Urea-resistant EPDM gaskets and hoses VW TL 52686 - Replacement of carbon black N990 with Aktisil VM 56

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VM-1/0320/09.2020

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1 Introduction

In order to make diesel engines more eco-friendly, selective catalytic reduction (SCR) was established for exhaust gas aftertreatment using an urea solution (Ad-Blue®; AUS 32).

As soon as the AdBlue® is injected into the hot exhaust gas stream, a hydrolysis reaction produces ammonia and CO_2. The ammonia is then required in the downstream SCR catalytic converter to convert nitrogen oxides (NOx) to water and elemental nitrogen.
If the engine and exhaust system are at operating temperature, the SCR catalytic converter removes up to 90 percent of the nitrogen oxide emissions from the exhaust gas. Currently (as of 2020), an estimated 20 million vehicles from German corporate brands are equipped with such exhaust gas aftertreatment. In order to meet future environmental protection limits, this technology is also indispensable.[1]

Due to this interaction of basicity and temperature, the stress on the elastomer components must not be neglected and is dependent on a strong performance of the formulation and the raw materials.

In this study we compare Aktisil VM 56 with a thermal Carbon Black N990 and present the advantages of a surface-treated Neuburg Siliceous Earth grade.

[1] Source: https://www.vda.de/de/themen/innovation-und-technik/antriebstechnik/abgas-technik.html

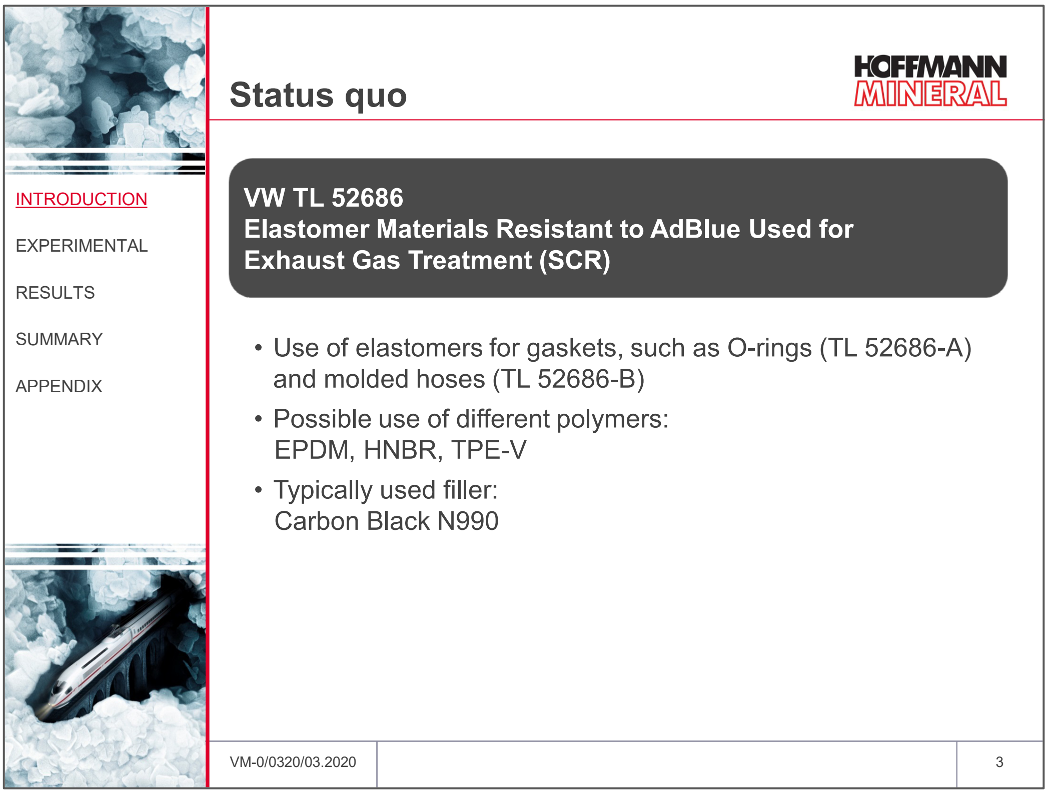

Fig. 1

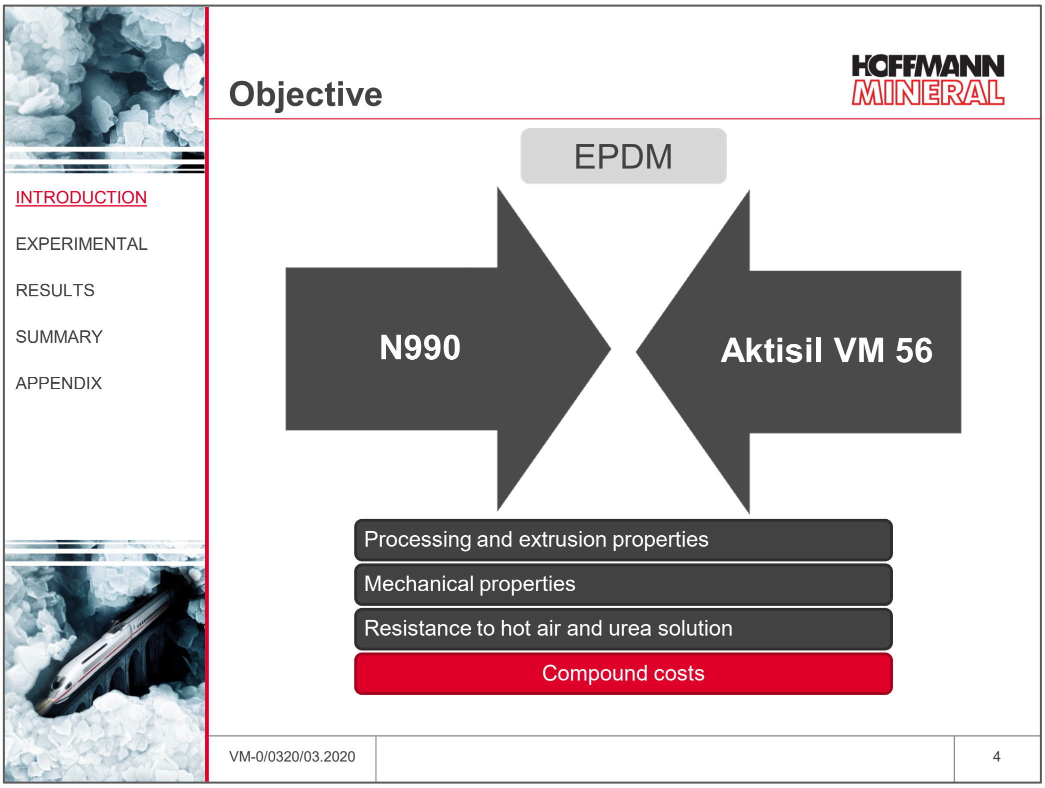

Fig. 2

The Volkswagen specification „VW TL 52686“ is dealing with elastomer materials resistant to Ad-Blue® used for exhaust gas treatment (SCR; selective catalytic reduction). It provides for the usage of either an EPDM or a HNBR type for seals and molded hoses. The application of hydrogenated acrylonitrile butadiene rubber provides great resistance to diesel fuel. This is necessary if the driver is falsely refuelling the vehicle and the components of the exhaust gas aftertreatment system are flooded with diesel fuel.

However, since a HNBR rubber is more expensive than EPDM rubber and offers no other application-related advantages, this study uses EPDM based formulation. The standard would also allow the use of a cross-linked TPE (thermoplastic-elastomer), but only for a filler neck.

2 Experimental

2.1 Formulation, Fillers, Mixing/Vulcanization

Formulation

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Material	Description	phr	phr
Keltan 4450S	Ethylene Propylene Diene Rubber, amorphous, ML 1+4 (125 °C): 42 MU	100	100
Carbon Black N990	Carbon Black MT	120	
Aktisil VM 56	NSE, surface treated		120
Process Oil P460	Paraffinic plasticizer	20	20
Vulkanox HS/LG	Antioxidant, TMQ	1	1
TAC GR 70	Triallylcyuanurate, 70%, coagent	1	1
Perkadox 14-40B-pd-s	Di(tert-butylperoxyisopropyl) benzene peroxide	5	5
Total		**247**	**247**

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Fig. 3

When designing the formulation, care must be taken to use as little plasticizer and additives as possible in order to suppress the potential impairment of the catalytic reduction - due to impurities that separate from the component. In addition, peroxide crosslinking is highly recommended, since a sulfur-crosslinked mixture reacts further in the alkaline environment and could therefore lead to disadvantageous properties *(Fig. 3)*.

Fillers, Characteristics

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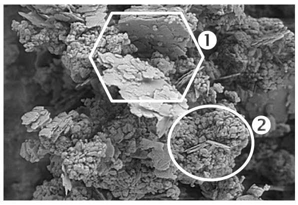
		CB N990	Aktisil VM 56
Density	[g/cm^3]	1.8	2.6
Particle size d_{50}	[µm]		2.2
Particle size d_{97}	[µm]		10
Sieve residue > 40 µm	[mg/kg]		20
Sieve residue 45 µm/325 mesh	ppm	18	
Oil absorption	[g/100g]		45
DBP absorption	[ml/100 g]	38	
Specific surface area BET	[m²/g]		9
CTAB surface area	[m²/g]	7	
Functionalization		none	Vinyl



❶ lamellar: kaolinite
❷ corpuscular: silica

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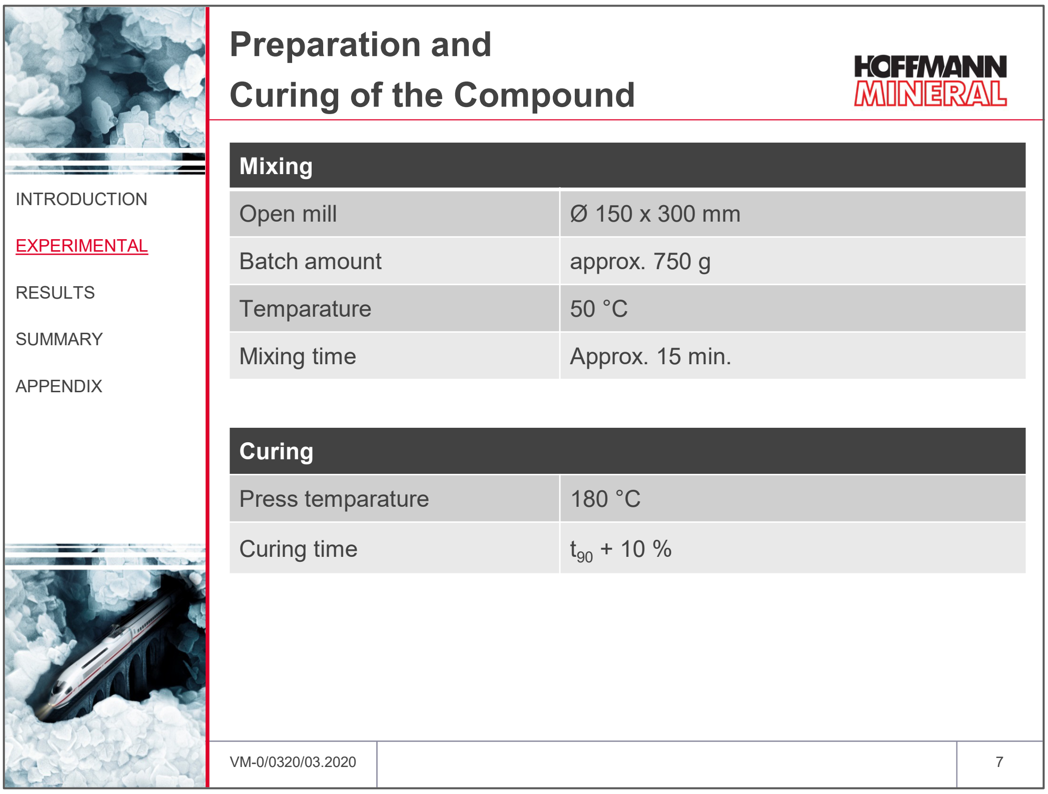
Fig. 4

The typical properties of Carbon Black N990 do not show big differences vs. the Neuburg Siliceous Earth; one of the biggest differences is the density of 1.8 vs. 2.6 g/cm³ *(Fig. 4)*.



Preparation and Curing of the Compound

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Mixing	
Open mill	Ø 150 x 300 mm
Batch amount	approx. 750 g
Temparature	50 °C
Mixing time	Approx. 15 min.

Curing	
Press temparature	180 °C
Curing time	t_{90} + 10 %

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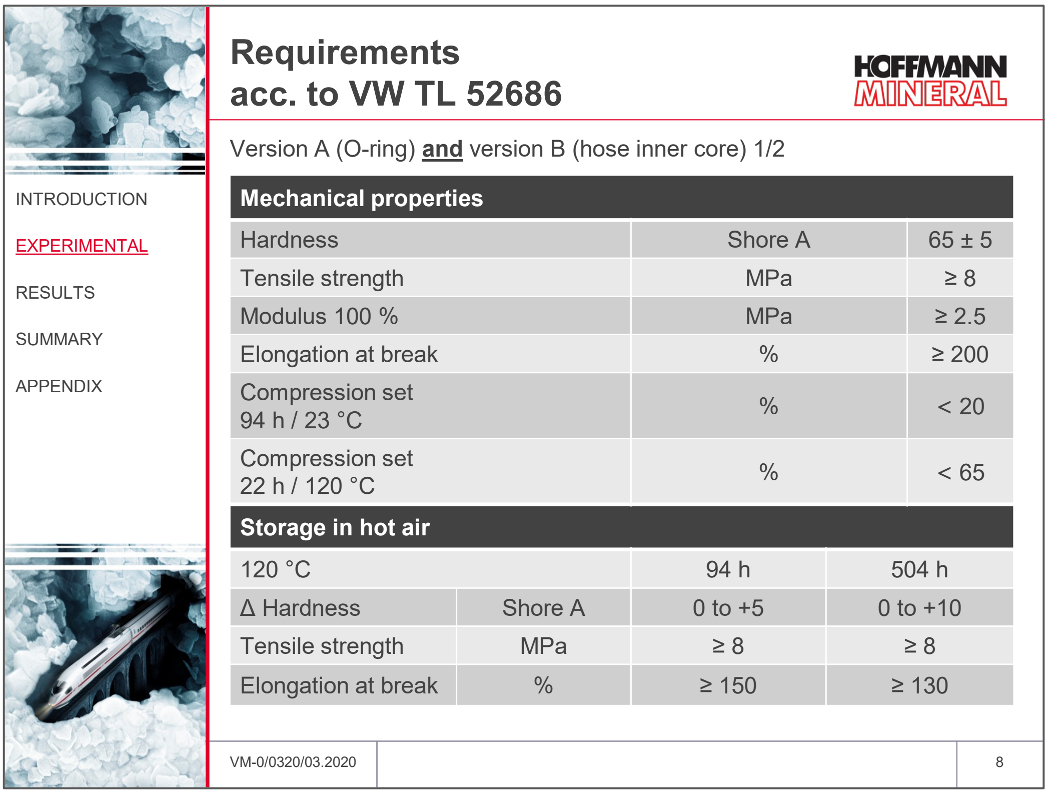
Fig. 5

The compound was made up using a open mill (Schwabenthan Polymix 150 L). The rubber was added to the roller at 50 °C, followed by the remaining ingredients in the order given in the formulation, at the same time keeping the roller at a constant temperature. Mixing time was around 15 minutes on average.
The compounds were cured in an electrically heated press at 180 °C. The duration of the vulcanization was the conversion time t_{90} + 10 % *(Fig. 5)*.

2.2 Requirements according to VW TL 52686



Requirements acc. to VW TL 52686

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Version A (O-ring) **and** version B (hose inner core) 1/2

Mechanical properties		
Hardness	Shore A	65 ± 5
Tensile strength	MPa	≥ 8
Modulus 100 %	MPa	≥ 2.5
Elongation at break	%	≥ 200
Compression set 94 h / 23 °C	%	< 20
Compression set 22 h / 120 °C	%	< 65

Storage in hot air			
120 °C		94 h	504 h
Δ Hardness	Shore A	0 to +5	0 to +10
Tensile strength	MPa	≥ 8	≥ 8
Elongation at break	%	≥ 150	≥ 130

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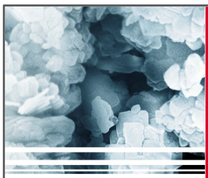
Fig. 6



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Requirements acc. to VW TL 52686

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Version A (O-ring) **and** version B (hose inner core) 2/2

Storage in urea solution , 32 %, ISO 22241			
80 °C		94 h	504 h
Δ Hardness	Shore A	± 5	± 5
Tensile strength	MPa	≥ 8	≥ 8
Elongation at break	%	≥ 200	≥ 200
Δ Weight	%	0 to +3	0 to +5

- **Tests**

  Based on DIN with test parameters VW standards TL 52686

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Fig. 7

Since the requirements for version A (O-ring) and version B (hose inner layer) are exactly the same, we can offer a uniform formulation for the processing fields of injection molding and extrusion.
The hose outer layer (also version B) was not processed, since it does not have to meet any specifications related to urea solution.

3 Results

3.1 Rheological properties

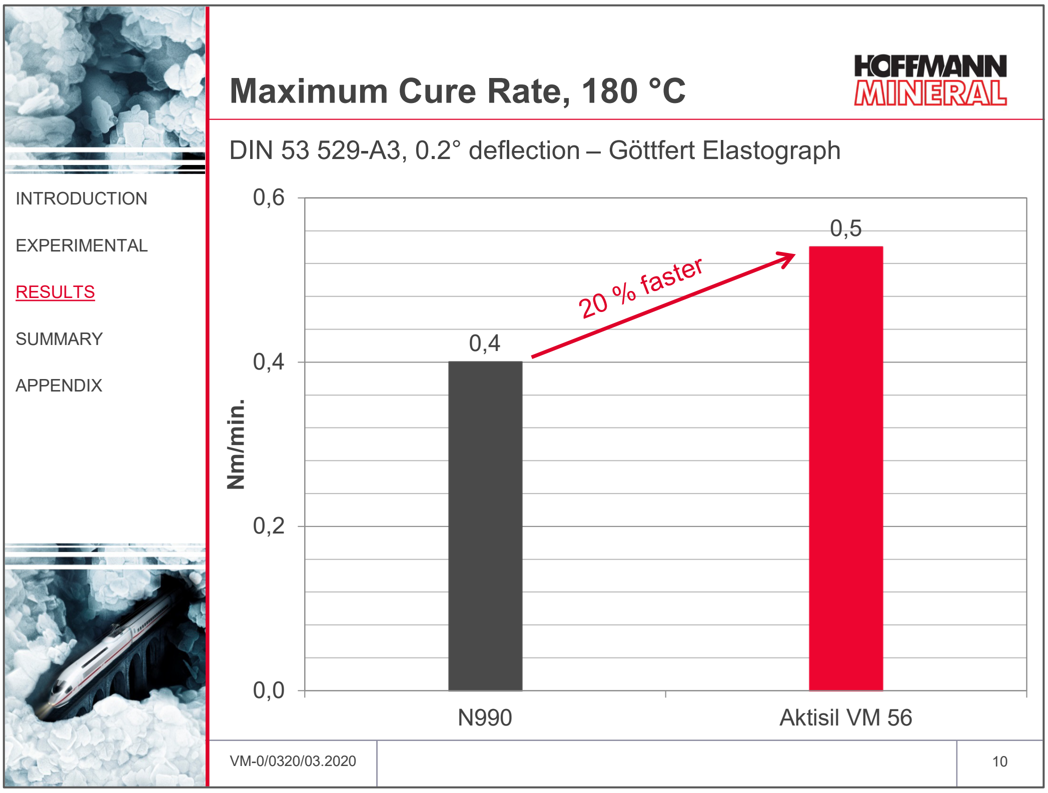


Fig. 8

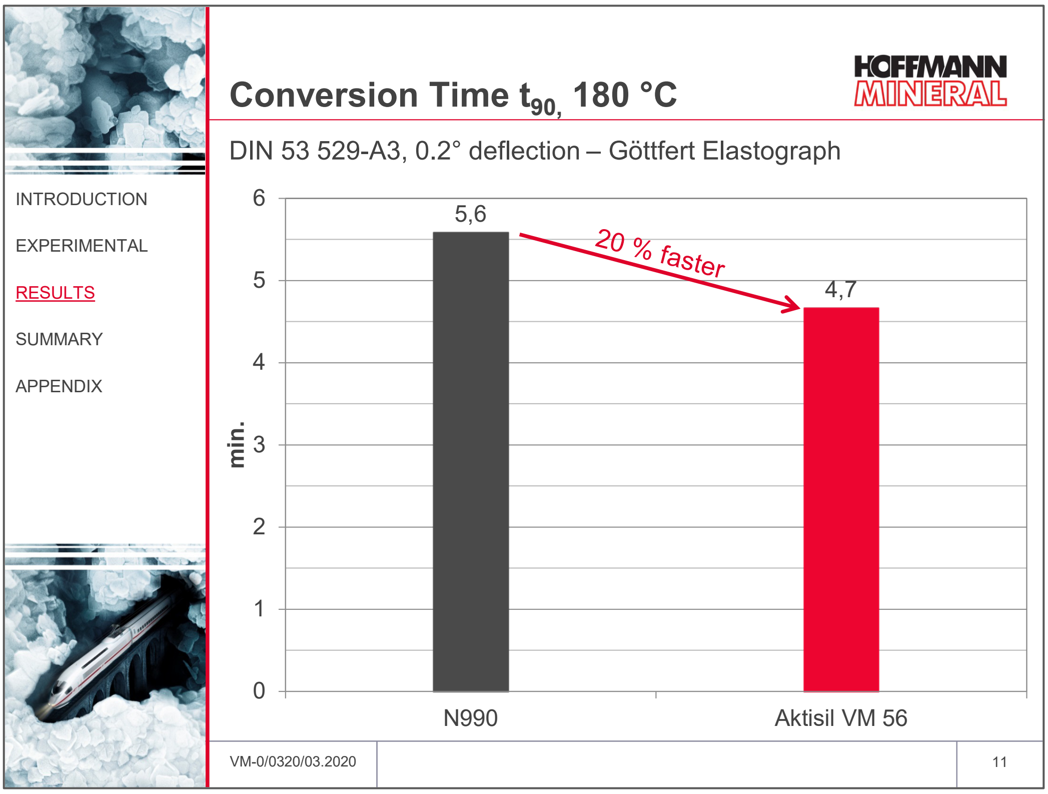


Fig. 9

The use of Aktisil VM 56 increases the maximum cure rate by 20 percent *(Fig. 8)*. This also results in a 20 percent reduction in conversion time t_{90}; from 5.6 minutes for carbon black to 4.7 minutes with the Aktisil VM 56 *(Fig. 9)*.
This should make it possible to shorten the cycle time in production.

3.2 Mechanical properties

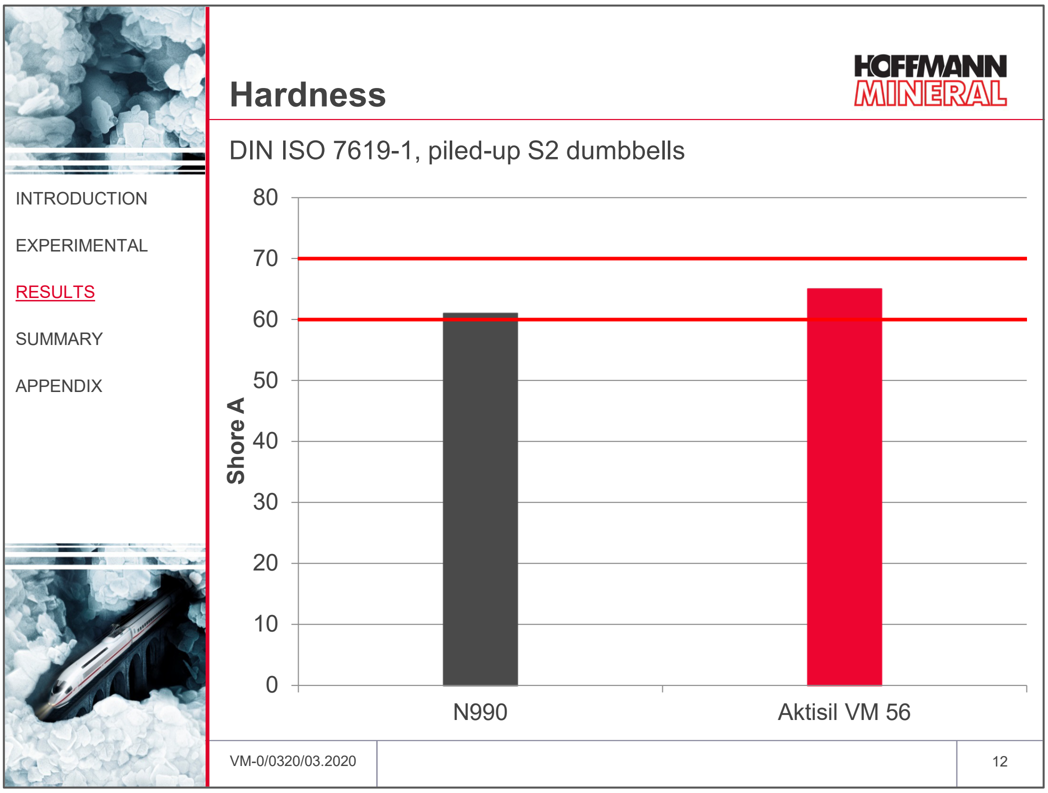


Fig. 10

With the same filler dosage, the compound with Neuburg Siliceous Earth has a hardness of 65 Shore A, wherein carbon black filled mixture with 61 Shore A is at the lower specification limit *(Fig. 10).*

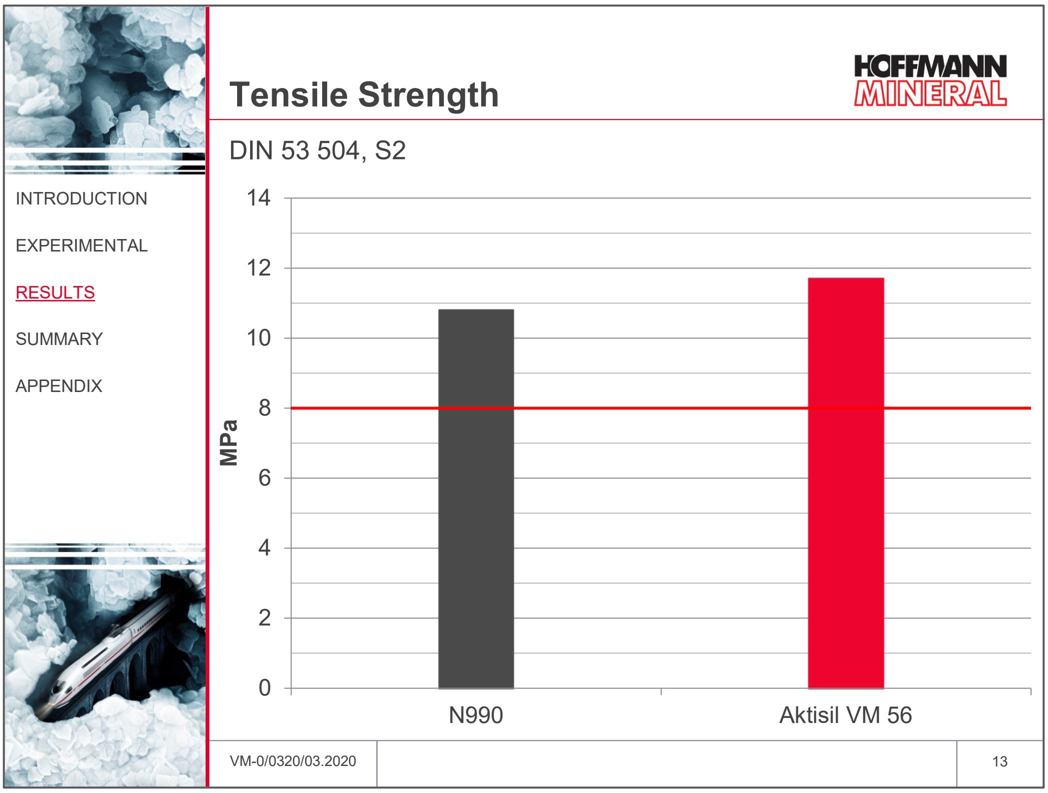


Fig. 11

The specification limit of 8 MPa is well exceeded by both fillers, whereby the Aktisil VM 56 results in a higher tensile strength (11.7 MPa) *(Fig. 11).*

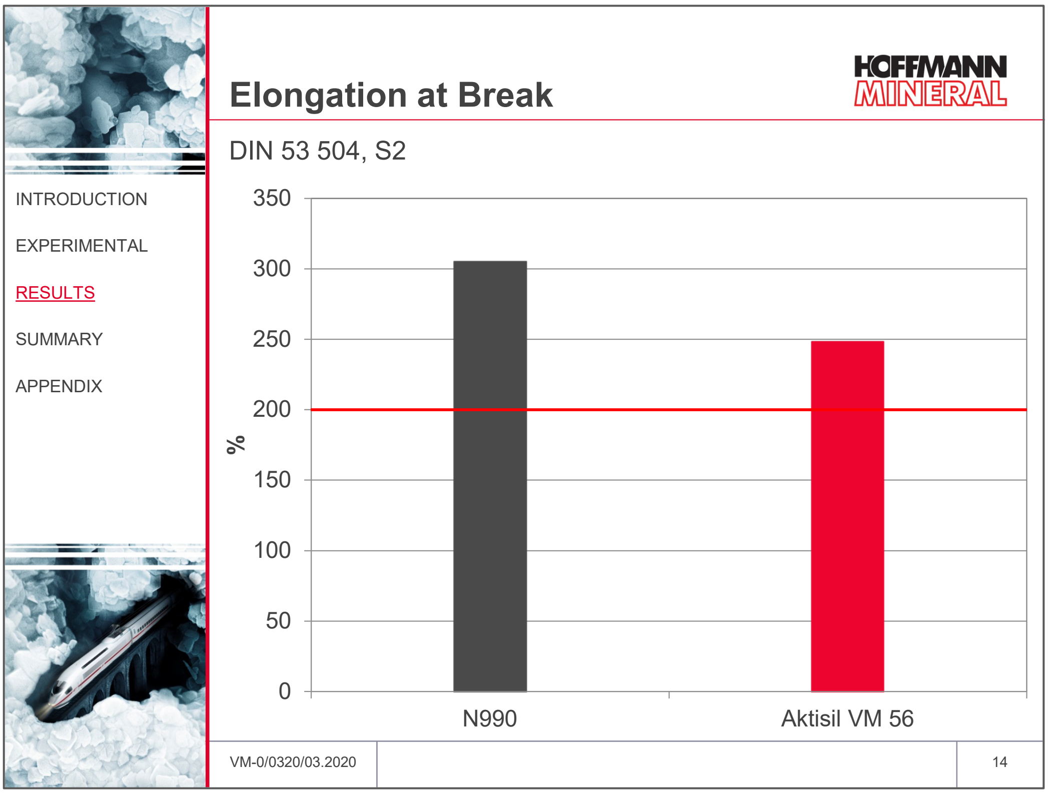


Fig. 12

Both fillers achieve the required elongation at break *(Fig. 12).*

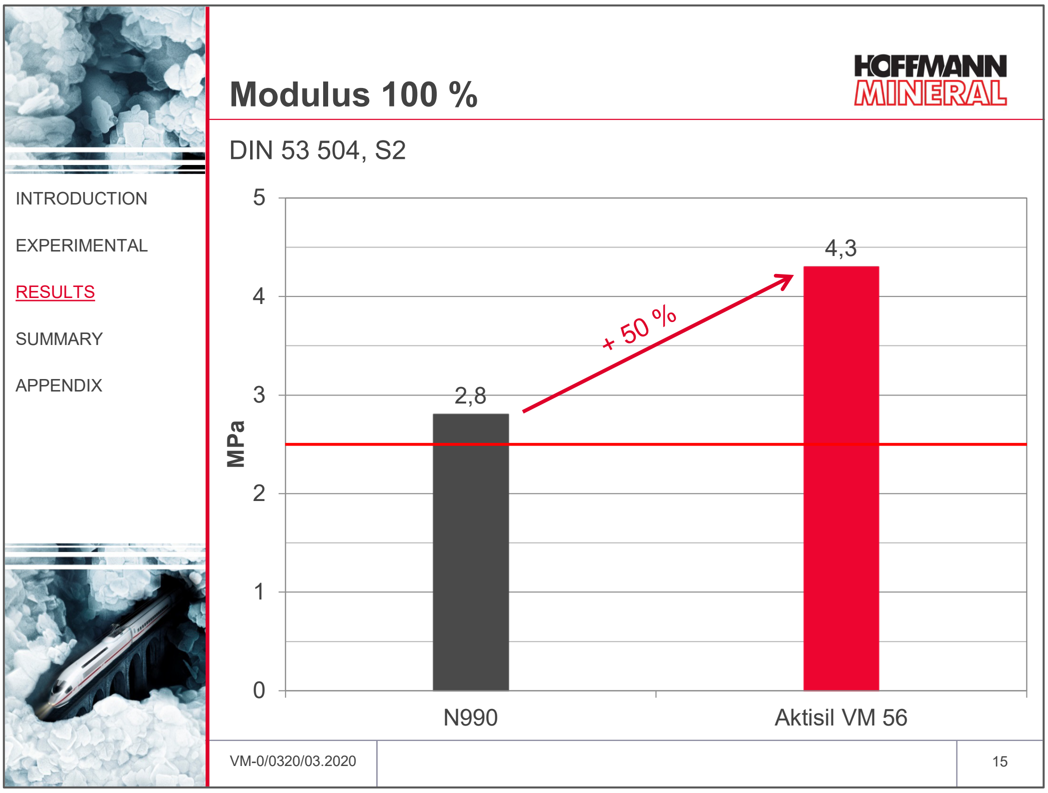


Fig. 13

In addition, Aktisil VM 56 leads to a 50 percent higher modulus at 100 % elongation (4.3 MPa). With the 2.8 MPa achieved by the N990, it is just meeting the specification of 2.5 MPa *(Fig. 13).*

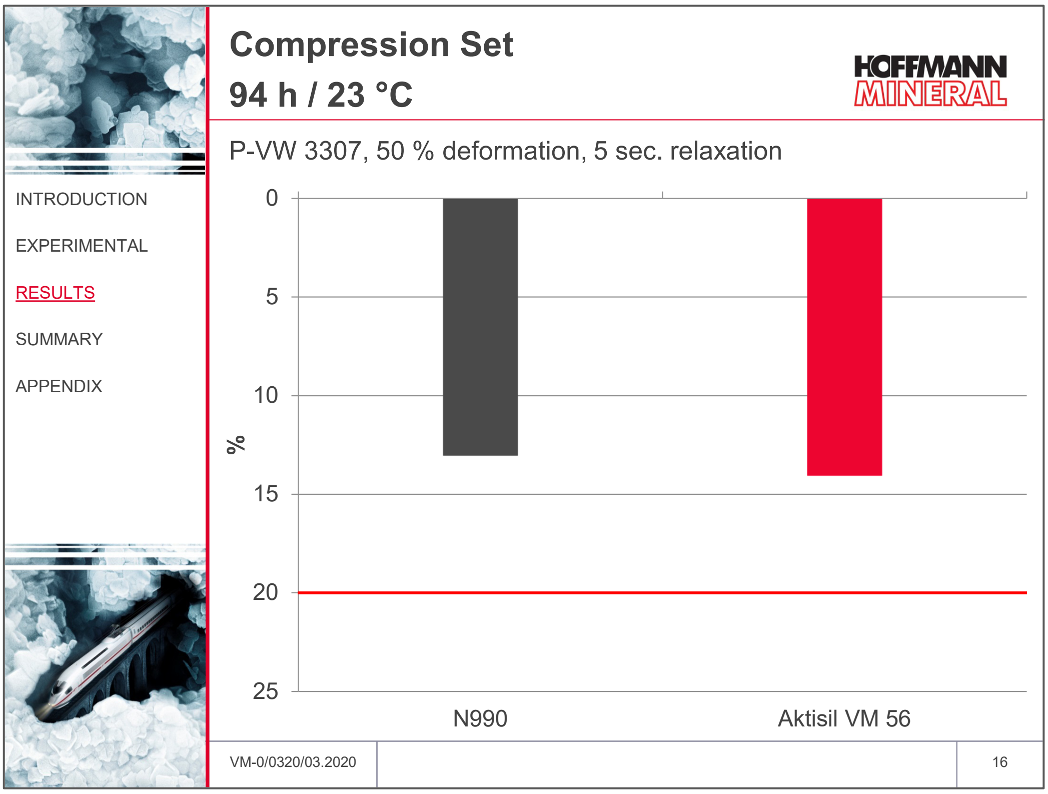


Fig. 14

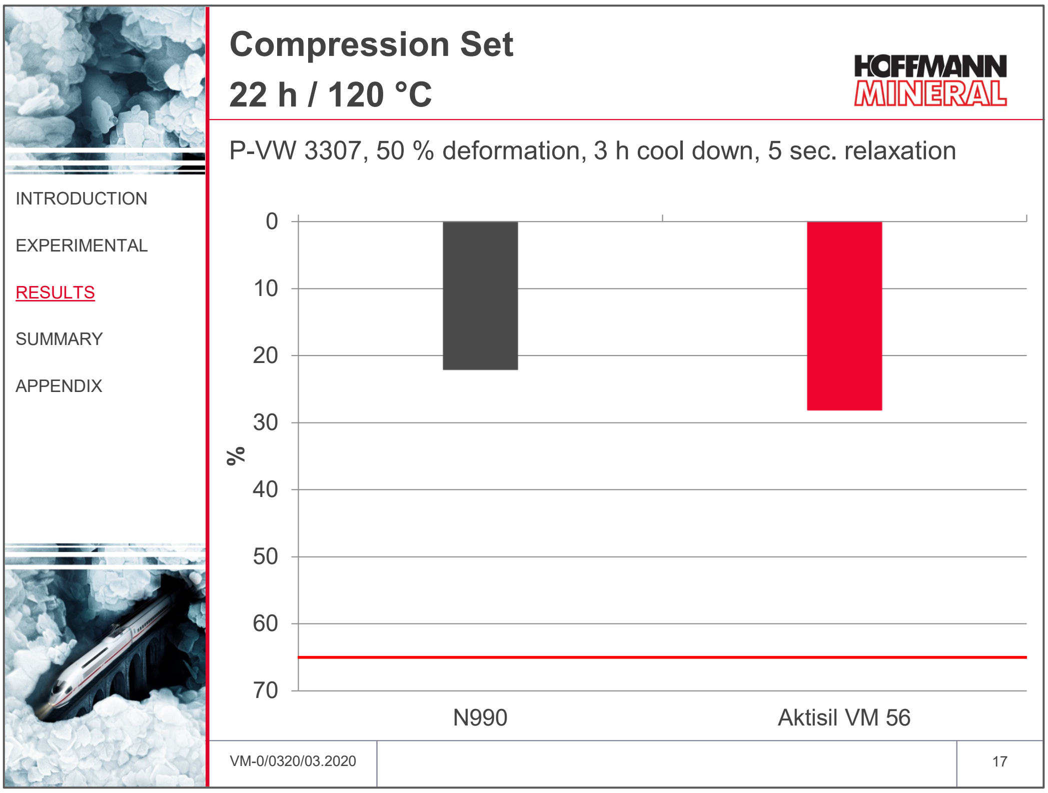


Fig. 15

Both compounds have the required low compression sets *(Fig. 14 and Fig. 15).*

3.3 Hot air resistance

The hot air aging duration was 94 hours or 504 hours.
Both compounds can easily reach the required specifications and offer more than sufficient safety for the use at increased temperature *(Fig.16, Fig. 17 and Fig. 18).*

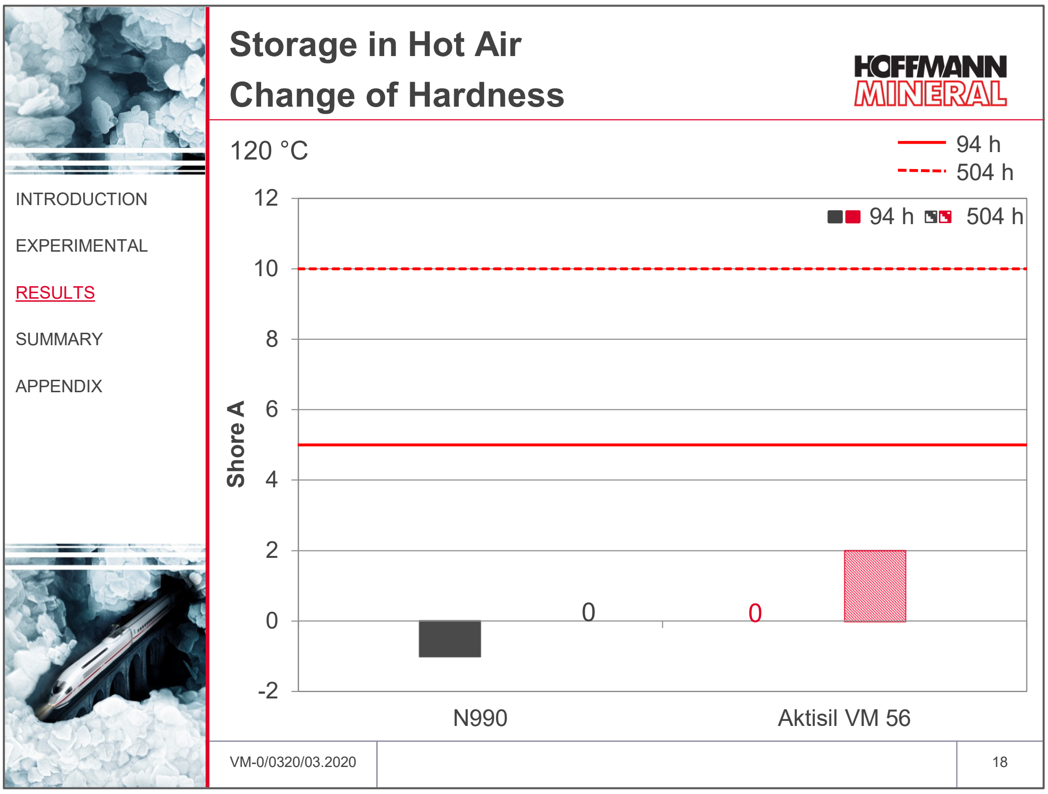


Fig. 16

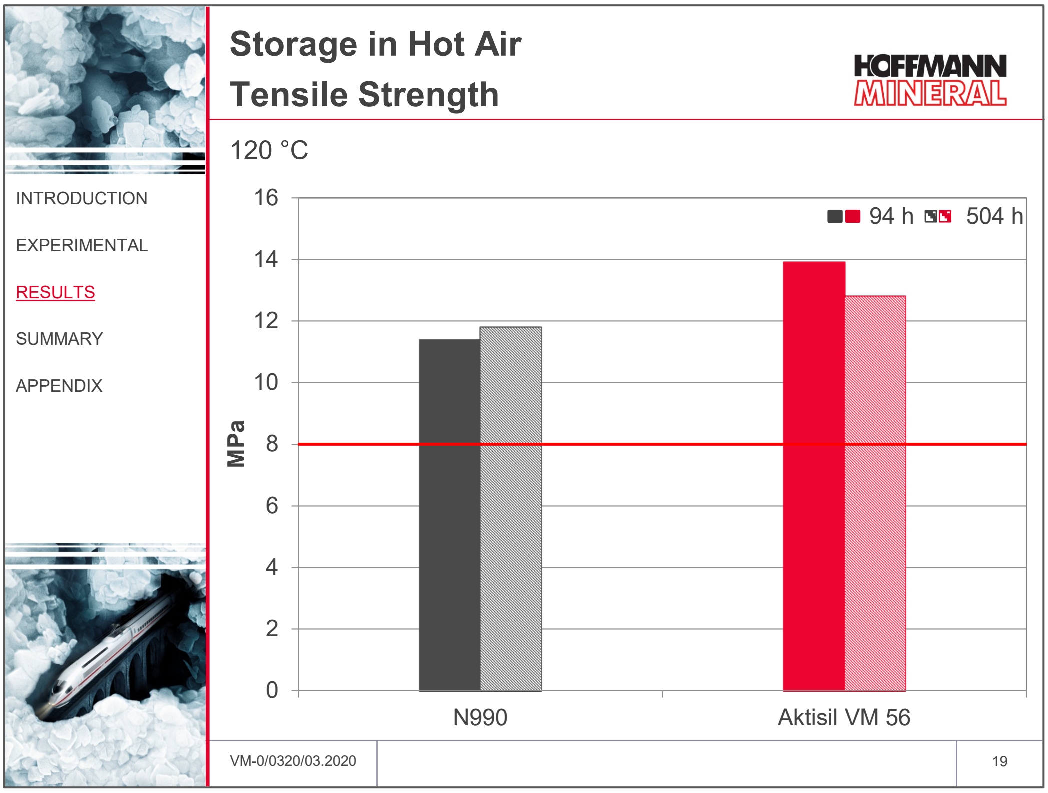
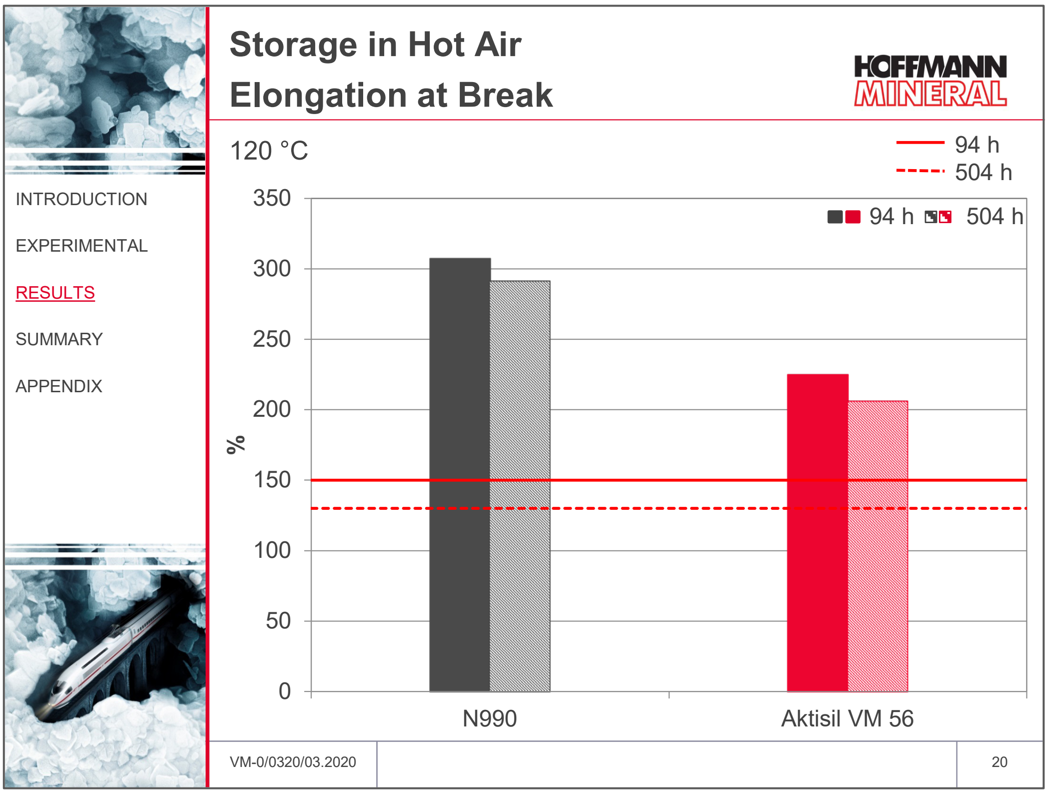


Fig. 17


Storage in Hot Air
Elongation at Break
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120 °C
94 h
504 h
94 h
504 h
350
300
250
200
150
100
50
0
%
N990
Aktisil VM 56
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20
Fig. 18

3.4 Urea resistance

The storage in urea solution takes place at 80°C, as the hydrolysis reaction to ammonia and water already takes place.

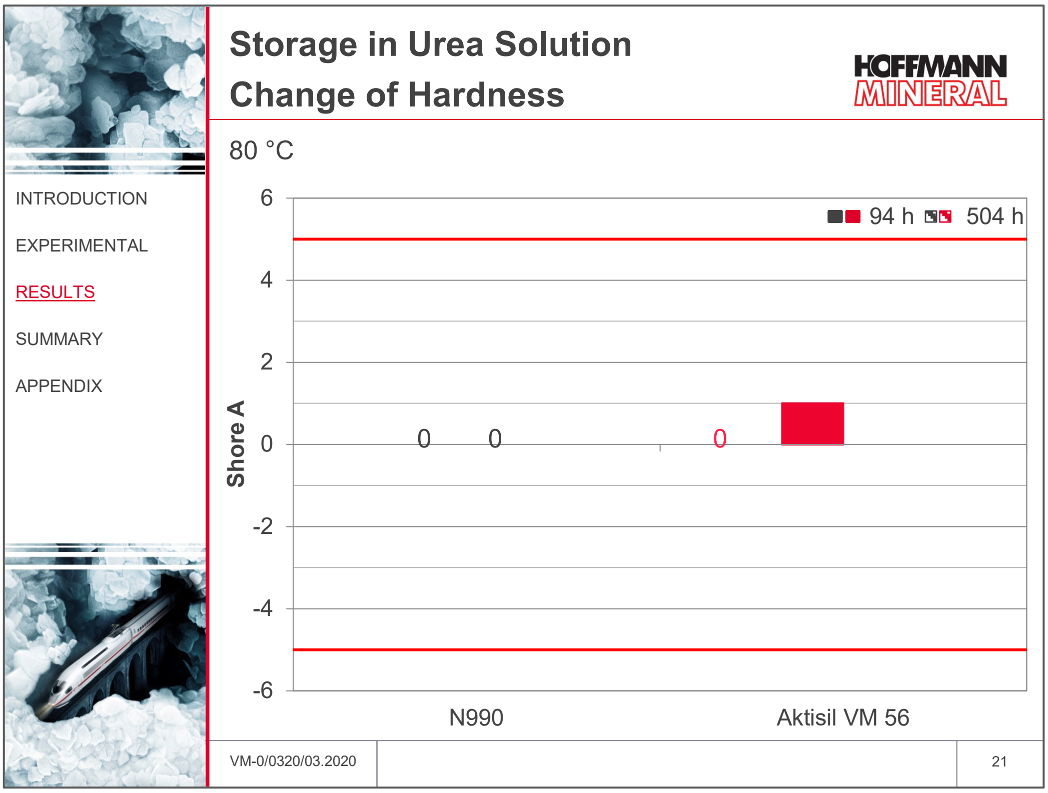


Fig. 19

Like the carbon black, the Aktisil VM 56 offers excellent resistance to AdBlue® and shows no change in hardness *(Fig. 19)* and no change in weight *(Fig. 22)* after storage. The tensile strength *(Fig. 20)* and the elongation at break *(Fig. 21)* are also at an excellent distance from the specification limit.

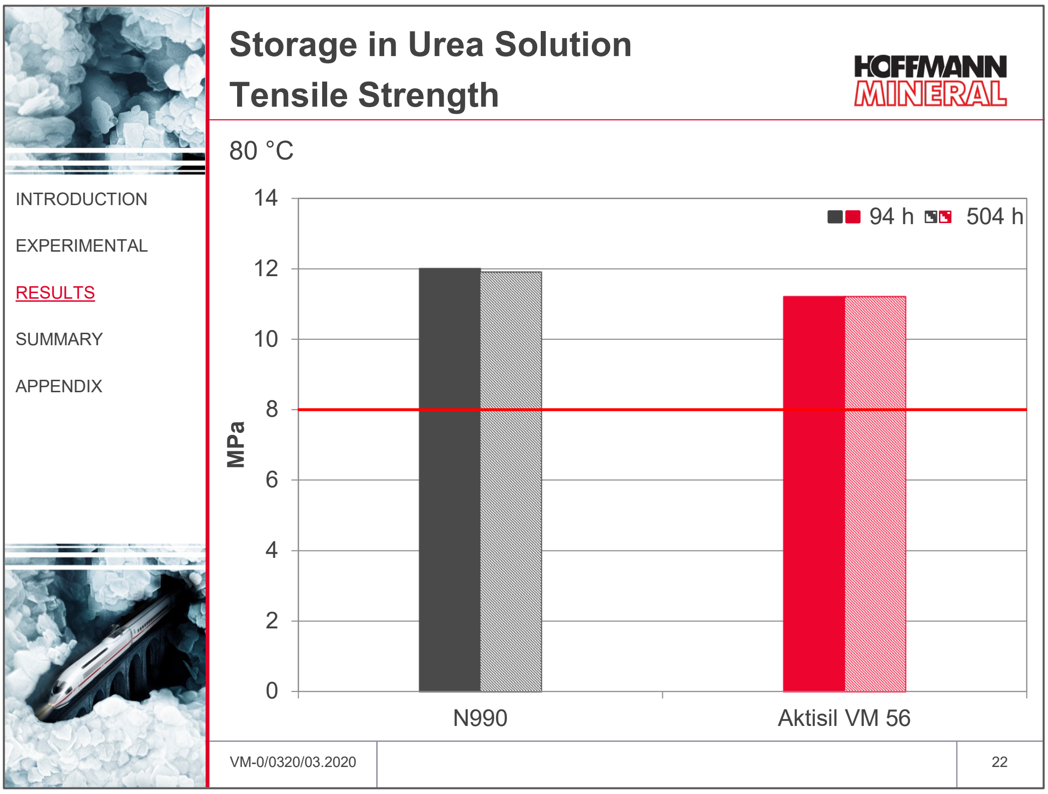
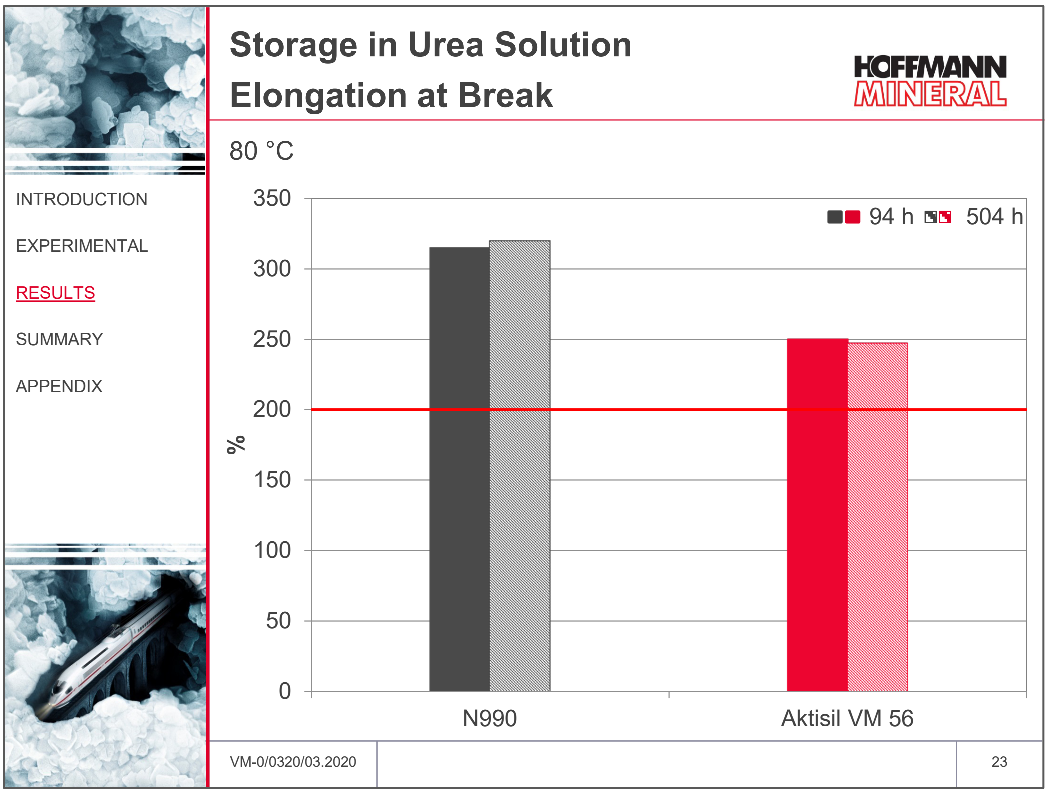


Fig. 20



Storage in Urea Solution
Elongation at Break
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80 °C
94 h
504 h
%
350
300
250
200
150
100
50
0
N990
Aktisil VM 56
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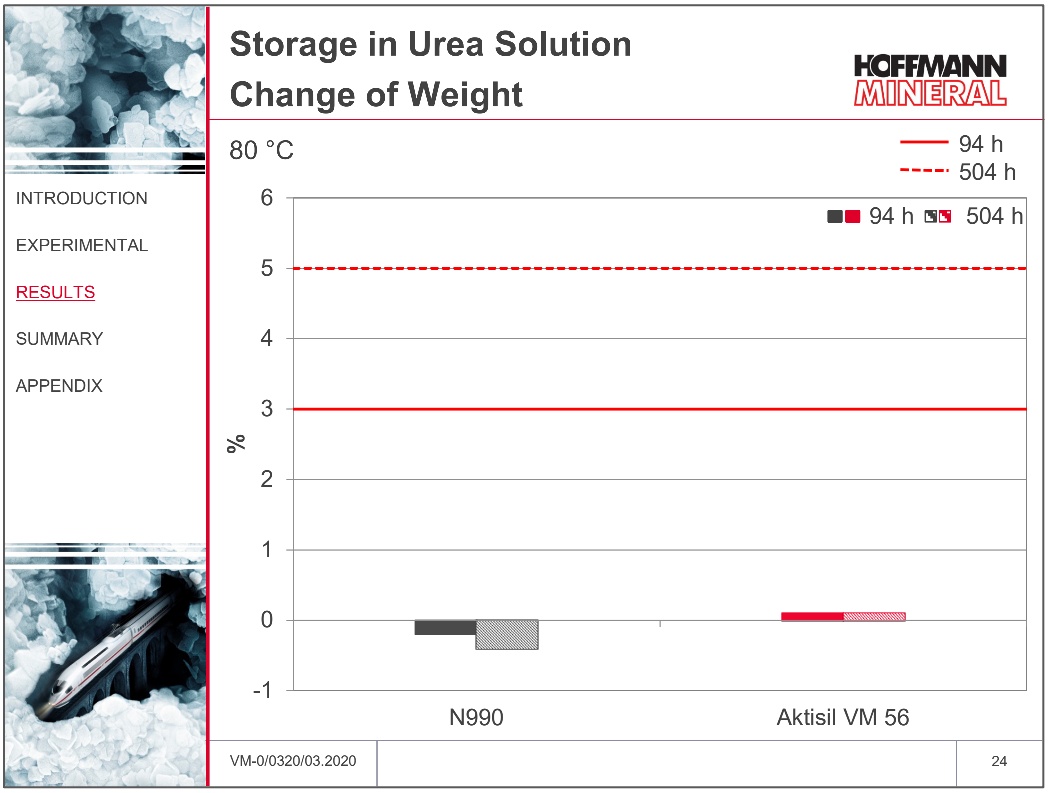
23

Fig. 21



Storage in Urea Solution
Change of Weight
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80 °C
94 h
504 h
94 h
504 h
%
6
5
4
3
2
1
0
-1
N990
Aktisil VM 56
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24

Fig. 22

3.5 Blooming

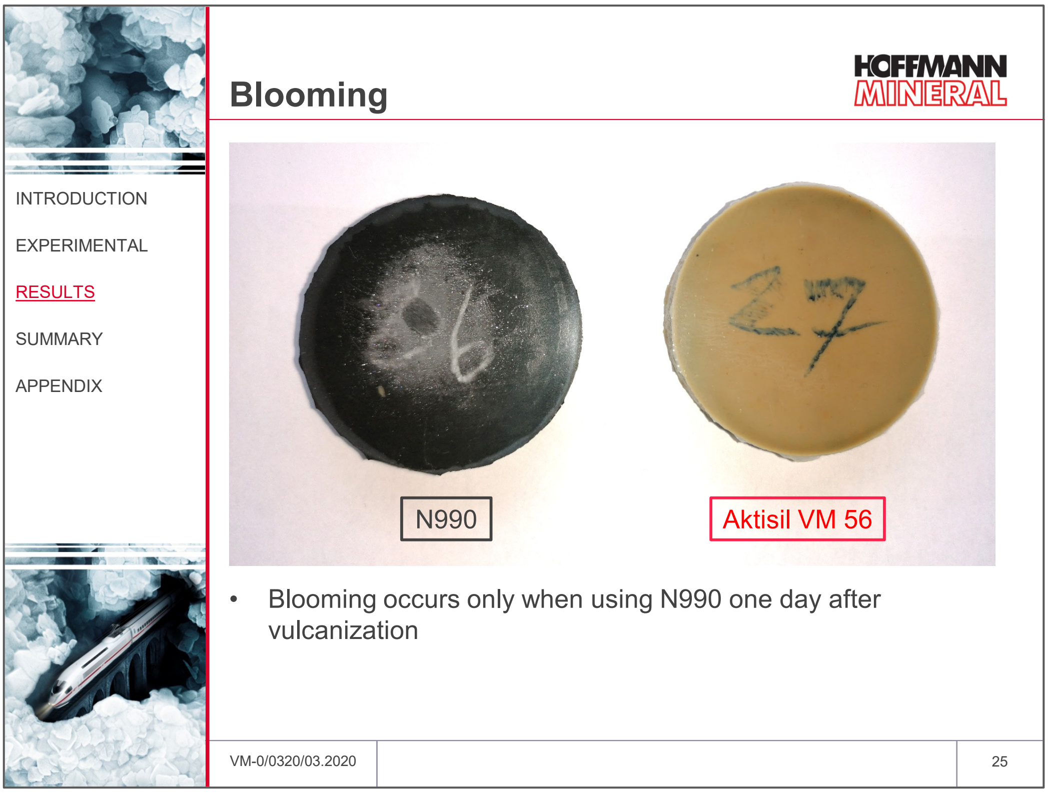

Fig. 23

As shown in *Figure 23* the compound with the carbon black tends to blooming of decomposition product of the peroxide. This occurs already one day after vulcanization as a white, crystalline powder on the surface of the test specimen.

The powder suggests that it is a di(2-hydroxyisopropyl)benzene, since according to the manufacturer, this can be a major solid decomposition product of the peroxide "Perkadox 14", which is used.
Other possible decomposition products - such as diacetylbenzene - can be excluded, since the melting range of these products is below 120°C, which would be the temperature of the hot air aging. After the aging there is still white powder on the surface.

The Aktisil VM 56 eliminates the blooming and thus contamination of the surface and can save an entire process step for cleaning the products.

3.6 Hose Extrusion

The compounds have been extruded with a haul-off speed of 5 m/min. on a laboratory extruder "Polytest 30 R" from Schwabenthan. The hoses were not vulcanized after the extrusion.
For more detailed information, see Figures 24 and 25.

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Hose Extrusion

Extruder		Schwabenthan Polytest 30 R
Screw diameter	[mm]	30
Working length	[mm]	450
Temperature set point head / zone 1 / zone 2	[°C]	110 / 70 / 70
Profile		see below
Feed strips		Cold untreated
Haul-off speed		5 m/min.

Tube Extrusion Die

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Fig. 24

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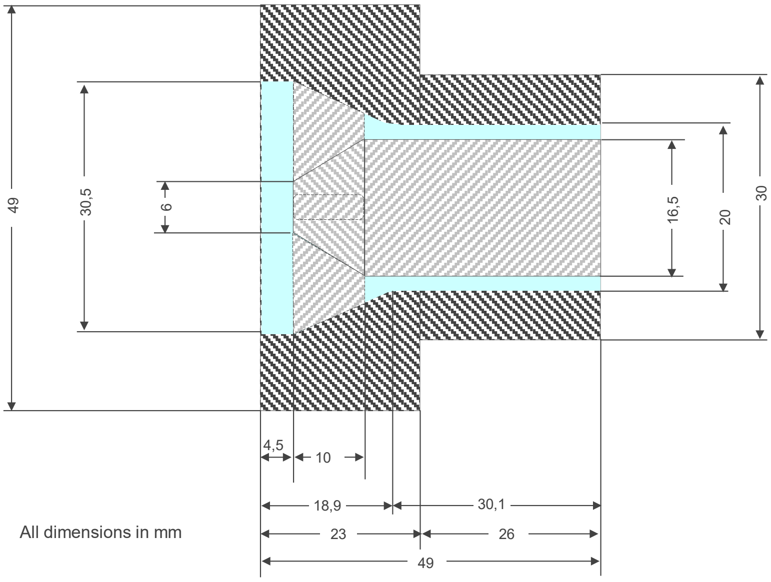
Tube Extrusion Die



All dimensions in mm

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Fig. 25

Fig. 26

Figure 26 depicts the hose extrusion photos, showing the advantages of using Aktisil VM 56.
The hose with the Carbon Black N990 has a rippled and uneven surface, whereas the hose with the Neuburg Siliceous Earth grade has an even and smooth surface. In addition, the Aktisil VM 56 results in a higher collapse resistance.

3.7 Cost aspects

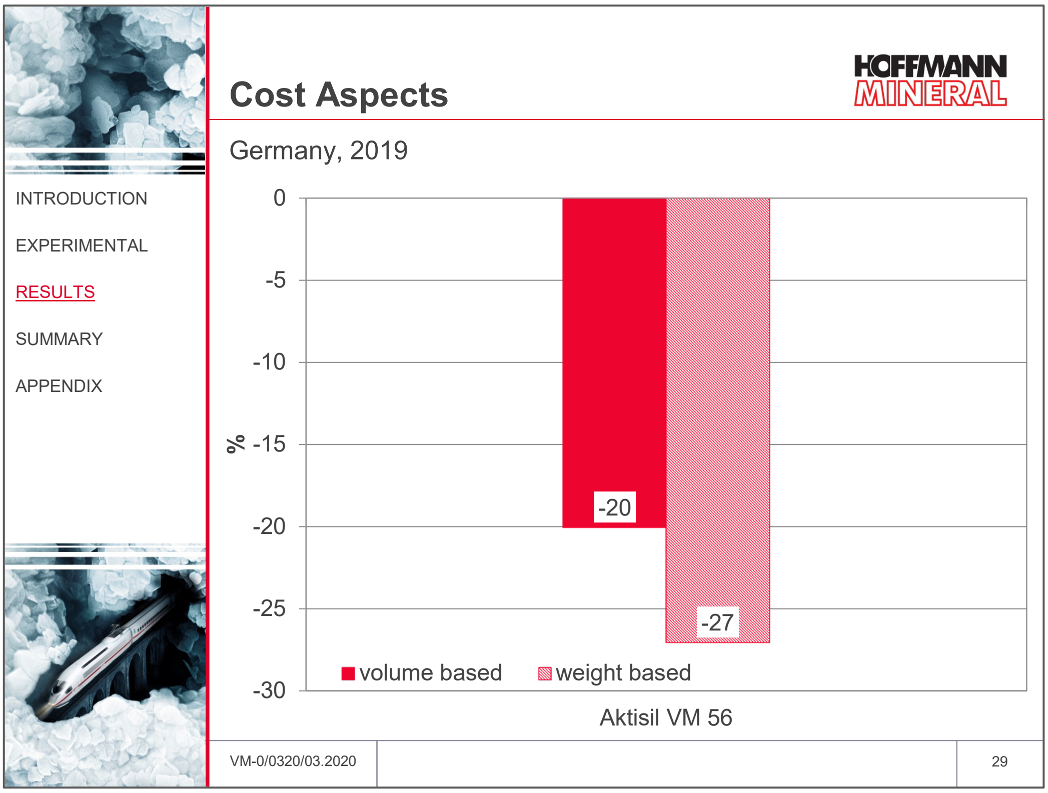

Fig. 27

With the use of the Aktisil VM 56, a marked reduction of the compound raw material costs can be realized. While the weight-based costs are reduced by up to 27 percent, the volume-based reduction is still 20 percent despite the higher density of Neuburg Siliceous Earth *(Fig. 27)*.
While the carbon black prices often fluctuate strongly, the costs for Neuburg Siliceous Earth remain calculable with a minimal increase over long time.

4 Summary

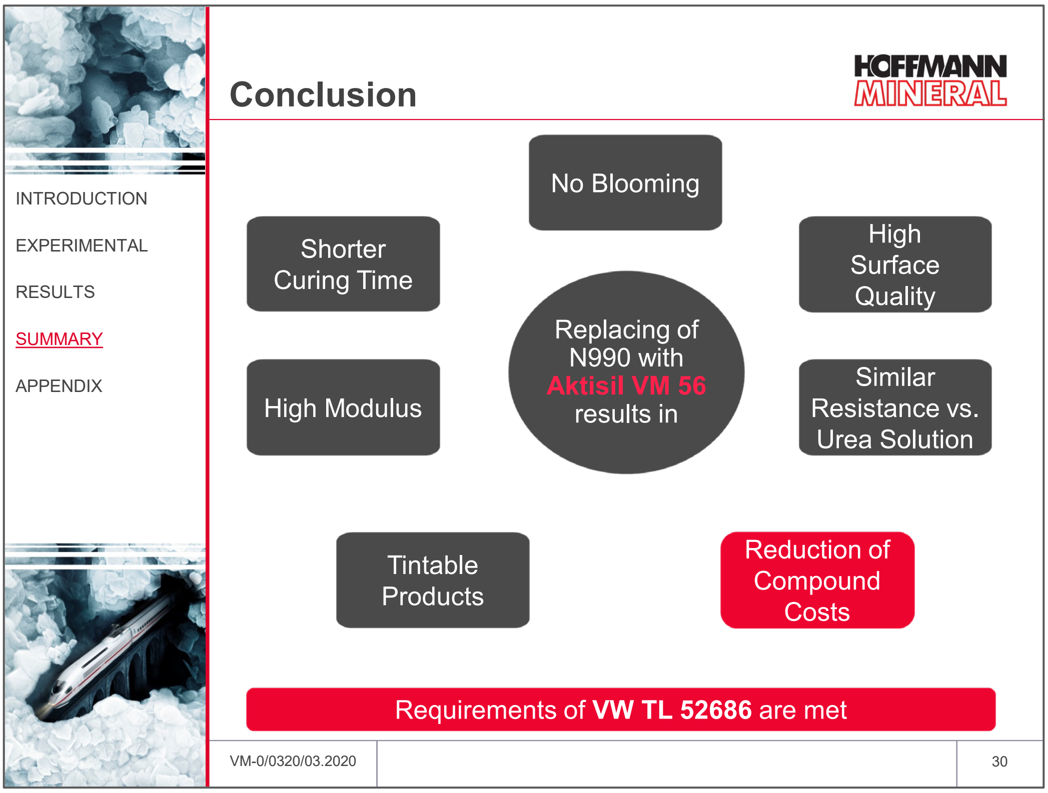

Fig. 28

The replacement of Carbon Black N990 by Aktisil VM 56 leads to a number of advantages:

- The shorter curing time results in a shorter cycle time in production.
- A modulus increase by 50 percent at 100% elongation.
- An absolute comparable resistance against urea solution / AdBlue®.
- Better surface quality and improved collapse resistance during extrusion.
- The Aktisil VM 56 prevents blooming of decomposition products, making a subsequent cleaning step unnecessary.
- Thanks to the non-black color of Neuburg Siliceous Earth the vulcanizates can be processed into tintable components.
- Compound raw material costs are extremely reduced by using Aktisil VM 56.

5 Appendix / table of results

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		N990	Aktisil VM 56
Rheology			
Mooney viscosity, ML 1+4, 120 °C	MU	46	53
Mooney scorch time, ML +5, 120 °C	min	77	56
Rotorless curemeter M_{min} 180 °C	Nm	0.09	0.09
Rotorless curemeter M_{max} 180 °C	Nm	1.03	0.96
Rotorless curemeter $M_{max\text{-}min}$ 180 °C	Nm	0.95	0.87
Rotorless curemeter V_{max} 180 °C	Nm / min	0.40	0.54
Rotorless curemeter t_5 180 °C	min	0.46	0.39
Rotorless curemeter t_{10} 180 °C	min	0.59	0.47
Rotorless curemeter t_{90} 180 °C	min	5.58	4.66
Rotorless curemeter tan delta 180°C		0.04	0.04

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Fig. 29

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		N990	Aktisil VM 56
Mechanical properties			
Hardness	Sh. A	61	65
Tensile Strength	MPa	10.8	11.7
Modulus 50 %	MPa	1.4	2.0
Modulus 100 %	MPa	2.8	4.3
Elongation at break	%	305	248
Tear resistance	N / mm	3.1	3.1
Rebound elasticity	%	59	59
Compression set, 94 h / 23 °C, VW	%	13	14
Compression set, 22 h / 120 °C, VW	%	22	28
Compression set, 24 h / 23 °C, 25 % Def.	%	5	6
Compression set, 24 h / 120 °C, 25 % Def.	%	7	10

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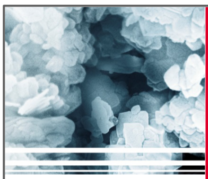
Fig. 30



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Storage in hot air; 120 °C; Measuring after 30 minutes		N990	Aktisil VM 56	N990	Aktisil VM 56
		94 h		504 h	
Hardness	Sh. A	60	65	61	67
Tensile Strength	MPa	11.4	13.9	11.8	12.8
Modulus 50 %	MPa	1.5	2.3	1.6	2.3
Modulus 100 %	MPa	2.9	5.1	3.1	5.2
Elongation at break	%	307	225	291	206
Tear resistance	N / mm	3.2	2.7	3.2	2.6
Δ Hardness	Sh. A	-1	0	0	2
Δ Tensile strength	%	5.1	18.8	8.9	9.1
Δ Modulus 50%	%	4.0	12.8	10.6	15.4
Δ Modulus 100%	%	3.8	20.7	12.3	23.1
Δ Elongation at break	% rel.	0.6	-9.4	-4.6	-17.2
Δ Tear resistance	%	1.6	-11.8	2.9	-16.3

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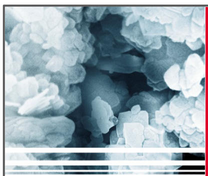
Fig. 31



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Storage in urea solution 80 °C; cool down 90 minutes		N990	Aktisil VM 56	N990	Aktisil VM 56
		94 h		504 h	
Hardness	Sh. A	61	66	61	65
Tensile strength	MPa	12.0	11.2	11.9	11.2
Modulus 50 %	MPa	1.5	2.0	1.5	2.0
Modulus 100 %	MPa	2.9	4.1	2.9	4.1
Elongation at break	%	315	250	320	247
Δ Hardness	Sh. A	0	1	0	0
Δ Tensile Strength	%	11.0	-4.7	9.7	-4.7
Δ Modulus 50%	%	5.1	0.2	5.3	1.8
Δ Modulus 100%	%	6.3	-3.5	6.3	-2.7
Δ Elongation at break	% rel.	3.2	0.6	5	-0.4
Δ Weight	%	-0.2	0.1	-0.4	0.1
Δ Volume	%	-0.3	0.1	-0.4	0.4

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Fig. 32