Molded NBR parts for automotive oil seals ASTM D2000 Replacement of carbon black N990 with Neuburg Siliceous Earth

Author: Karin Müller
Hubert Oggermüller

VM-1/0615/12.2023

Contents

1 Introduction

NBR seals are extensively used in the engineering and automotive industries *(Tab. 2)*; pertinent property requirements are given in the ASTM standard D2000. For rationalizing the property profile ad cost aspects, frequently carbon black N990 is used in addition to carbon black N550.

According to the price of fossile raw materials, the price of carbon blacks is often subject to considerable variations. The long term, however, doubtless shows an upwards trend. The price of mineral fillers is hardly affected by fossile raw materials, and over a long time just shows minor increases without severe variations.

In addition, temporarily there exist supply problems with carbon black N990, which can be avoided by the use of Neuburg Siliceous Earth.

Hoffmann Mineral assures viable supply times and reliable availability of the Neuburg Siliceous Earth portfolio.

2 Objectives

Replacement of carbon black N990 with Neuburg Siliceous Earth for cost reduction at unchanged property levels. The guideline for the assessment was ASTM D2000-08, material class CH *(Tab. 1).*

Requirements and Test Conditions

HOFFMANN MINERAL

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Base Values:

• Hardness:	70 +/- 5 Shore A
• Tensile Strength:	>10 MPa resp. >14 MPa
• Elongation at Break:	> 250 %
• Compression Set:	< 25 % at 100 °C and 22 h

Grade 2:

- Reference Liquid IRM 901 70 h at 125 °C
- Reference Liquid IRM 903 70 h at 125 °C
- Reference Liquid C 70 h at 23 °C
- Hot Air 70 h at 125 °C

Grade 3:

- Reference Liquid IRM 901 70 h at 150 °C
- Reference Liquid IRM 903 70 h at 150 °C
- Hot Air 70 h at 125 °C

VM-1/0615/12.2023 5

Table 1

3 Experimental

3.1 Compound Formulations

Base Formulation
70 Shore A

HOFFMANN MINERAL

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

		phr
Krynac 2950 F	NBR, 30 % ACN, ML 1+4 (100 °C) 53 MU	100.0
Zinkoxyd aktiv	Zinc Oxide	5.0
Stearic Acid	Processing Aid	0.5
Agerite Resin D	Antioxidant	2.0
Corax N550	FEF Carbon Black	60.0
Carbon Black N990	**MT Carbon Black**	**50.0**
Mediaplast NB-4	Ester Plasticizer	10.0
Vulkacit Thiuram/C	Accelerator, TMTD	2.5
Vulkacit CZ/C	Accelerator, CBS	2.0
Sulfur	Curing Agent	0.2
		232.2

VM-1/0615/12.2023 6

Table 2

Krynac 2950 F	NBR, 30 % ACN, ML1+4 (100 +C) 53 MU
Zinkoxyd aktiv	Zinc oxide
Stearic acid	Processing aid
Agerite Resin D	Antioxidant, 1.2-Dihydro-2.2.4-trimethylchinoline
Corax N550	FEF carbon black
Carbon black N990	Thermal black
Mediaplast NB-4	Ester plasticizer
Vulkacit Thiuram/C	Cure accelerator, Tetramethyl thiuramdisulfide, TMTD
Vulkacit CZ/C	Cure accelerator, N-Cyclohexyl-2-benzothiazole-sulfenamide, CBS
Ground sulfur	Curing agent, sulfur

This base formulation is representative of NBR moldings for oil seals in the automotive sector. The total carbon black addition of 110 phr consists of 60 phr Corax N550 and 50 phr carbon black N990. The plasticizer part is only 10 phr, which explains that a 1:1 replacement arrives at a hardness of 70 Shore A.

INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

Fillers, Characteristics

HOFFMANN MINERAL

		Carbon black N990	Aktisil PF 216	Aktifit AM	Silfit Z 91	Sillitin Z 86	Sillitin N 75*
Density	[g/cm³]	1,8	2,6	2,6	2,6	2,6	2,6
Particle size d_{50}	[µm]		2,2	2,0	2,0	1,9	3,0
Particle size d_{97}	[µm]		10	10	10	9	16
Sieve residue > 40 µm	[mg/kg]		15	10	10	20	25
Sieve residue 45 µm/325 mesh	ppm	18					
Oil absorption	[g/100g]		60	55	55	55	45
DBP-absorption	[ml/100 g]	38					
Specific surface area BET	[m²/g]		9	7	8	12	12
CTAB-surface area	[m²/g]	7					
Functionalization		none	Tetra-sulfan	Amino	none	none	none

*The tests were carried out with Sillitin N 82. This product is no longer available. Recommended: Sillitin N 75.

VM-1/0615/12.2023 7

Table 3

The typical properties of carbon black N990 do not show big differences versus the siliceous earth grades. The density difference of 1.8 to 2.6 counts among the biggest disparities *(Tab. 3).*

3.2 Compound mixing and curing

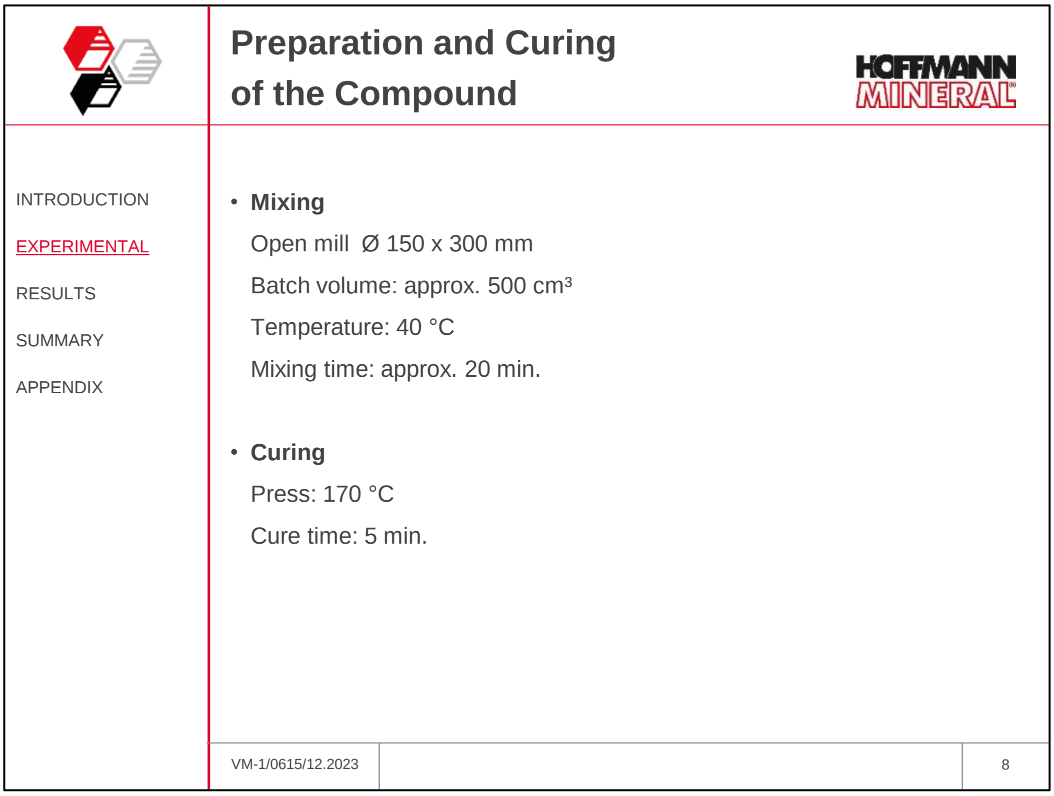

Fig. 1

All compounds were mixed on a laboratory mill (Schwabenthan Polymix 150 L) at 20 rpm and a batch size of 500 cm^3. The mixing times were adjusted according to the incorporation properties of the fillers, and registered.

Curing was done in an electrically heated press at 170 °C. The cure time was always 5 min, equally with the 2 mm sheets and the rebound and compression set samples *(Fig. 1).*

4 Results

4.1 Mooney viscosity and Mooney scorch time

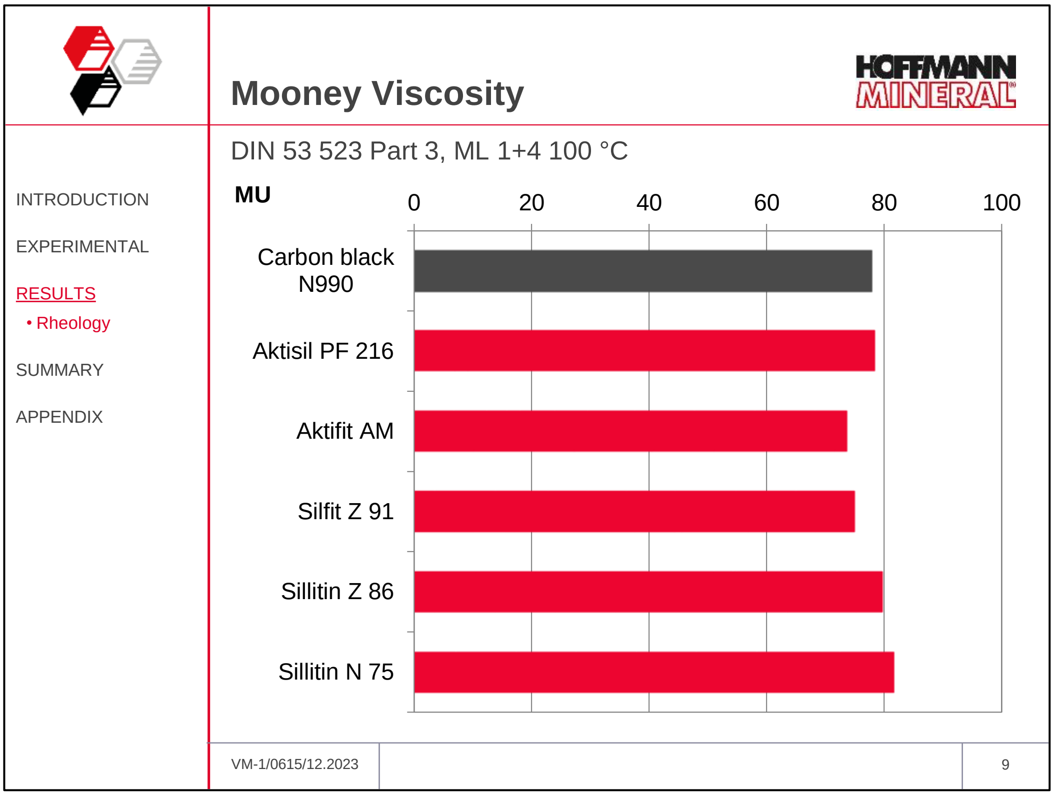

Fig.2

The replacement of carbon black N990 with Neuburg Siliceous Earth grades hardly at all affects the Mooney viscosity of the compounds. With Aktifit AM and Silfit Z 91, just a somewhat lower Mooney viscosity was obtained, which allows to expect a slight positive influence onto the processing properties of the compounds *(Fig. 2).*

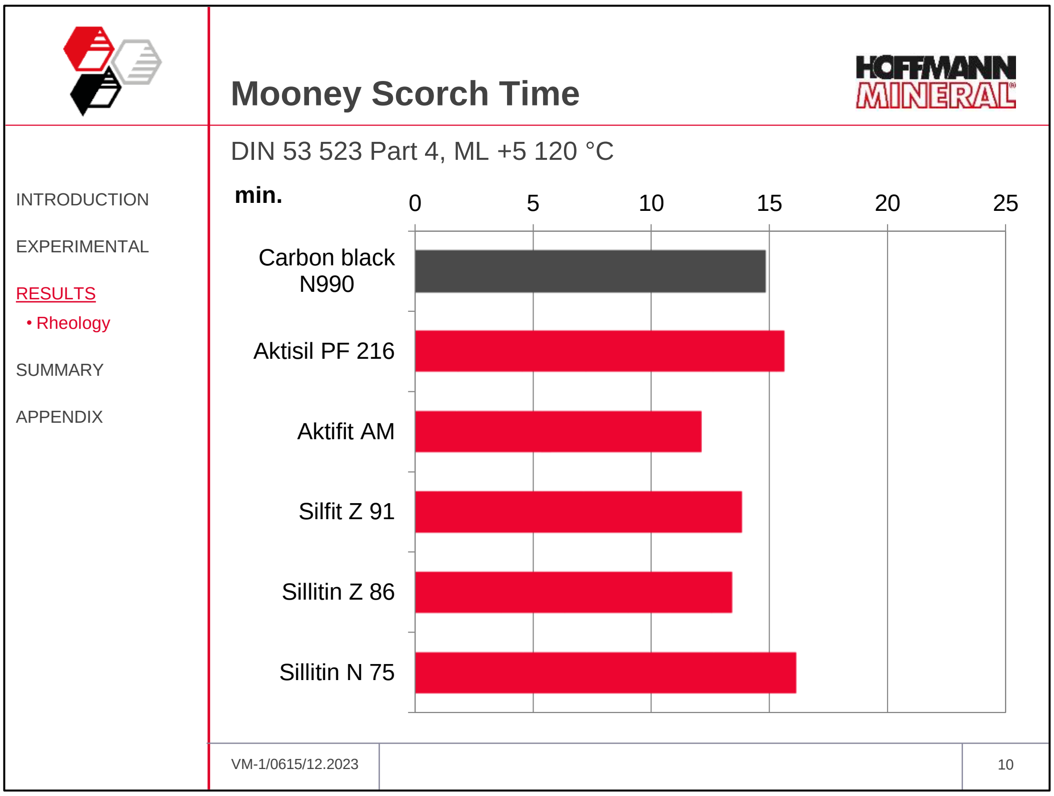

Fig. 3

The Mooney scorch time, an index for the scorch tendency of the compound during the processing, with Aktifit AM, Silfit Z 91 and Sillitin Z 86 will come out somewhat shorter. Aktisil PF 216 and Sillitin N 75 hardly show any influence *(Fig. 3)*

.

4.2 Cure characteristics

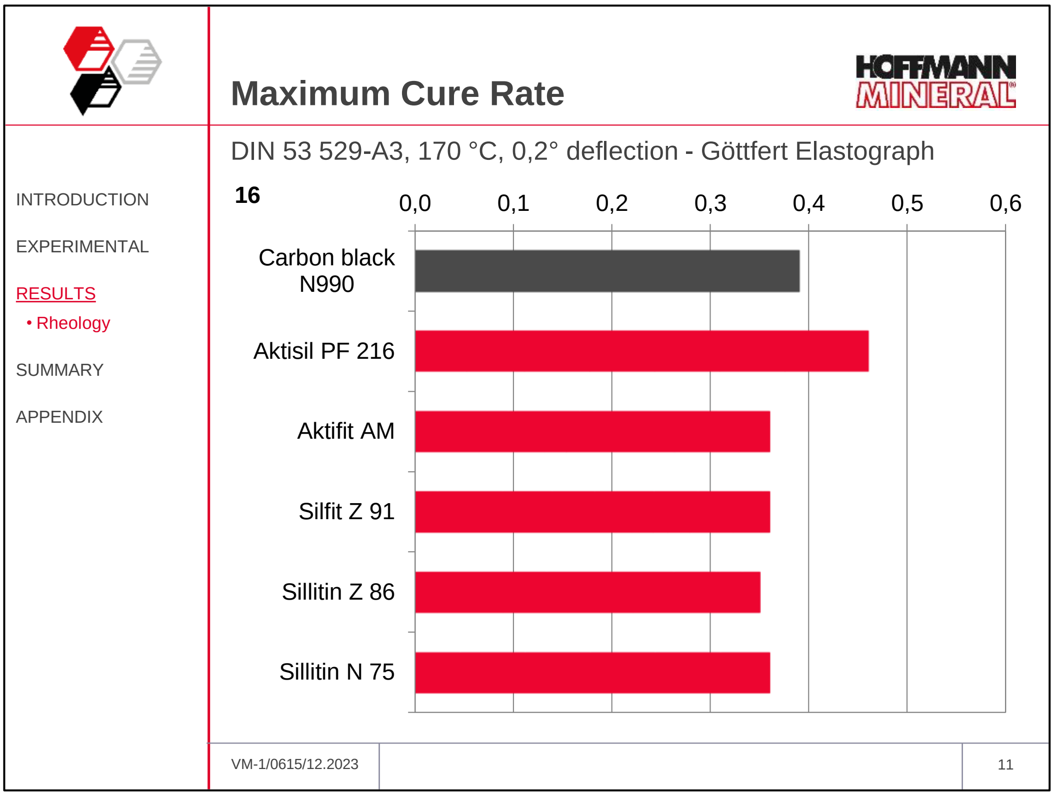

Fig. 4

With Aktisil PF 216 the maximum cure rate, compared with carbon black N990, shows a considerable increase. The other siliceous earth grades rather come out with a slightly lower maximum cure rate *(Fig. 4).*

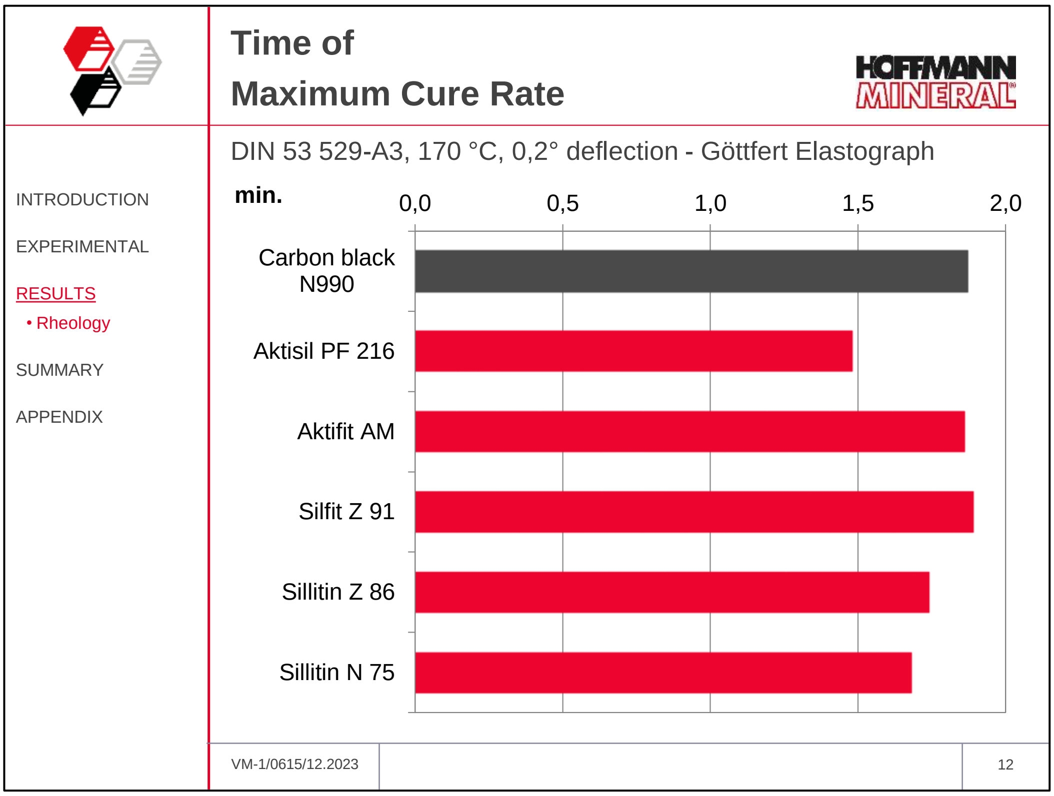

Fig. 5

The point of maximum cure rate will also be reached markedly faster with Aktisil PF 216. By contrast, Sillitin Z 86 and Sillitin N 75 only lead to marginal acceleration. Aktisil AM and Silfit Z 91 comes out equal with carbon black N990 *(Fig. 5.)*

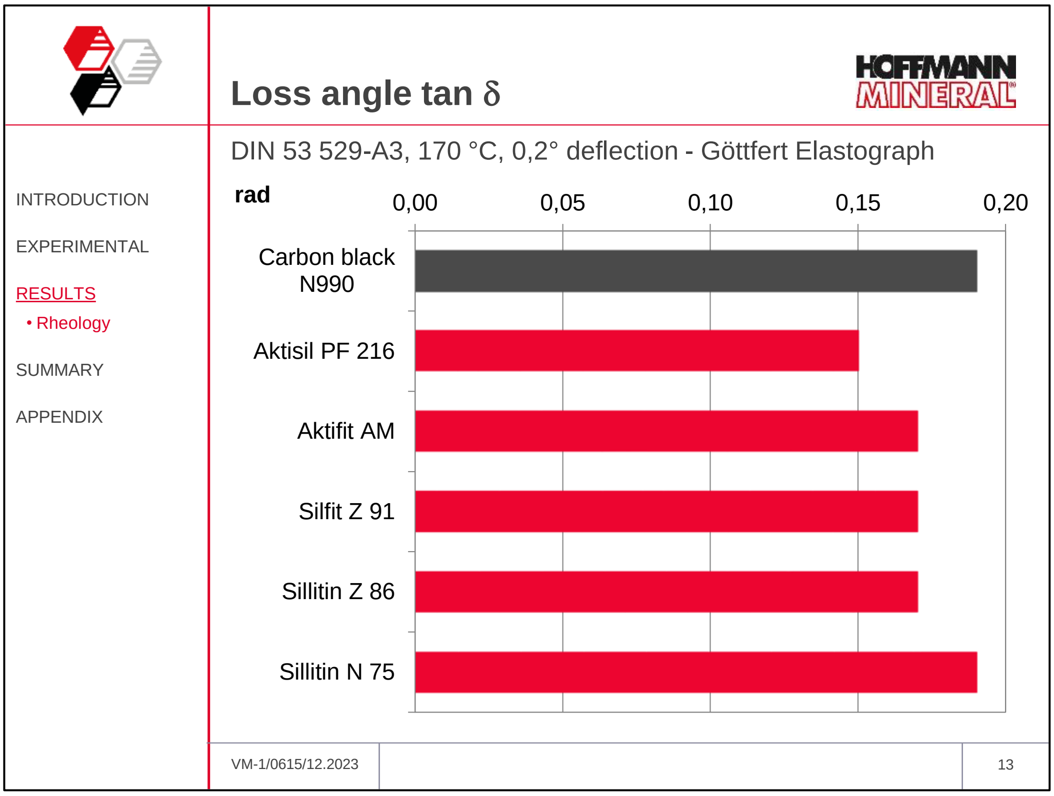

Fig. 6

The dynamic loss angle tan δ is slightly lower with Aktisil AM, Silfit Z 91 and Sillitin Z 86, with Aktisil PF 216 even markedly lower. Sillitin N 75 has remained on the same level as carbon black N990 *(Fig. 6).*

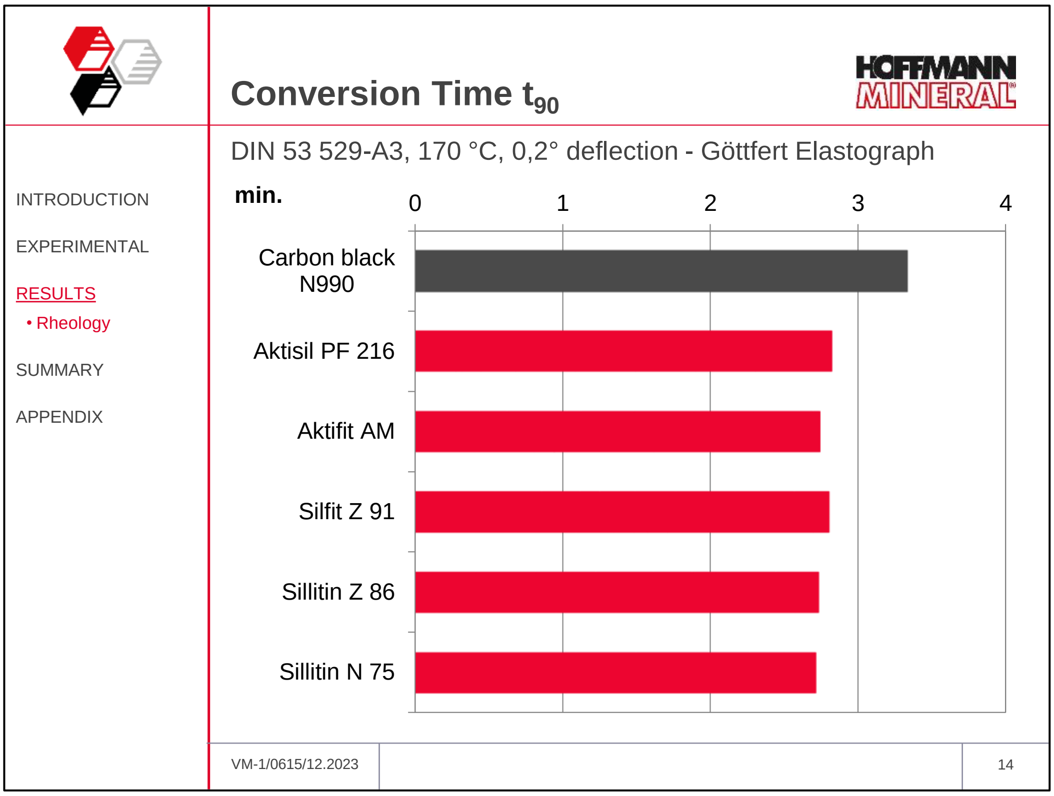

Fig. 7

The conversion time t_{90}, as an index of the required time to full cure, will be shortened by all the testes siliceous earth grades, which should allow shorter cycle times in processing *(Fig. 7).*

4.3 Initial Mechanical Properties

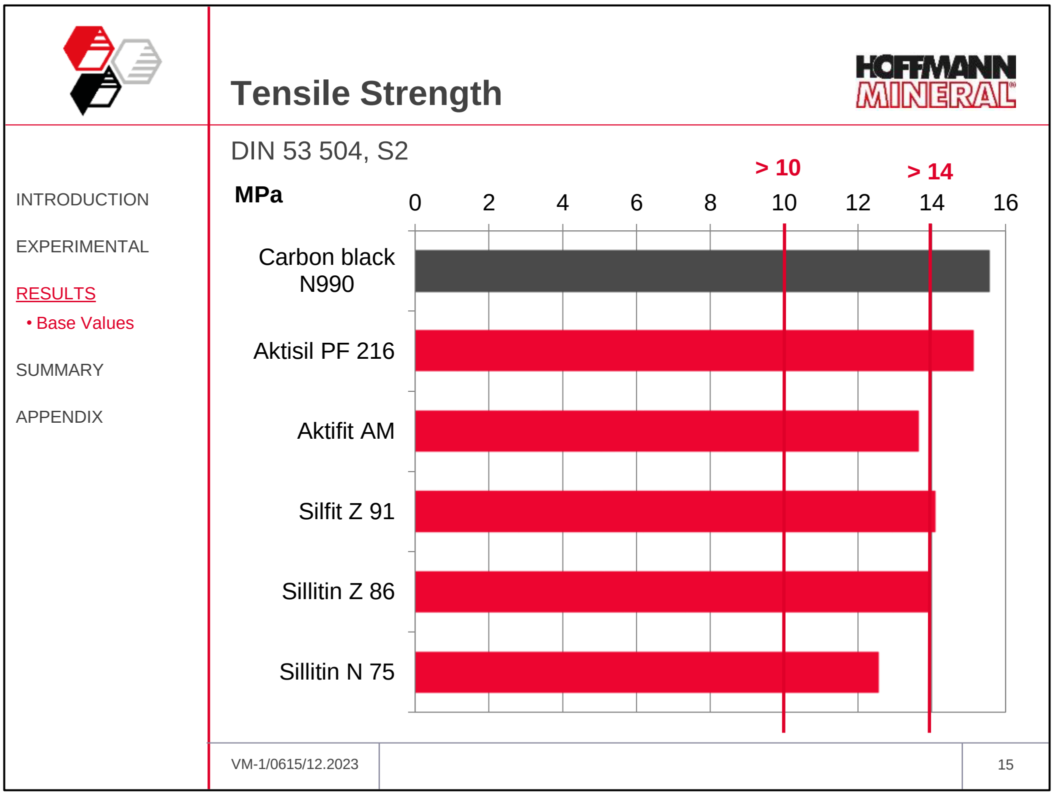

Fig. 8

In the materials class CH at a hardness level of 70+5 Shore A, there exist different requirements for the tensile strength. For a majority of applications, a tensile strength of >10 MPa is sufficient, a figure that will be met by all siliceous earth fillers. The next higher condition of >14 MPa will be even surpassed with Aktisil PF 216 *(Fig. 8).*

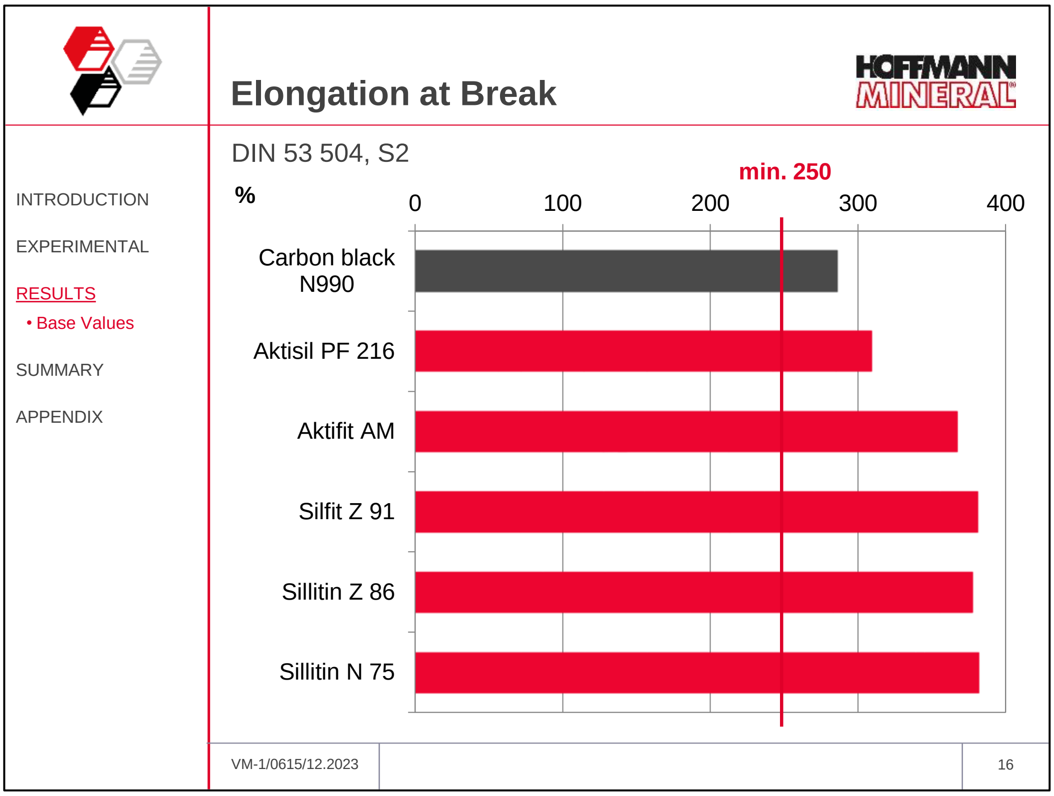

Fig. 9

The elongation at break shows an increase with all siliceous earth grades, and goes above the standard requirements even more distinctly *(Fig. 9).*

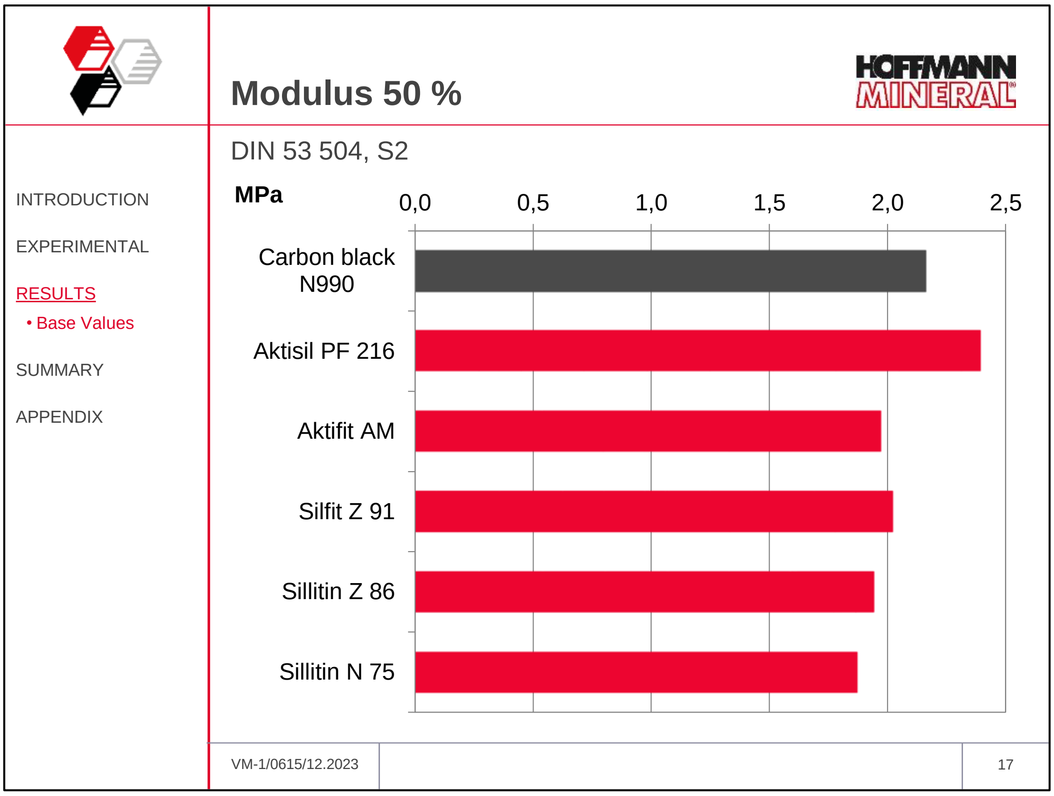

Fig. 10

The tensile modulus with Aktisil PF 216 comes out somewhat higher than with carbon black N990. The other siliceous earth grades rather deliver a lower modulus *(Fig. 10).*

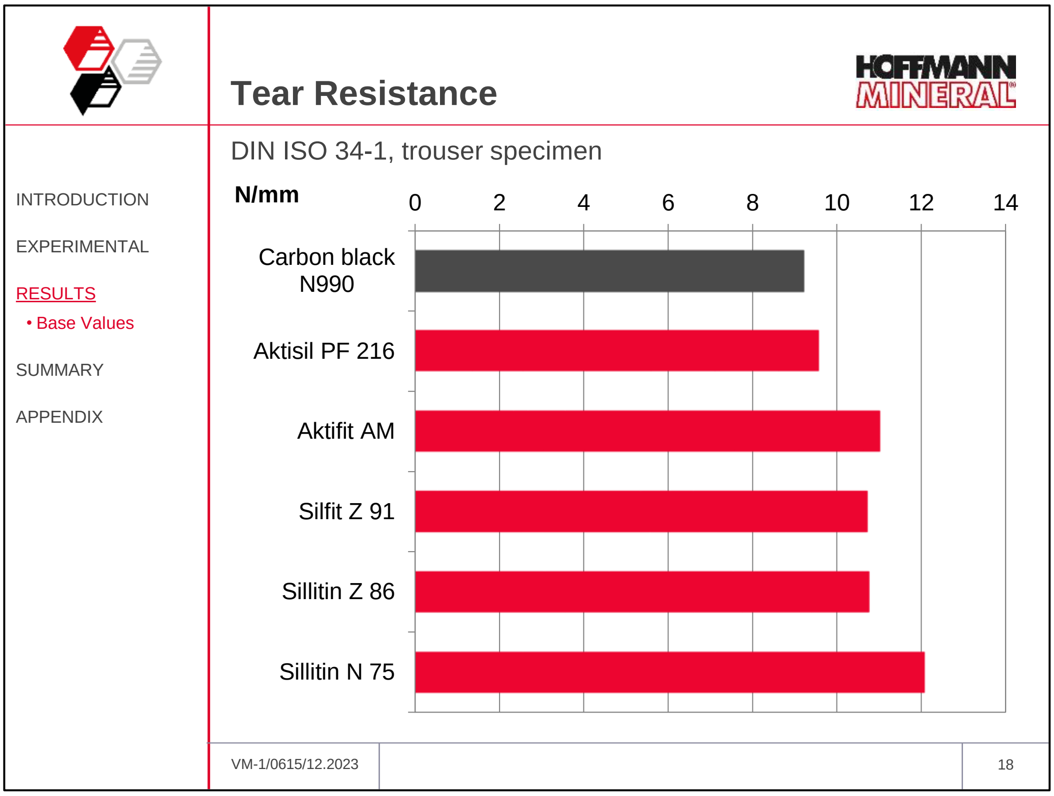

Fig. 11

The tear strength increases slightly when replacing carbon black N990 with Aktisil PF 216, or even markedly with the other discussed siliceous earth products *(Fig. 11).*

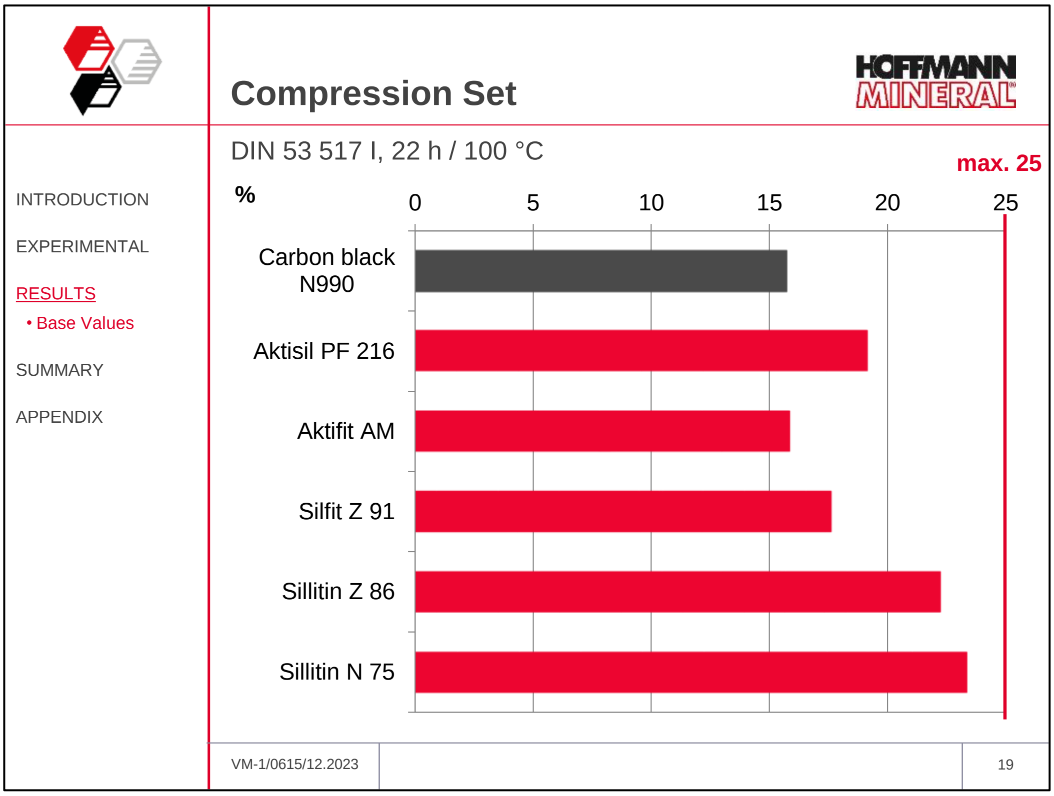

Fig. 12

Aktifit AM comes out at the same level with the carbon black N990 compound, and along with Silfit Z 91 gives the best results. With Sillitin Z 86, Sillitin N 75 and Aktisil PF 216 the compression set is somewhat higher, but all results remain within the requirements of the standard *(Fig. 12).*

4.4 Grade 2 - Immersion in Oil IRM 903 at 125 °C

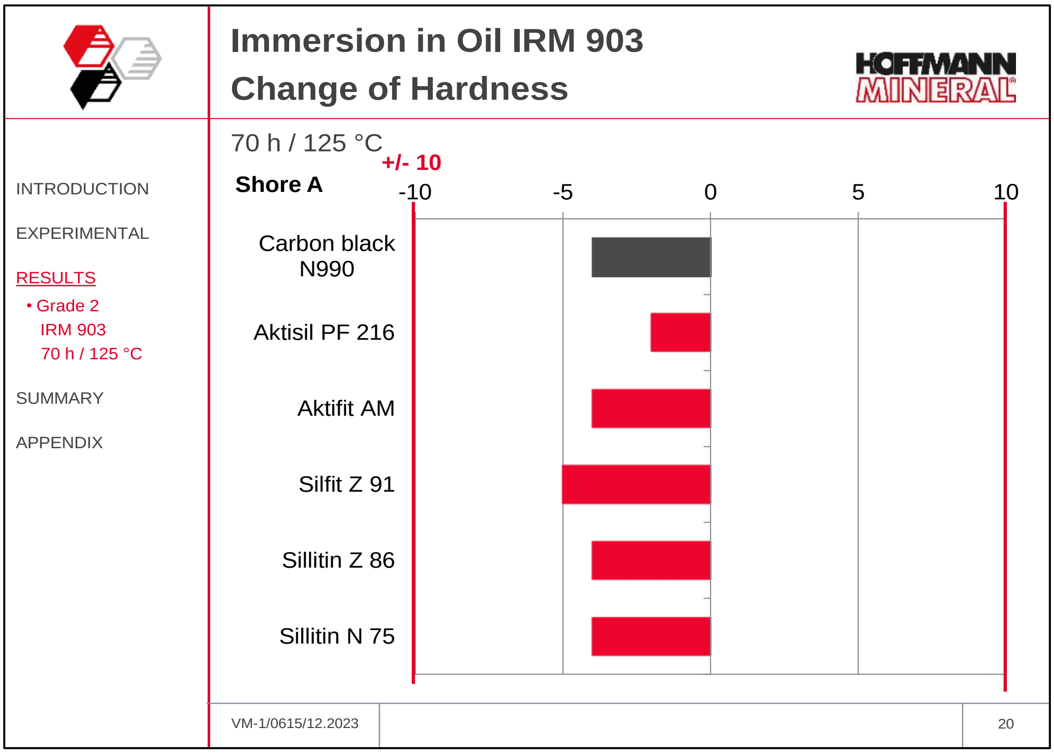

Fig. 13

As a further property, the resistance against the aggressive standard oil IRM 903 was tested at 125 °C. The hardness change comes out lowest with Aktisil PF 216. The other compounds show all a similar decrease, and thus remain at the level of the compound with carbon black N990 *(Fig. 13).*

4.5 Grade 2 – Immersion in Reference Fuel Liquid C at 23 °C

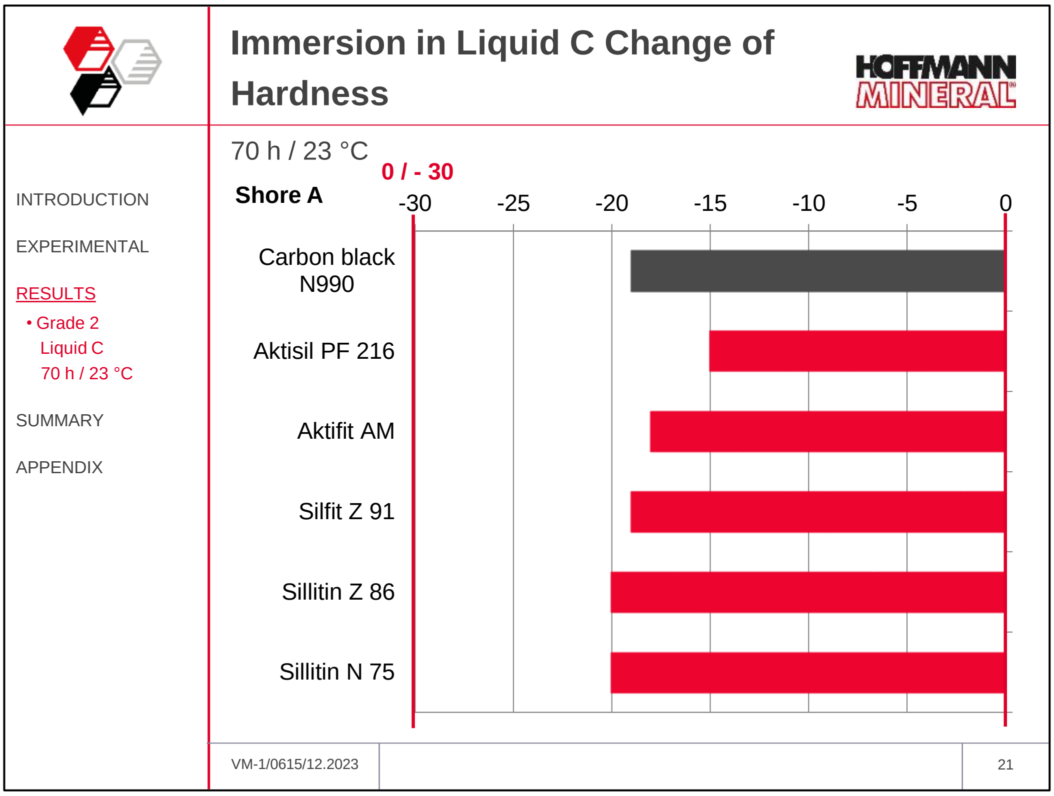

Fig. 14

A further property evaluated was the resistance against automotive fuel with the example of Reference Liquid C according to ASTM D471 and ISO 1817:2011. Here again, the hardness change is lower with Aktisil PF 216 in comparison with carbon black N990. The other compounds show a similar response as the straight carbon black compounds *(Fig. 14).*

4.6 Grade 3 - Immersion in Oil IRM 903 at 150 °C

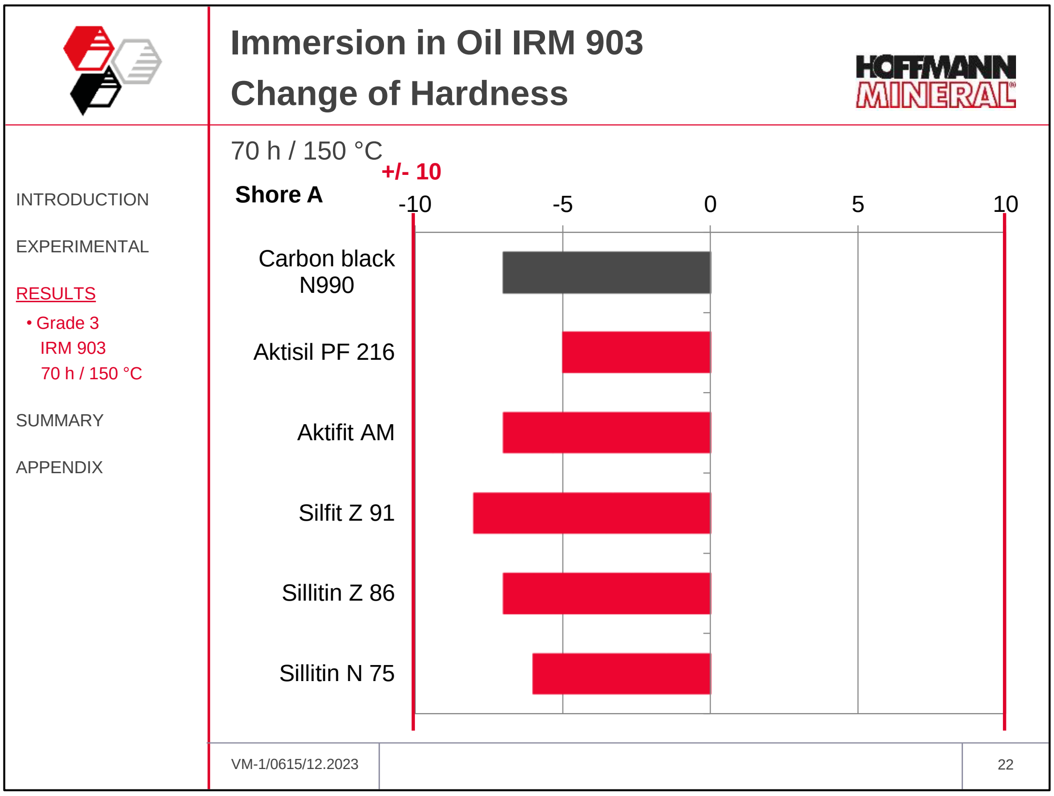

Fig. 15

The oil resistance was also evaluated at 150 °C with the aggressive standard oil IRM 903. Here once more Aktisil PF 216 offers a markedly lower hardness change compared with carbon black N990. The other siliceous earth fillers equally fulfill the standard requirements without problems *(Fig. 15).*

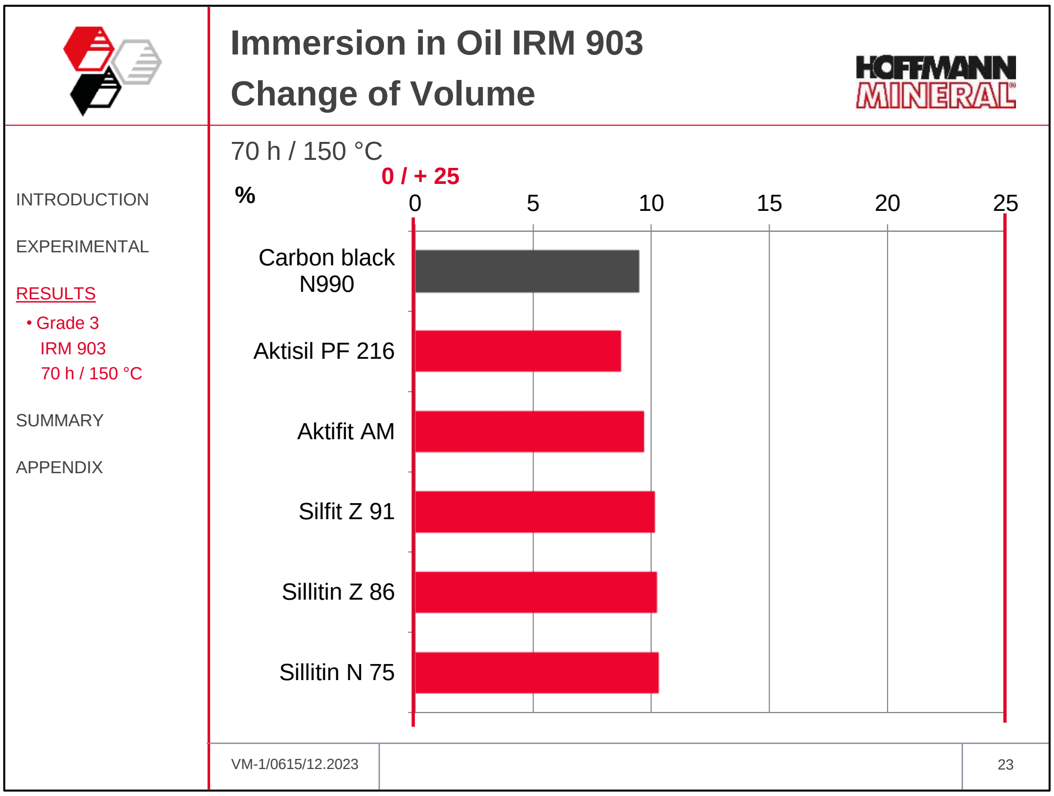

Fig. 16

Aktisil PF 216 throughout shows a lower tendency towards volume change than carbon black N990. The volume increase of the other siliceous earth compounds is only marginally higher compared with the carbon black N990 compound, without significant differences between the individual fillers *(Fig. 16).*

4.7 Cost aspects

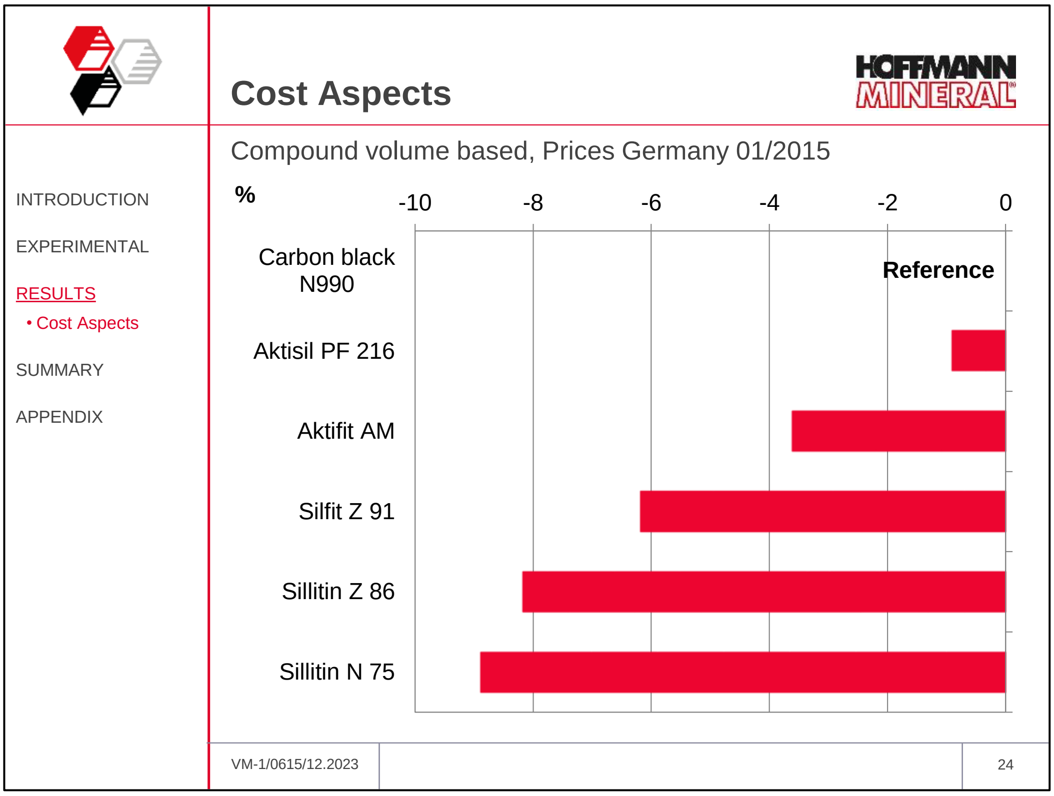

Fig. 17

The siliceous earth fillers allow to benefit of a distinct reduction of the compound raw material prices. This is all the more important, as in the indicated volume-related compound prices have already considered the different densities versus carbon black N990.

This way, with Aktisil AM and Silfit Z 91 a cost reduction of 4 resp. 6 % can be realized. More pronounced, Sillitin Z 86 and Sillitin N 75 allow to come up to a cost reduction of up to 9 %. Even Aktisil PF 216 still gives room to a small cost advantage *(Fig. 17).*

5 Summary

Aktisil PF 216, in comparison with carbon black N990, along with improved cure properties (loss angle, tan δ) and maintained tensile strength, gives rise to a reduced hardness change during immersion in Oil IRM 903 and in Reference Fuel Liquid C.

A good compression set and the absence of mold fouling characterize the action of Aktifit AM and Silfit Z 91 along with a cost reduction of approx. 4 to 6 %.

With Sillitin Z 86 as well as with Sillitin N 75, at the cost of small changes in properties a price advantage of up to 9 % can be realized.

In order to arrive at an optimum balance between physical properties and cost reduction, a combination of Sillitin and Aktisil PF 216 appears to offer the solution of choice. For example, a 50:50 blend results in a property profile that seems to rather approach Aktisil PF 216.

High availability and reliable supplies are further arguments in favor of the siliceous earth fillers.

In summary: Carbon black N990 can be replaced

- with technical advantages by Aktisil PF 216
- under cost reductions with other siliceous earth fillers

6 Appendix – Results without Particular Effects

The appendix summarizes further test results which do not show any particular effect of the filler exchange.
Initial values: torque min./max., conversion time t_5, hardness and rebound
Immersion in IRM 901 and 903: 70 h at 125 and 150 °C
Immersion in Reference Fuel Liquid C: 70 h at 23°C
Aging in hot air: 70 h at 125 °C

All compounds with the different siliceous earth grades meet the requirements of the ASTM D2000-08 standard.

6.1 Cure characteristics

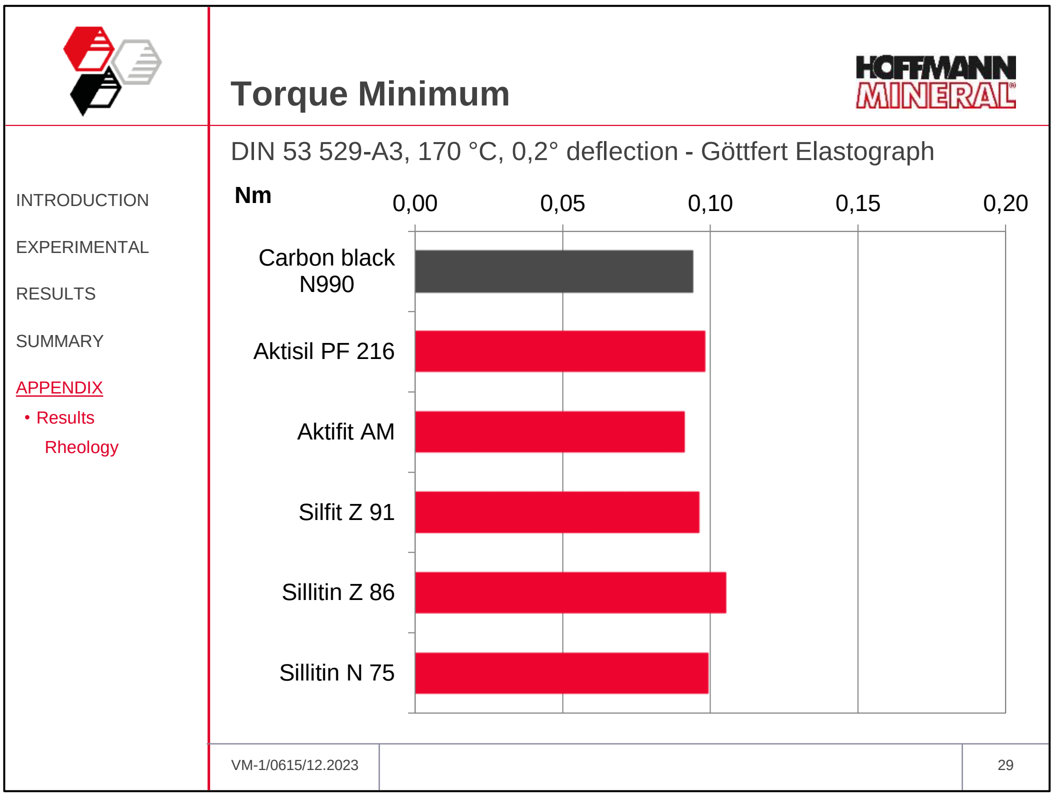

Fig. 18

When replacing carbon back N990 with siliceous earth, the minimum torque in the Vulkameter test largely remains at an unchanged level *(Fig. 18).*

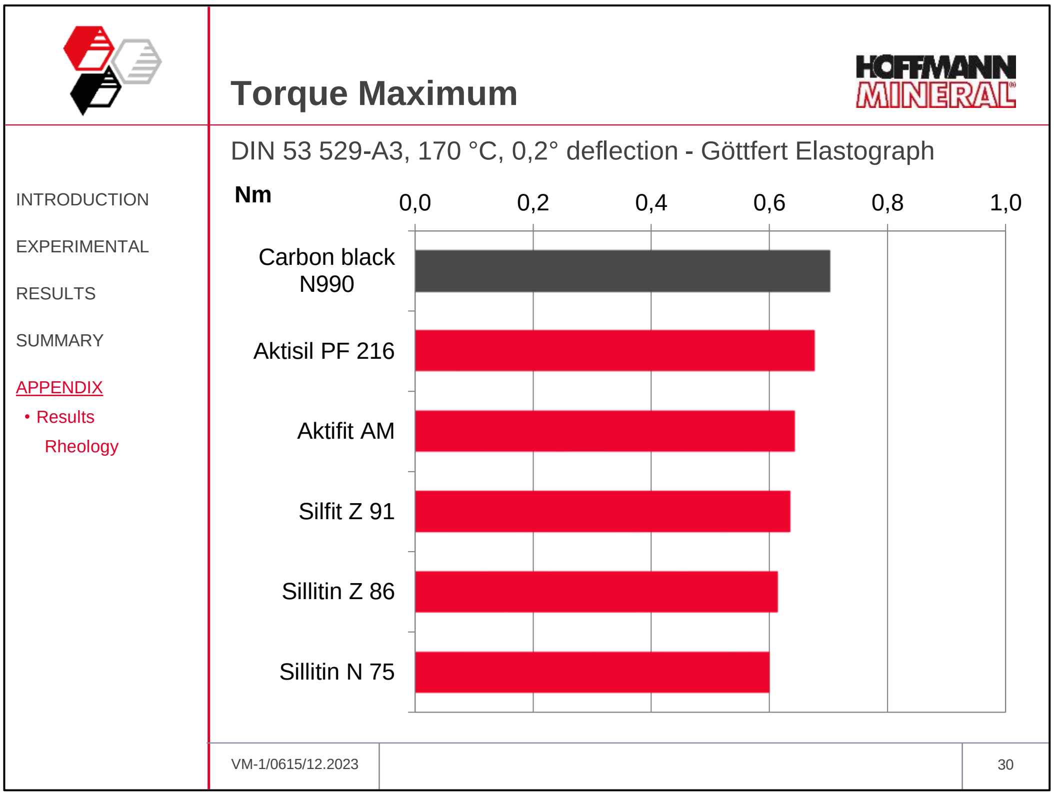

Fig. 19

The torque maximum with the siliceous earth fillers comes out slightly lower. Aktisil PF 216 approaches most closely the level of the straight carbon black compound *(Fig. 19).*

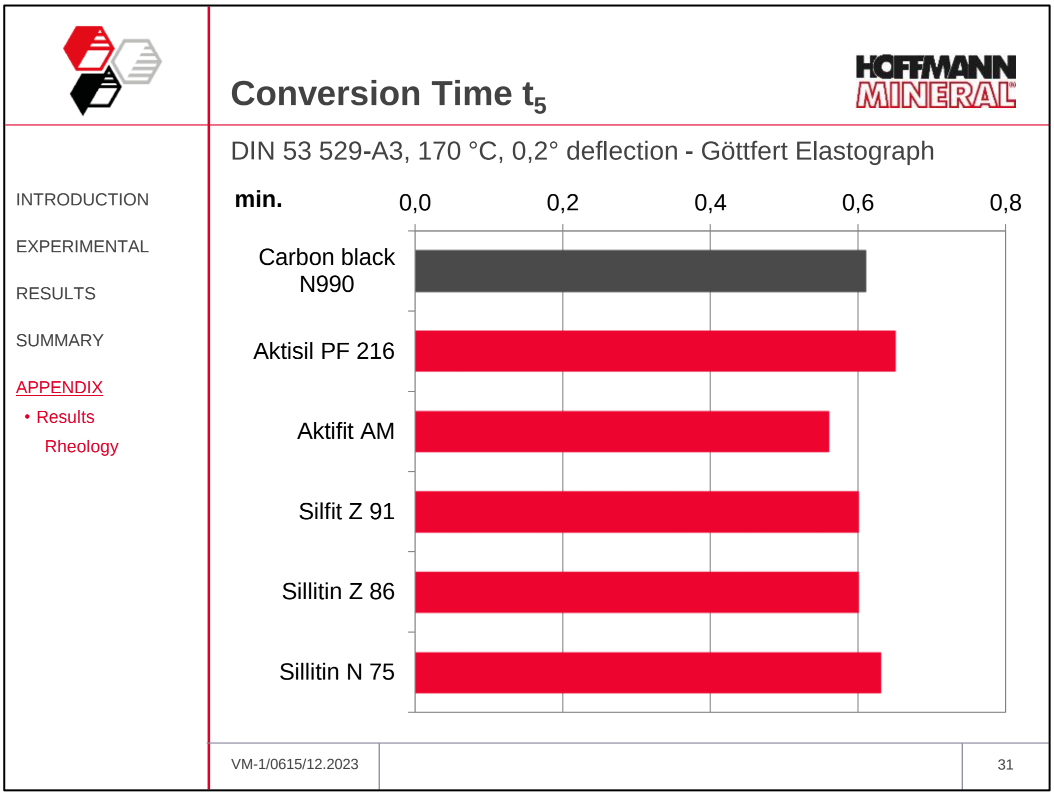

Fig. 20

The untreated siliceous earth grades give a conversion time t_5 at the level of the carbon black N990 compound. With Aktifit AM t_5 comes out slightly shorter, with Aktisil PF 216 somewhat longer *(Fig. 20).*

6.2 Initial Mechanical Properties

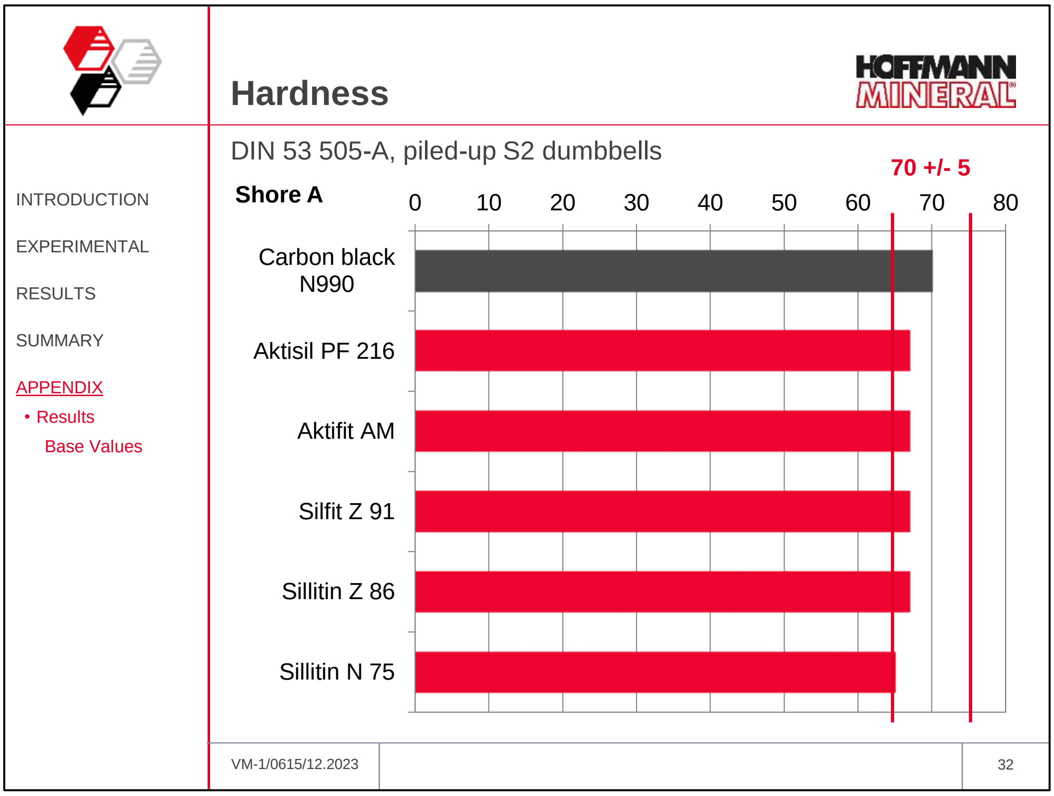

Fig. 21

The different compounds were adjusted throughout to a Shore A hardness of around 70. The 1:1 exchange of carbon black N990 with siliceous earth grades tends to result in a somewhat lower hardness, but the figures are still within the tolerance of the standard *(Fig. 21).*

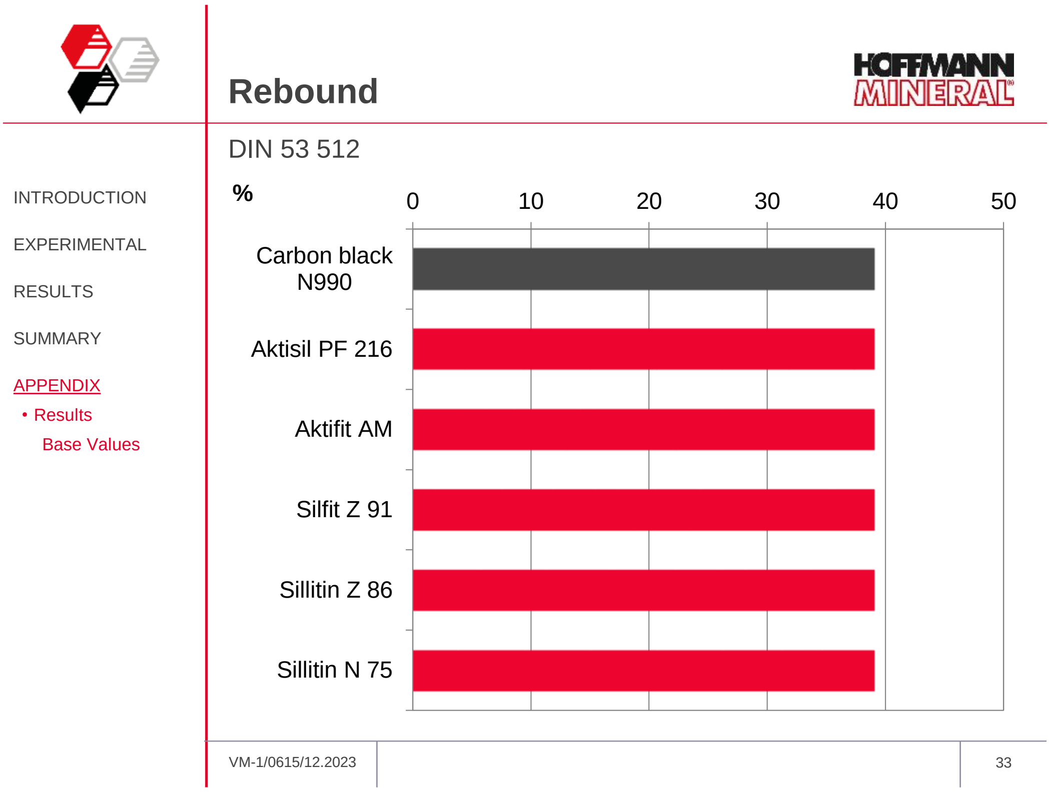

Fig. 22

The rebound resilience does not show any differences at all *(Fig. 22).*

6.3 Grade 2 - Immersion in Oil IRM 901 at 125 °C

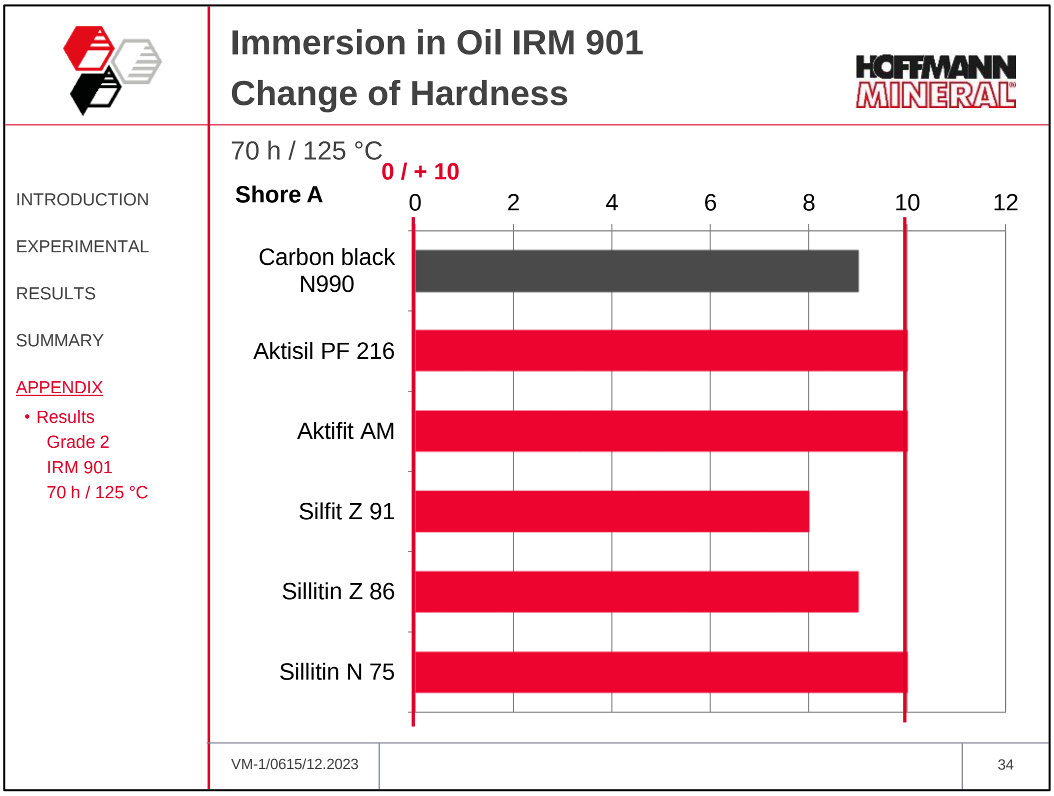

Fig. 23

Along with the oil resistance against standard oil IRM 903, pertinent properties ware also evaluated after immersion in IRM 901 at 125 °C. The hardness values change + few points from the carbon black N990, and just remain within the limits of the standard *(Fig. 23).*

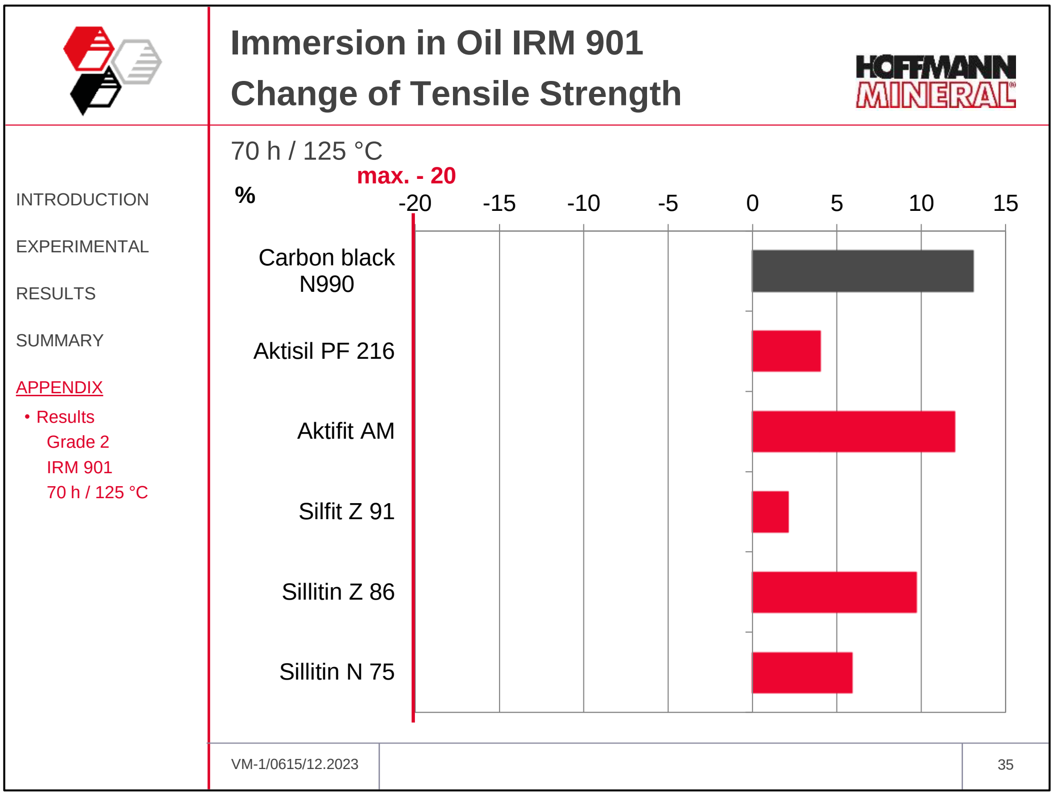

Fig. 24

The tensile strength change comes off very similar to the carbon black N990 compound. Here too all compounds without restrictions arrive within the requirements of the standard *(Fig. 24).*

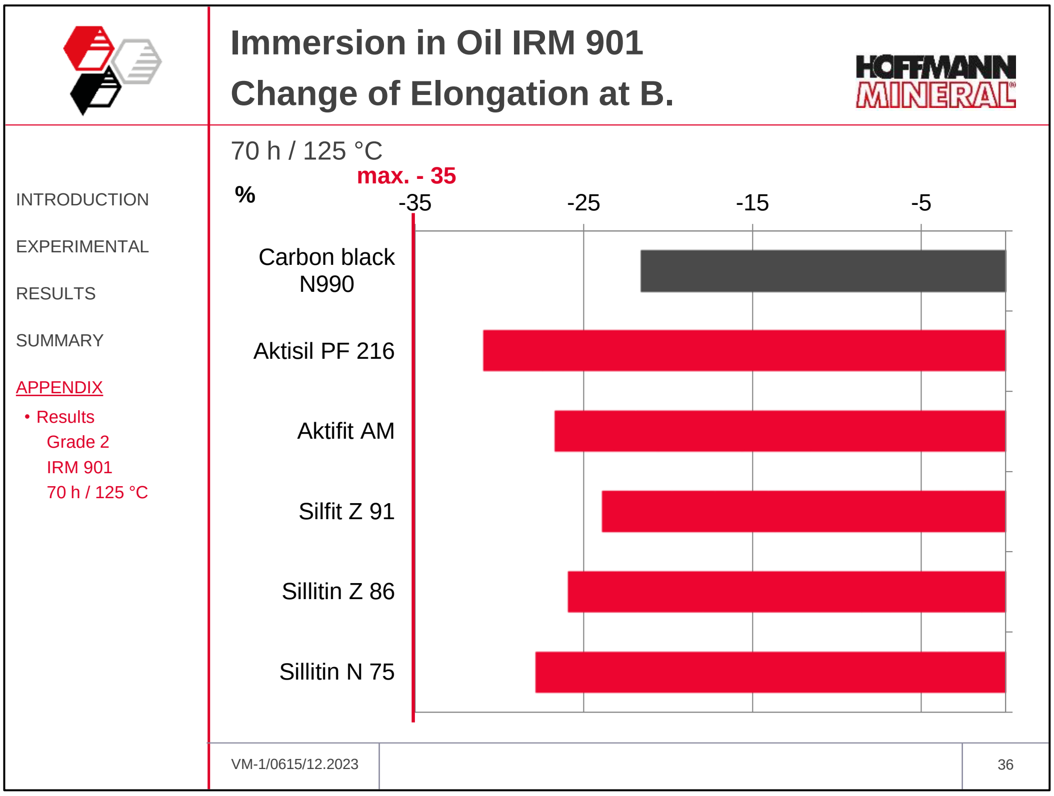

Fig. 25

The change of elongation at break with the tested siliceous earth grades basically is higher compared with carbon black N990, but all compounds throughout still fulfill the requirements of the ASTM D2000 standard *(Fig. 25).*

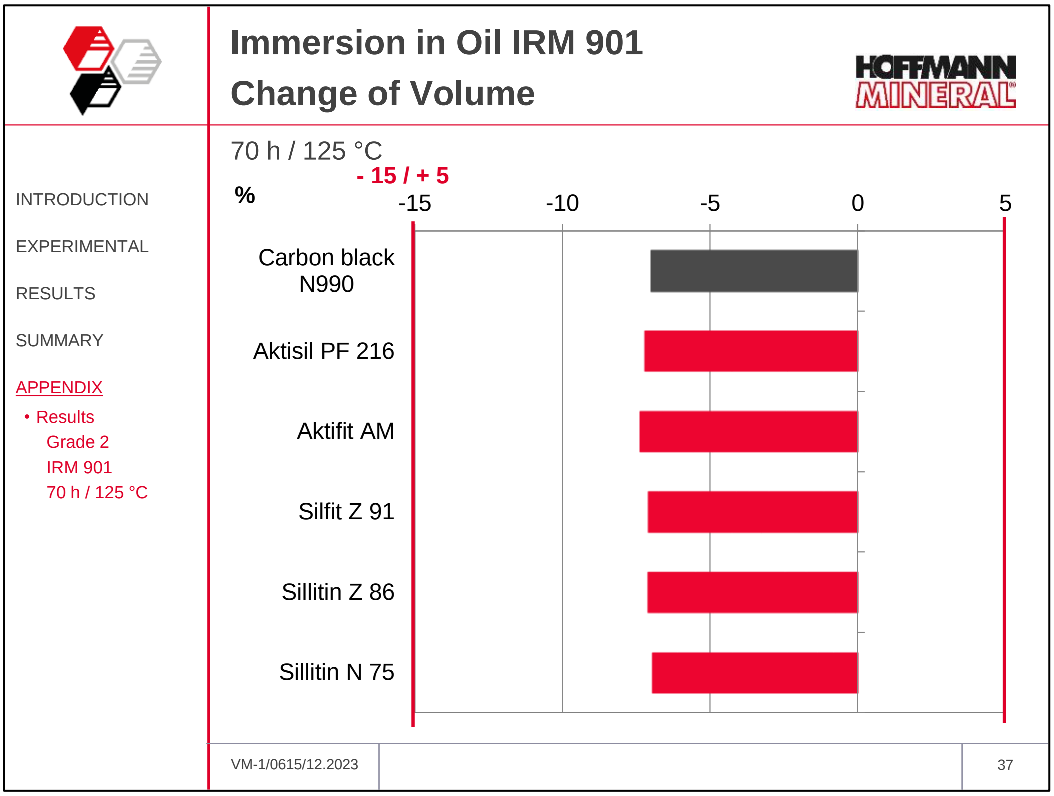

Fig. 26

The volume change of the siliceous earth compounds upon immersion in IRM 901 remains at the level of the straight carbon black compound without showing significant differences within the portfolio and without problems to meet the requirements of the standard *(Fig. 26).*

6.4 Grade 2 – Immersion in Oil IRM 903 at 125 °C

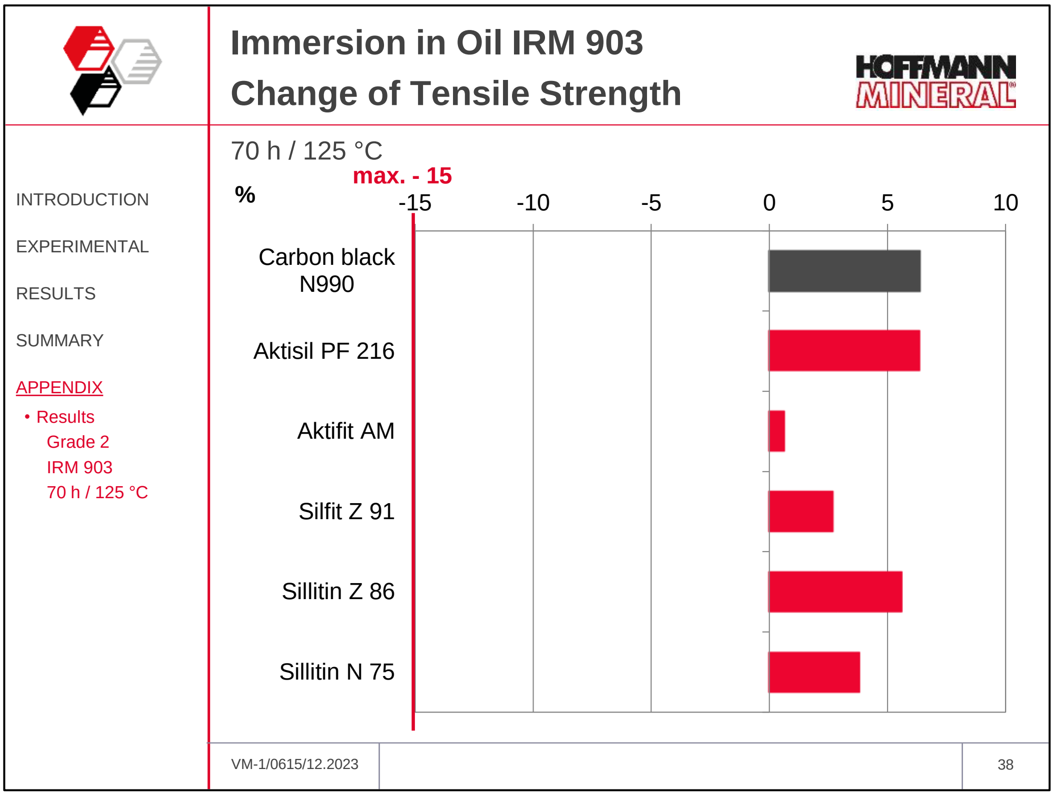

Fig. 27

The tensile strength changes in a comparable way in almost all of the compounds. And all versions easily meet the requirements of the standard *(Fig. 27).*

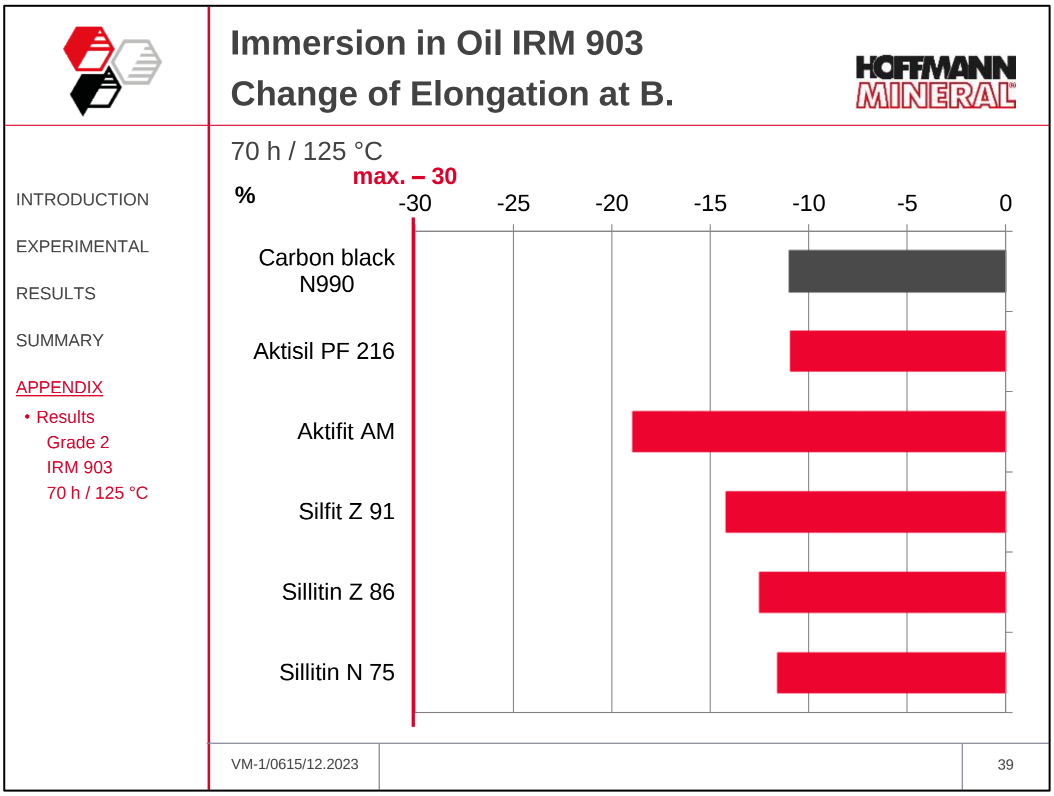

Fig. 28

Except for Aktisil AM, the change of the elongation at break comes out at the level of the straight carbon black compound. The requirements of the standard will, however, be met without problems by all compounds *(Fig. 28).*

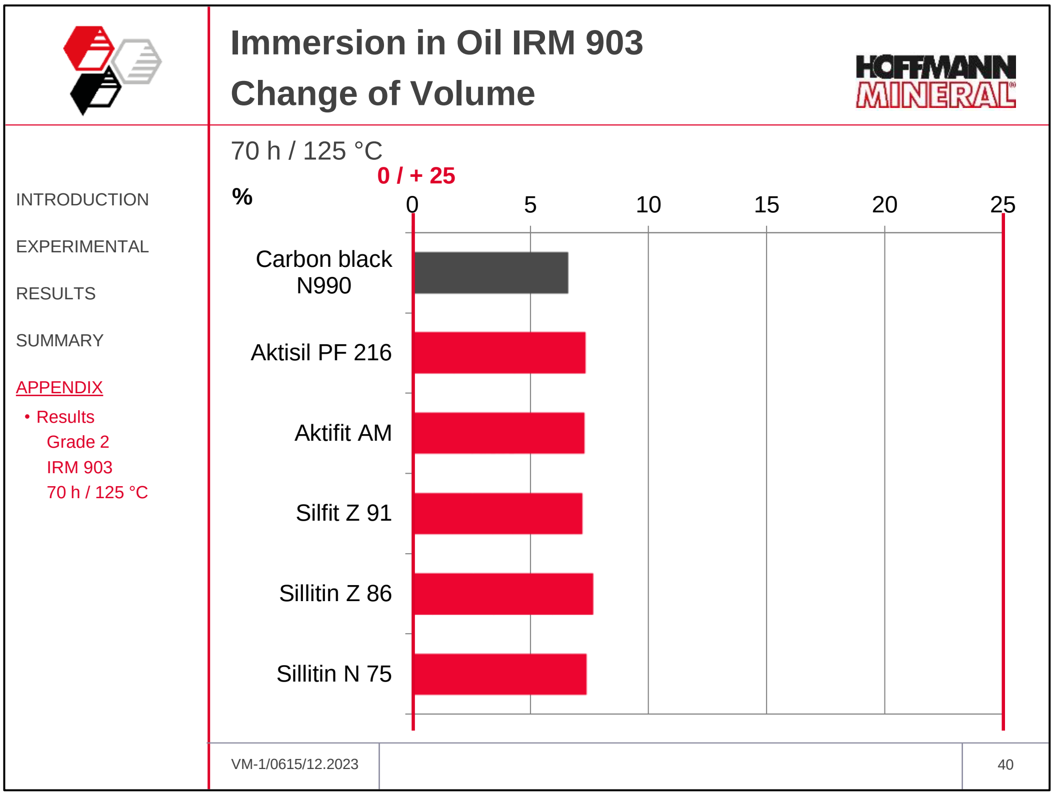

Fig. 29

The volume change with the siliceous earth fillers remains at the level of the straight carbon black compound with N990, without giving evidence of significant differences between the individual products. The requirements of the standard will be fulfilled without limitations *(Fig. 29).*

6.5 Grade 2 – Immersion in Reference Fuel Liquid C at 23 °C

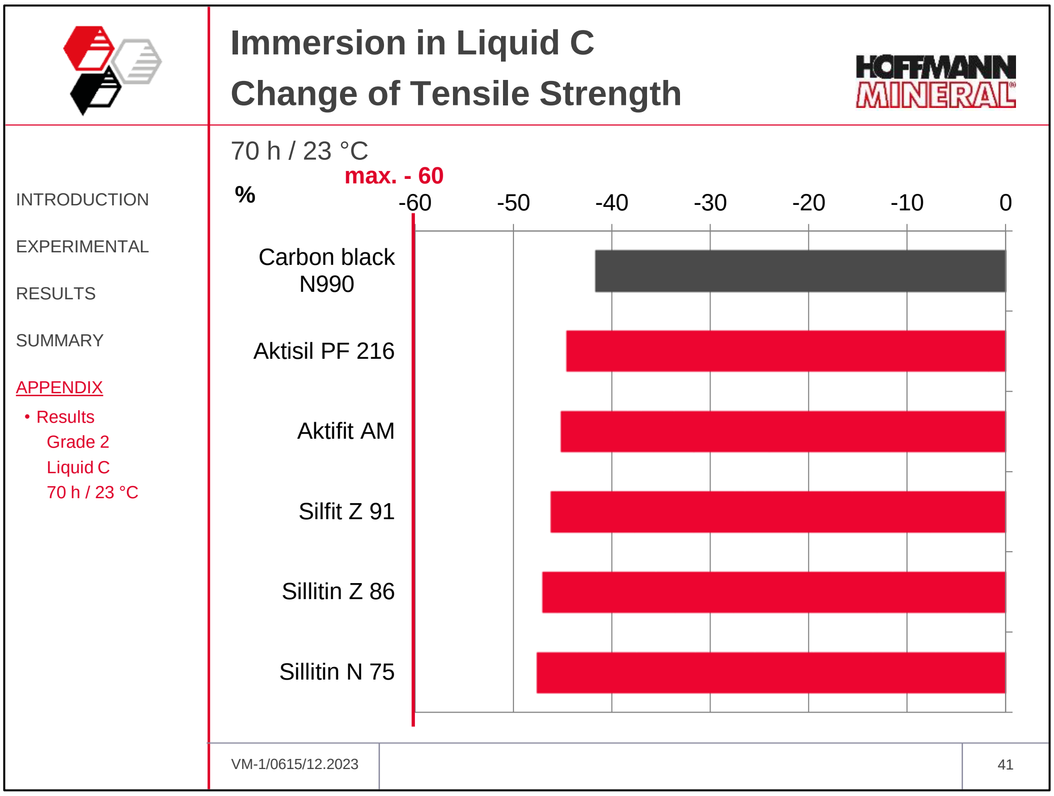

Fig. 30

Here too, the change of the tensile strength comes out rather comparable for the siliceous earth fillers, and safely remains within the requirements of the standard *(Fig. 30).*

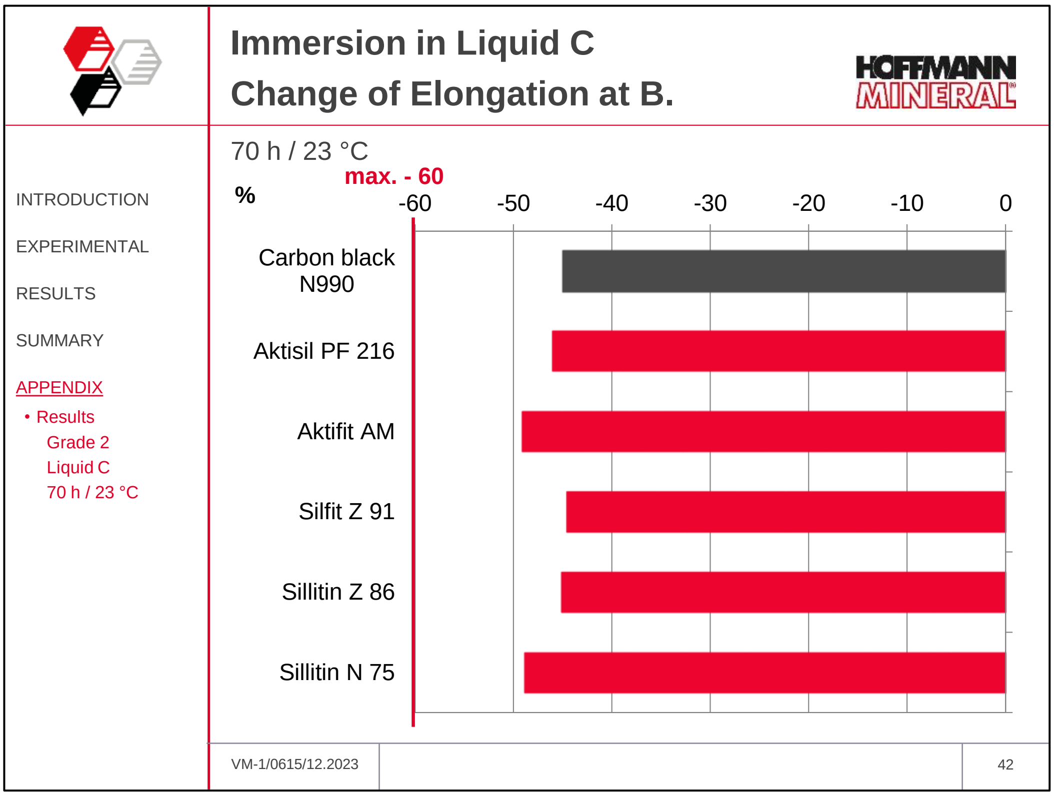

Fig. 31

The change of elongation at break with the siliceous earth fillers comes out similar to the straight carbon black compound, which means the requirements of the standard will be met safely *(Fig. 31).*

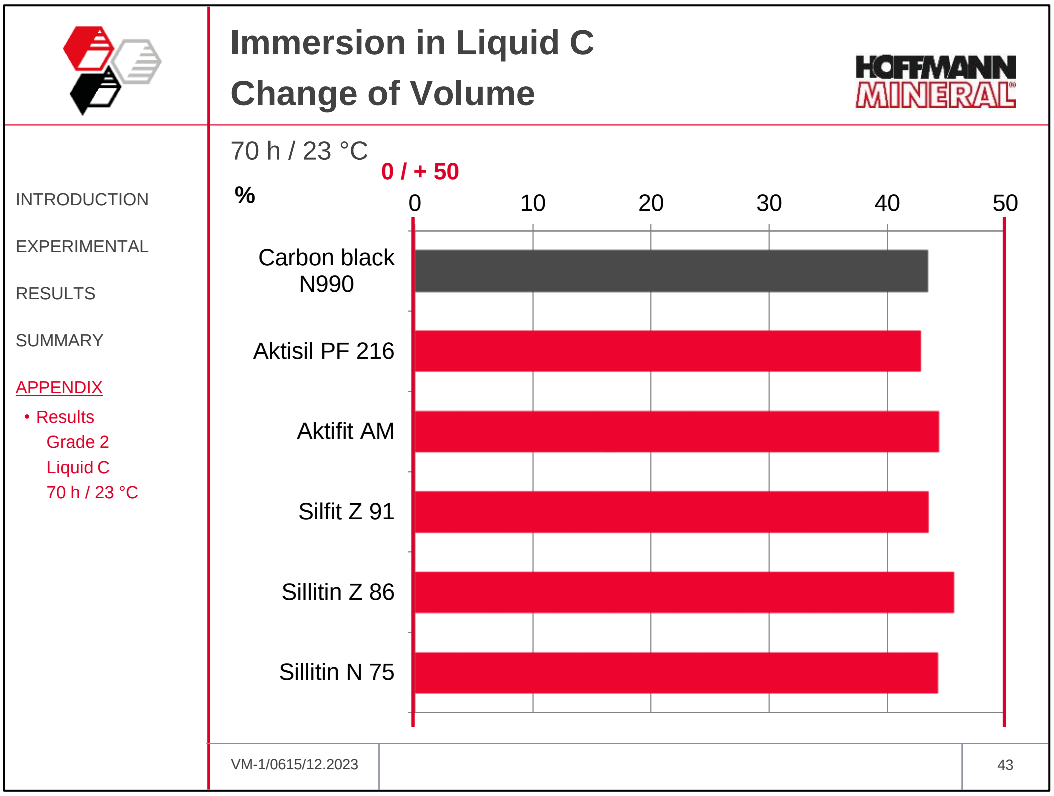

Fig. 32

The volume change with the siliceous earth fillers remains at the level of the straight carbon black compound and, therefore, within the limits of the pertinent standard *(Fig. 32).*

6.6 Grade 3 - Immersion in Oil IRM 901 at 150 °C

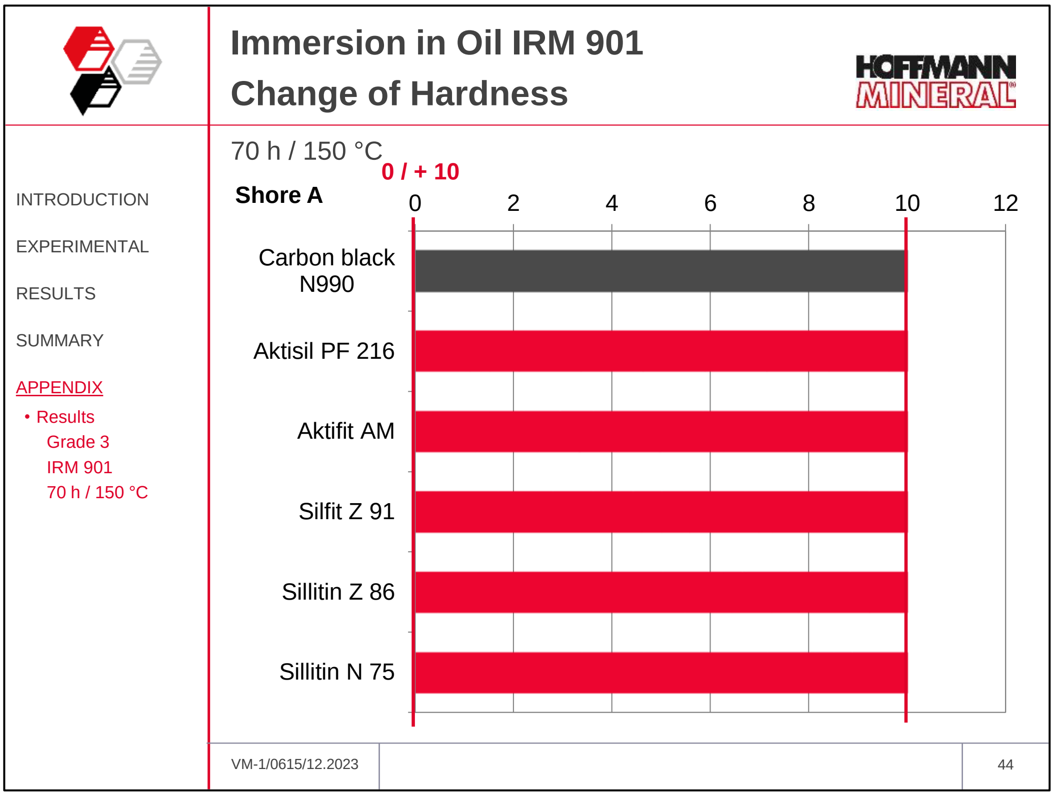

Fig. 33

Along with the oil resistance in standard oil IRM 903, further tests at 150 °C concerned the properties after immersion in Oil IRM 901. Here the hardness increases in the same way for all compounds included, so that the requirements of the standard are just fulfilled with borderline results *(Fig. 33).*

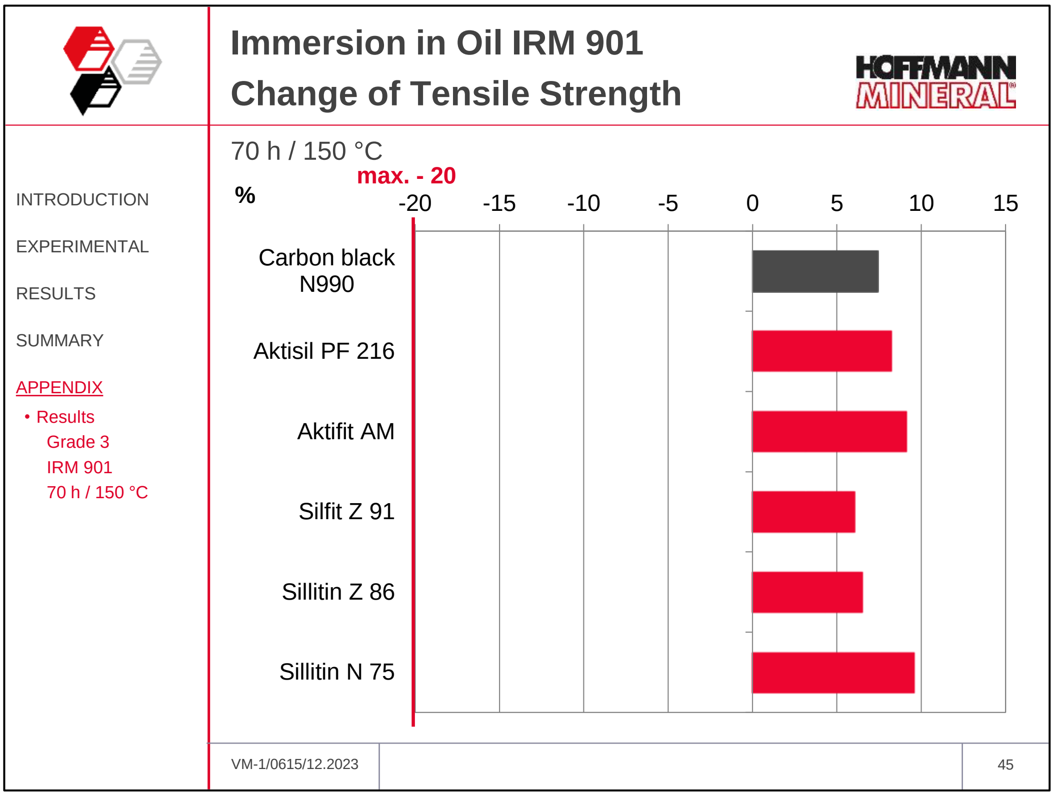

Fig. 34

The tensile strength increases similar to the carbon black compound. The requirements of the pertinent standard again are met by all compounds without difficulties *(Fig. 34).*

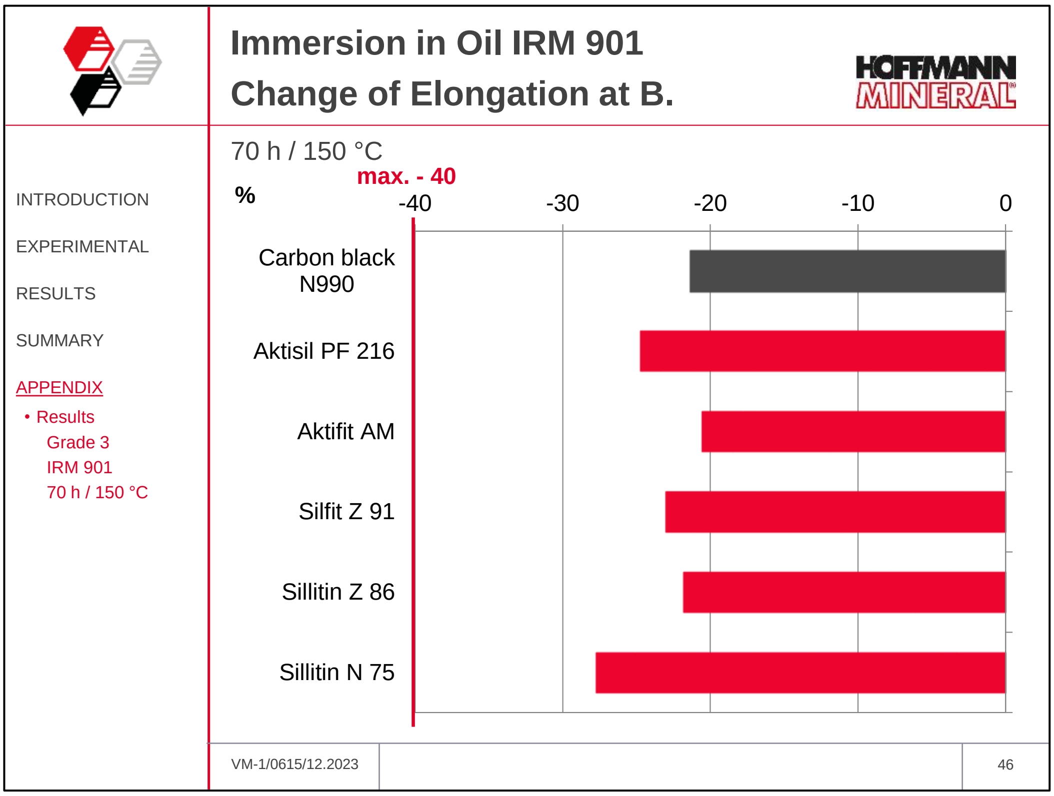

Fig. 35

The elongation at break of the siliceous earth compounds remains largely at the level of the control compound with carbon black N990. The standard requirements are met throughout *(Fig. 35).*

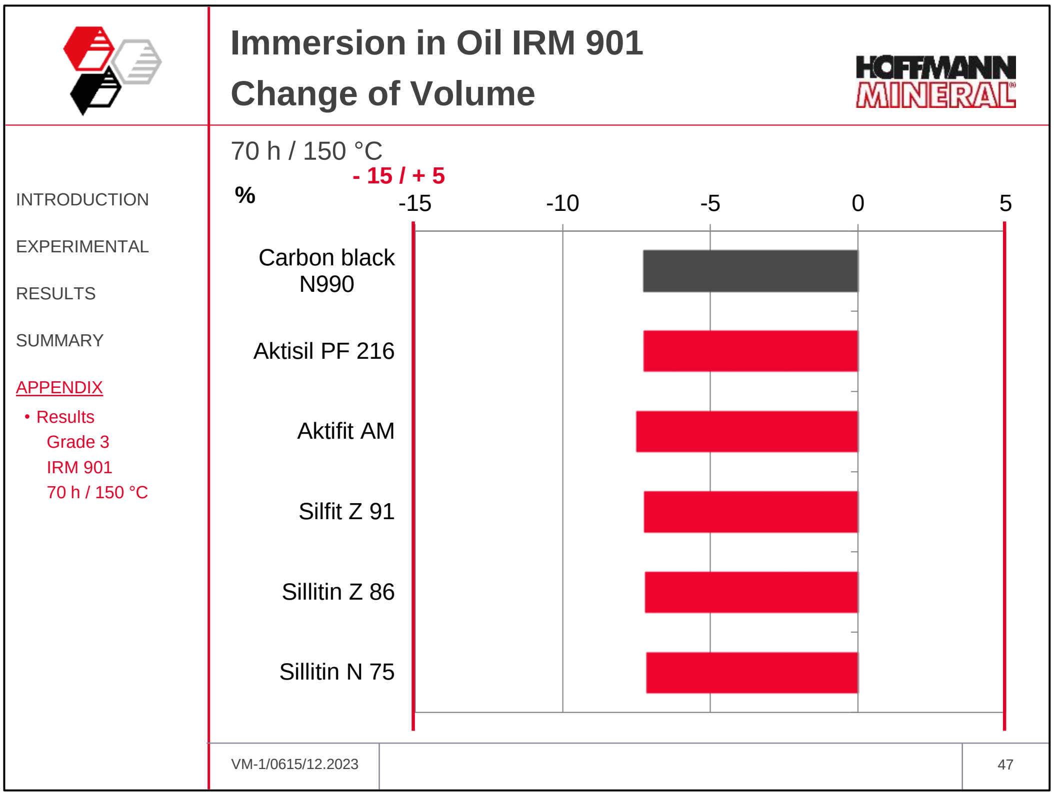

Fig. 36

The volume change of the siliceous earth compounds comes out at the same level as the carbon black compound, i.e. far from the requirement limits of the standard *(Fig. 36).*

6.7 Grade 3 - Immersion in Oil IRM 903 at 150 °C

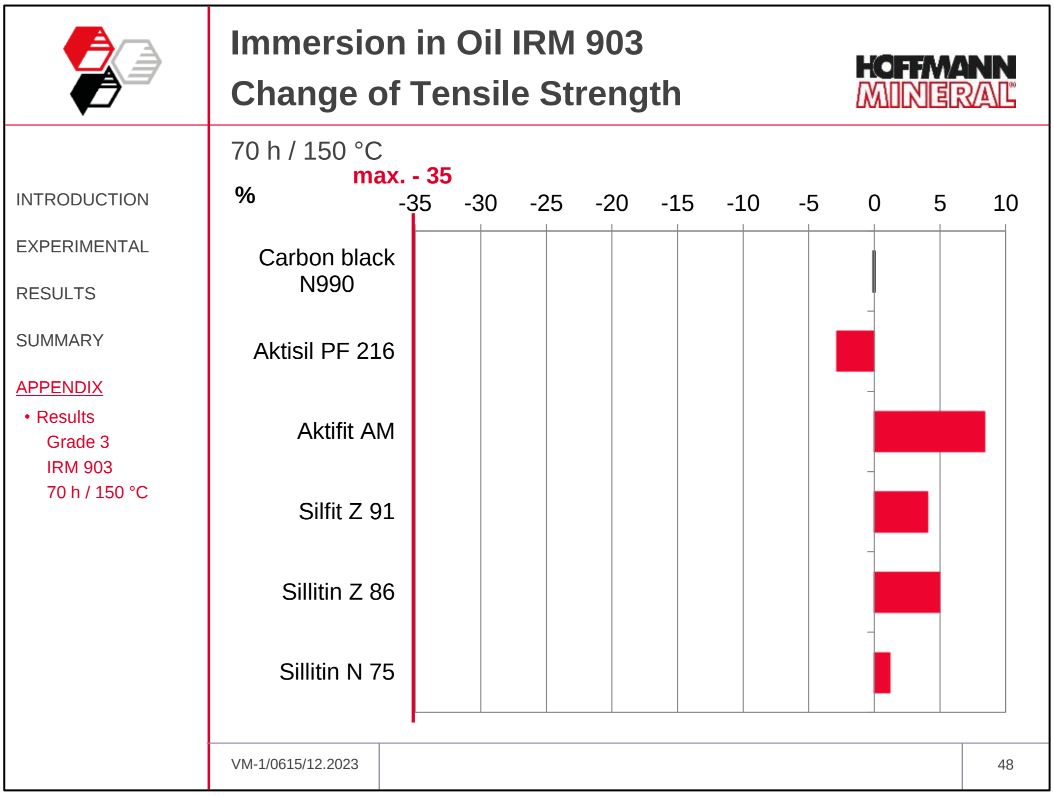

Fig. 37

The tensile strength changes positively or negatively while remaining close to the compound with carbon black N990, and the variations are so small that the requirements of the pertinent standard are met without problems *(Fig. 37).*

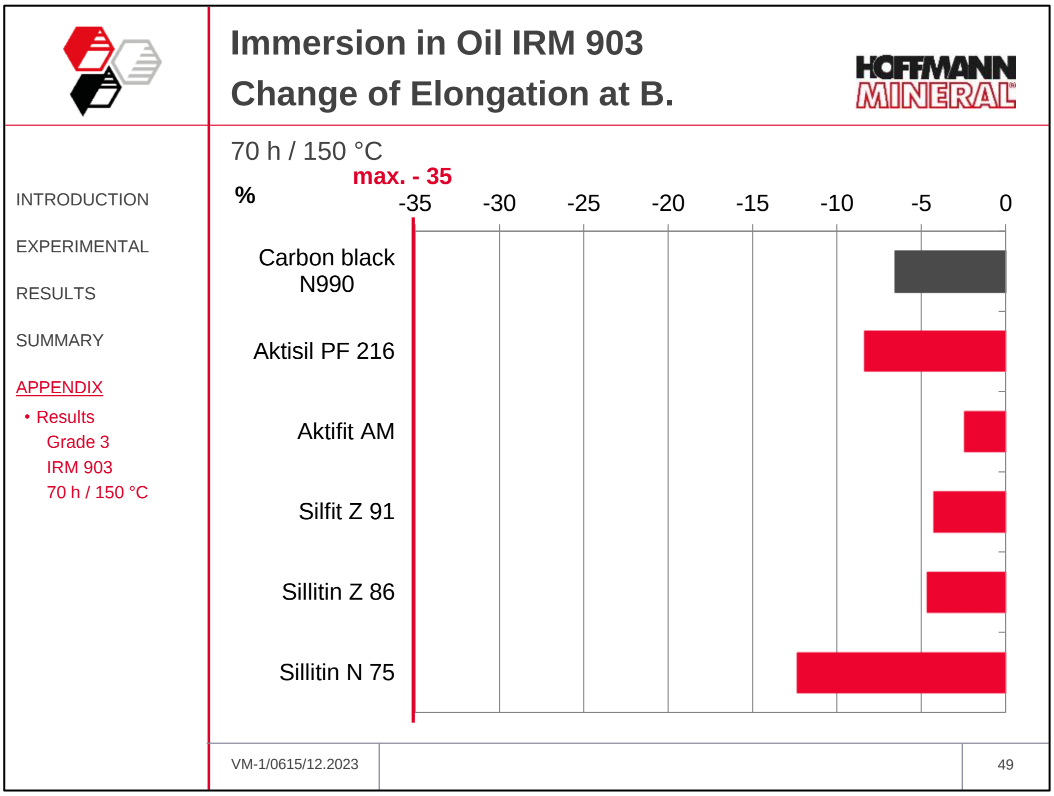

Fig. 38

The changes of elongation at break of the siliceous earth compounds are only marginally different from those of the carbon black N990 compound. The conditions of the pertinent standard are fulfilled here again without problems *(Fig. 38).*

6.8 Grade 2 + 3 – Aging in Hot Air at 125 °C

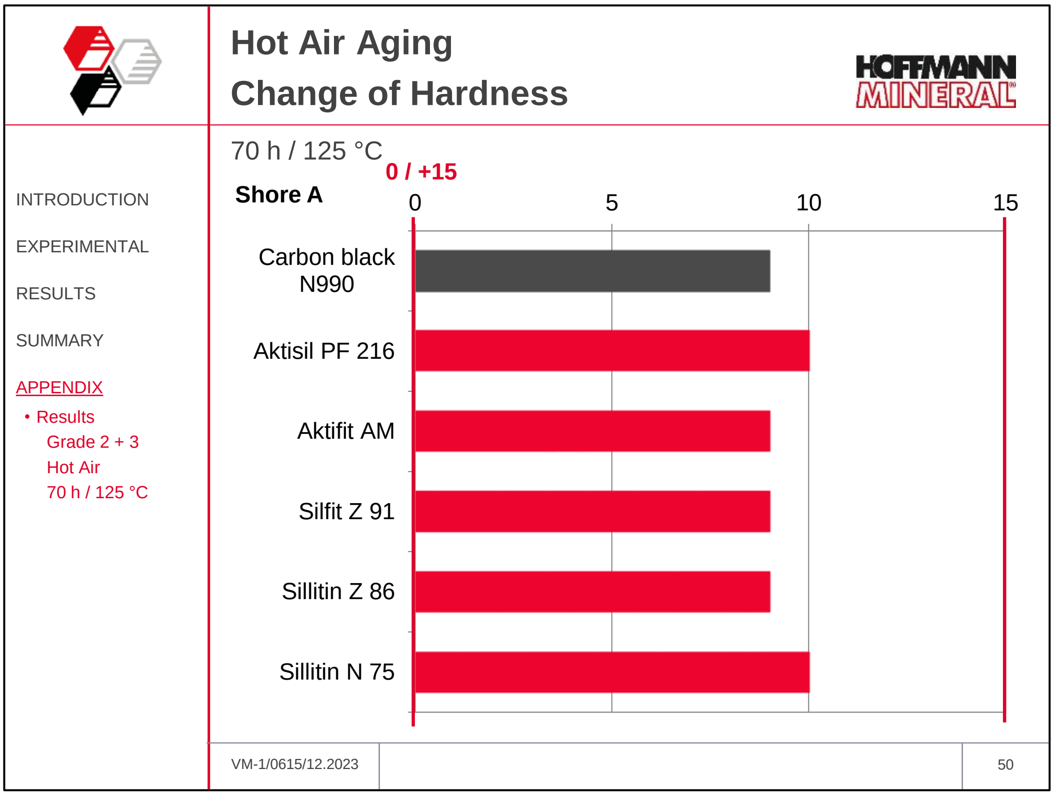

Fig. 39

Along with the swelling in oils, also hot air aging is part of the technical requirements of ASTM D2000. The hardness change of the individual siliceous earth compounds during hot air aging differs only marginally from the situation with the carbon black N990 compound. The conditions of the general standard are met easily *(Fig. 39).*

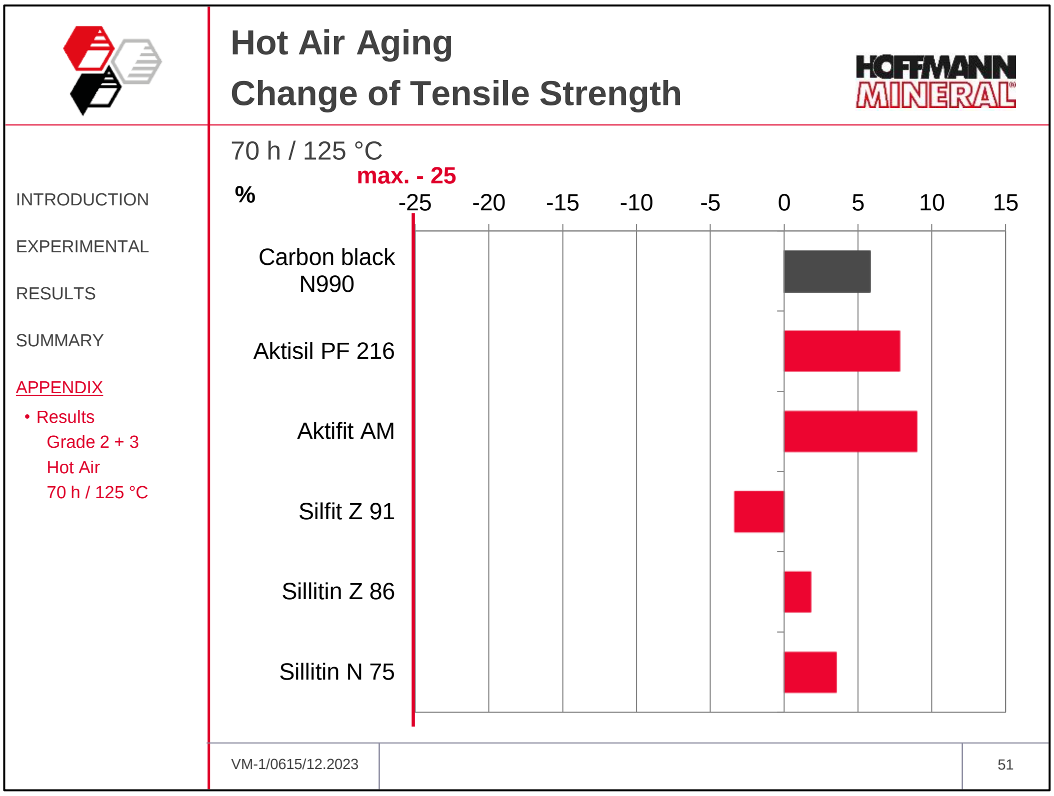

Fig. 40

The change of the tensile strength is hardly different from the straight carbon black compound with N990. This way, also the requirements of the pertinent standard can be met without limitations *(Fig. 40).*

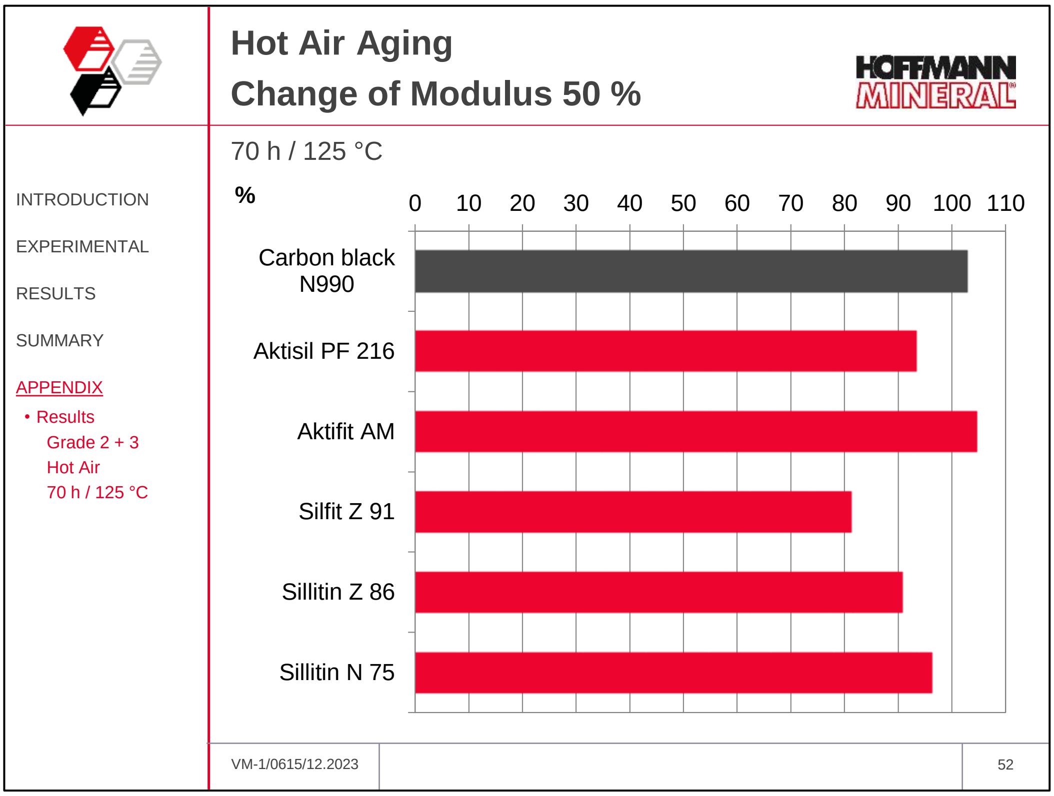

Fig. 41

The change of the tensile modulus at 50 % with carbon black N990 is already so important that the results for the siliceous earth compounds come out at a comparable level *(Fig. 41).*

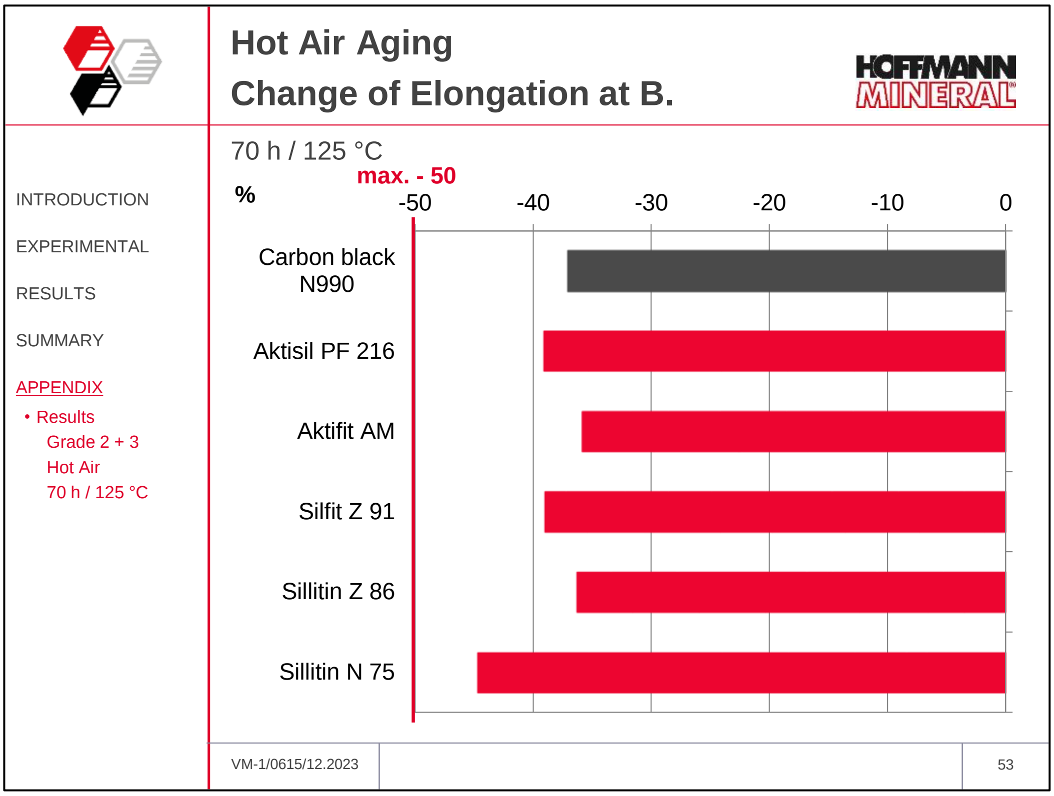

Fig. 42

The changes of elongation at break come out all at a similar level with the straight carbon black compound. The requirements of the pertinent standard will therefore, be met although partly just borderline *(Fig. 42).*