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Unternehmensgruppe Hoffmann

Neuburg Siliceous Earth in diaphragms for expansion vessels in water systems based on SBR, DIN EN 13831

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Contents

1 Introduction

The standard DIN EN 13831 "Closed expansion vessels with built in diaphragm for installation in water" describes the design of closed expansion vessels which are intended for the use in water systems.

The water systems for which these expansion vessels can be used according to DIN EN 13831 are, among others, heating circuits and fresh water systems.

With heating, the water volume in these systems will increase. In order to arrange with this higher volume, expansion vessels are used which include an elastic diaphragm.

This diaphragm is an elastomeric component which can be produced of different polymers, e.g. IIR, NBR, NR, EPDM or SBR. In typical formulations, carbon black N550 serves as filler.

In the present study, the property profile of an SBR based formulation which simply contains carbon black, will be compared with different versions where part of N550 is replaced by Neuburg Siliceous Earth.

The effect of this partial replacement of carbon black with Neuburg Siliceous Earth on the cost of the compounds will also be discussed.

2 Experimental

2.1 Formulation and compound preparation

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY

Base Formulation

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Material	Description	phr
Buna SB 1502	SBR rubber Styrene: 23 %, ML 1+4 (100 °C): 50 MU	100
N550	Carbon Black FEF	90
Nytex 4700	naphtenic plasticizer	45
Dispergator FL	Process aid	1.4
Lipoxol 4000	Process aid, PEG	0.86
Zinkoxyd aktiv	Vulcanization activator	3
Stearic acid	Vulcanization activator / process aid	2
Vulkanox HS/LG	Antioxidant, TMQ	0.4
Vulkanox 4020/LG	Antioxidant, p-phenylendiamine	0.4
Sulfur	Vulcanizing agent	1.9
Rhenogran TMTD-70	Accelerator, TMTD, 70 %	1.5
Rhenogran MBTS-80	Accelerator, MBTS, 80 %	1.5
Total		**247.96**

VM-0/0116/01.2016

Fig. 1

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY

Formulation Variations

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in phr	N550	-N550, +Sillitin Z 86		
TMTD / MBTS	**1.5 / 1.5**	**1.5 / 1.5**	**1.5 / 1.5 - PEG**	**2 / 1 - PEG**
N550	90	60	60	60
Sillitin Z 86	-	60	60	60
Lipoxol 4000	0.86	0.86	-	-
Rhenogran TMTD-70	1.5	1.5	1.5	2
Rhenogran MBTS-80	1.5	1.5	1.5	1
Total	**247.96**	**277.96**	**277.10**	**277.10**

VM-0/0116/01.2016

Fig. 2

Fig. 1 gives the formulation based on sulfur cured SBR which served as starting point for the present study.

Fig. 2 indicates the formulation variations in which a part of the carbon black was replaced by the Neuburg Siliceous Earth grade Sillitin Z 86. Along with the effects of the different filler system, also the influences of PEG and of a modified accelerator ratio were evaluated.

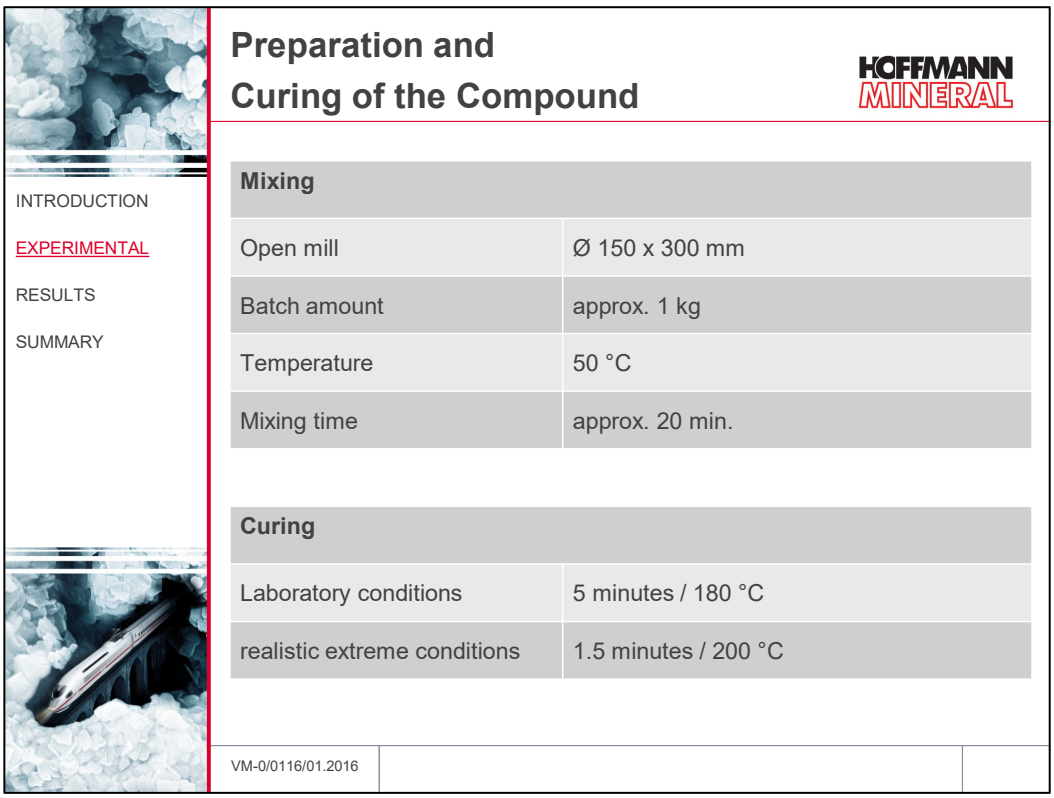


Fig. 3

The compounds were prepared on a laboratory mill (Schwabenthan Polymix 150L). The rubber was given onto the mill at 50 °C and milled to a uniform sheet. Subsequently, the filler and the plasticizer were added in two portions each. With the second portion, also the processing aids and antioxidants were introduced. When all the fillers and additives were incorporated, the sulfur-accelerator system was added. After working in all ingredients, the compound was homogenized by cutting and laying in triangles. The typical mixing time added up to about 20 minutes.

Curing took place under laboratory conditions for 5 minutes at 180 °C; for the extreme injection molding conditions the samples were cured closer to practical industrial situations for 1.5 minutes at 200 °C.

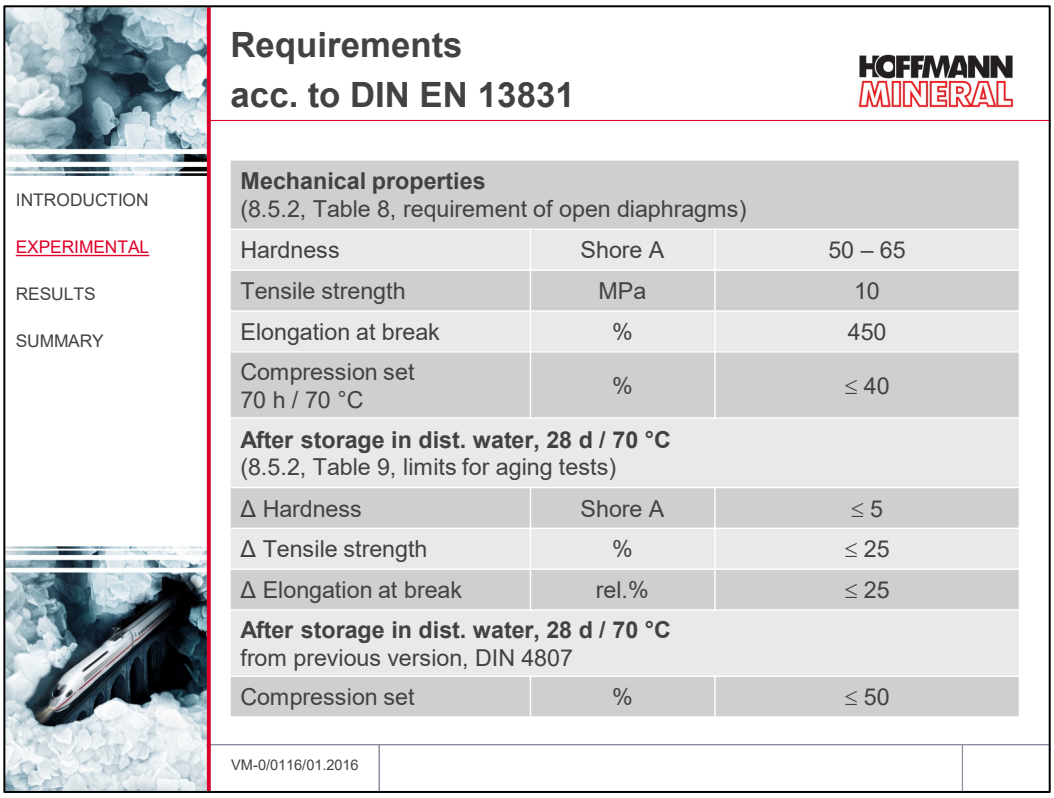
2.2 Requirements

Fig. 4 reviews the requirements of DIN EN 13831.

The results discussed here are compared with the specification for open diaphragms. With respect to compression set, this specification is stricter than the conditions for closed membranes, and is, therefore, more critical to apply.

In DIN EN 13831 the compression set after exposure to water is no longer specified, while there had been a requirement in the previous standard version DIN 4807.

The respective test here was carried out in addition.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

Requirements acc. to DIN EN 13831

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Mechanical properties (8.5.2, Table 8, requirement of open diaphragms)		
Hardness	Shore A	50 – 65
Tensile strength	MPa	10
Elongation at break	%	450
Compression set 70 h / 70 °C	%	≤ 40
After storage in dist. water, 28 d / 70 °C (8.5.2, Table 9, limits for aging tests)		
Δ Hardness	Shore A	≤ 5
Δ Tensile strength	%	≤ 25
Δ Elongation at break	rel.%	≤ 25
After storage in dist. water, 28 d / 70 °C from previous version, DIN 4807		
Compression set	%	≤ 50

VM-0/0116/01.2016

Fig. 4

3 Results

3.1 Rheology

The partial replacement of N550 with Sillitin Z 86 leads to a somewhat lower viscosity (Fig. 5) and at the same time clearly gives rise to an extended scorch time by a factor of more than 2 (Fig. 6).

The curing properties confirm the reduced viscosity as indicated by the results for the torque minima (Fig. 7).

The conversion times t_5 (Fig. 8) and t_{90} (Fig. 9) come out somewhat increased with the partial replacement of N550 by Sillitin Z 86 as indicated by the tests at 180 °C. During injection molding the shear forces generally lead to an increased temperature which is why the curing behavior was also determined at 200 °C. At this temperature, practically no differences exist any longer with respect to the conversion times. In particular, the optimization of the accelerator system with Sillitin Z 86 (TMTD:MBTS = 2:1) leads to conversion times comparable with N550 alone.

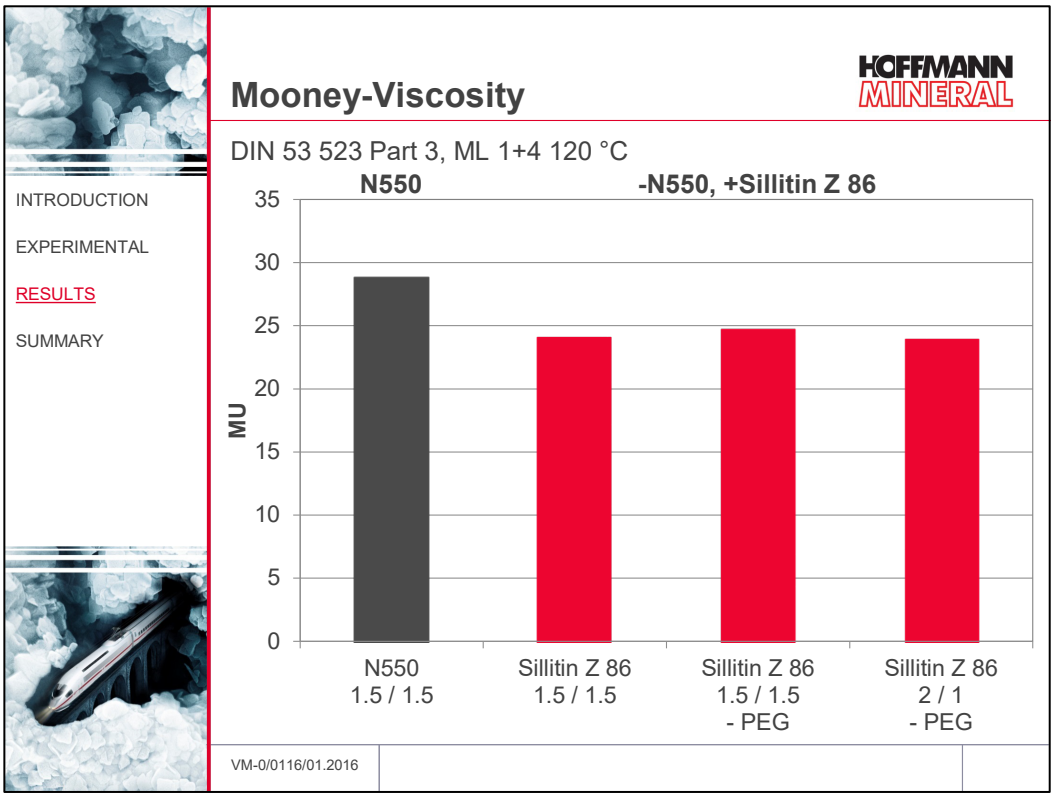

Mooney-Viscosity
HOFFMANN MINERAL
DIN 53 523 Part 3, ML 1+4 120 °C
N550
-N550, +Sillitin Z 86
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
MU
35
30
25
20
15
10
5
0
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
VM-0/0116/01.2016

Fig. 5

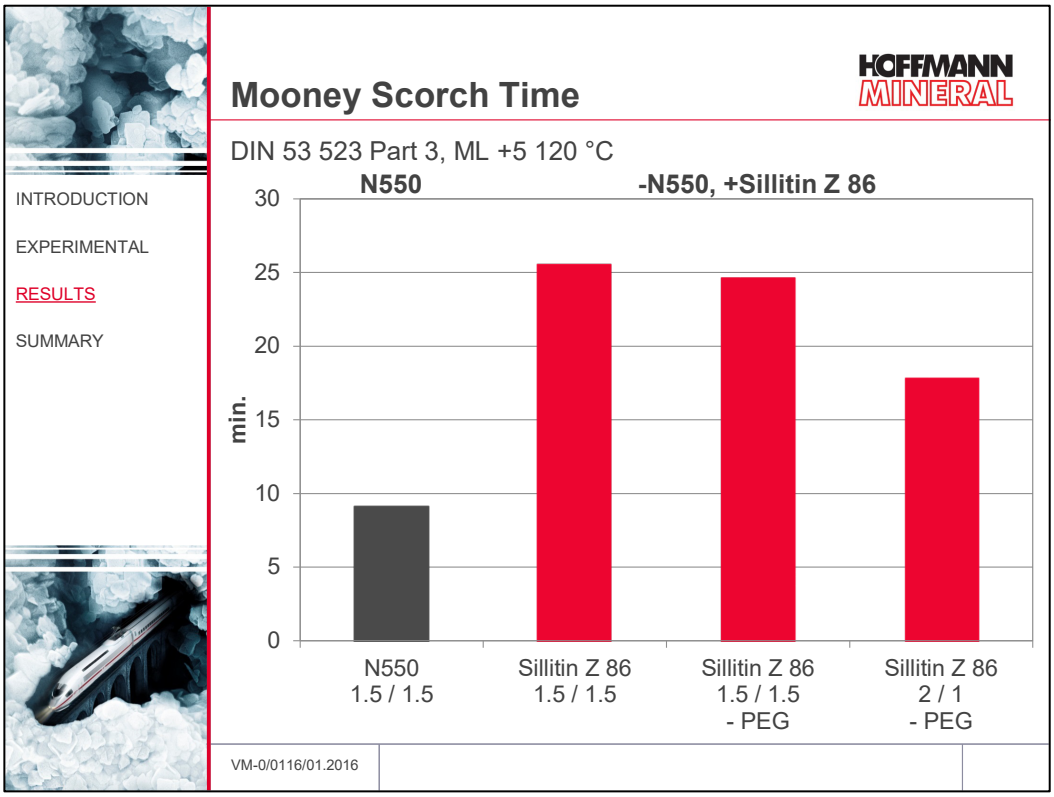

Mooney Scorch Time
HOFFMANN MINERAL
DIN 53 523 Part 3, ML +5 120 °C
N550
-N550, +Sillitin Z 86
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
min.
30
25
20
15
10
5
0
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
VM-0/0116/01.2016

Fig. 6

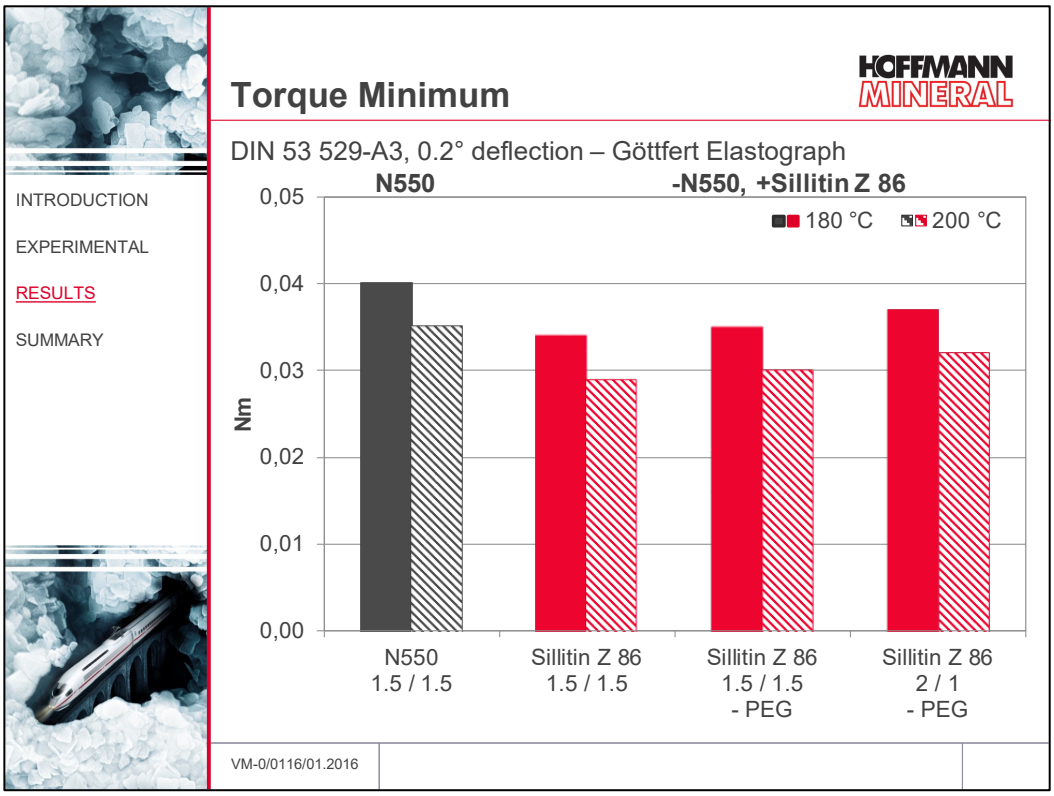

Torque Minimum
HOFFMANN MINERAL
DIN 53 529-A3, 0.2° deflection – Göttfert Elastograph
N550
-N550, +Sillitin Z 86
180 °C
200 °C
Nm
0,05
0,04
0,03
0,02
0,01
0,00
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 7

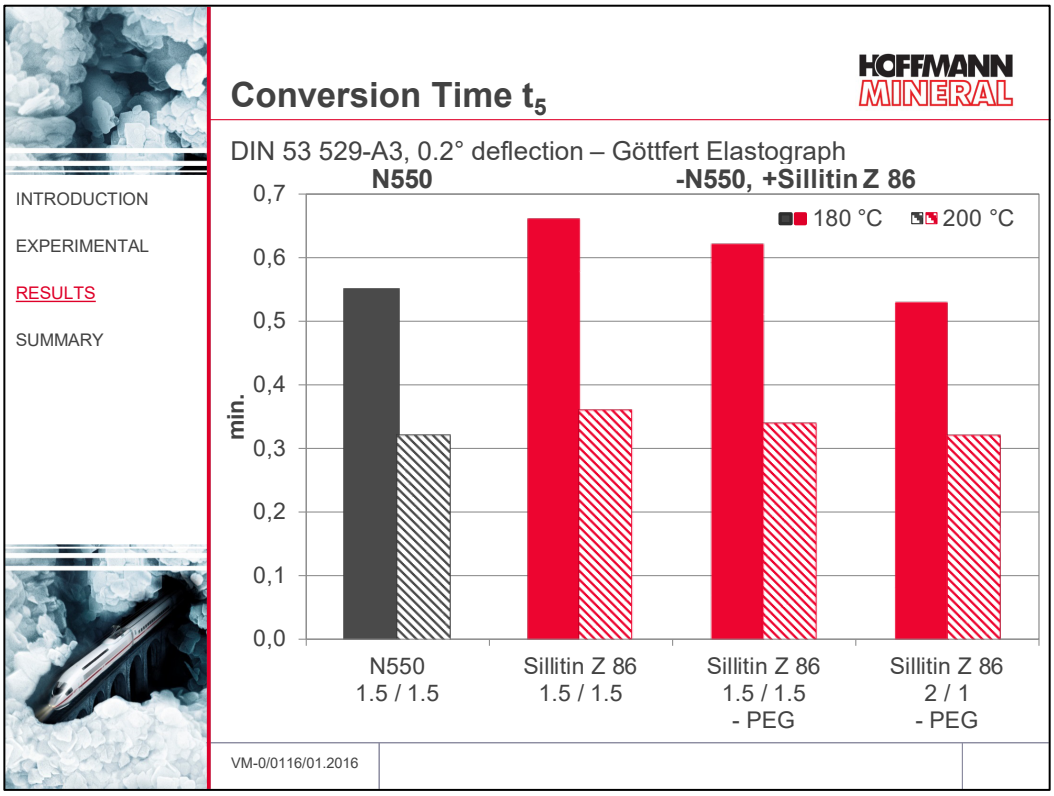

Conversion Time t5
HOFFMANN MINERAL
DIN 53 529-A3, 0.2° deflection – Göttfert Elastograph
N550
-N550, +Sillitin Z 86
180 °C
200 °C
min.
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 8

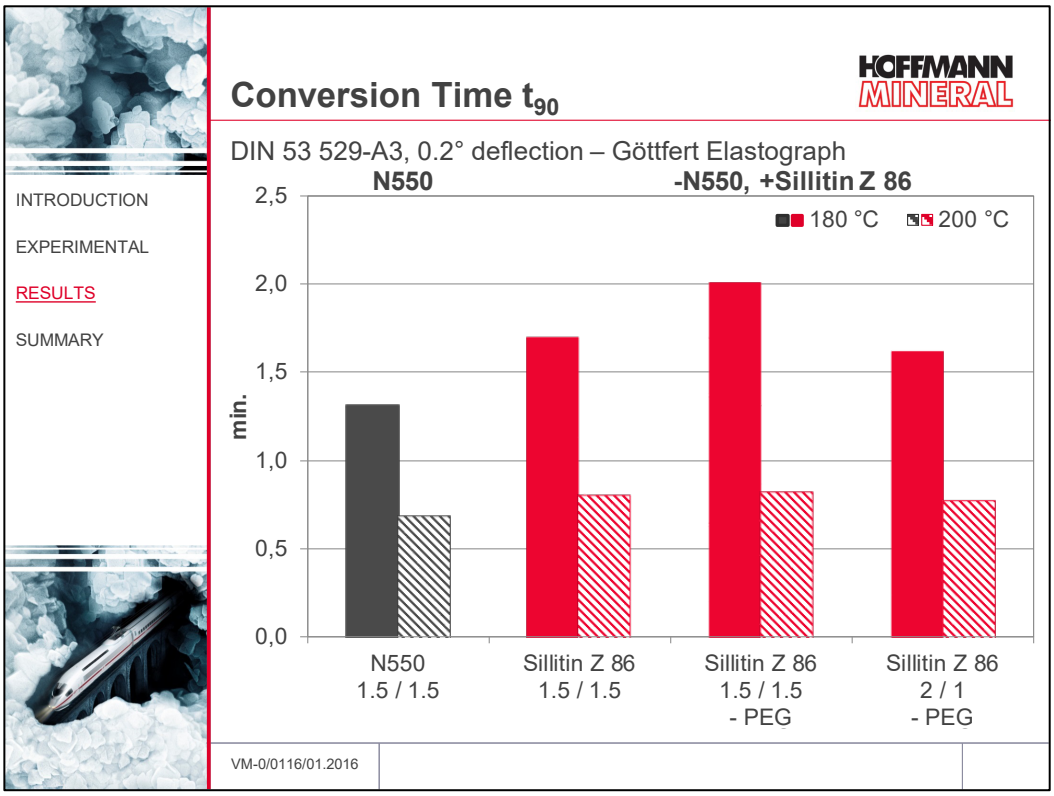


Fig. 9

3.2 Mechanical properties

The partial replacement of N550 with Sillitin Z 86 tends to somewhat reduce the hardness (Fig. 10) but the requirement of DIN EN 13831 can still be fulfilled with all tested versions. When curing at 200 °C for 1.5 minutes as closer to industrial conditions, the hardness becomes rather borderline but this can be corrected by the slight change of the accelerator system.

While PEG exerts no significant influence on the results discussed so far, its addition results in a slight decrease of the tensile strength (Fig. 11).
When working without PEG addition, the tensile strength increases by about 1 MPa, a result that can be important in limiting cases. By this action, with an identical compound formulation, the tensile strength with Sillitin Z 86 can be increased to the level of N550.

Along with this working without PEG gives rise to a slight increase of the elongation at break (Fig. 13). The requirements of DIN EN 13831 are met without any problems with all variants including Sillitin Z 86 while here the straight carbon black comes out noticeably weaker, i.e. largely below the limit value of 450 %.

Apart from the increased elongation at break caused by Sillitin Z 86 the use of the Neuburg Siliceous Earth is also able to improve the tear resistance compared with the carbon black alone (Fig. 13). Working without PEG or simultaneously modifying the accelerator system are able to further improve the already very good tear resistance obtained with Sillitin Z 86.

It is true that DIN EN 13831 does not specify a minimum value for the tear resistance. The test is, however, indicated to point to non-destructive demolding operations after injection molding processes. With this in mind, the higher results of the samples which were cured for 1.5 minutes at 200 °C should be of particular interest.

Fig. 14 shows the compression set results of the cured compounds. Although the compression set comes out higher after the partial replacement of N550 with Sillitin Z 86 the requirement of DIN EN 13831 can still be met. When looking at the results for the more industry-close curing conditions the advantage of using the modified accelerator system becomes very evident. Sillitin Z 86 here comes off only 5 % higher than the straight carbon black.

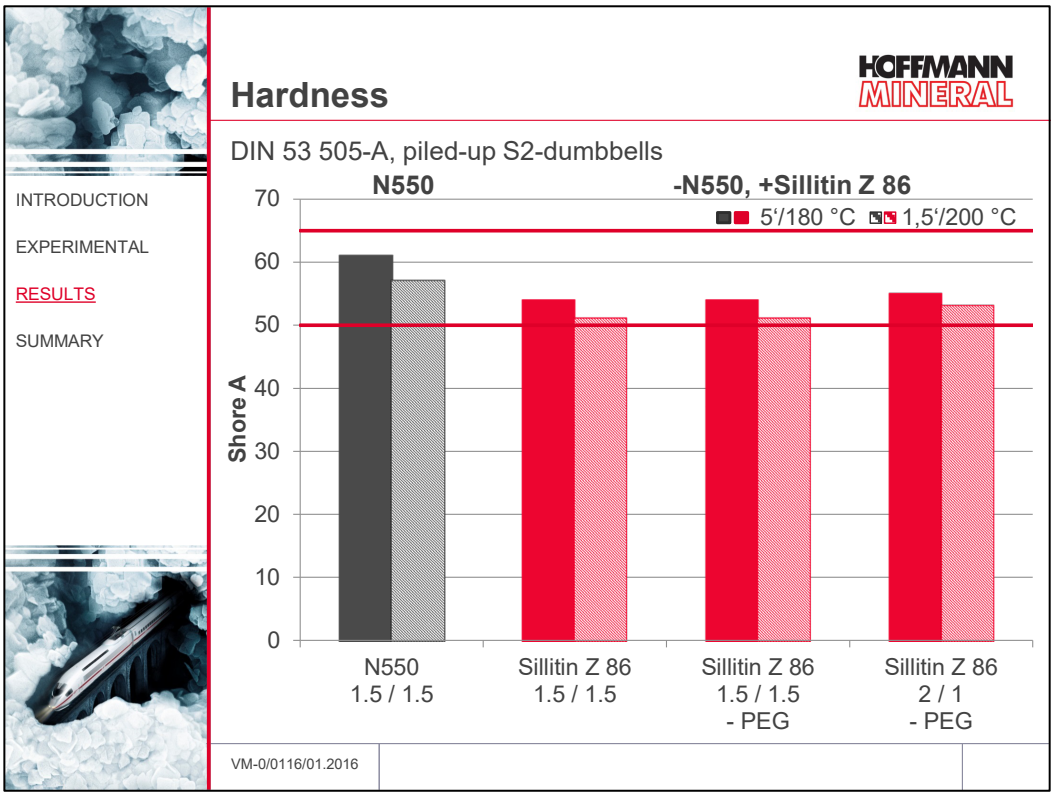

Hardness
HOFFMANN MINERAL
DIN 53 505-A, piled-up S2-dumbbells
N550
-N550, +Sillitin Z 86
5'/180 °C
1,5'/200 °C
Shore A
70
60
50
40
30
20
10
0
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 10

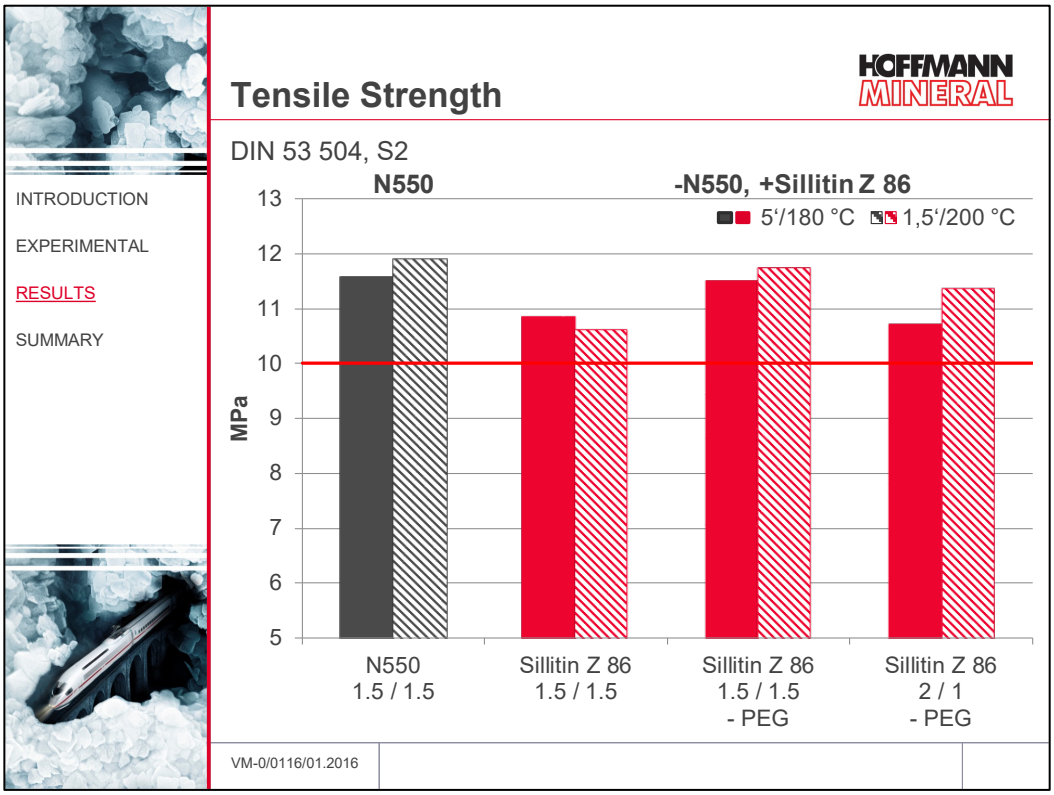

Tensile Strength
HOFFMANN MINERAL
DIN 53 504, S2
N550
-N550, +Sillitin Z 86
5'/180 °C
1,5'/200 °C
MPa
13
12
11
10
9
8
7
6
5
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 11

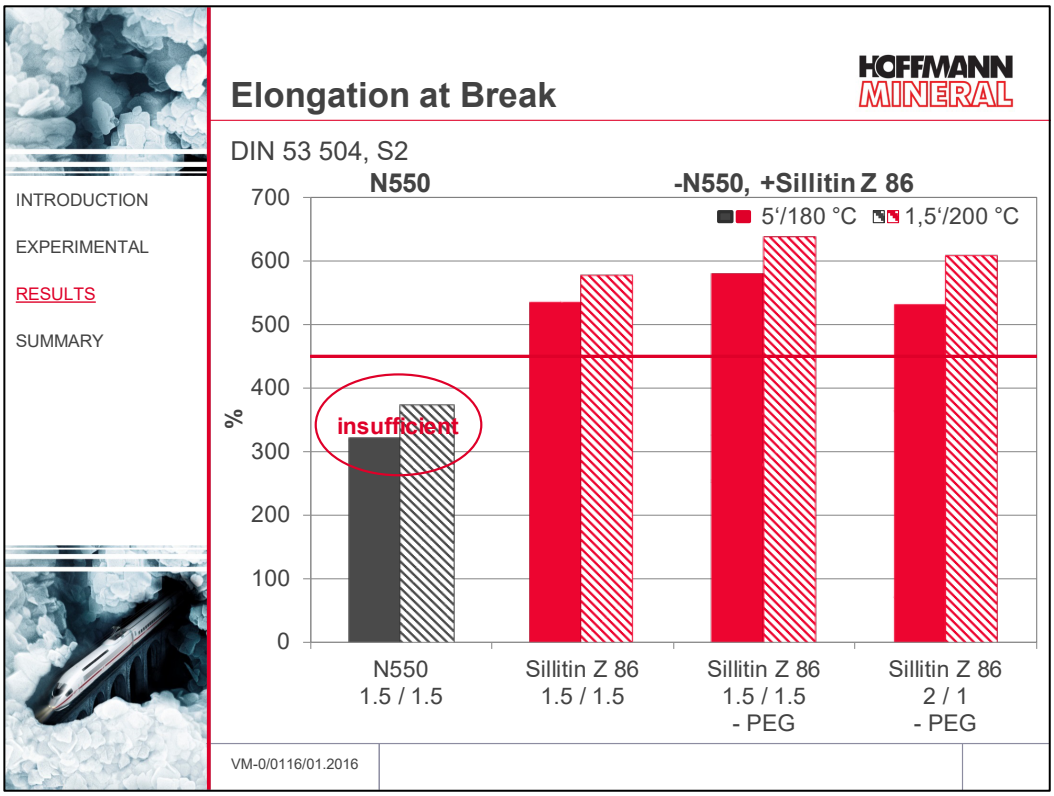

Elongation at Break
HOFFMANN MINERAL
DIN 53 504, S2
N550
-N550, +Sillitin Z 86
5'/180 °C
1,5'/200 °C
%
700
600
500
400
300
200
100
0
insufficient
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 12

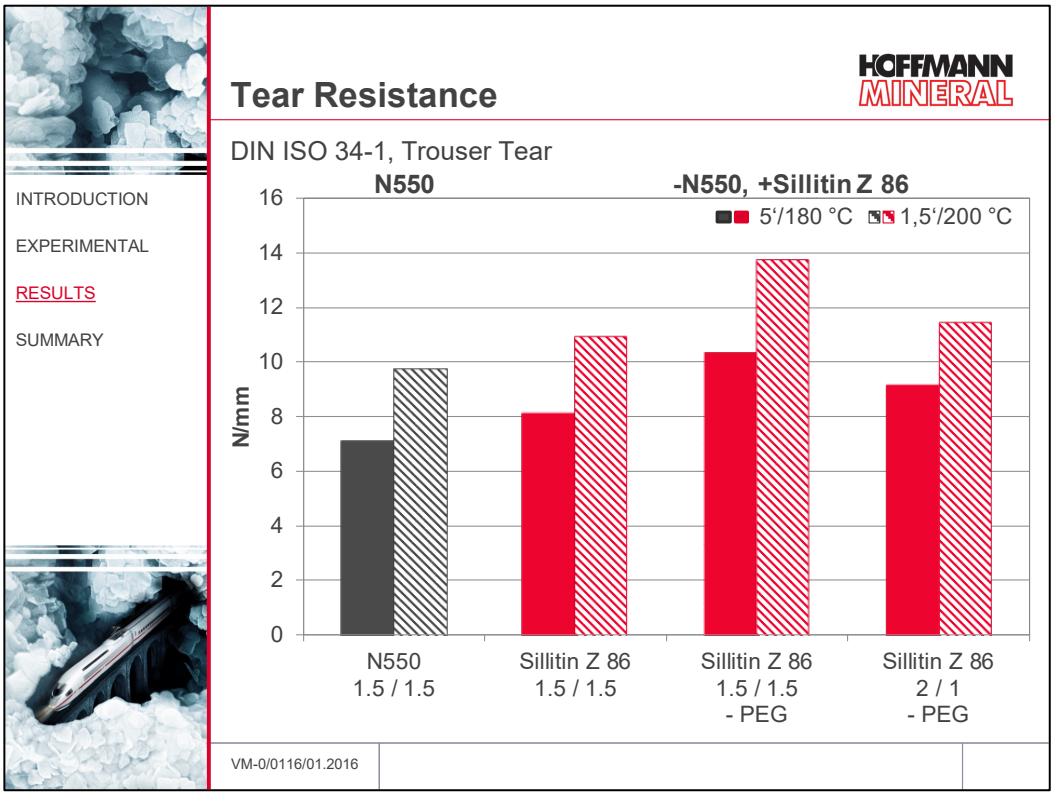

Tear Resistance
HOFFMANN MINERAL
DIN ISO 34-1, Trouser Tear
N550
-N550, +Sillitin Z 86
5'/180 °C
1,5'/200 °C
N/mm
16
14
12
10
8
6
4
2
0
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 13

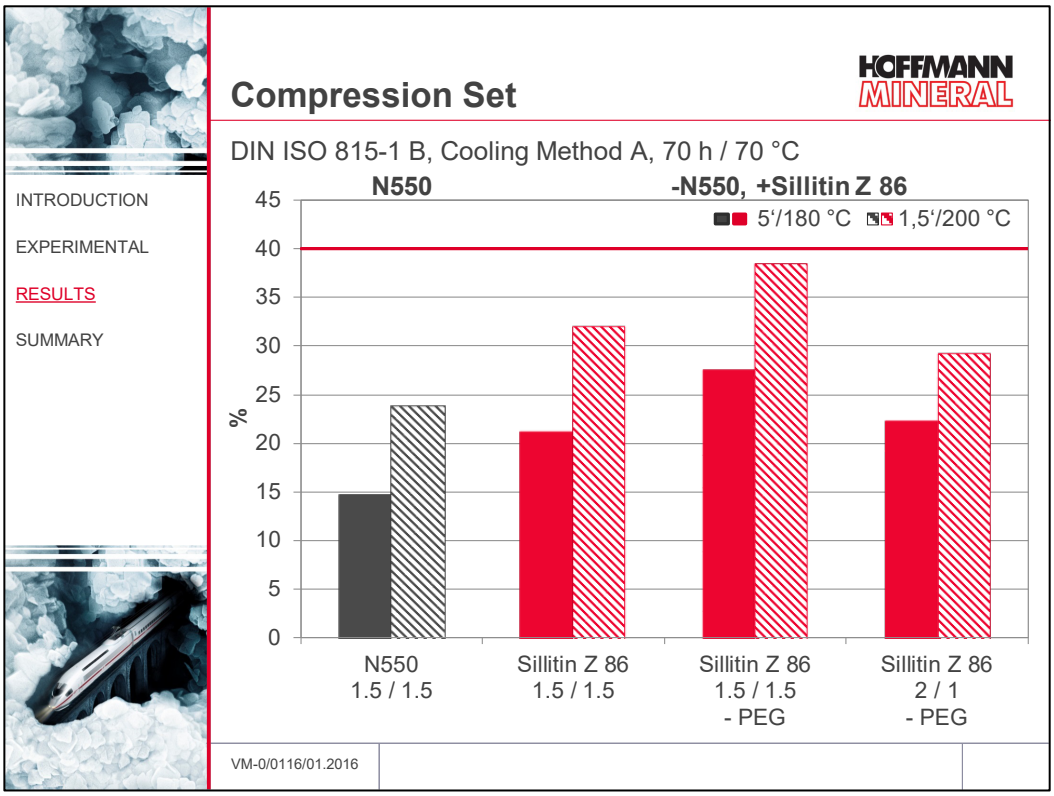


Fig. 14

3.3 Water immersion

The samples were immersed in distilled water for 28 days at 70 °C.

Fig. 15 shows the change of hardness as a result of the exposure.
The compounds containing Sillitin Z 86 become a little softer but with -2 Shore A this decrease is not very pronounced.

With unchanged formulation the tensile strength decreases slightly with Sillitin Z 86 compared with the straight carbon black (Fig. 16). If the compound does not contain any PEG the tensile strength indicates practically no change with the immersion in water.

The elongation at break shows a slight decrease of a similar order for all compounds (Fig. 17).

As already mentioned, a compression set specification is not included in DIN EN 13831. The earlier standard DIN 4807, however, also contained a compression set requirement.
Fig. 18 shows the results vs. the requirements of DIN 4807. With the partial replacement of N550 with Sillitin Z 86 the compression set shows increased levels. The limiting value of DIN 4807 can, however, be observed with all compound versions.

As confirmed by the results all requirements concerning the mechanical properties after immersion in water can be met with all tested compound variants without any problems.

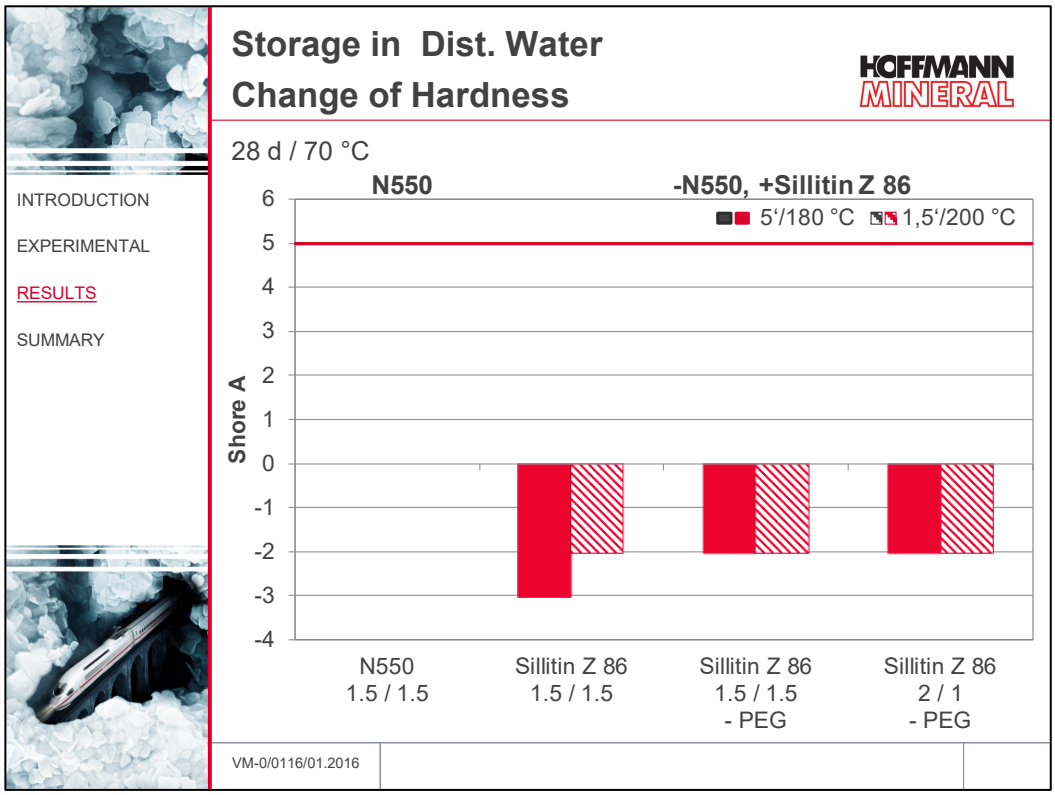

Storage in Dist. Water
Change of Hardness
HOFFMANN MINERAL
28 d / 70 °C
N550
-N550, +Sillitin Z 86
5'/180 °C
1,5'/200 °C
Shore A
6
5
4
3
2
1
0
-1
-2
-3
-4
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 15

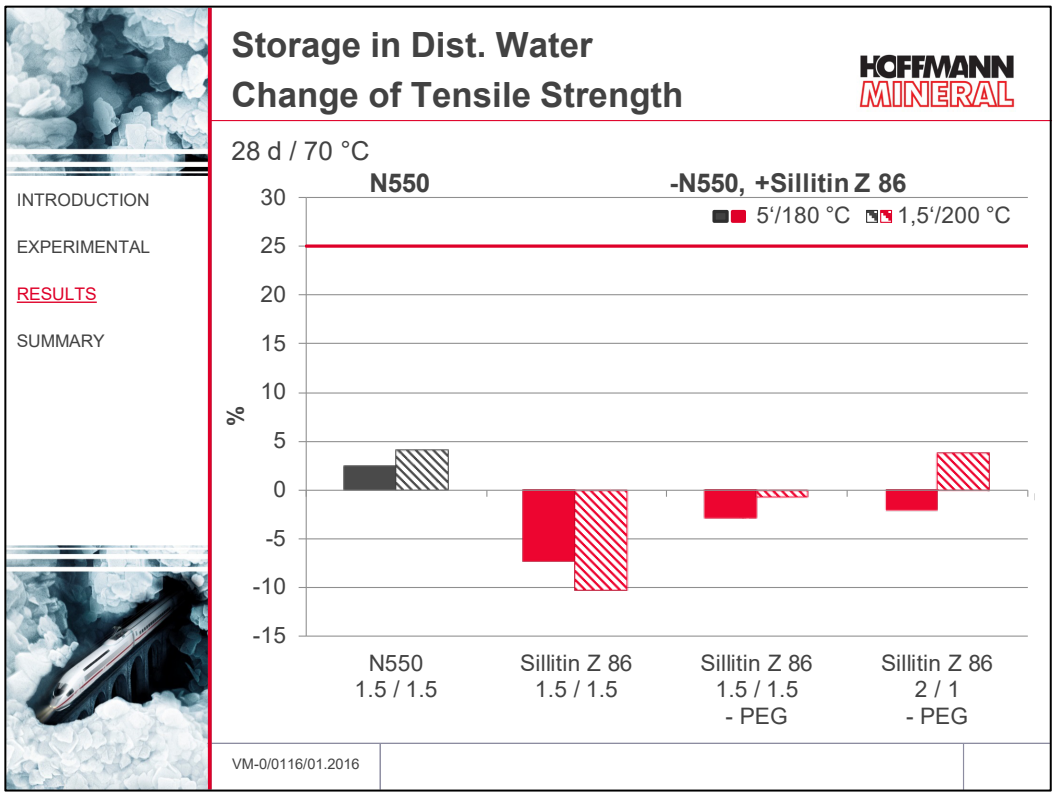

Storage in Dist. Water
Change of Tensile Strength
HOFFMANN MINERAL
28 d / 70 °C
N550
-N550, +Sillitin Z 86
5'/180 °C
1,5'/200 °C
%
30
25
20
15
10
5
0
-5
-10
-15
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 16

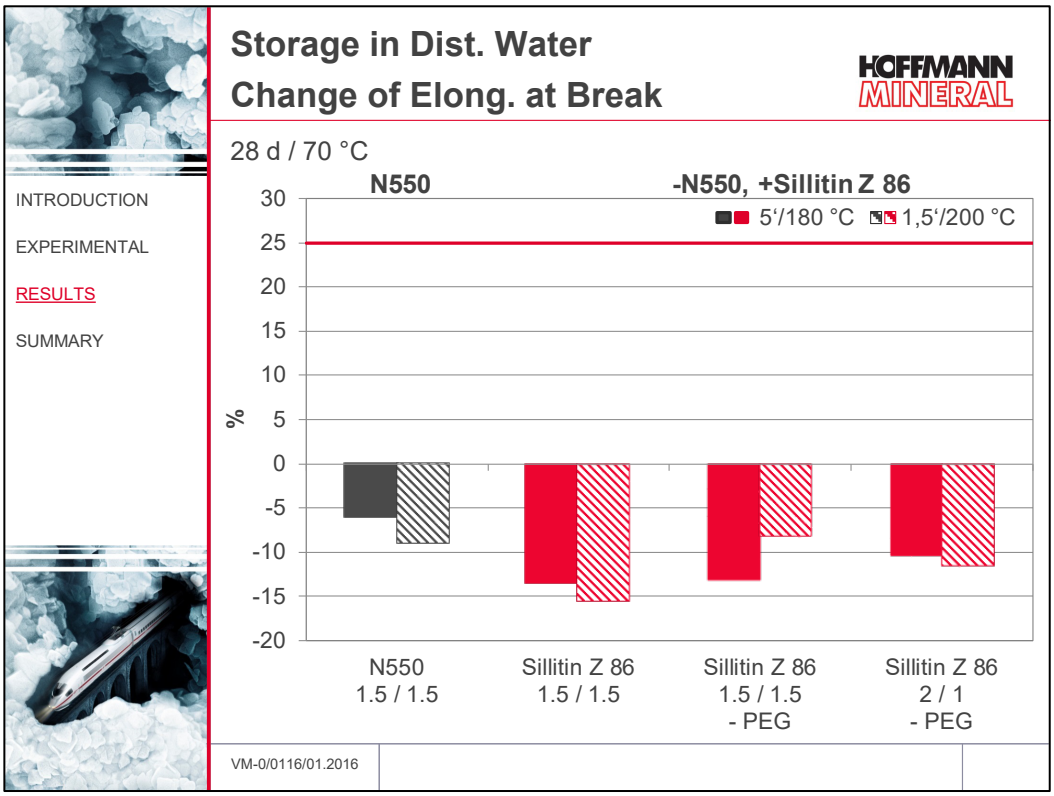

Storage in Dist. Water
Change of Elong. at Break
HOFFMANN MINERAL
28 d / 70 °C
N550
-N550, +Sillitin Z 86
5'/180 °C
1,5'/200 °C
%
30
25
20
15
10
5
0
-5
-10
-15
-20
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 17

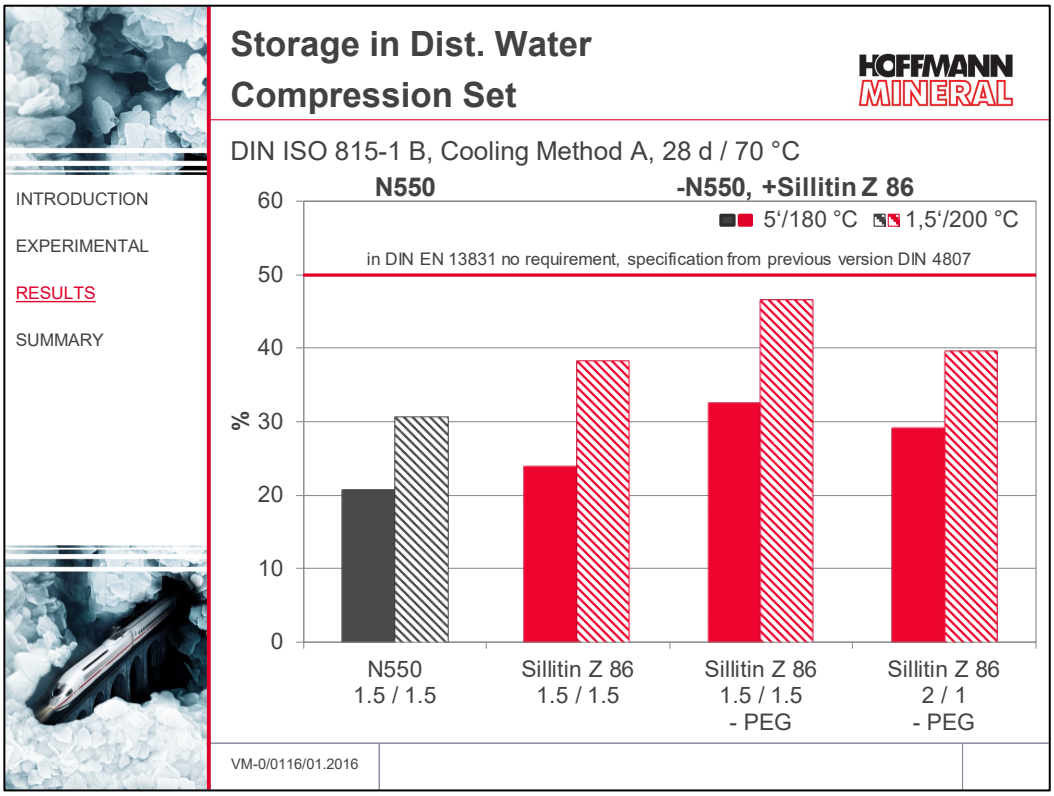

Storage in Dist. Water
Compression Set
HOFFMANN MINERAL
DIN ISO 815-1 B, Cooling Method A, 28 d / 70 °C
N550
-N550, +Sillitin Z 86
5'/180 °C
1,5'/200 °C
in DIN EN 13831 no requirement, specification from previous version DIN 4807
%
60
50
40
30
20
10
0
N550 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5
Sillitin Z 86 1.5 / 1.5 - PEG
Sillitin Z 86 2 / 1 - PEG
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
VM-0/0116/01.2016

Fig. 18

3.4 Compound costs

As shown in Fig. 19, the partial replacement of N550 with Sillitin Z 86 is able to slightly reduce the volume related compound costs. When looking at the weight related situation, the price reduction with more than 10 % is markedly more pronounced.

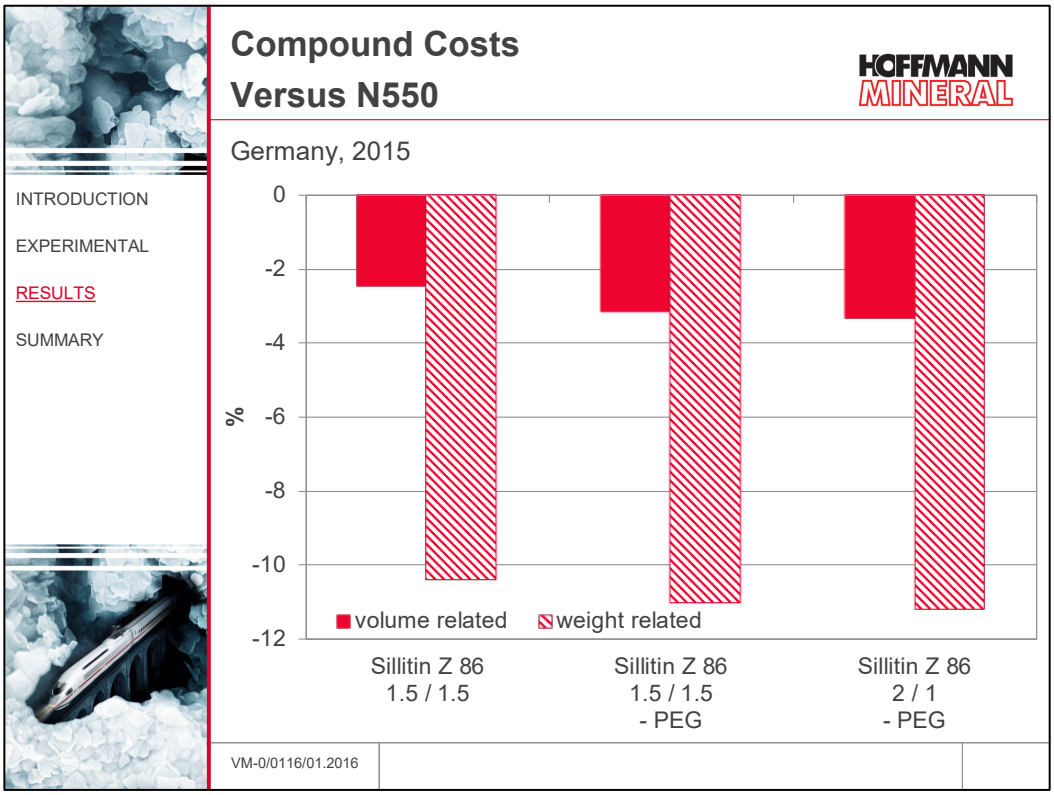


Fig. 19

The calculations were based on prices in Germany, 2015.

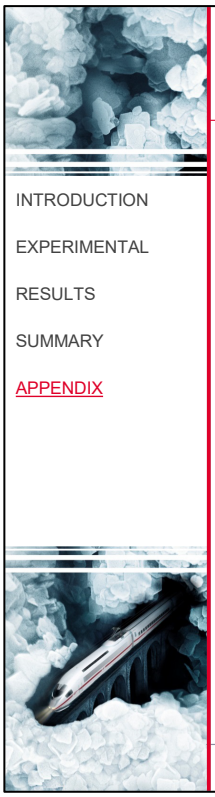
4 Summary

The partial replacement of carbon black N550 by the Neuburg Siliceous Earth grade Sillitin Z 86 gives rise to the following effects:

- higher filler loading (total phr)
- reduced compound costs
- reduced viscosity
- higher tear resistance
- higher elongation at break

In summary, the requirements of DIN EN 13831 can be met without any problems.

5 Numerical results in table form



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

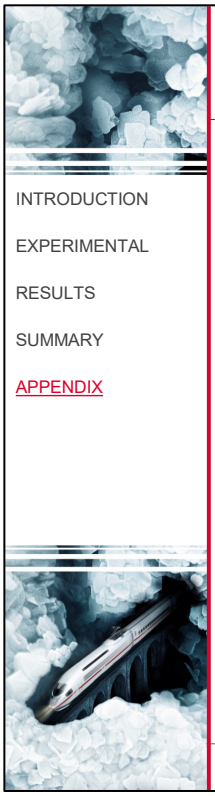
APPENDIX

Table of Results
Curing at 180 °C

HOFFMANN MINERAL

		N550	-N550, +Sillitin Z 86		
	TMTD / MBTS	1.5 / 1.5	1.5 / 1.5	1.5 / 1.5 -PEG	2 / 1 - PEG
Rheology					
Mooney viscosity, ML 1+4, 120 °C	MU	29	24	25	24
Mooney scorch time, ML +5, 120 °C	min.	9.1	26	25	18
Rotorless curemeter M_{min} 180 °C	Nm	0.040	0.034	0.035	0.037
Rotorless curemeter V_{max} 180 °C	Nm/min.	0.96	0.49	0.36	0.47
Rotorless curemeter t_5 180 °C	min.	0.55	0.66	0.62	0.53
Rotorless curemeter t_{90} 180 °C	min.	1.3	1.7	2.0	1.6
Mechanical properties – cure conditions 5 min. / 180 °C					
Hardness	Sh. A	61	54	54	55
Tensile strength	MPa	11.6	10.8	11.5	10.7
Elongation at break	%	320	535	580	532
Modulus 50 %	MPa	1.5	1.1	1.1	1.2
Modulus 100 %	MPa	3.4	1.9	1.9	2.1
Tear resistance	N/mm	7.1	8.1	10	9.1
Compression set 70 h / 70 °C, 25 % defl.	%	15	21	28	22

VM-0/0116/01.2016



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

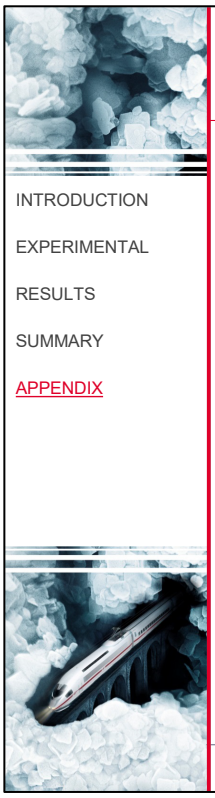
Table of Results
Curing at 180 °C

HOFFMANN MINERAL

		N550	-N550, +Sillitin Z 86		
	TMTD / MBTS	1.5 / 1.5	1.5 / 1.5	1.5 / 1.5 -PEG	2 / 1 - PEG
Storage in dist. water, 28 d / 70 °C					
Hardness	Sh. A	62	54	54	55
Tensile strength	MPa	11.2	9.4	10.2	10.9
Elongation at break	%	283	443	470	482
Modulus 100 %	MPa	3.7	1.9	1.9	1.9
Compression set 25 % defl.	%	21	24	32	29
Δ Hardness	Sh. A	0	-3	-2	-2
Δ Tensile strength	%	+2	-7	-3	-2
Δ Elongation at break	rel.%	-6	-13	-13	-10
Δ Modulus 100 %	%	+10	+1	-2	-11
Δ Weight	%	+1.3	+2.4	+1.2	+1.0
Δ Volume	%	+1.9	+3.3	+2.3	+1.4

The storage in water was conducted with specimens that had been stored for some time. In order to evaluate the influence of this temporary storage, the inital values were determined before starting the storage in water. There was practically no change, except of the hardness which showed a slight increase.
The changes after storage in water were calculated with the values of the temporarily stored specimens.

VM-0/0116/01.2016



INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Table of Results
Curing at 200 °C

HOFFMANN MINERAL

		N550	-N550, +Sillitin Z 86		
	TMTD / MBTS	1.5 / 1.5	1.5 / 1.5	1.5 / 1.5 -PEG	2 / 1 - PEG
Rheology					
Mooney viscosity, ML 1+4, 120 °C	MU	29	24	25	24
Mooney scorch time, ML +5, 120 °C	min.	9.1	26	25	18
Rotorless curemeter M_{min} 200 °C	Nm	0.035	0.029	0.030	0.032
Rotorless curemeter V_{max} 200 °C	Nm/min.	1.34	0.82	0.73	0.85
Rotorless curemeter t_5 200 °C	min.	0.32	0.36	0.34	0.32
Rotorless curemeter t_{90} 200 °C	min.	0.7	0.8	0.8	0.8
Mechanical properties – cure conditions 1.5 min. / 200 °C					
Hardness	Sh. A	57	51	51	53
Tensile strength	MPa	11.9	10.6	11.7	11.4
Elongation at break	%	372	578	639	608
Modulus 50 %	MPa	1.3	1.0	1.0	1.0
Modulus 100 %	MPa	2.7	1.6	1.7	1.8
Tear resistance	N/mm	10	11	14	11
Compression set 70 h / 70 °C, 25 % defl.	%	24	32	38	29

VM-0/0116/01.2016

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Table of Results
Curing at 200 °C

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		N550	-N550, +Sillitin Z 86		
	TMTD / MBTS	1.5 / 1.5	1.5 / 1.5	1.5 / 1.5 -PEG	2 / 1 - PEG
Storage in dist. water, 28 d / 70 °C					
Hardness	Sh. A	60	53	52	53
Tensile strength	MPa	11.2	9.8	10.7	11.3
Elongation at break	%	315	502	549	522
Modulus 100 %	MPa	3.2	1.6	1.6	1.7
Compression set 25 % defl.	%	31	38	47	40
Δ Hardness	Sh. A	0	-2	-2	-2
Δ Tensile strength	%	+4	-10	-1	+4
Δ Elongation at break	rel.%	-9	-15	-8	-11
Δ Modulus 100 %	%	+20	-6	-10	-10
Δ Weight	%	+1.8	+1.8	+1.3	+1.4
Δ Volume	%	+2.6	+2.7	+1.9	+1.8

The storage in water was conducted with specimens that had been stored for some time. In order to evaluate the influence of this temporary storage, the inital values were determined before starting the storage in water. There was practically no change, except of the hardness which showed a slight increase.
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