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Unternehmensgruppe Hoffmann

Silfit Z 91

in Conventional and

Non-Conductive Car Body Seals

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1 Introduction

Car body seals can be subdivided into two kinds, i.e. conventional and electrically insulating (non-conductive) compounds.

The major filler in the conventional seals is carbon black. Mineral fillers here are used to improve the surface quality of the extruded sections.

The automotive industry has been using for several years increasing amounts of light metals such as aluminum and magnesium. In combinations with steel and conventionally formulated seals electrochemical corrosion can occur at the less noble metal. In order to avoid this, electrically insulating seal sections are required. The use of non-conductive fillers makes it possible to produce such insulating seals.

For this purpose, Neuburg Siliceous Earth is outstandingly suitable because of its high electrical resistivity, which means the carbon black loading and thus the conductivity of the compound can be brought down.

Until now, only non-calcined Siliceous Earth fillers have found application in this field. As Hoffmann 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.

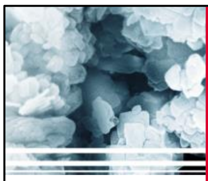
In the present study, the effect of Silfit Z 91 in a conventional and an electrically insulating formulation for car body seals is evaluated in comparison with Sillitin, Sillikolloid and a calcined clay.

In particular, basic properties and extrusion characteristics will be highlighted.

Furthermore, the effect of the calcined Silfit Z 91 on filler-induced deposits (plating) will be evaluated. The occurrence of plating tends to negatively affect the surface quality of extruded 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



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Base Formulation
Car Body Seal

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	conventional	non-conductive
Keltan 8340 A	100.00	100.00
Zinkoxyd aktiv	5.00	5.00
Stearic Acid	1.00	1.00
PEG 3000	2.00	2.00
Calcium oxide	5.50	5.50
Corax N 550/30	**110.00**	**60.00**
Mineral filler	**50.00**	**155.00**
Sunpar 2280	65.00	65.00
Rhenogran DPG-80	0.50	0.50
Rhenogran MBTS-80	1.30	1.30
Rhenogran ZBEC-70	2.00	2.00
Rhenogran S-80	0.75	0.75
Rhenogran CLD-80	1.00	1.00
Rhenogran TP-50	2.00	2.00
Vulkalent E/C	0.50	0.50
Rhenogran CBS-80	0.50	0.50
Total	**347.05**	**402.05**

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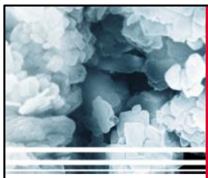
Keltan 8340 A:	EPDM, amorphous
Zinkoxyd aktiv:	zinc oxide active
Stearic Acid:	processing aid
PEG 3000:	polyethylene glycol
Calcium oxide:	drying agent
Corax N 550/30:	carbon black
Sunpar 2280:	paraffinic oil, plasticizer
Rhenogran DPG-80:	diphenylguanidine (80 %)
Rhenogran MBTS-80:	dibenzothiazolyl disulfide (80 %)
Rhenogran ZBEC-70:	zinc dibenzyldithiocarbamate (70 %)
Rhenogran S-80:	sulfur (80 %)
Rhenogran CLD-80:	caprolactam disulfide (80 %)
Rhenogran TP-50:	zinc dialkyldithiophosphate (50 %)
Vulkalent E/C:	cure retarder
Rhenogran CBS-80:	cyclohexyl benzothiazolesulfenamide (80%)
Mineral filler:	see 2.2 "Mineral fillers and compound preparation"

2.2 Mineral fillers and compound preparation



Fillers, Characteristics

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		Calcined Clay	Neuburg Siliceous Earth		
		Polestar 200 R	Sillitin Z 86	Sillikolloid P 87	Silfit Z 91
Particle Size d_{50}	[µm]	3.6	1.4	1.1	2.0
Particel Size d_{97}	[µm]	19	6.9	4.3	10
Oil Absorption	[g/100g]	60	48	53	59
Specific surface area (BET)	[m²/g]	6.5	11	12	7.6
Calcination		yes	none	none	yes

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

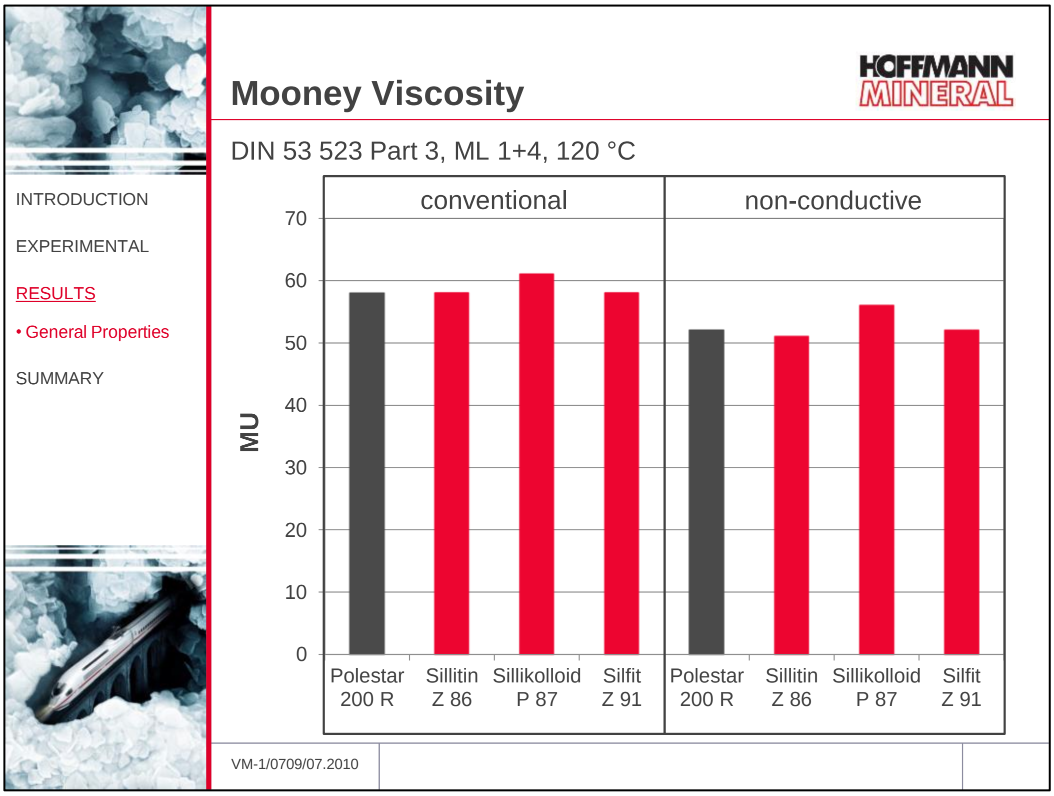
The calcined clay is somewhat coarser than the Neuburg Siliceous Earth grades. The oil absorption and the specific surface area are in a comparable range with Silfit Z 91.

The specific surface areas of the two standard Siliceous Earth grades are higher compared with the fillers mentioned above. Sillikolloid P 87 offers the lowest grain size of all fillers included, and thus has the highest degree of fineness. Sillitin Z 86 with regard to the grain size fits in between Sillikolloid P 87 and Silfit Z 91, in fact very close to the calcined Silfit grade. The oil absorptions of Sillitin Z 86 and Sillikolloid P 87 are on a comparable level, somewhat below Silfit Z 91.

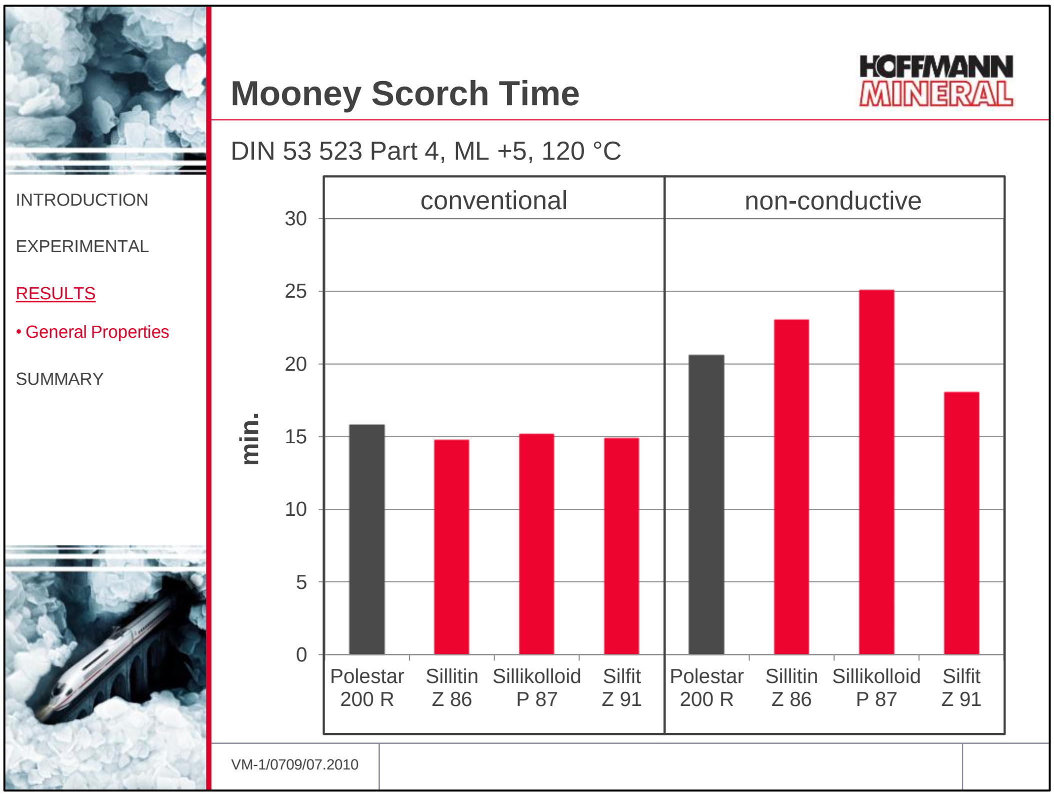
The compounding was done on a laboratory mill (Schwabenthan Polymix 150 L).
The rubber was fed to the mill at 50 °C, subsequently all other components were added at constant mill temperature in the sequence of the formulation. A typical mixing time was 15 minutes.

3 Results

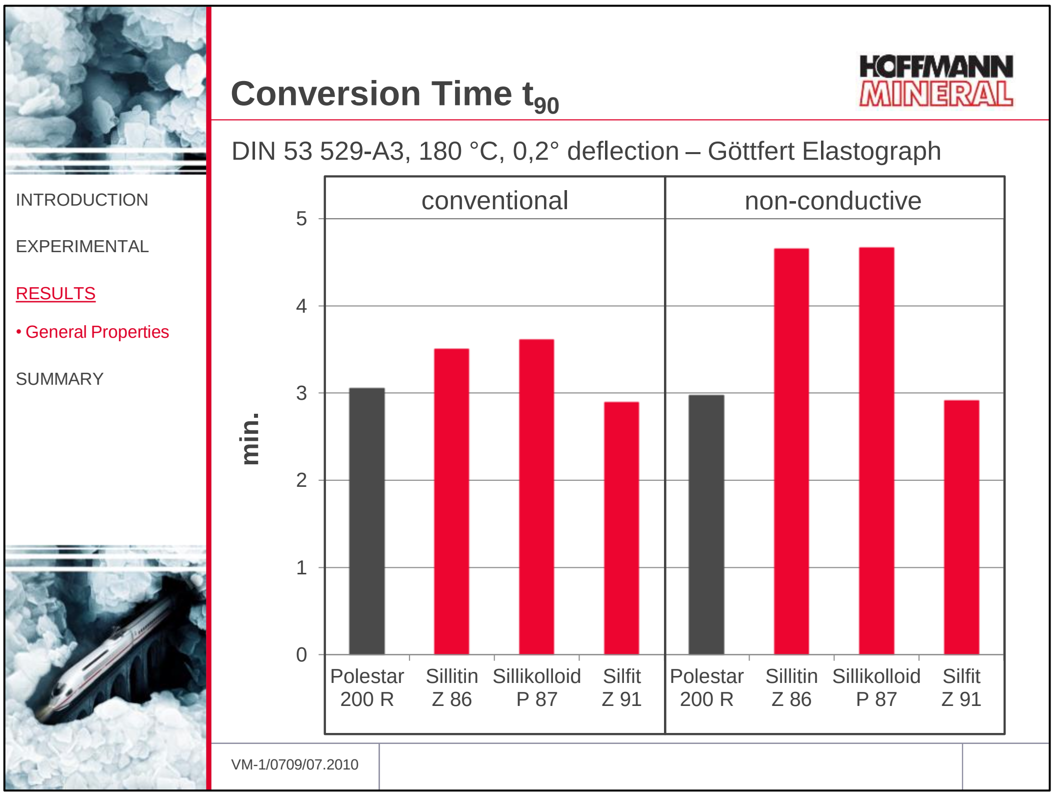
3.1 Viscosity, scorch and cure characteristics



The graph indicates that Silfit Z 91 does not give any significant differences versus the standard Siliceous Earth grades and the calcined clay.
The partial replacement of carbon black by mineral filler leads in all compounds to a slight reduction of the viscosity.



The viscosity increase from the minimum by 5 units with all fillers takes sufficiently long time. In the conventional formulation, all compounds come out with about 15 minutes.
The partial replacement of carbon black increases the scorch time with the calcined clay and the standard Siliceous Earth grades considerably, with Silfit Z 91, by contrast, only moderately.

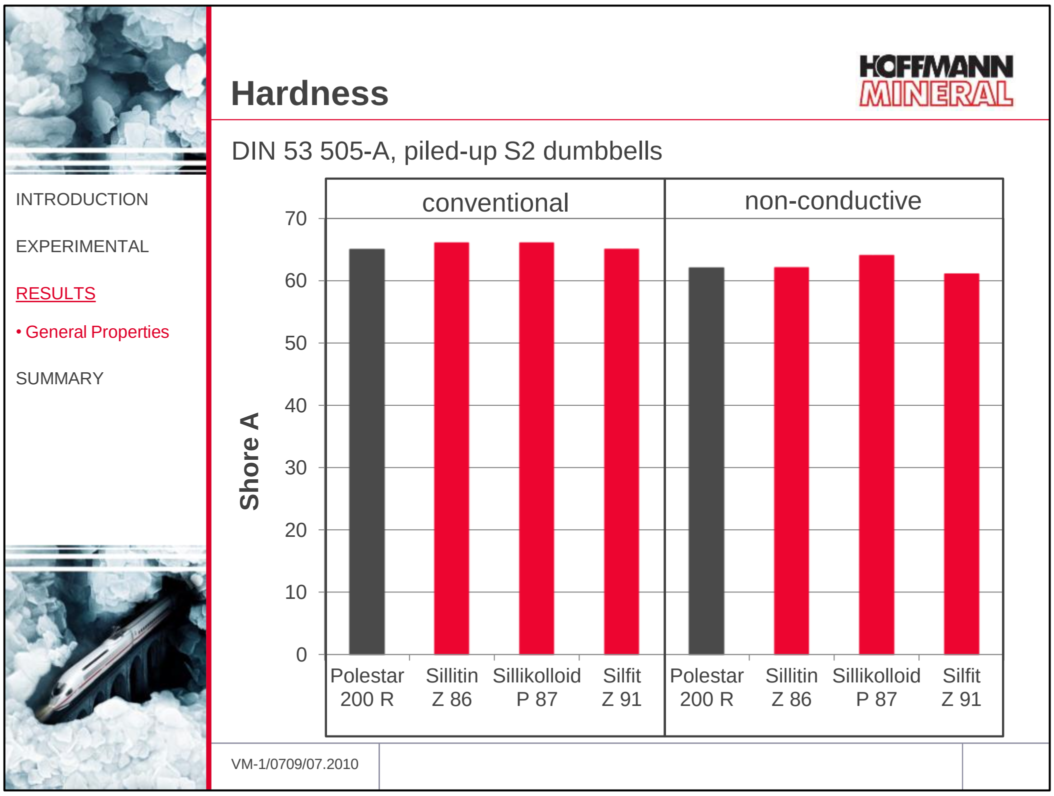


The conversion times t_{90} are fairly short for all compounds. The trend towards shorter conversion times of the calcined products comes out more pronounced in the non-conductive formulation. This way, Silfit Z 91 offers a markedly shorter t_{90} than Sillitin Z 86 or Sillikolloid P 87.

3.2 Cured rubber properties

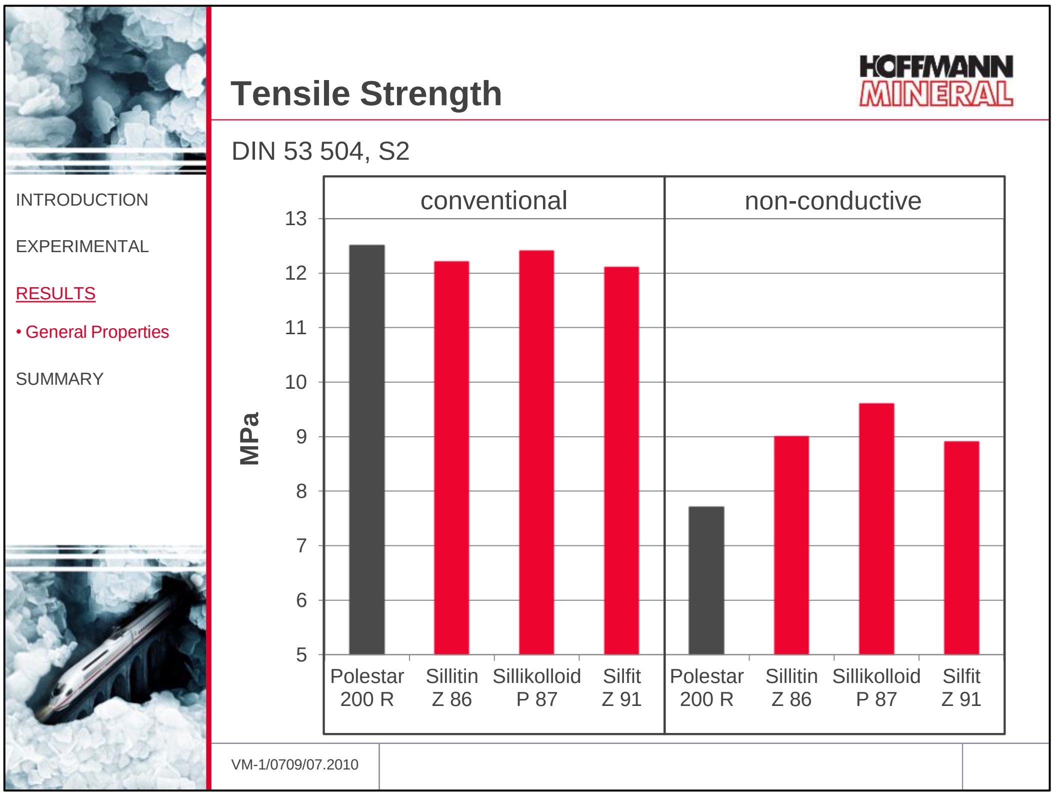
The compounds were press cured at 180 °C.

For 2 mm sheets, 6 minutes were used, and 8 minutes for the thicker samples for compression set testing.



Hardness was determined on three piled-up S2 dumbbells. No significant difference can be found between the individual fillers.

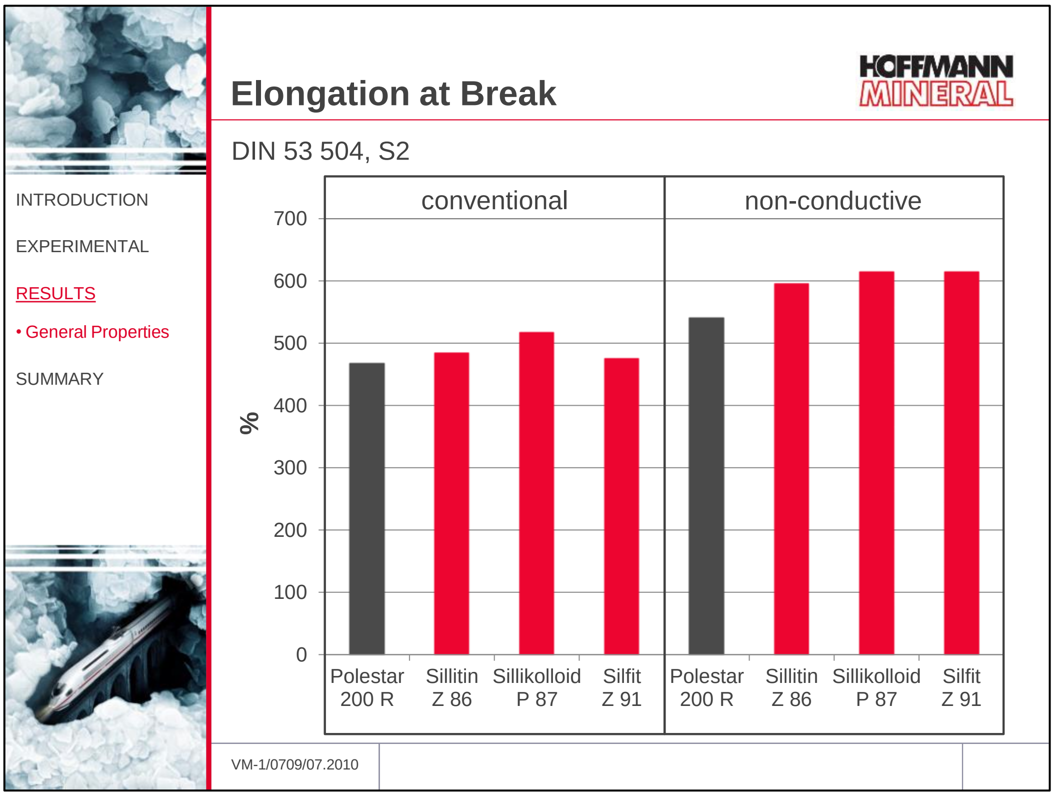
The partial replacement of carbon black by mineral filler in a 1 : 2 ratio in all cases leads to largely equal hardness, which should allow a good comparison for the other cured rubber properties.



In the conventional formulations, the tensile strength does not show any significant difference between the individual fillers.

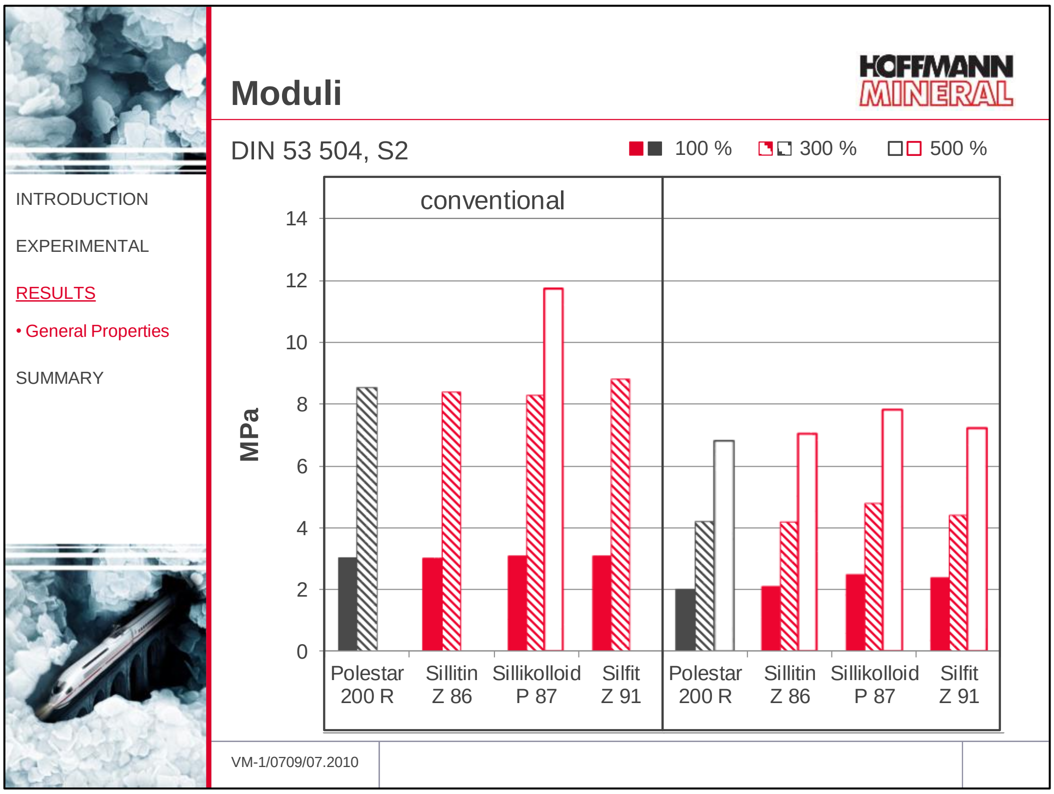
In the non-conductive compounds, the use of Neuburg Siliceous Earth grades results in a higher tensile strength compared with the calcined clay. Sillitin Z 86 and Silfit Z 91 are about on the same level, with Sillikolloid P 87 somewhat higher. As already mentioned, all compounds of this study have been mixed on a laboratory mill. That means that the components including the filler were dispersed ideally.

Since Silfit Z 91 has excellent dispersion properties even at low shearing forces, it is supposed to be well dispersed in a compound mixed in an internal mixer. Therefore, with Silfit Z 91 a higher tensile strength level than with the standard Siliceous Earth grades could be obtained and the advantage over calcined clay could be even more pronounced.

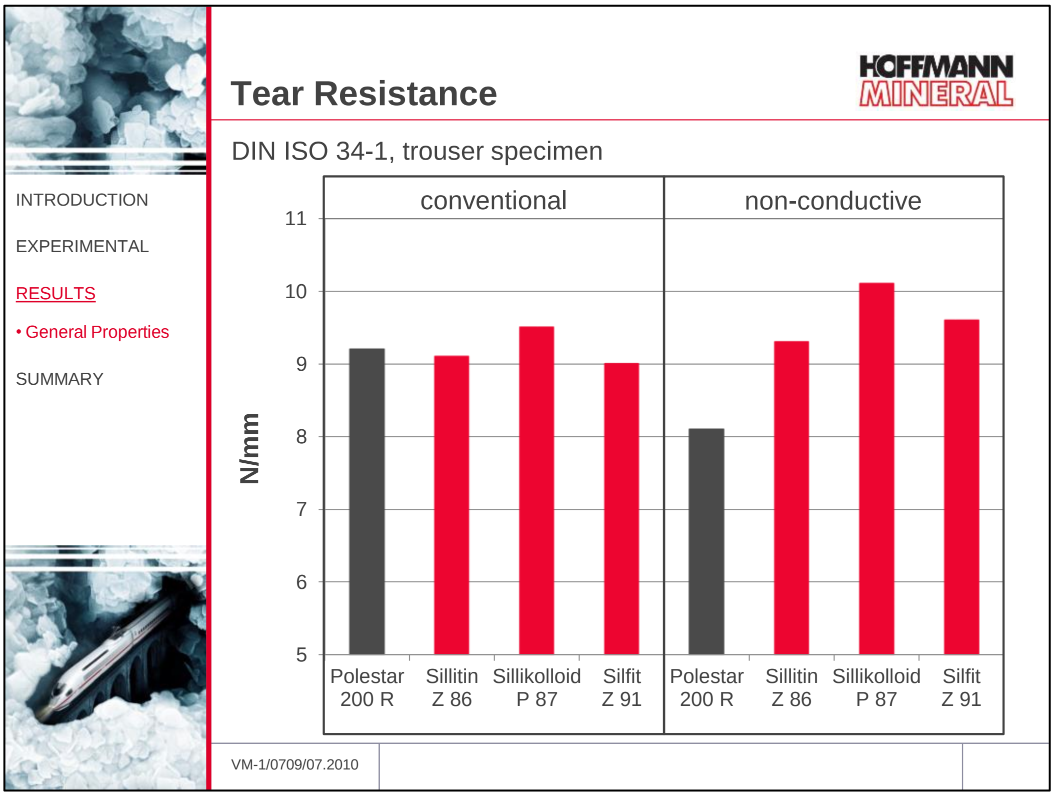


As shown in the graph, in the conventional compounds the highest elongation at break is obtained with Sillikolloid P 87; Silfit Z 91, Sillitin Z 86 and the calcined clay come out at a somewhat lower level.

For the non-conductive compounds, the level of the elongation at break is generally somewhat higher. For Silfit Z 91 and Sillitin Z 86 this increase comes out so important that both become comparable with Sillikolloid P 87, which here again delivers a level higher than the calcined clay.

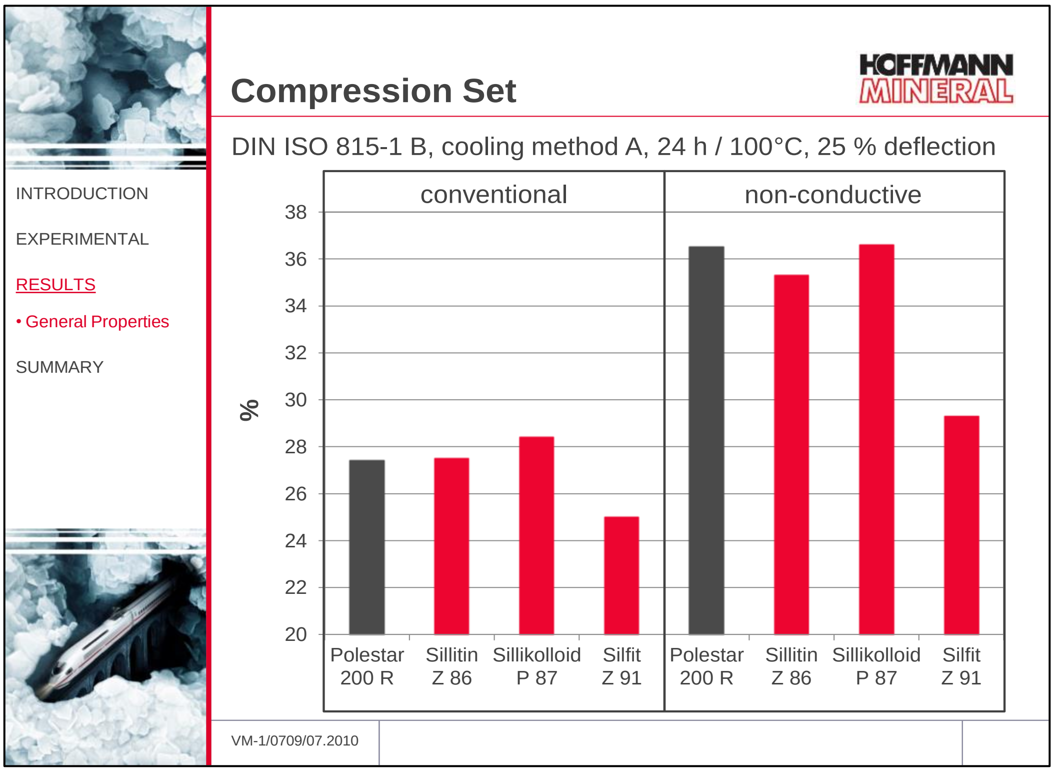


The moduli obtained with the individual fillers are on a comparable level, both for the conventional and for the non-conductive formulations. The partial replacement of carbon black in the non-conductive compounds results for all formulations in a lower level of the moduli compared with the conventional approach.

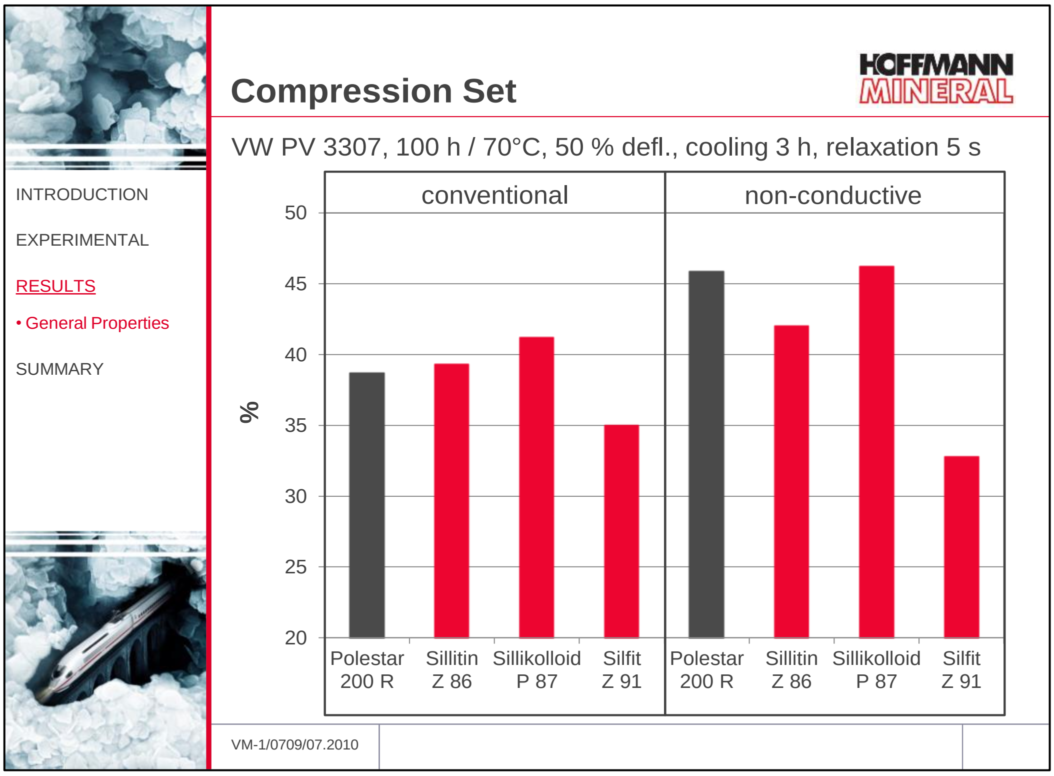


The filler selection in the conventional formulations has no significant effect on the tear resistance, as shown in the graph.

If the portion of mineral filler is increased, such as in the non-conductive compounds, the tear resistance is reduced in the compound with calcined clay, while the compounds with Neuburg Siliceous Earth products offer somewhat higher results. The highest tear resistance is obtained with Sillikolloid P 87, and Sillitin Z 86 and Silfit Z 91 come off at a comparable level just slightly lower.



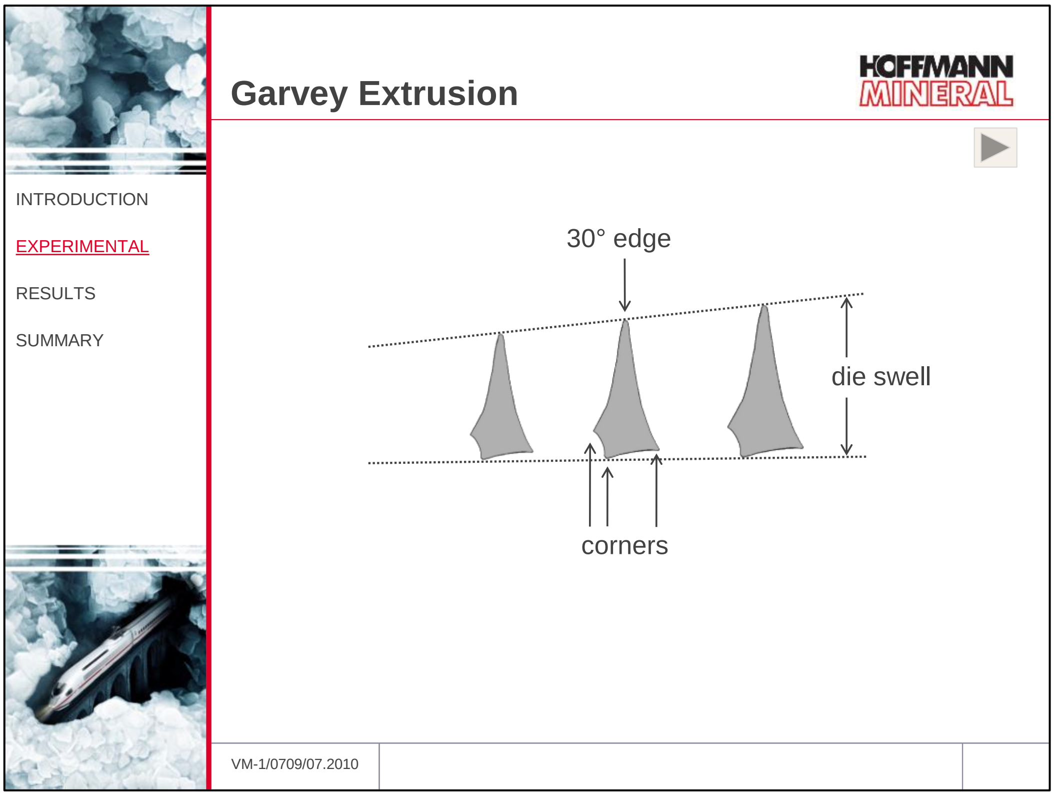
The test conditions for the compression set according to DIN ISO 815, B were 24 hours at 100 °C under 25 % deflection. The figure shows that in the conventional as well as in the non-conductive compounds the calcined clay and the standard Siliceous Earth grades impart a similar level. Silfit Z 91, by contrast, allows arriving at the lowest compression set results both in the conventional and in the non-conductive formulations.



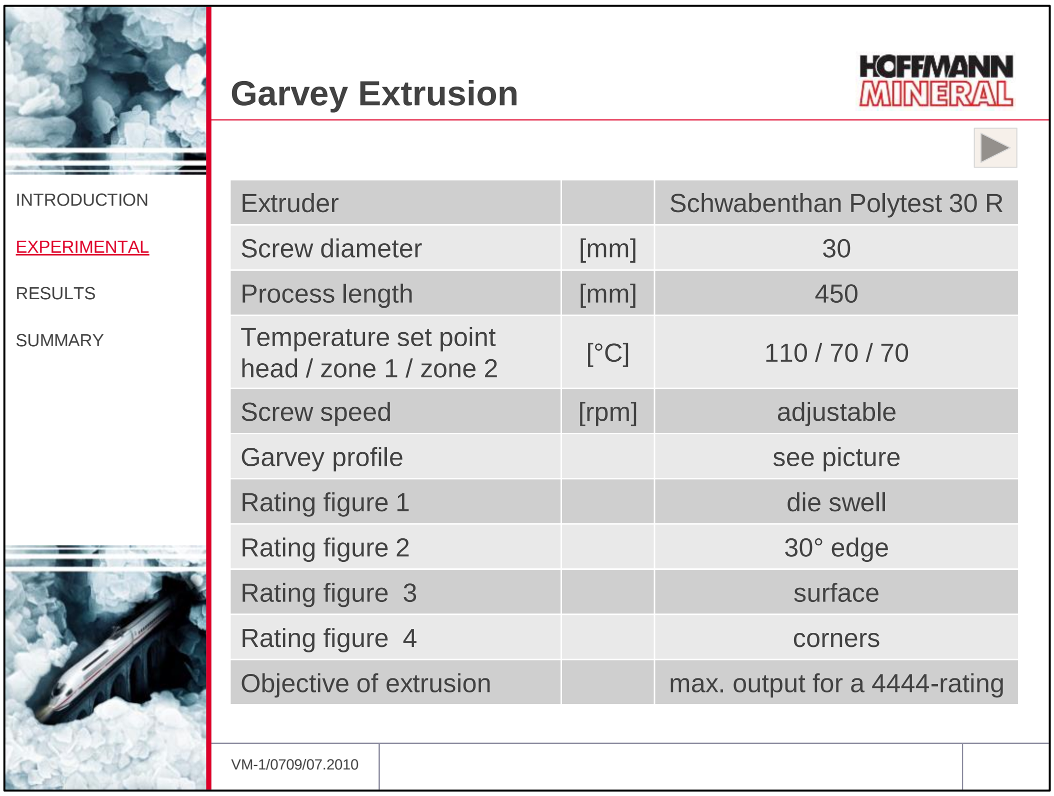
The test conditions for the compression set according to the VW test standard 3307 were 70 hours at 100 °C under 50 % deflection, cooling down for 3 hours (still under deflection), and a relaxation time of 5 seconds .
Even under these demanding test conditions the compounds with Silfit Z 91 yield the lowest compression set, while the other fillers more or less come out at a comparable level.Furthermore it becomes evident that the replacement of carbon black by Silfit Z 91 does not bring about an increase of the compression set, as is the case with the standard Siliceous Earth grades and also the calcined clay.

3.3 Extrusion properties

In order to enable a quality assessment, extrusion tests according to Garvey were carried out. Apart from the usual reporting of length output, the special die geometry allows to judge edge formation, surface quality and swelling of the extrusions.



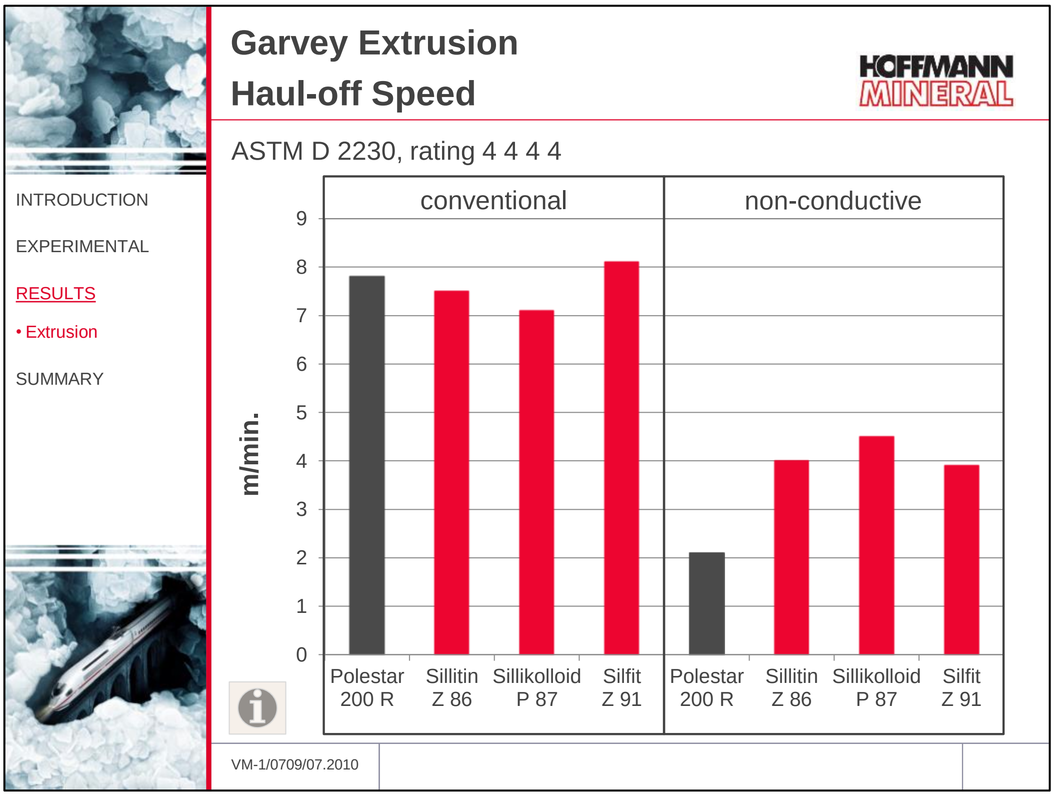
The following table lists the parameters of the extrusion test:



Extruder		Schwabenthan Polytest 30 R
Screw diameter	[mm]	30
Process length	[mm]	450
Temperature set point head / zone 1 / zone 2	[°C]	110 / 70 / 70
Screw speed	[rpm]	adjustable
Garvey profile		see picture
Rating figure 1		die swell
Rating figure 2		30° edge
Rating figure 3		surface
Rating figure 4		corners
Objective of extrusion		max. output for a 4444-rating

For each compound, it was tried to arrive at a maximum length output for a „4444“ rating (4 is the best rating in the Garvey test, so 4444 confirms very good swelling, 30° edge, surface quality and corner shaping).

The qualitative assessment was made according to ASTM D2230 on uncured extruded sections.



As can be seen in the graph, the conventional versions come out with marginal differences with respect to the maximum output for qualitatively good extrusions.

The electrically non-conductive compounds are characterized by a reduced length output. With the Neuburg Siliceous Earth grades, this reduction, however, is less pronounced as with the calcined clay. The two standard Siliceous Earth grades and the calcined Silfit Z 91 arrive at comparable throughput rates, and this markedly above the calcined clay.

3.4 Plating - Filler induced deposits

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.

The filler selection, apart from other factors, can play a significant role with respect to the occurrence of plating.

In order to arrive at a meaningful statement with regard to the fillers tested here, the standard plating test was carried out with a special compound.

Base Formulation Die Plating

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	≙ conventional		≙ non-conductive	
Vistalon 8600	100	100	100	100
Sunpar 2280	75	75	75	75
Corax N 550/30	**90**	**90**	**60**	**60**
Sillitin Z 86	**50**		**110**	
Silfit Z 91		**50**		**110**

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Vistalon 8600: EPDM, amorphous
Sunpar 2280: paraffinic oil, plasticizer
Corax N 550/30: carbon black

For the tests, a modified formulation was used which contained only the polymer, the plasticizer, the carbon black and the mineral filler, in order to exclude other potential effects with regard to the development of deposits.
The loading of the carbon black / mineral filler blends in the above formulation were adjusted in accordance with the proportions between conventional and non-conductive car body seal compounds.

Experimental Parameters

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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

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This table lists the parameters of the plating test.

Measuring Device

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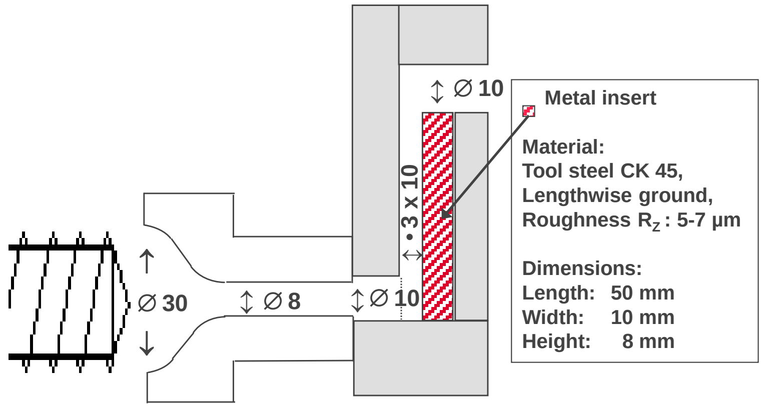

all dimensions in mm

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Here the dimensions of the adapted die and the measuring device are indicated.

Deposits on the Metal Insert

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• Plating

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	≙ conventional		≙ non-conductive	
	Sillitin Z 86	Silfit Z 91	Sillitin Z 86	Silfit Z 91
extruded amount [kg]	5	5	5	5
throughput [g/min.]	546	570	616	600

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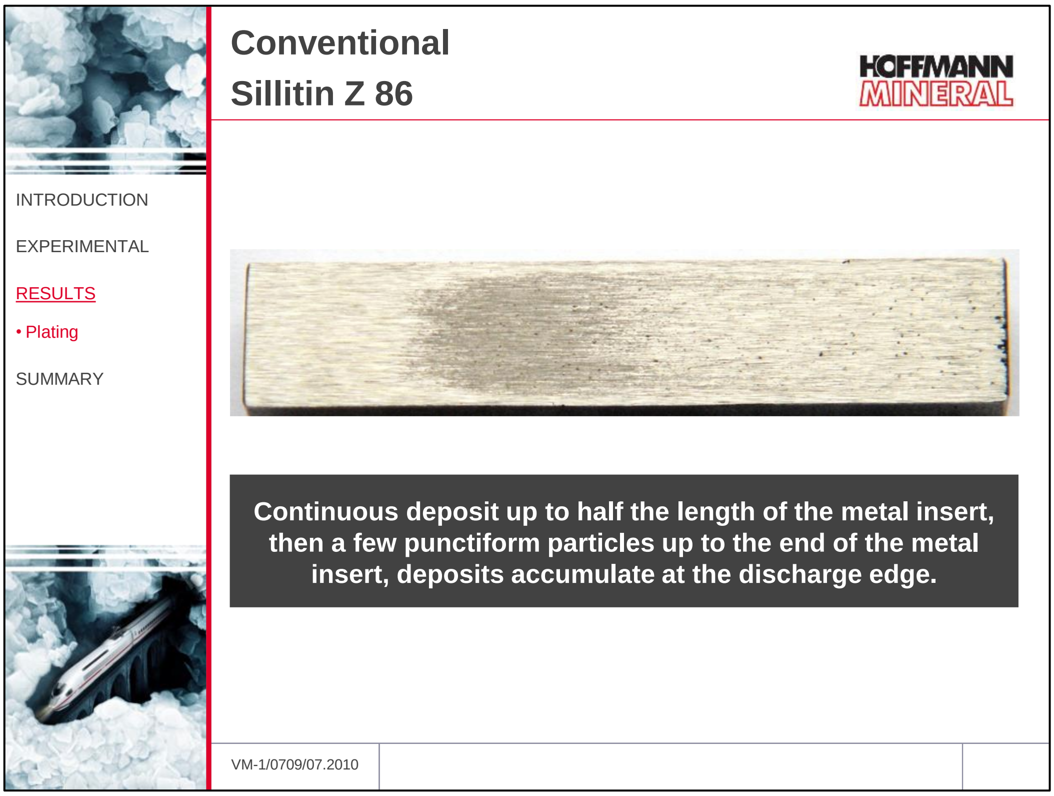
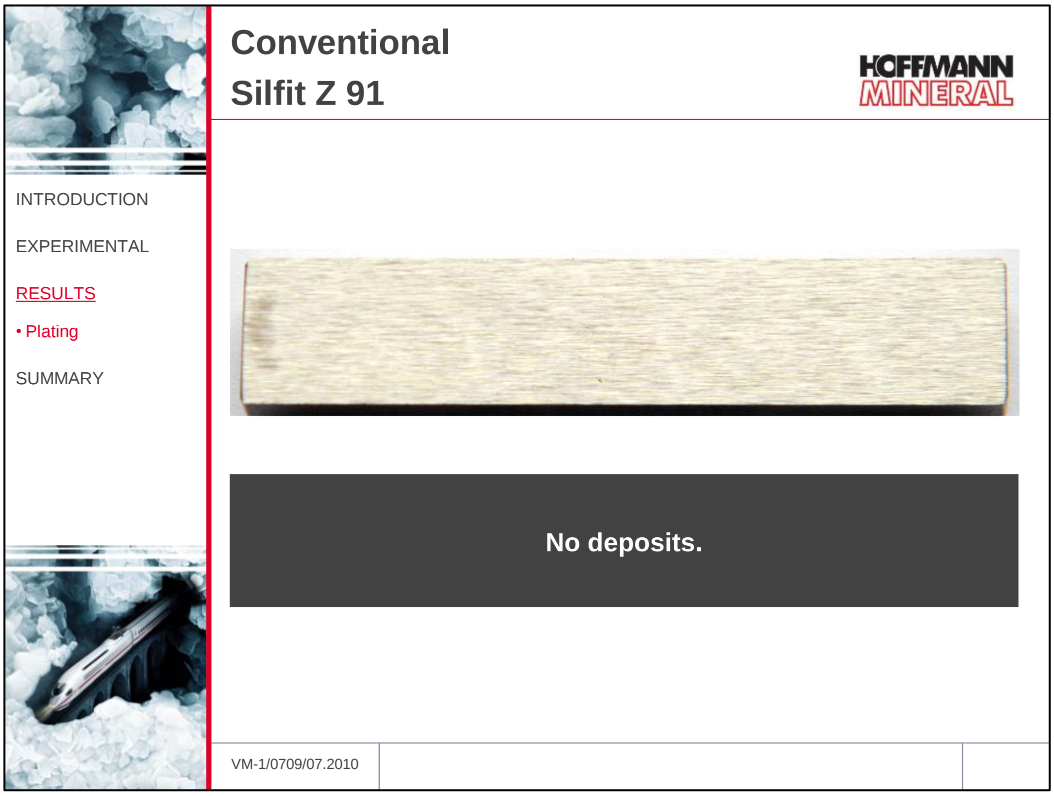
Of each compound, 5 kg were extruded, after which the metal inserts were removed and visually assessed.

As the table shows, the mass throughput with the non-conductive compound is higher than what can be obtained with the traditional formulations. This results in a higher shear rate which will generally cause increased deposits.– as has been demonstrated in the study on „Die- Plating“.

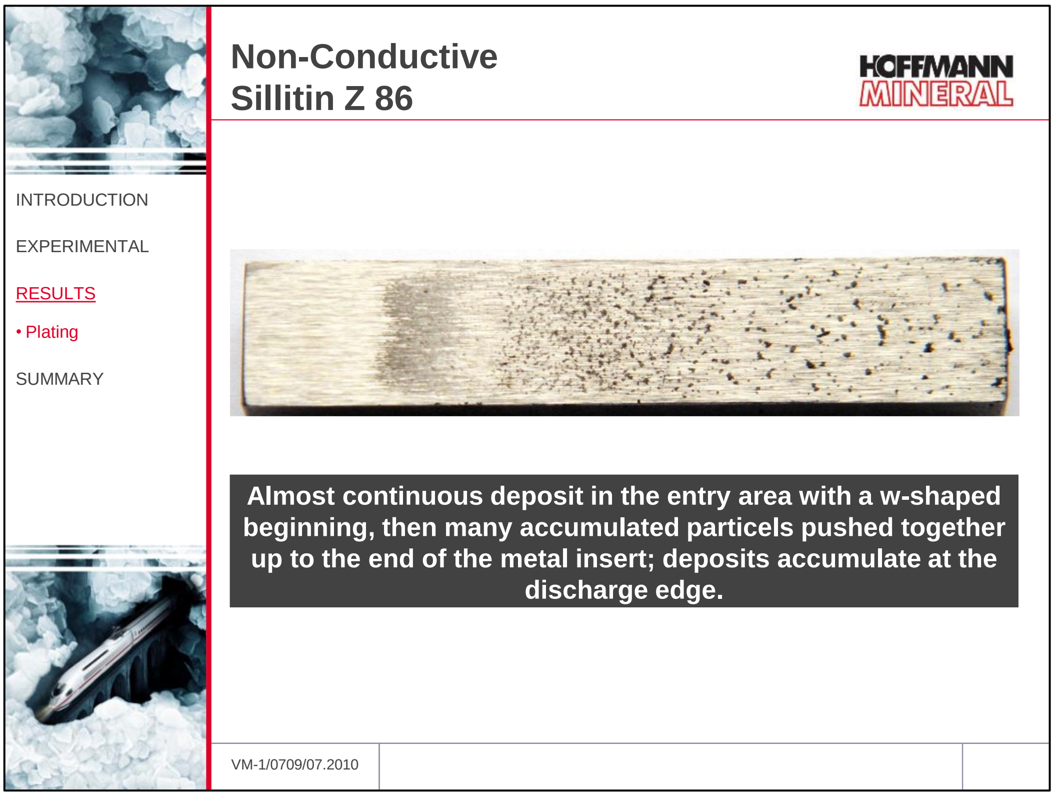
The overall images of the metal inserts show this for Sillitin Z 86, while Silfit Z 91 in all formulations remains free from deposits.



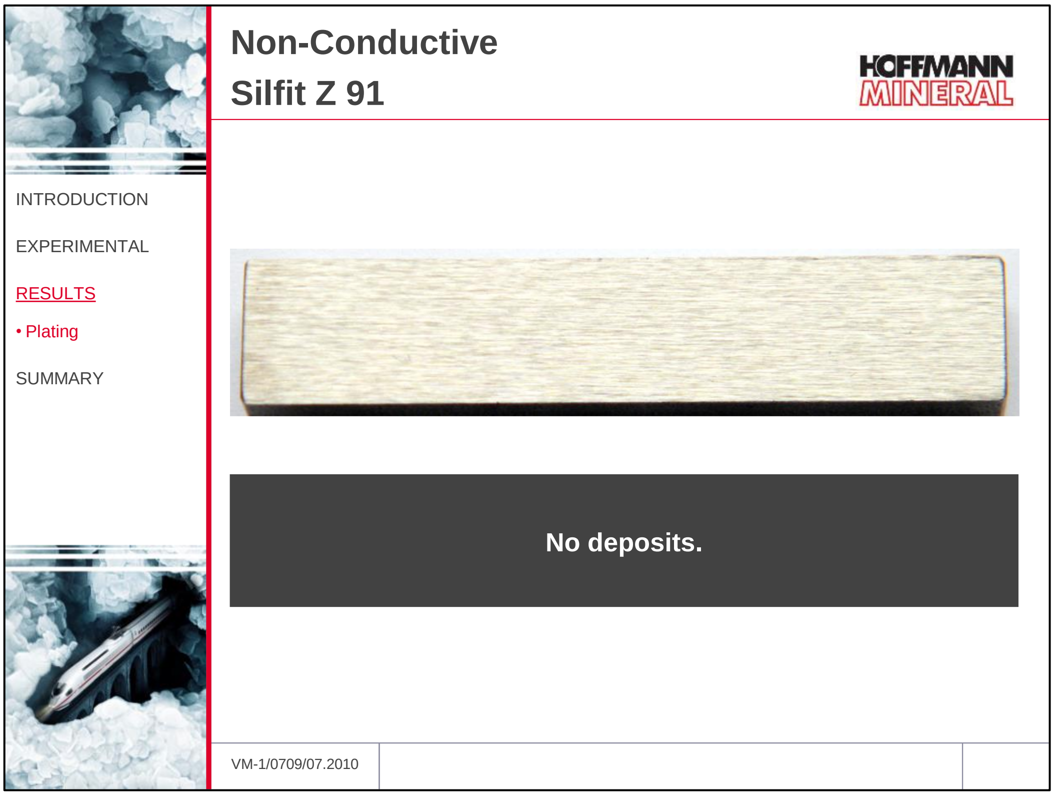
With the conventional formulation loaded with Sillitin Z 86, a continuous deposit is formed on half of the metal insert and then some punctiform particles are detected up to its end, with a certain accumulation at the exit edge. At the end of the test, deposits are also visible on the surface opposite the metal insert. The visual evaluation at 100x magnification confirms these results.
Sillikolloid P 87 gives similar characteristics.



As evident from the figure, with Silfit Z 91 no deposits can be spotted on the metal insert. The visual evaluation at 100x magnification confirms this result.



With Sillitin Z 86 in the electrically non-conductive compound, a continuous deposit is formed at the entry area with a w-shaped onset. After that, many pushed-together particle accumulations are visible up to the end of the metal insert, which gather close together at the exit edge. Deposits can be seen on the surface opposite the metal insert, too. The visual assessment at 100x magnification confirms this result.
Sillikolloid P 87 shows similar characteristics.



Similar to the conventional formulation, also in the non-conductive compound which contains a higher mineral filler loading, Silfit Z 91 does not give rise to any deposits. The visual observation at 100x magnification confirms this result. Filler induced deposits, therefore, can be largely or even totally avoided by working with Silfit Z 91.

4 Summary

With Silfit Z 91, in principle similar general and extrusion properties can be obtained as with Sillitin / Sillikolloid. This special grade, therefore, fits smoothly into the product range of Neuburg Siliceous Earth.

Silfit Z 91 positively affects the conversion time t_{90}, which means faster cure.

In conventional car body seal compounds, Silfit Z 91 leads to general properties which are similar to those with calcined clay.

In addition, Silfit Z 91 leads to a better compression set than the calcined clay.

This improved compression set with Silfit Z 91 comes out even more pronounced in the non-conductive formulation.

Versus calcined clay, Silfit Z 91 allows here to arrive at a higher tensile strength and at the same time at a higher tear resistance.

Another advantage of Silfit Z 91 in comparison with calcined clay is the higher extrusion rate which makes it possible to produce even complex section geometries faster, i.e. with reduced costs. This will be further boosted, as already mentioned, by the shorter time to full cure.

Moreover, Silfit Z 91 helps to avoid filler induced deposits during the extrusion process. This way, there are no downtimes due to stoppage of the extrusion line for cleaning purposes.

In total, Silfit Z 91 offers a very favorable property profile, which maintains and even improves the strong points of Sillitin / Sillikolloid such as extrusion characteristics and compression set, and this without showing the tendency towards plating even under unfavorable working conditions.