Potable water seal EPDM

E-DIN EN 681-1 (07/16)

Partial replacement of carbon black

by Neuburg Siliceous Earth

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VM-1/0520/09.2021

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1 Introduction

Our drinking water is one of the best controlled foods. Even the slightest contamination can lead to health problems. Due to this reason, the requirements for the formulation components of elastomers used in drinking water are very high and defined in the positive list of the German Federal Environment Agency (Umweltbundesamt, UBA) for drinking water. The Positive List is divided into Part 1 - fully evaluated substances, Part 2 - not fully evaluated substances and Part 3 - list of rubbers.

Part 2 - the partially evaluated substances - is accepted until December 2016 and extended until December 2021. According to the current status (September 2021), from January 2022 onwards only the updated raw materials from Part 1 should be relevant.

The basic formulation was based on a recipe recommendation of the company Arlanxeo on the basis of EPDM. To meet the requirements of hot air aging, a variant cross-linked with peroxide was chosen. The raw materials used were selected on the basis of the Positive List Part 1 and Part 3 (as of July 2021).

Purex HS 45, a grade with reduced PAH content, is gradually replaced by the Neuburg Siliceous Earth products Sillitin Z 86 and Aktisil VM 56 at 25 %, 37 % and 50 % respectively. Here, cost reduction by using the Siliceous Earth compared with the straight carbon black compound is an important criterion.

Carbon black is characterized by high price fluctuations, long-term rising cost levels and temporary supply bottlenecks, whereas Neuburg Siliceous Earth is characterized by only slightly price increases in a long term, high calculability, availability and reliable delivery times.

For drinking water applications, there are also decisive aspects to be considered, such as the requirement for a PAH[1] content of 10% of the required limit value in the German Drinking Water Ordinance (as of 2011). This is influenced by the PAH content in the carbon black. The lower the carbon black content, the less PAHs are present in the rubber compound, which in turn reduces the potential for PAHs in drinking water.
Neuburg Siliceous Earth generally meets the purity requirements of the German Federal Institute for Risk Assessment (BfR) Part 1 A LII.

The aim of this investigation is to partially replace the carbon black by Neuburg Siliceous Earth in compliance with the standard DIN EN 681-1 (draft 07/16) **Elastomeric seals - Material requirements for pipe joint seals used in water and drainage applications – Part 1: Vulcanized rubber.**

The following specifications were selected for this purpose:

- WB Cold drinking water supply (T ≤ 50 °C) and continuously hot drinking water supply (T ≤ 110 °C)

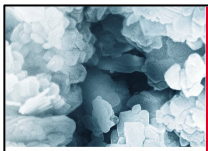
- WD Cold non drinking water supply (T ≤50 °C) and continuously hot non drinking water supply (T ≤110 °C)

- Hardness 70 IRHD (+/- 5 IRHD)

[1] Polycyclic aromatic hydrocarbons

2 Experimental

2.1 Base formulation and fillers



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Base Formulation

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		phr
Keltan®2650	EPDM amorphous	100.0
Zinkoxyd aktiv	Zinc oxide	3.0
Stearic acid	Processing aid	0.3
Purex HS 45	**FEF-Carbon black, reduced PAH content**	80.0
Caldic PIB 190	Polyisobutylene, Plasticizer	15.0
Safic Chem OMB	BPH, 2,2'-methylene-bis-(4-methyl-6-tert. butylphenol), Antioxidant	0.75
Luperox 101-XL 45	DHBP, 2,5-Dimethyl-2,5-Di(tert-butyl peroxide)hexane, Peroxide / Crosslinker	5.33
TAC 70	Triallyl cyanurate, Activator	0.7
Total		**205.08**

All selected raw materials meet the criteria of the UBA Positive List for the production of elastomers in contact with drinking water Part 1 and Part 3 (as of July 2021).

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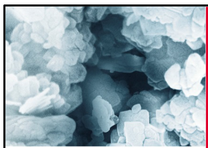
Table1

The base formulation represents a formula for the application area of potable water seals peroxide cross-linked 70 +/-5 IRHD. The mixture proposal was made available to us by the company Arlanxeo.



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Formulation Variations

HOFFMANN MINERAL

Dosages in phr for equal hardness

Purex HS 45	Carbon black replacement level	Sillitin Z 86	Aktisil VM 56
80			
60	25 %	40	40
50	37 %	60	60
40	50 %	80	80

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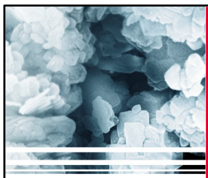
Table 2

To obtain an equal hardness, Purex HS 45 was replaced by Sillitin Z 86 and Aktisil VM 56 in a ratio of 1 : 2 phr.



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Fillers and Characteristics

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		Purex HS 45	Sillitin Z 86	Aktisil VM 56
Density	[g/cm³]	1.8	2.6	2.6
Particle size d_{50}	[µm]		1.9	2.2
Particle size d_{97}	[µm]		9.0	10
Sieve residue > 40 µm	[mg/kg]		20	20
Sieve residue 45 µm / 325 mesh	ppm	≥ 50		
Oil absorption	[g/100g]		55	45
Jod adsorption	[mg/g]	43 +/- 5		
Specific surface area BET	[m²/g]		12	9
STSA surface area	[m²/g]	39 +/- 5		
Functionalization		none	none	Vinyl

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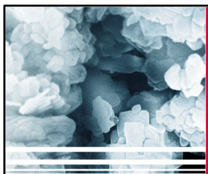
Table 3
Carbon black Purex HS 45 is used as a typical filler. With its specific surface area of about 40 m²/g, it differs markedly from Neuburg Siliceous Earth grades, which was taken into account in the formulation by a correspondingly increased phr dosage. Aktisil VM 56 is an activated SILLITIN Z 86, produced by modifying the surface with a vinyl functional group.

2.2 Preparation and curing of the compounds



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Preparation and Curing of the Compounds

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- **Mixing**
  Open mill Ø 150 x 300 mm
  Batch volume: approx. 800 cm³
  Temperature: 50 °C
  Mixing time: approx. 20 min.
- **Curing**
  Press: 180 °C
  Curing time: t_{90} + 10 % resp. 12 min.
- **Post cure**
  Unless otherwise stated, 2 h / 125 °C

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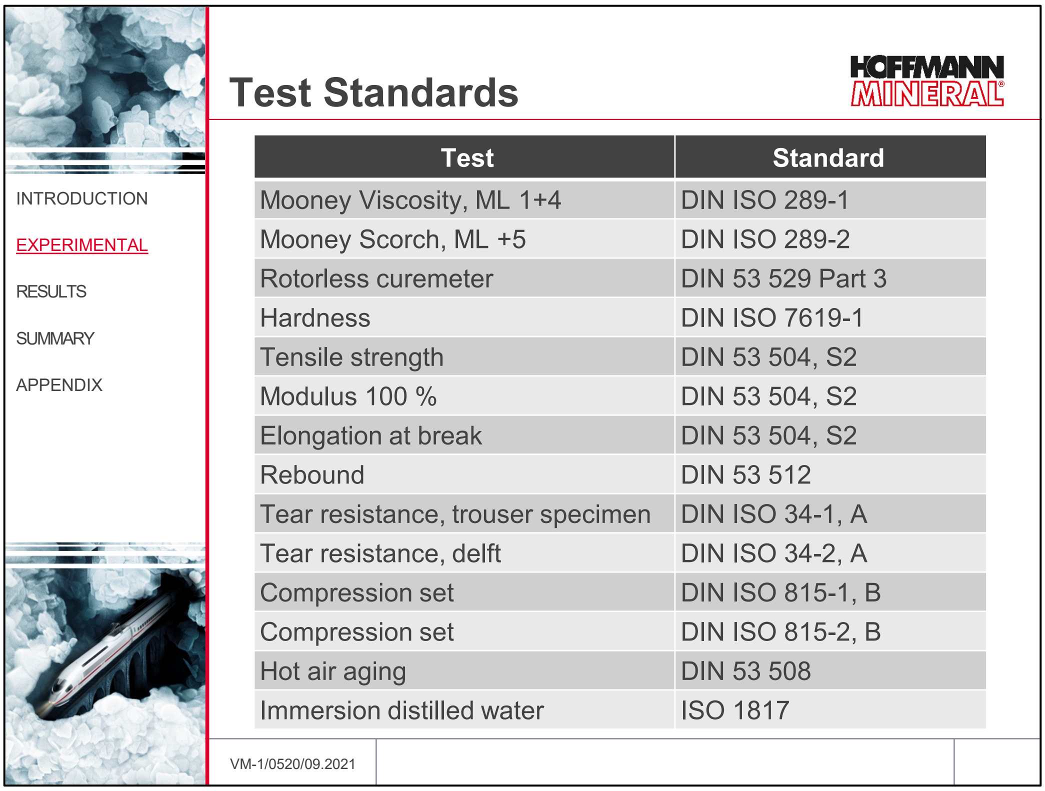
Fig. 1
The compounding was done on a laboratory rolling mill (Schwabenthan Polymix 150 L). The rubber was fed onto the mill at 50 °C, followed by mixing in all the remaining ingredients in the order shown in the recipe while keeping temperature constant and homogenized by cutting and folding triangles. The typical mixing time was 20 minutes.

The cure time was usually t90 + 10 % at 180 °C. Only when indicated, as for the compression set, it was increased to 12 minutes or the test specimens were additionally post cured for 2 h / 125 °C after the regular vulcanization time of t90 + 10 %.

2.3 Test Standards



Test	Standard
Mooney Viscosity, ML 1+4	DIN ISO 289-1
Mooney Scorch, ML +5	DIN ISO 289-2
Rotorless curemeter	DIN 53 529 Part 3
Hardness	DIN ISO 7619-1
Tensile strength	DIN 53 504, S2
Modulus 100 %	DIN 53 504, S2
Elongation at break	DIN 53 504, S2
Rebound	DIN 53 512
Tear resistance, trouser specimen	DIN ISO 34-1, A
Tear resistance, delft	DIN ISO 34-2, A
Compression set	DIN ISO 815-1, B
Compression set	DIN ISO 815-2, B
Hot air aging	DIN 53 508
Immersion distilled water	ISO 1817

Table 4

The values shown in the following diagrams and at the end in the result tables refer to tests performed in accordance with the standards mentioned in table 4.

In this study, the hardness was measured in Shore A, which typically provides slightly lower values than in IRHD procedure.

3 Results

3.1 Rheology

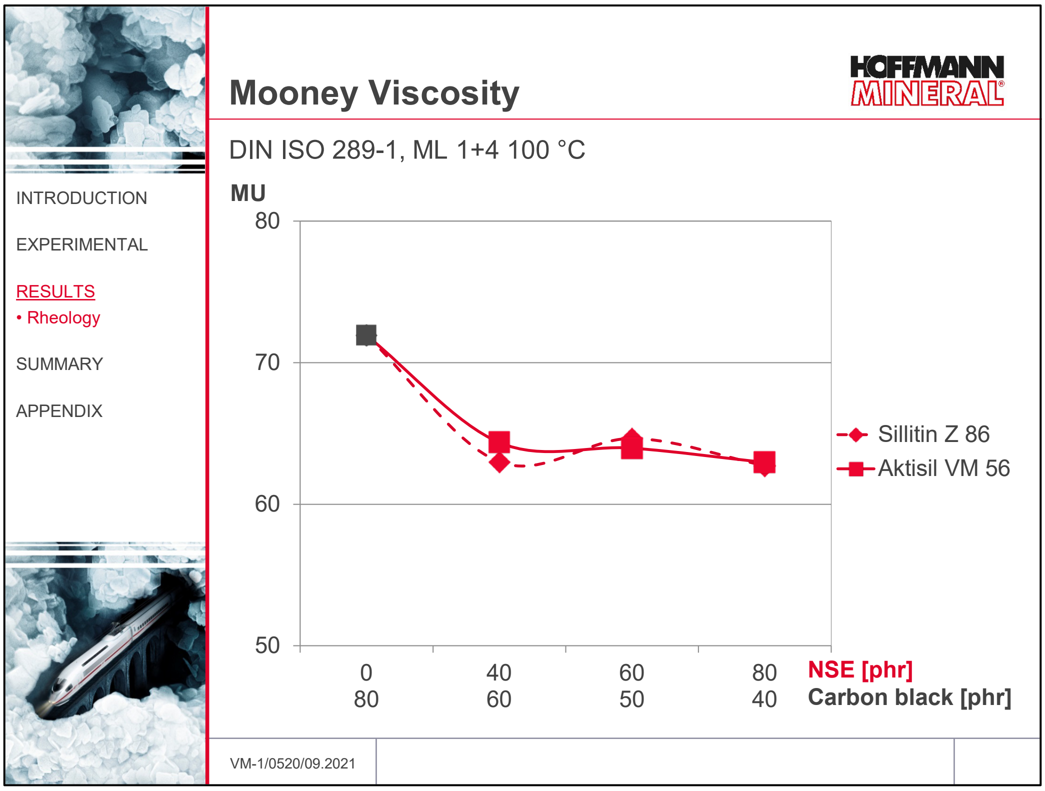


Fig. 2
The increasing proportion of Neuburg Siliceous Earth achieves a slight reduction in viscosity, which typically indicates improved processing properties.

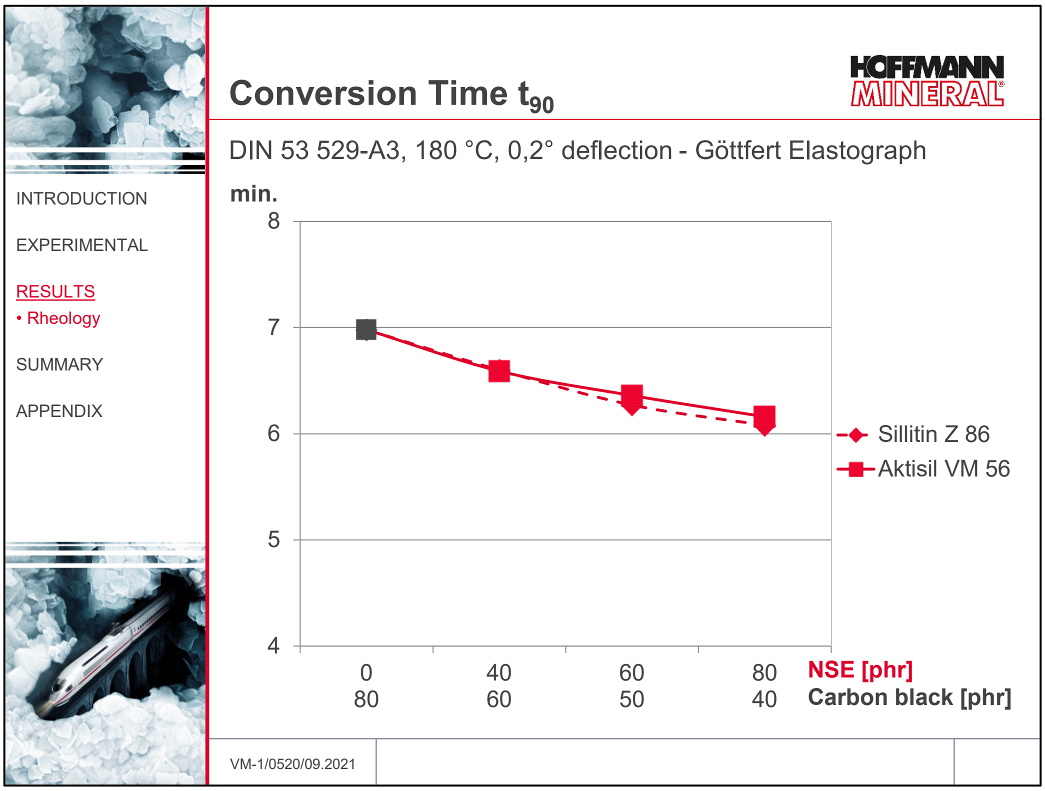


Fig. 3
The conversion time t_{90}, as an indicator of the vulcanization time, shows a tendency to shorten with increasing Neuburg Siliceous Earth content, which allows higher productivity to be achieved.

3.2 Mechanical properties

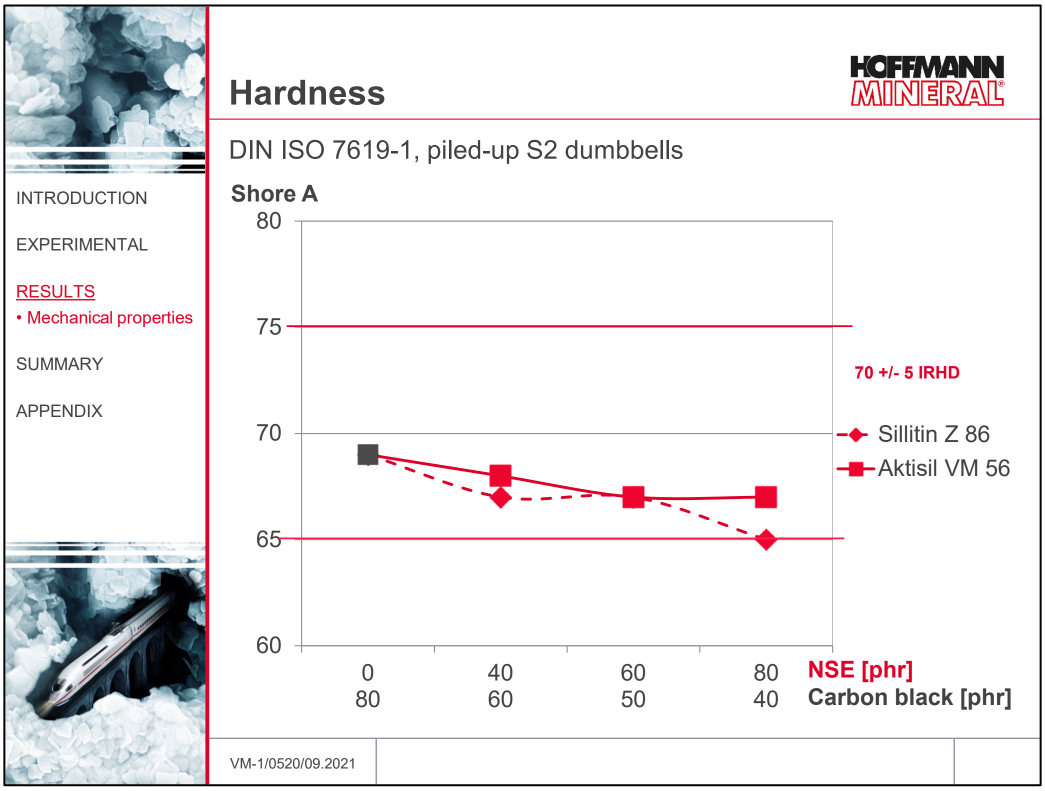


Fig. 4

The hardness is slightly lower with the selected exchange ratio of carbon black 1 against 2 phr Neuburg Siliceous Earth. In the case of Sillitin Z 86 at an exchange ratio of 50 %, it is just within the specification, whereas Aktisil VM 56 maintains a higher hardness.

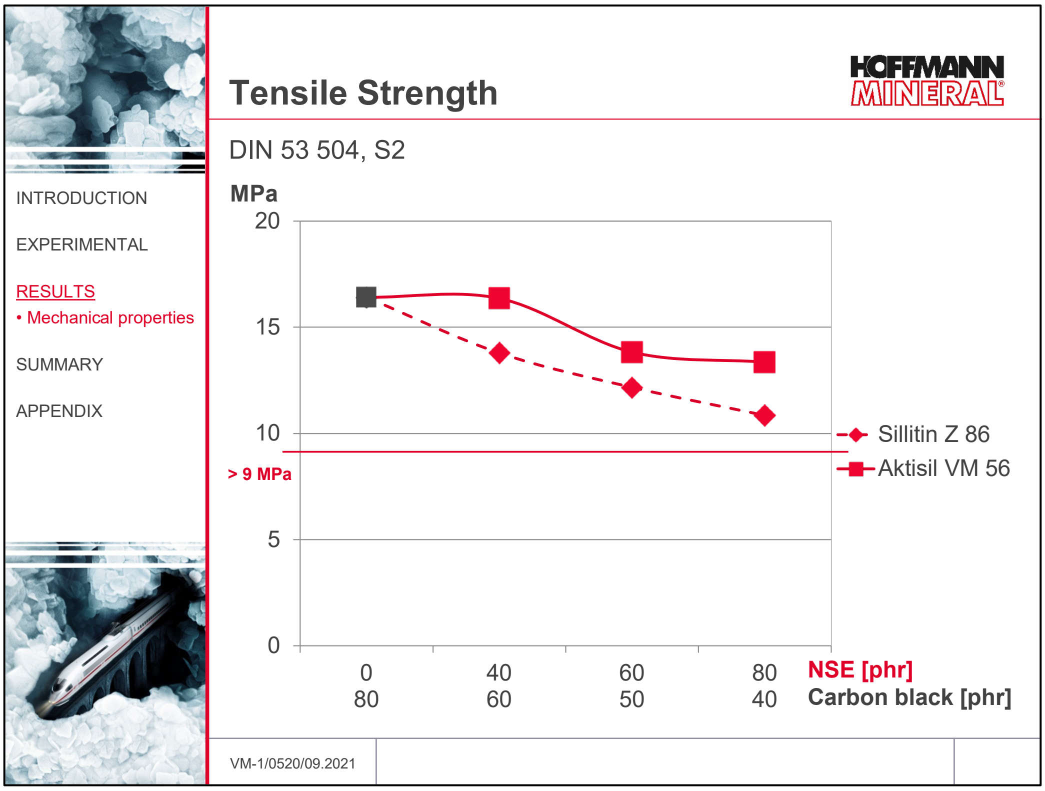


Fig. 5

Despite the decreasing tendency for the tensile strength with increasing Neuburg Siliceous Earth content, it is still well above the required limit of 9 MPa.

With Aktisil VM 56, the overall level is generally higher than with Sillitin Z 86, and with 25 % carbon black replacement even at the same level as the straight carbon black compound.

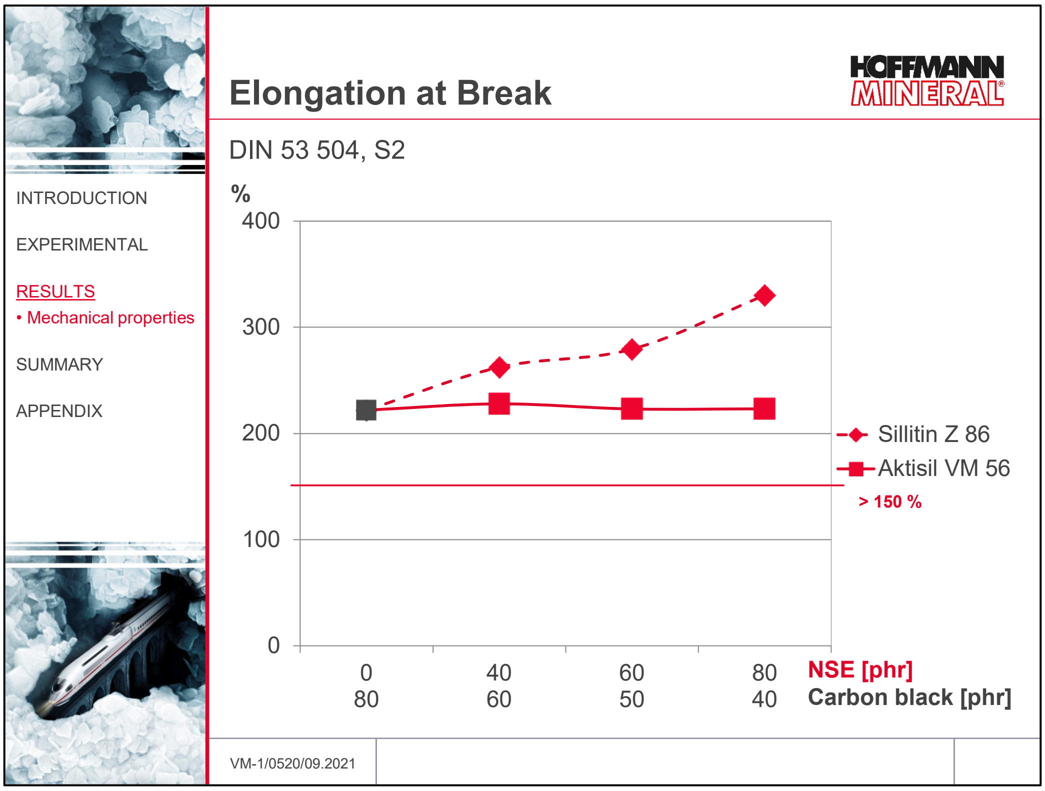


Fig. 6
With increasing Sillitin Z 86 concentration, the elongation at break is noticeably increased, while it remains unchanged with each Aktisil VM 56 dosage. Thus with Sillitin Z 86 it is even more clearly above the specified limit value of 150 %.

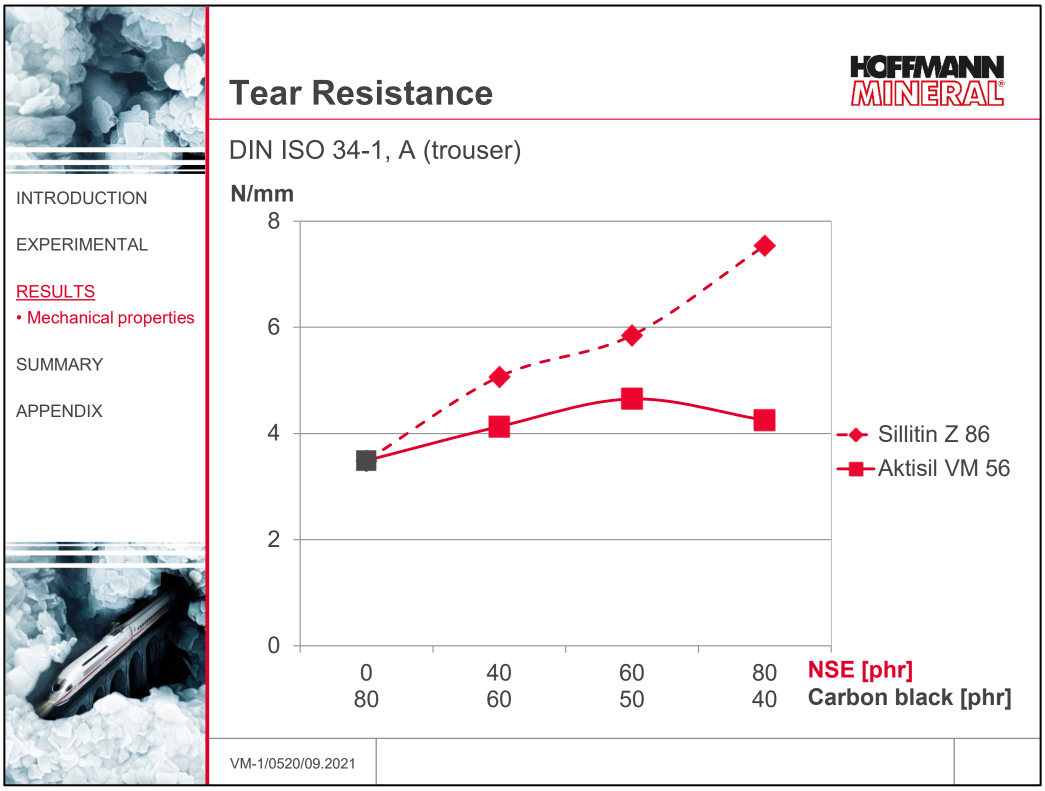


Fig. 7
The tear resistance, determined as trouser specimen, rises markedly with higher Sillitin Z 86 contents. With Aktisil VM 56 it increases only slightly.

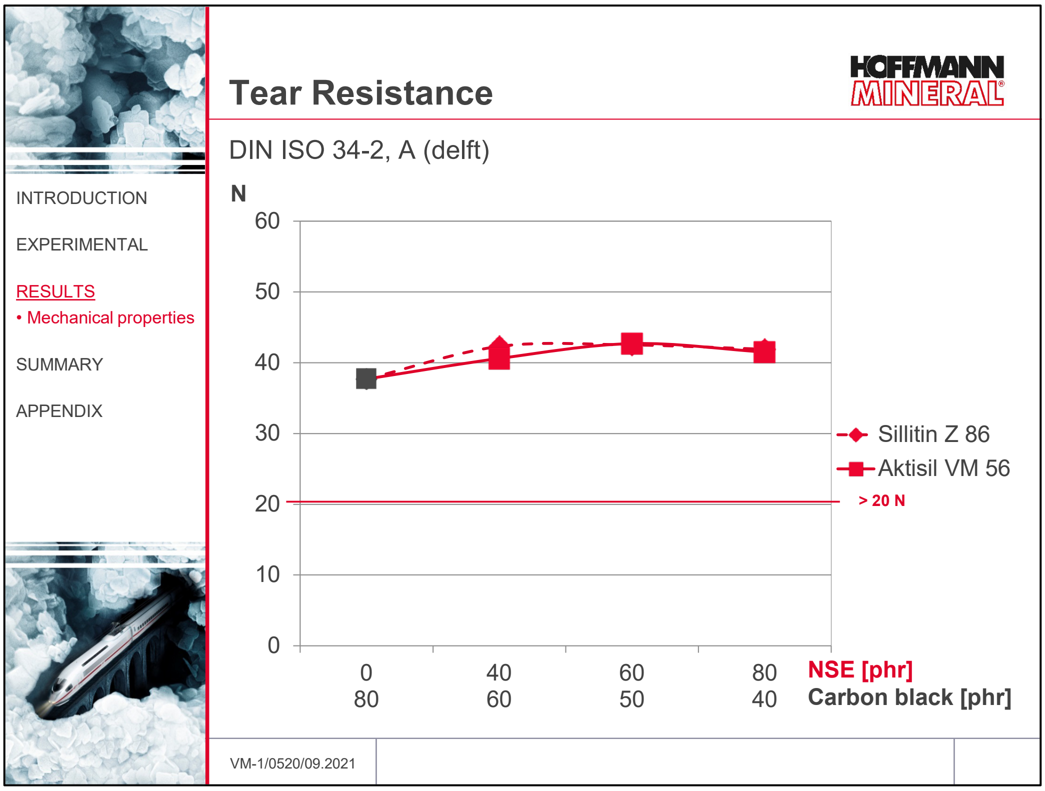


Fig.8

In the case of the tear resistance using the delft specimen, both Neuburg Siliceous Earth grades show only a slightly increasing trend. All values are significantly above the standard´s requirement of 20 Newton.

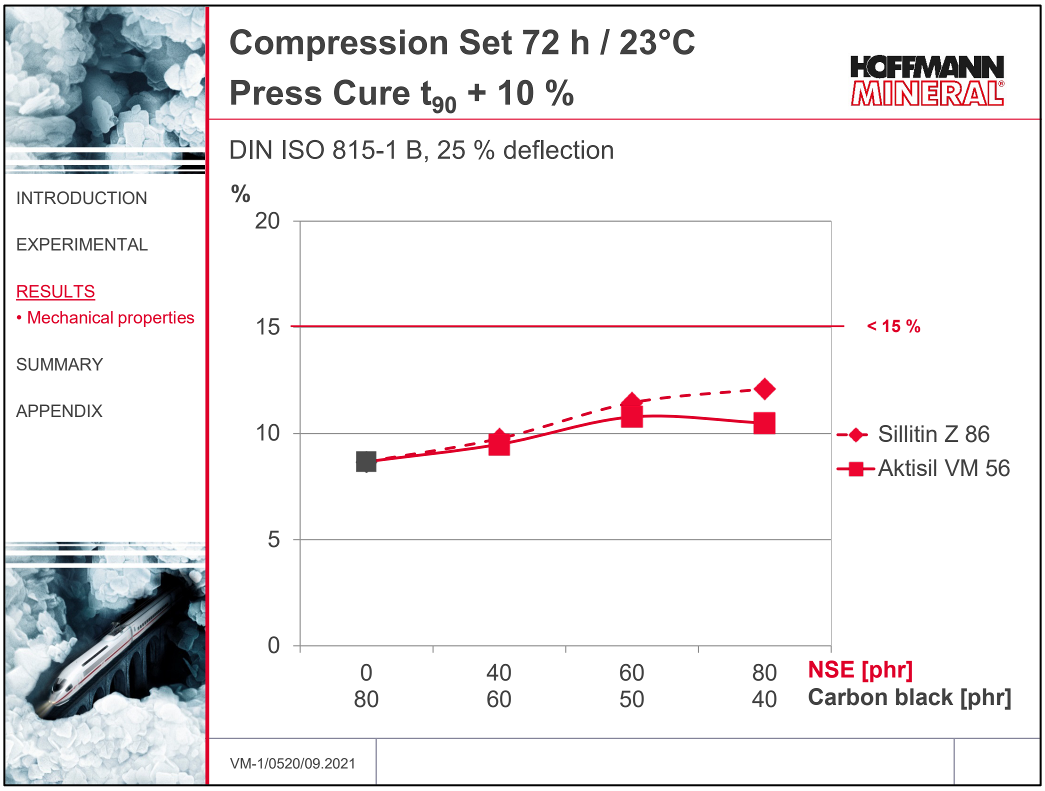


Fig. 9

With a higher Neuburg Siliceous Earth content the compression set at 23 °C tends to increase, but is still well below the specified limit of maximum 15 %.

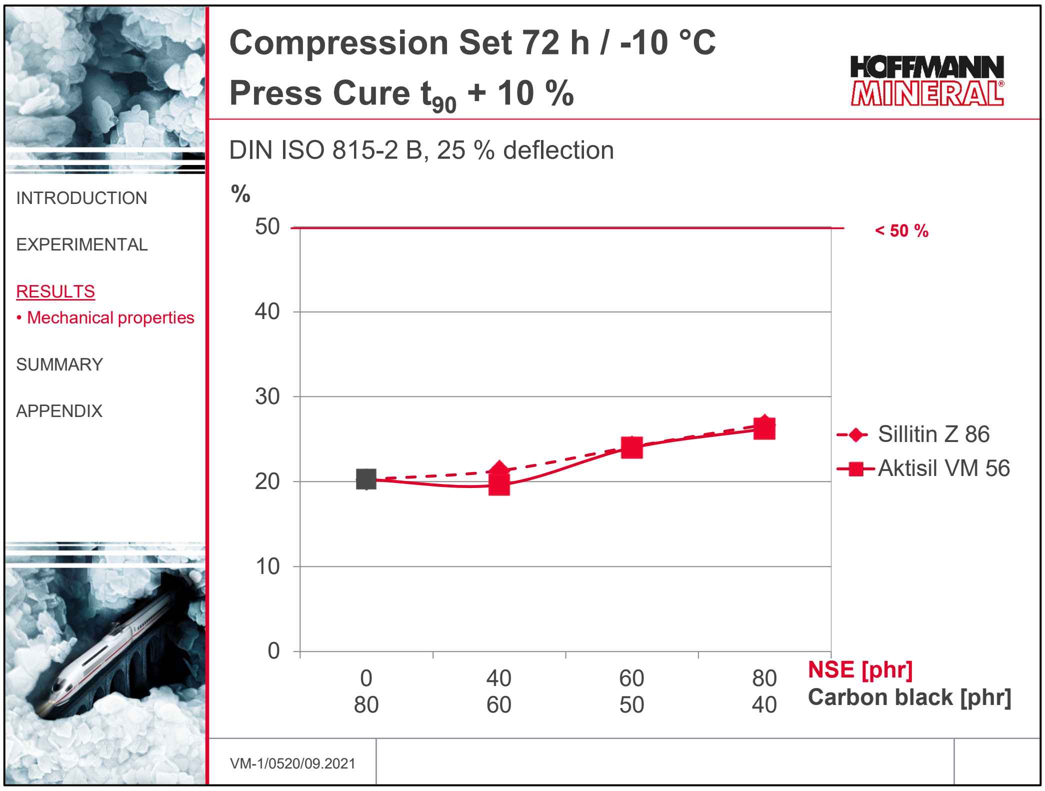


Fig. 10

The compression set at -10 °C is also slightly higher with increasing mineral filler content. However, the values are still well below the specified limit value of max. 50 %.

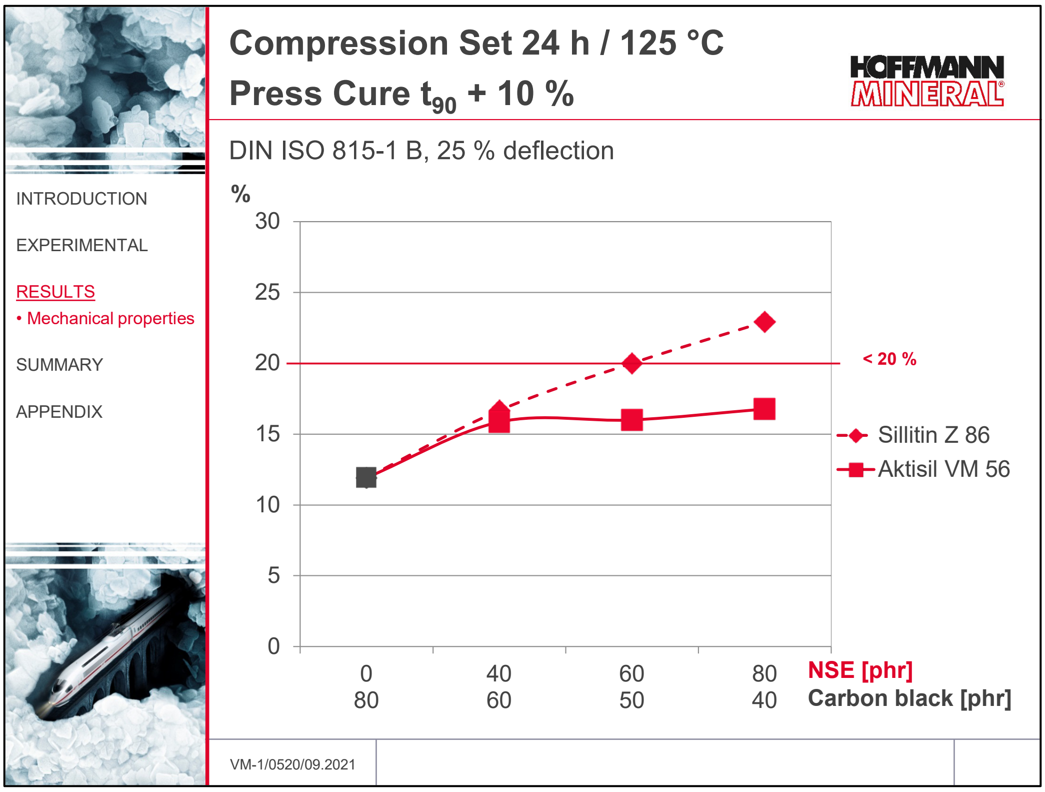


Fig. 11

Aktisil VM 56 even at the highest carbon black exchange rate of 50 % reliably complies with the standard of max. 20 % for compression set at 125 °C. Sillitin Z 86, on the other hand, complies with the specification only at 25 % carbon black replacement. In order to comply with the specification at higher carbon black replacement, additional measures are required such as post cure or a longer curing time of the test specimens, see figures 12 and 13.

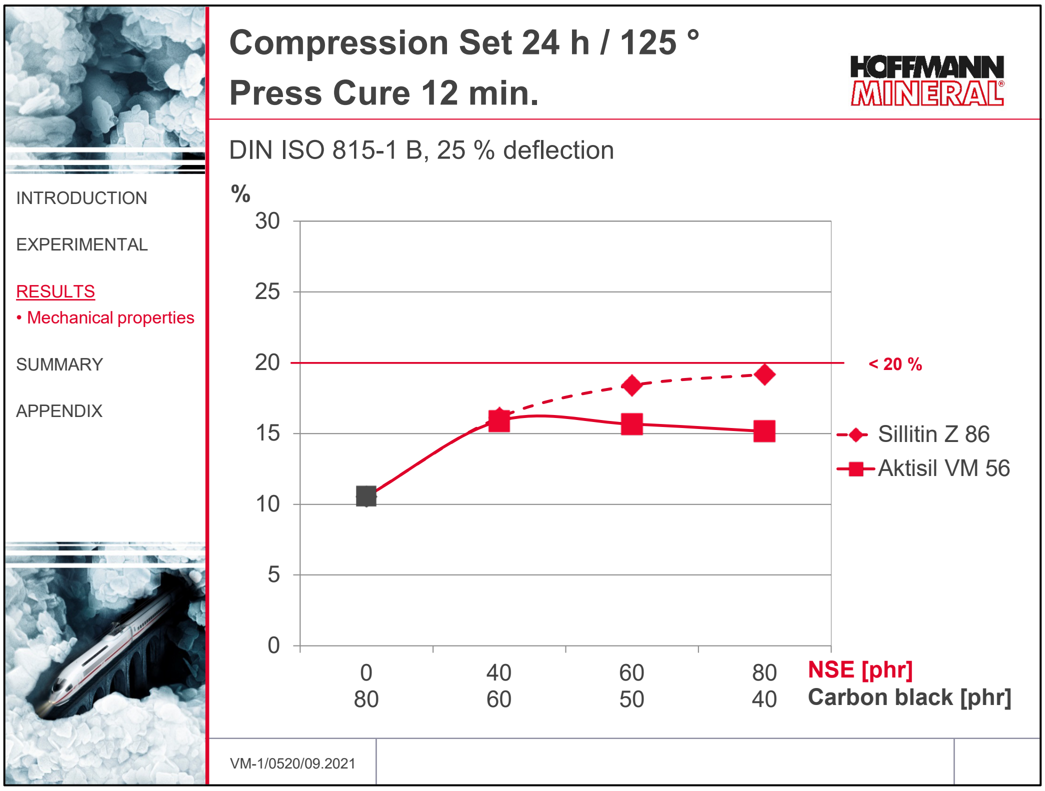


Fig. 12

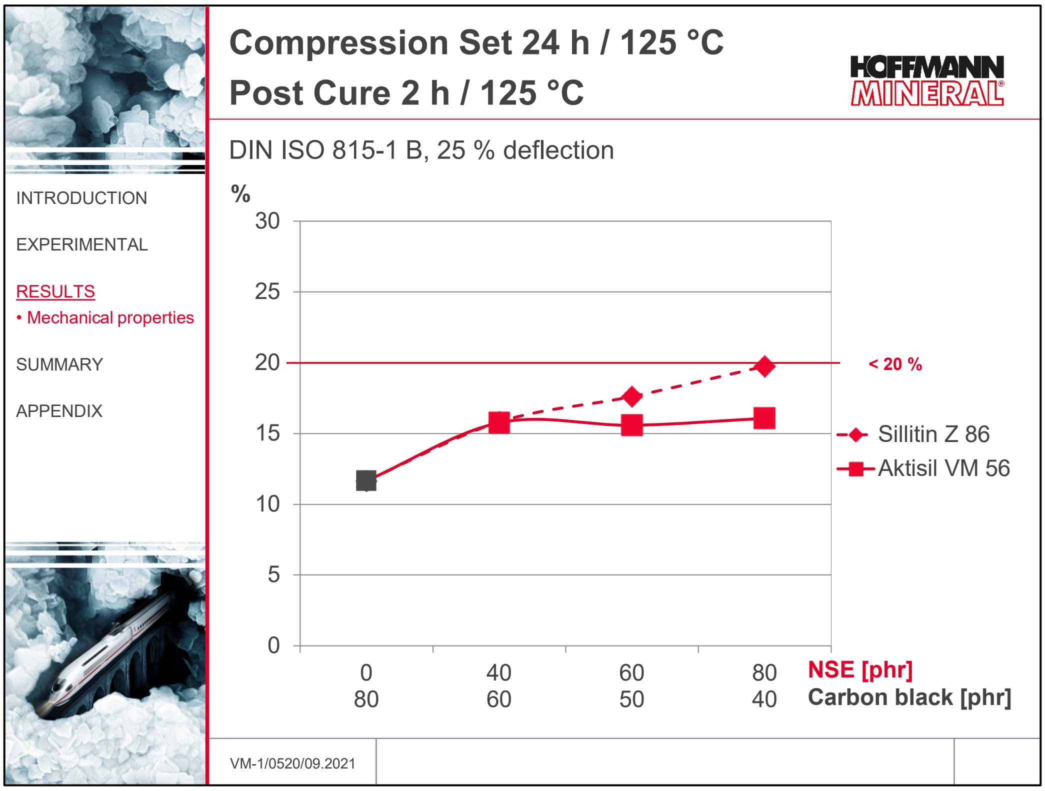


Fig. 13

The measures, as mentioned in the text under figure 11, have positively influenced the compression set results of Sillitin Z 86 using higher carbon black replacement levels of 37 % and 50 % to such an extent that it is, albeit only slightly, within the specification of 20 %. With Aktisil VM 56 no significant influence can be found.

3.3 Immersion in distilled water

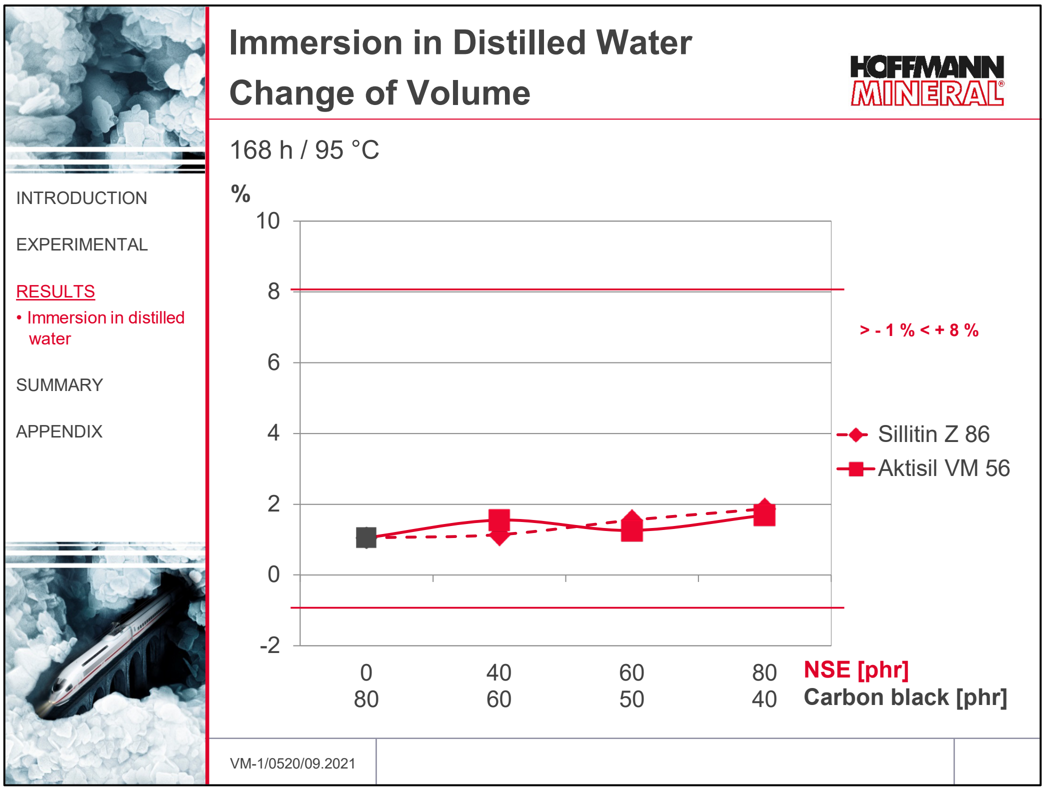


Fig. 14

The marginal fluctuations of the volume change after water storage are subject to the scatter of measured values. Under all replacement levels all variants are similar to the straight carbon black compound, well within the requirement profile of the standard from -1 to + 8 %.

3.4 Hot air aging

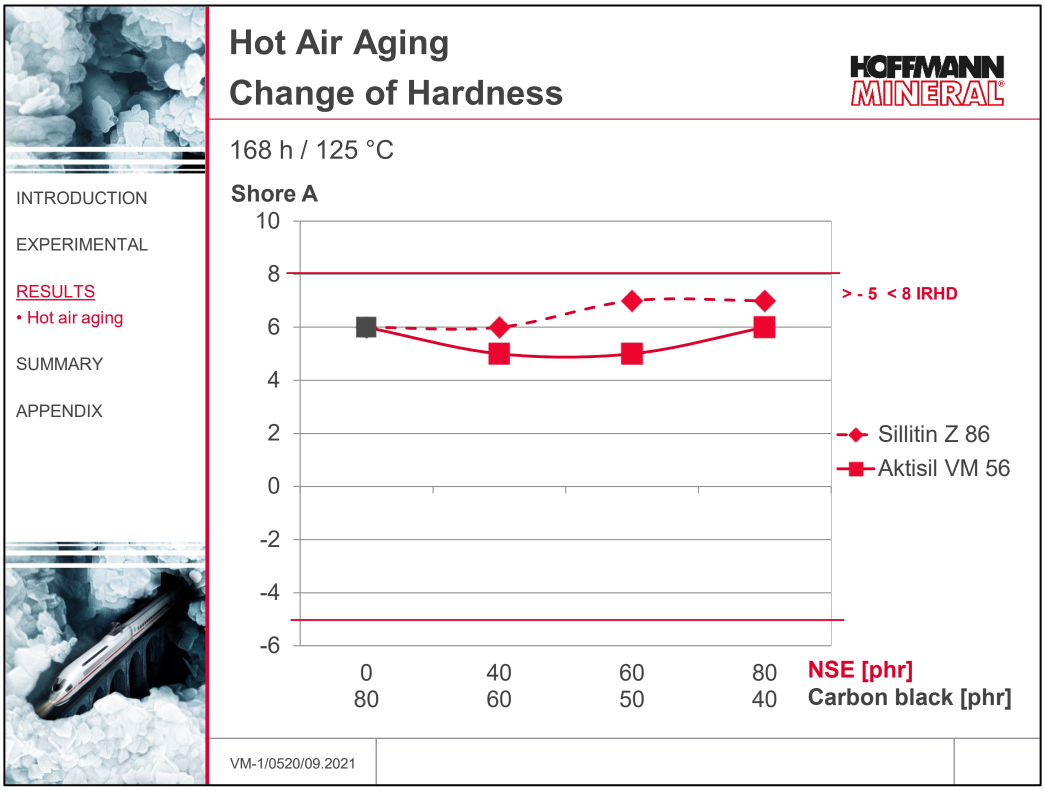


Fig. 15

Both Sillitin Z 86 and Aktisil VM 56 have only a marginal influence on the hardness change and are similar to the straight carbon black result. The specified limit of the standard of - 5 to + 8 IRHD is maintained.

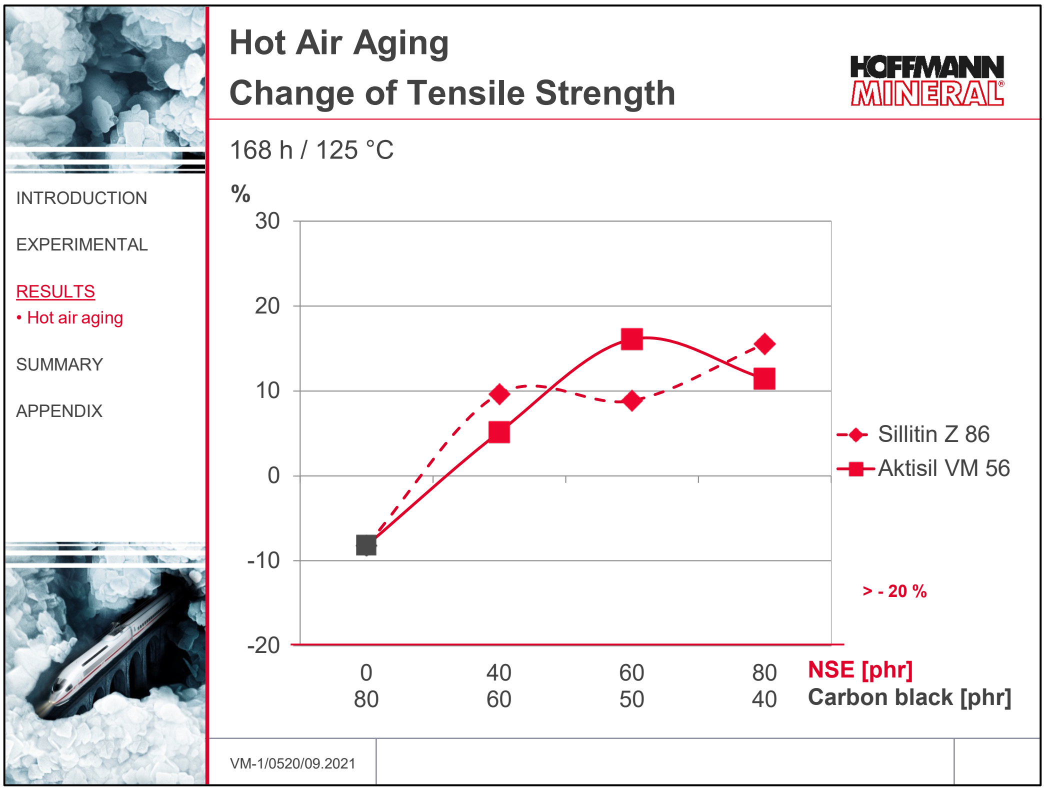


Fig. 16

All Neuburg Siliceous Earth grades and dosages result in positive changes of the tensile strength, well away from the specified limit of - 20 %, whereas the pure carbon black compound results in a negative change.

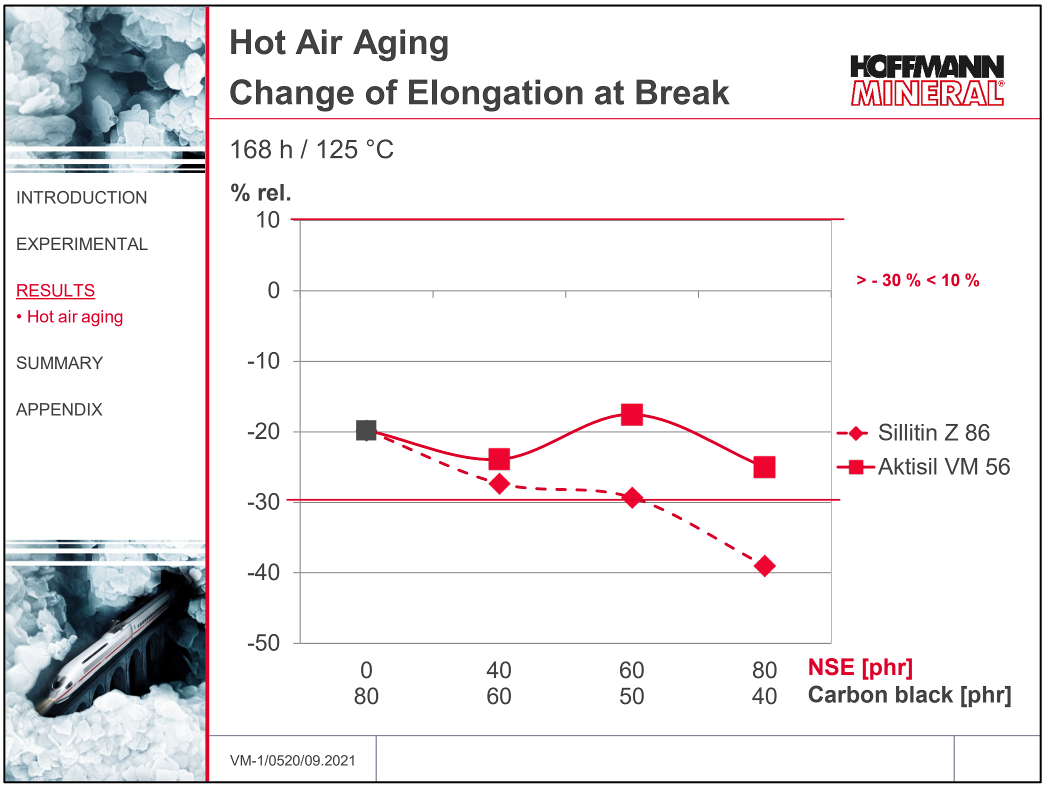


Fig. 17
With Aktisil VM 56, under all exchange conditions, the change of elongation at break after hot air aging is roughly at the level of the pure carbon black compound, which is within the standard range of +10 to -30 % relative.
Sillitin Z 86 barely meets the elongation at break change at carbon black replacement level of 25 %, 37 % is only borderline, and 50 % requires formulation optimization.

3.5 Cost aspects

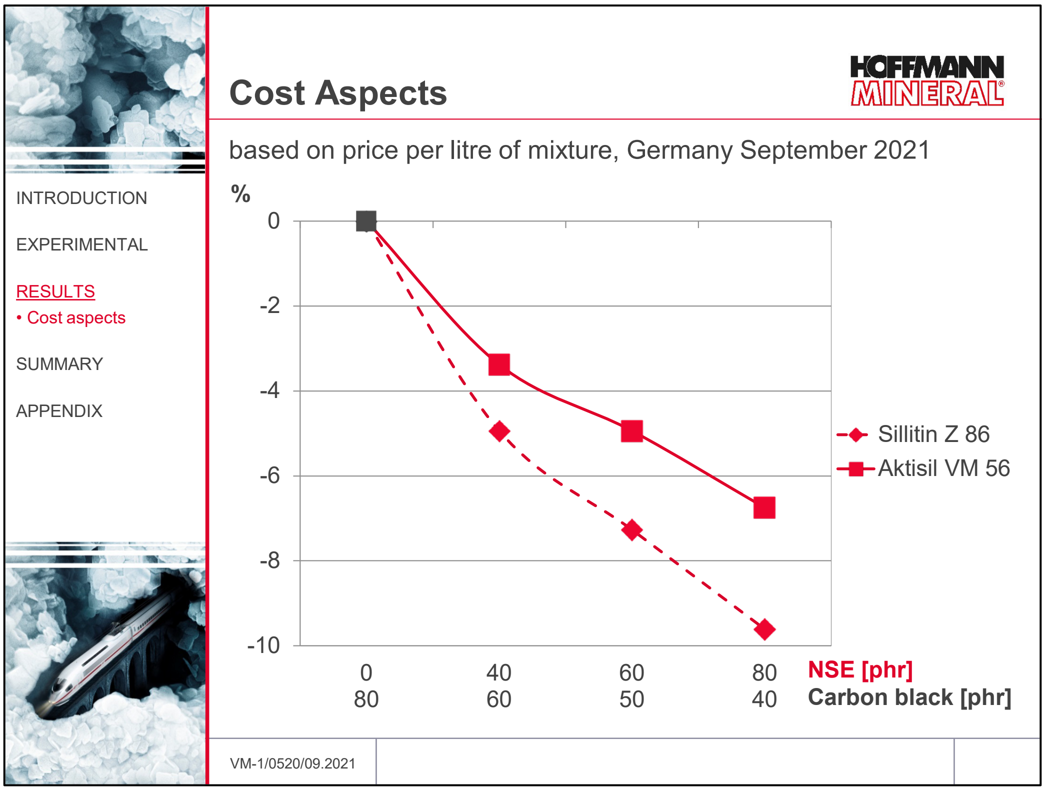


Fig. 18

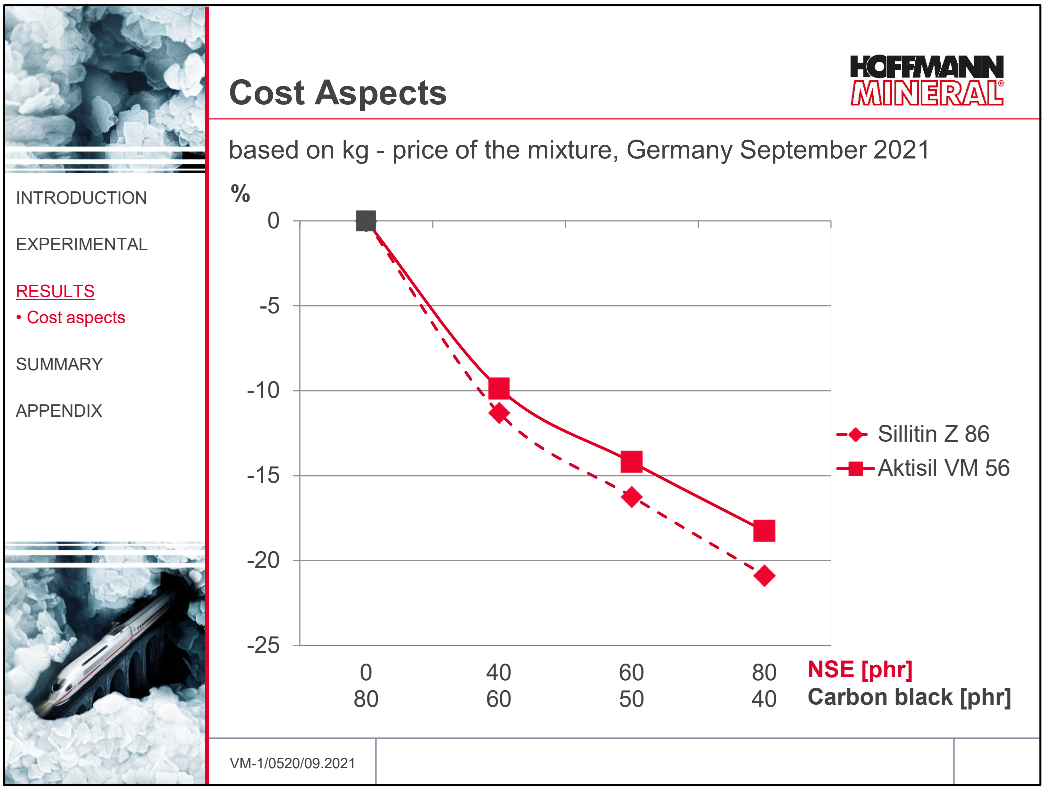


Fig. 19

The higher the concentration of Neuburg Siliceous Earth grades, the lower the compound price.

With Sillitin Z 86, due to the lower filler price, the compound costs are reduced even more than with Aktisil VM 56.

4 Summary

Aktisil VM 56

- Significant cost reduction
- Fulfils the requirement profile of the standard even up to 50 % carbon black replacement at a high level
- Lower Mooney viscosity and shorter conversion time t_{90}

Sillitin Z 86

- Even more significant cost reduction potential than with Aktisil VM 56
- Positive effect on tear resistance DIN ISO 34-1 trouser specimen
- Lower Mooney viscosity and shorter conversion time t_{90}
- 25 % Carbon black replacement:

  Fulfils requirement profile
- 37 % Carbon black replacement:
  - Requires longer conversion time or post cure due to compression set requirement
  - Change of elongation at break after hot air ageing is borderline
- 50 % Carbon black replacement:

  Most cost-effective variant, however requires formulation optimization:
  For example, by replacing the antioxidant BPH with polymeric TMQ, both compression set and properties after hot air aging are significantly improved.
  Polymeric TMQ currently listed in Positive List part 2 of the German Federal Environment Agency (as of September 2021).

5 Table of results

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		Purex HS 45	Sillitin Z 86 + Purex HS 45			Aktisil VM 56 + Purex HS 45		
		80 phr	40 phr 60 phr	60 phr 50 phr	80 phr 40 phr	40 phr 60phr	60 phr 50 phr	80 phr 40 phr
Rheology								
Mooney viscosity, ML 1+4, 100 °C	MU	72	63	65	63	64	64	63
Mooney viscosity, ML 1+4, 120 °C	MU	53	47	50	47	47	48	48
Temperature curemeter	°C	180						
Rotorless curemeter M_{min}	Nm	0.10	0.08	0.09	0.08	0.08	0.08	0.08
Rotorless curemeter M_{max}	Nm	0.80	0.76	0.73	0.70	0.79	0.70	0.71
Rotorless curemeter M_{max}-M_{min}	Nm	0.71	0.68	0.65	0.62	0.71	0.62	0.63
Rotorless curemeter V_{max}	Nm/min .	0.22	0.24	0.24	0.24	0.24	0.23	0.25
Rotorless curemeter t_5	min.	0.47	0.48	0.47	0.46	0.48	0.47	0.45
Rotorless curemeter t_{90}	min.	7.0	6.6	6.3	6.1	6.6	6.4	6.2

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Table 5

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		80 phr	40 phr 60 phr	60 phr 50 phr	80 phr 40 phr	40 phr 60phr	60 phr 50 phr	80 phr 40 phr
Mechanical properties after press cure								
Hardness	Sh. A	69	67	67	65	68	67	67
Tensile strength	MPa	16	14	12	11	16	14	13
Modulus 100 %	MPa	5.0	4.7	4.6	3.8	5.5	5.2	5.3
Elongation at break	%	222	262	279	330	228	223	223
Tear resistance Trouser tear	N/mm	3.5	5.1	5.9	7.5	4.1	4.7	4.3
Tear resistance Delft	N	38	42	43	42	41	43	42
Compression set, 72 h / 23 °C, 25 % defl.	%	8.7	9.8	11	12	9.5	11	10
Compression set, 72 h / -10 °C, 25 % defl.	%	20	21	24	27	20	24	26
Compression set, 24 h / 125 °C, 25 % defl. Press cure t_{90} + 10 %	%	12	17	20	23	16	16	17
Compression set, 24 h / 125 °C, 25 % defl. Press cure 12 min.	%	11	16	18	19	16	16	15
Compression set, 24 h / 125 °C, 25 % defl. Post cure 2 h / 125 °C	%	12	16	18	20	16	16	16

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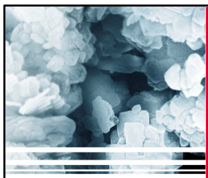
Table 6



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		Purex HS 45	Sillitin Z 86 + Purex HS 45			Aktisil VM 56 + Purex HS 45		
		80 phr	40 phr 60 phr	60 phr 50 phr	80 phr 40 phr	40 phr 60phr	60 phr 50 phr	80 phr 40 phr
Mechanical properties after immersion in distilled water 168 h / 95 °C								
Hardness	Sh. A	70	67	66	64	69	68	67
Tensile strength	MPa	17	15	13	11	16	14	14
Elongation at break	%	208	289	325	391	239	247	250
Δ Hardness	Sh. A	+1	0	-1	-1	+1	+1	0
Δ Tensile strength	%	+3.8	+6.5	+9.5	+4.6	-2.3	+2.4	+2.0
Δ Elongation at break	%	-6.4	+10	+16	+18	+5.0	+11	+12
Change of volume	%	+1.1	+1.1	+1.6	+1.9	+1.6	+1.3	+1.7
Mechanical properties after hot air aging 168 h / 125 °C								
Hardness	Sh. A	75	73	74	72	73	72	73
Tensile strength	MPa	17	15	14	13	15	16	15
Elongation at break	%	169	194	212	215	170	188	176
Δ Hardness	Sh. A	+6	+6	+7	+7	+5	+5	+6
Δ Tensile strength	%	-8.2	+9.7	+8.9	+16	-5.2	-16	-11
Δ Elongation at break	%	-20	-27	-29	-39	-24	-18	-25

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Table 7