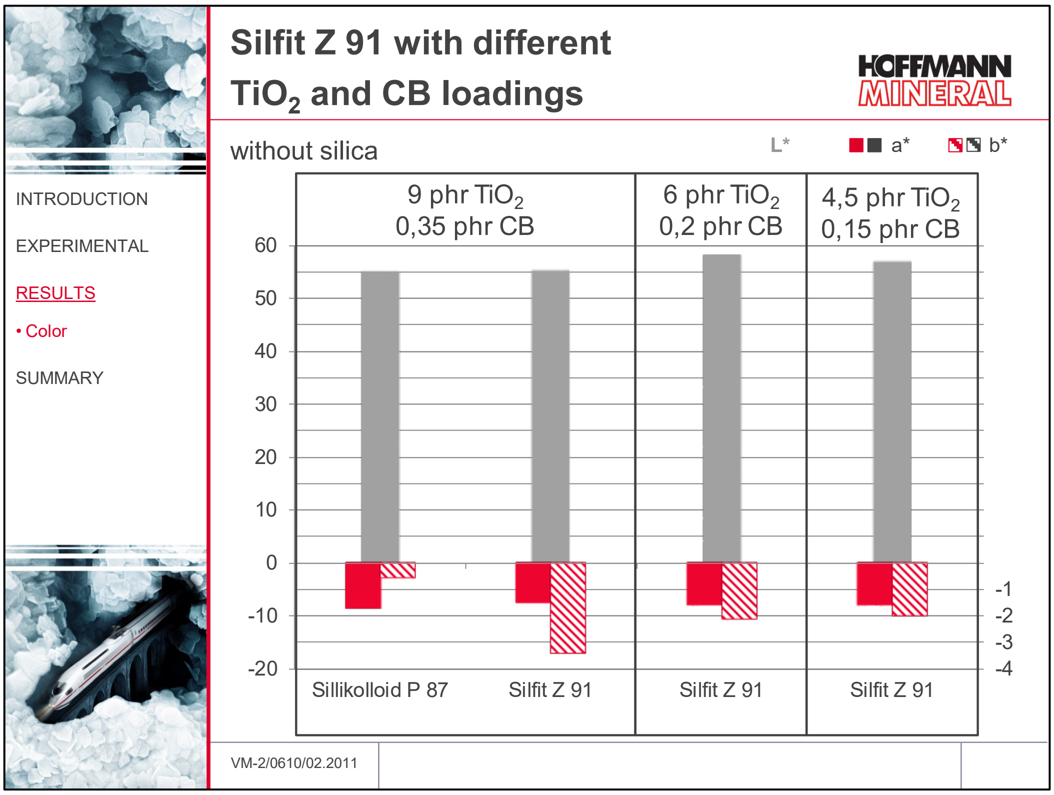
As can be seen in the graph, there is no difference between the individual fillers for the brightness (L*, grey bars). The results come out comparable for all fillers, and this also with and without silica.

Regarding the a* results (green bars), similarly no big differences are observed between the fillers. It is true that the two standard Siliceous Earth grades and the two calcined fillers come out grouped together, but the differences between the two groups are not very pronounced. This is also the case for the replacement of the silica.

A more marked differentiation, however, is evident with the b* values of the individual compounds (blue bars). For instance, the b* result of the Silfit Z 91 compound is clearly lower than the b* levels of the two compounds with the Siliceous Earth standard grades. This indicates that the yellowish tint of the cured rubber compounds with the standard Siliceous Earth grades comes out much reduced with Silfit Z 91 as filler. The comparison of Silfit Z 91 with calcined clay does hardly show any difference in color quality, the two b* figures are almost identical.

The replacement of the silica increases the yellowish tint of the compounds loaded with standard Siliceous Earth grades, as evident from the higher b* results in the right half of the above diagram.
Similar to the compound with calcined clay, the replacement of silica has no effect onto the color results of the Silfit Z 91 compound.
With this, Silfit Z 91 ensures an invariable color quality without the need for corrections by any further addition of color pigments.

Inversely, this means that for compounds so far loaded with standard Siliceous Earth grades, the dosage of color pigments can be reduced when working with Silfit Z 91 without any negative effects on the color quality.



In the base formulation, for color adjustment 9 phr titanium dioxide and 0.35 phr carbon black are added. With Silfit Z 91 results a definitely lower yellowish tint than, for example, with Sillikolloid P 87 (as evident from the negativity of the blue bars: the lower, the lower the yellow contribution, which means the higher the blue portion).

If in the Silfit Z 91 compound the TiO_2 concentration is reduced to 6 phr and the carbon black to 0.2 phr, the b* result will be increased, resulting optically in a slightly higher yellowish tint. In comparison with the Sillikolloid P 87 compound which contains the original amount of pigments, Silfit Z 91 still gives rise to a markedly lower yellowish tint.

A further decrease of the TiO_2 and carbon black additions in direction of about half the original loadings has no effect on the color values. This means in theory further reduced additions of TiO_2 and carbon black would appear possible.

Via a reduced addition of color pigments - in this case TiO_2 and carbon black - the compound costs could be decreased, and a slight cost saving in comparison to working with Sillikolloid P 87 could be achieved.

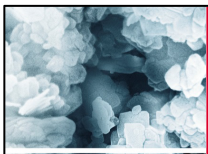
3.6 Plating - Filler induced mold fouling

Plating means the occurrence of undesirable deposits in the compound flow channel and at the extrusion die when extruding rubber compounds. With time, such deposits not only result in a contaminated extrudate surface, but also in reduced dimensional accuracy leading to production of scrap material and lastly expensive stopping times of the unit for exchange of dies or cleaning purposes. Similar phenomena are also observed during injection molding.

In order to arrive at a statement about the mold fouling with regard to the discussed washing machine gasket, the internal Hoffman-Mineral standard plating test was carried out.

The formulation tested largely corresponded to the tests already discussed. But only the compounds with Neuburg Siliceous Earth without silica were tested, as they contained a higher portion of mineral fillers, and therefore should lead to a more meaningful result with respect to plating.

The compounds for these tests were mixed without curing chemicals.



Experimental Parameters

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INTRODUCTION

EXPERIMENTAL

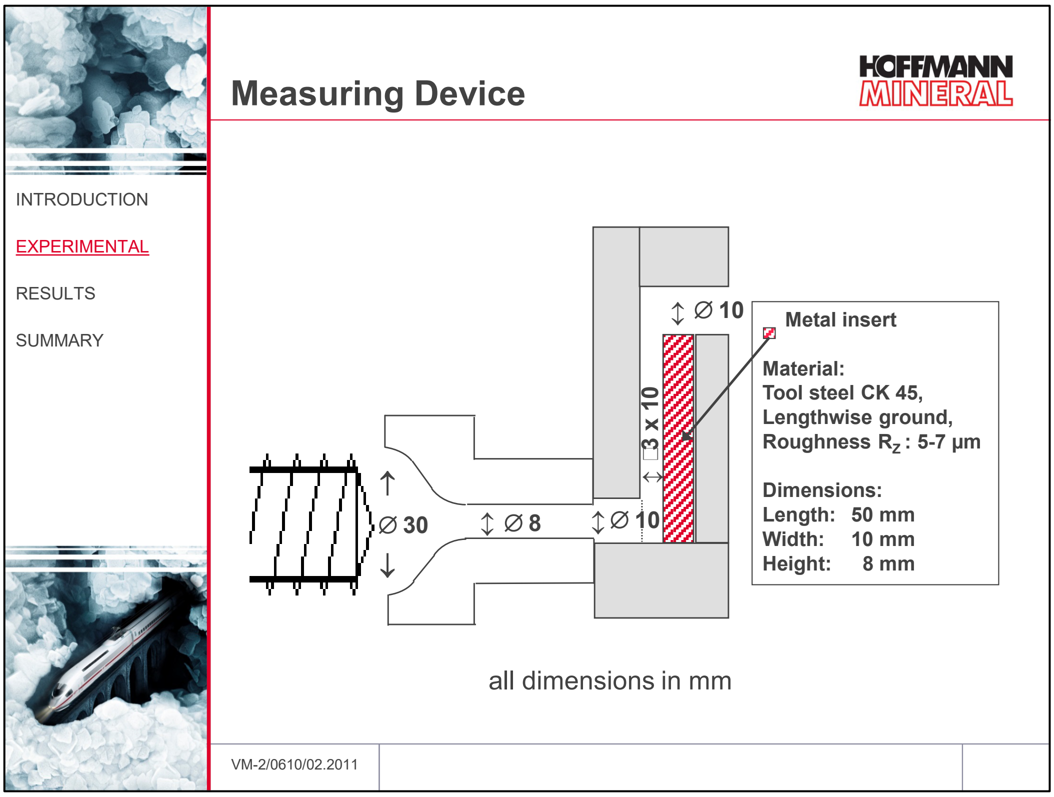
RESULTS

SUMMARY

Extruder		Schwabenthan Polytest 30 R
Screw diameter	mm	30
Process length	mm	450
Temperature set point head / zone 1 / zone 2	°C	60 / 60 / 60
Cooling (zone 1 and 2)		¼ turn open
Screw speed	rpm	100
Measuring channel l x w x h	mm	50 x 10 x 3
Metal insert material		Tool steel CK 45, lengthwise ground
Metal insert roughness R_z (across the flow direction)	µm	5-7
Feed strips	mm	30 x 6

VM-2/0610/02.2011

The upper figure indicates the parameters of the plating test.



This graph illustrates the dimensions of the exit die and the test equipment.

Deposits on the Metal Insert

HOFFMANN MINERAL

INTRODUCTION

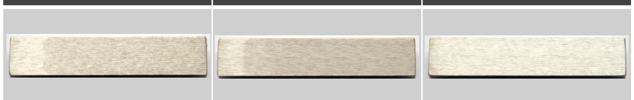
EXPERIMENTAL

RESULTS

• Plating

SUMMARY

	Sillitin N 85	Sillikolloid P 87	Silfit Z 91
extruded amount [kg]	2.5	2.5	5
throughput [g/min.]	388	404	454



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Of the compounds loaded with the standard Siliceous Earth grades Sillitin N 85 and Sillikolloid P 87, no more than 2.5 kg were extruded, as already noticeable deposits could be detected on the metal inserts. This will be further discussed in the following.

The above table also indicates clearly that the mass throughput with Silfit Z 91 is higher than with the two standard Siliceous Earth grades.

INTRODUCTION

EXPERIMENTAL

RESULTS

• Plating

SUMMARY

Sillitin N 85

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almost continuous deposit on the whole metal insert

VM-2/0610/02.2011

During the extrusion of 2.5 kg of the compound with Sillitin N 85, on the metal insert there is an almost continuous layer. At the end of the test, deposits are also visible on the surface across from the metal insert in the exit area.
The visual assessment at 100x magnification confirms these results.

INTRODUCTION

EXPERIMENTAL

RESULTS

• Plating

SUMMARY

Sillikolloid P 87

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continuous compact deposit on the whole metal insert

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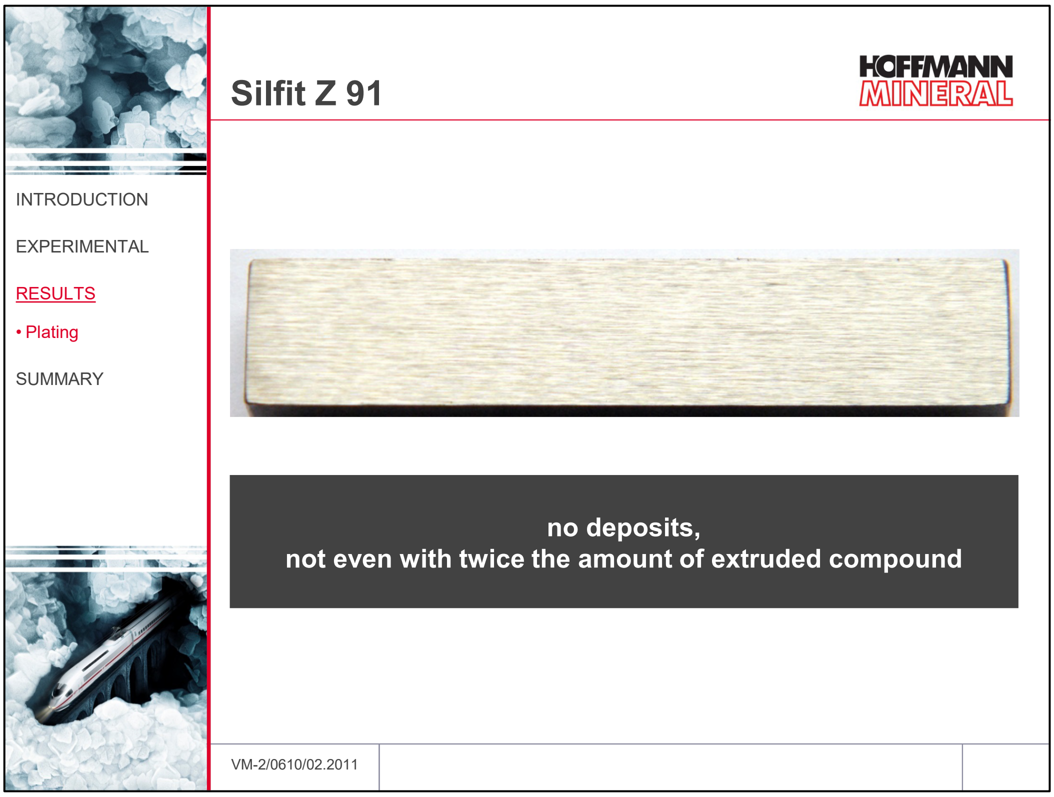
During the extrusion of 2.5 kg of the compound with Sillikolloid P 87 a continuous layer of deposit is formed on the total surface of the metal insert. At the end of the test, deposits are observed also on the total surface opposite the metal insert, which increase towards the exit region. Over the whole, markedly more deposit is found than with Sillitin N 85.
The visual assessment at 100x magnification confirms these results.



In contrast to the previously mentioned fillers even after extruding twice the amount (5 kg) of the compound with Silfit Z 91 neither with the naked eye nor at 100x magnification deposits are made out on the metal insert.

Mold fouling caused by fillers, therefore, can be largely or even totally avoided by working with Silfit Z 91. Detailed judgments, however, will only be obtained by tests under production conditions.

4 Summary

With Silfit Z 91, basic properties can be obtained which are between those with Sillitin N 85 and Sillikolloid P 87. As a result, this new filler fits easily into the product range of Neuburg Siliceous Earth.

Compared with calcined clay, Silfit Z 91 imparts higher tensile and tear resistance, in particular when the silica in the compound is replaced.

Apart from the higher tensile strength and tear resistance, the faster cure rate and thus shorter conversion time t_{90} speaks in favor of replacing the silica. Furthermore, the study has confirmed that the replacement of the silica with a higher amount of mineral filler does not give rise to any negative effects.

The immersion in detergent is another aspect that justifies the replacement of the silica. Due to marginal changes of hardness, tensile strength and elongation at break, the benefits of Silfit Z 91 regarding the mechanical properties remain. Additionally, a smaller change of volume can be accomplished by the substitution of silica.

In view of the very bright and neutral color of Silfit Z 91, the addition of color pigments – in this case titanium dioxide and carbon black – can be reduced without negatively affecting the color quality of the compound.

A further benefit of Silfit Z 91 is the reduction or total elimination of filler induced mold fouling. As a result, there will be no down times due to stoppage of the production units for maintenance and cleaning purposes. Moreover, the new filler helps to ensure a consistent and outstanding surface quality.