Comparison of mineral fillers in non-conductive car body seals

Author: Karin Müller

HOFFMANN MINERAL

We supply material for good ideas

Content

Status Quo

Since a few years, the automotive industry increasingly has been working with light metals such as aluminum and magnesium. In contact with steel and conventionally formulated sealing profiles, electrochemical corrosion can occur at the less noble metal. In order to avoid that this happens, electrically insulating sealing sections are required.

In the pertinent compounds, consequently, the loading of the traditional major filler carbon black has to be reduced and must be compensated by non-conductive fillers. Here mineral fillers are the materials of choice, as they have already been used as co-fillers, but primarily with respect to esthetic effects at the extruded rubber surface. In the modified formulations, the mineral filler now has to assume the load-carrying properties of the section.

Objective

This leads to the question:

Which mineral filler to use?

The present study will show the basic effects of individual filler types, and thus facilitate a selection close to the requirements.

Emphasis is placed on Neuburg Siliceous Earth products, which also offer themselves to demonstrating the effects of a surface treatment with funktional groups (Aktisil grades).

Part 1:

Laboratory trials

Part 1:
Laboratory Trials

HOFFMANN MINERAL

The starting point was a guide formulation for window duct and channel seals from DSM Elastomers Europe with a medium filler loading (40 vol.-% EPDM).

With respect to the requirements of automotive companies, the following laboratory results wer to be obtained:

- Hardness 60 to 70 Shore A
- Tensile strength > 8 MPa
- Compression set 22 h / 70 °C < 20 %
- Volume Resistivity > 10^9, ideally > 10^{10} Ω*cm

Base Formulation

EPDM – 65 Shore A

	phr
Keltan 8340 A	100.00
Zinc Oxide activ	5.00
Stearic acid	1.00
Lipoxol 3000	2.00
Kezadol GR	5.50
Carbon black N 550	135.00
Sunpar 2280	65.00
Rhenogran DPG-80	0.50
Rhenogran MBTS-80	1.30
Rhenogran ZBEC-70	2.00
Rhenogran S-80	0.75
Rhenodure S/G	1.00
Rhenocure TP/G	2.00
Vulkalent E/C	0.50
Santocure CBS pdr-d	0.50
Total	**322.05**

Preliminary Tests

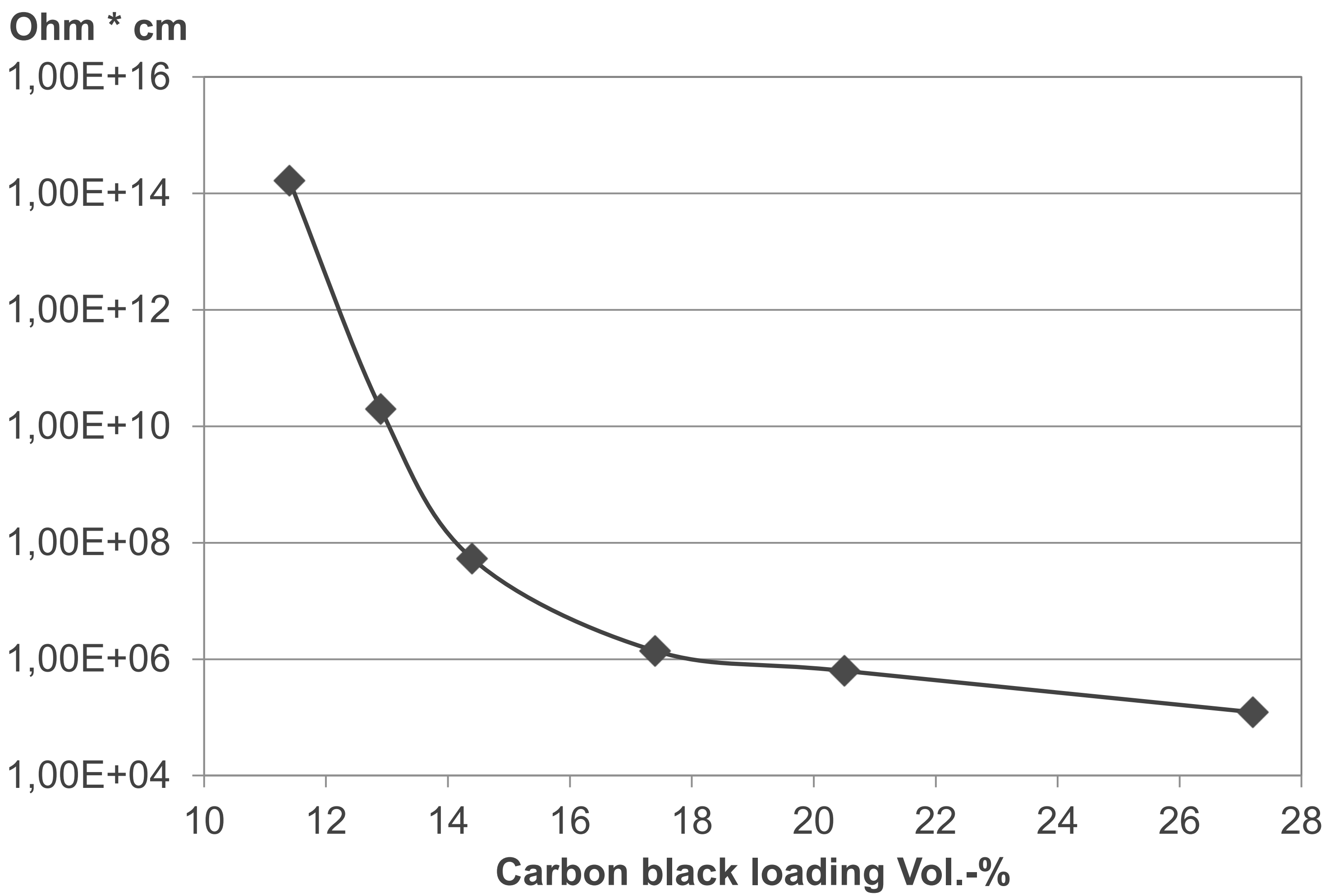
Test for determining the volume resistivity as a function of the loading of carbon black / mineral filler at nearly identical hardness of 65 Shore A

	phr					
Carbon black N 550	135	105	90	75	67,5	60
Sillitin Z 86	0	65	95	125	140	155

	Vol.-%					
Carbon black N 550	27.2	20.5	17.4	14.4	12.9	11.4
Sillitin Z 86	0.0	8.7	12.6	16.4	18.3	20.2

Volume Resistivity

as a function of carbon black loading at constant hardness



Selected Loading
Carbon Black / Mineral Filler

	phr
Carbon black N 550	60
Mineral Filler	155

	Vol.-%
Carbon black N 550	11.4
Mineral Filler	20.4

Fillers, Characteristics

HOFFMANN MINERAL

Filler Class	Product	Particle size d_{50} [µm]	Particle size d_{97} [µm]	Oil absorption [g/100g]	Spezific surface area BET [m²/g]
Neuburg Siliceous Earth	Sillitin N 85	3.0	16	45	10
	Sillitin Z 86	1.9	9	55	11
	Sillitin P 87	1.5	6	55	12
	Aktisil MM	2.2	10	45	7
	Aktisil PF 216	2.2	10	50	8
Calcium Carbonate	Surface treated $CaCO_3$	2.7	24	20	2
	$CaCO_3$	2.4	13	30	5
Talc	American Talc	4.7	17	50	11
Clay	English calcined Clay	3.5	18	60	8
	English soft Clay	7.7	34	45	7
	English hard Clay	1.8	11	50	30
	English Clay	3.0	12	55	13

Preparation and Curing of the Compound

- **Mixing**

  Open mill Ø 150 x 300 mm

  Batch volume: approx. 1000 g

  Temperature: 50 °C

  Mixing time: approx. 20 min.

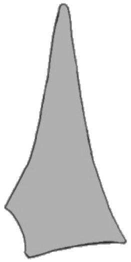
- **Curing**

  Press, 170 °C, t_{90} + 10 %

Extrusion

In accordance with ASTM D 2230

- Schwabenthan Extruder Polytest 30R
  D = 30 mm, L/D ratio = 15
- Temperature profile:
  70 / 70 / 110 °C
- Variations:
  Constant screw speed 50 rpm
- Garvey rating:
  1st digit: Die swell
  2nd digit: 30° edge
  3rd digit: Surface
  4th digit: Corners



- Assessment
  1 = poor to 4 = very good
- Maximum rating: 4 x 4 = 16

Volume Resistivity

DIN IEC 93

Test outline:

- Dimension of plates: 10 x 10 cm
- Thickness of plates: about 2 mm
- Electrode set-up: circular plate electrode with protective ring
- Test method: Voltage / Amperage method
- Test voltage: 100 V
- Recording time: 1 min. after application of voltage
- Test temperature: 23 °C
- Evaluation:

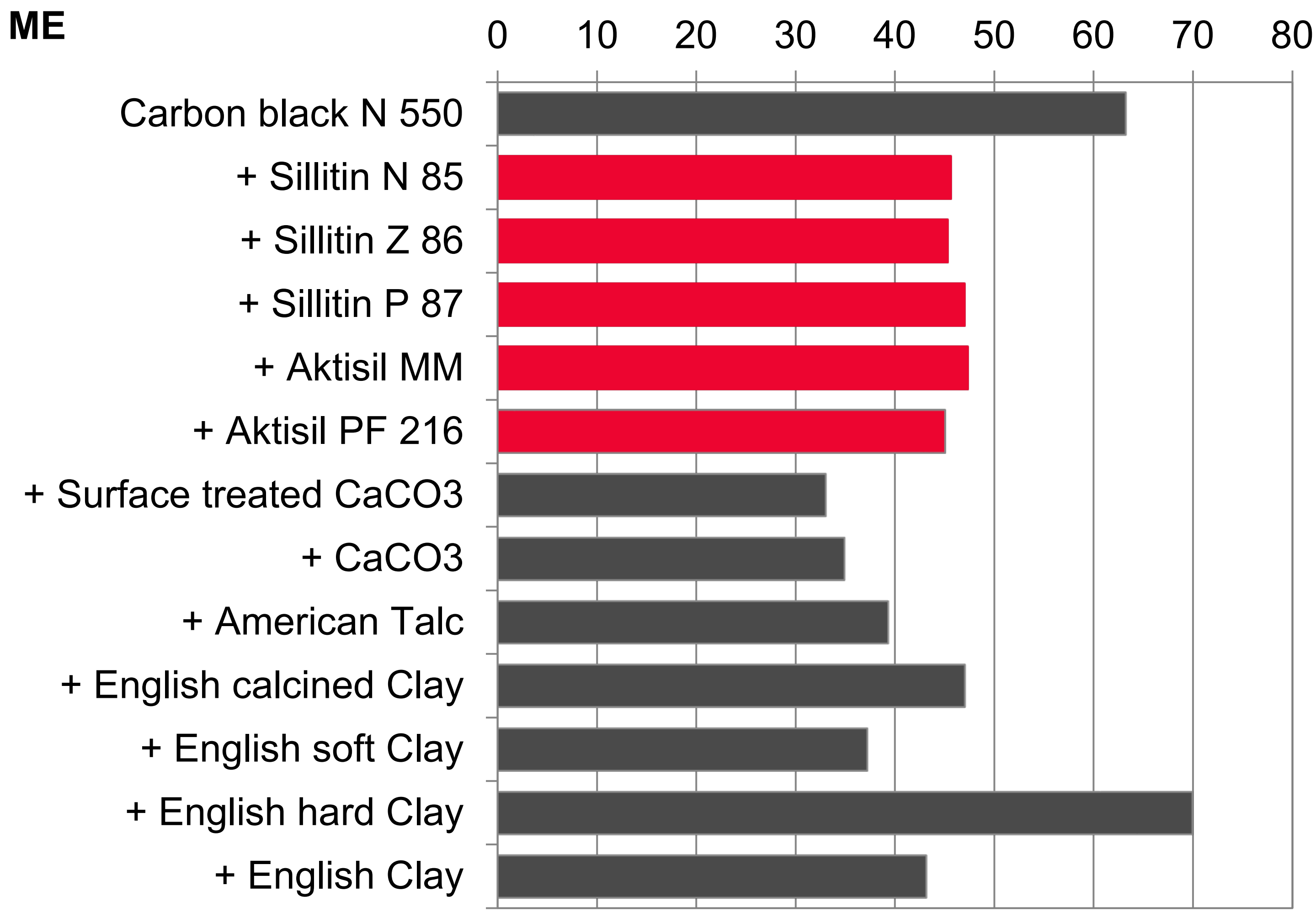
$$\rho = R_X * A / h$$

with

ρ volume resistivity in Ω*cm
R_X volume resistance in Ω
A effective surface area of the protected electrode (24 cm²)
h median thickness of test plate in cm

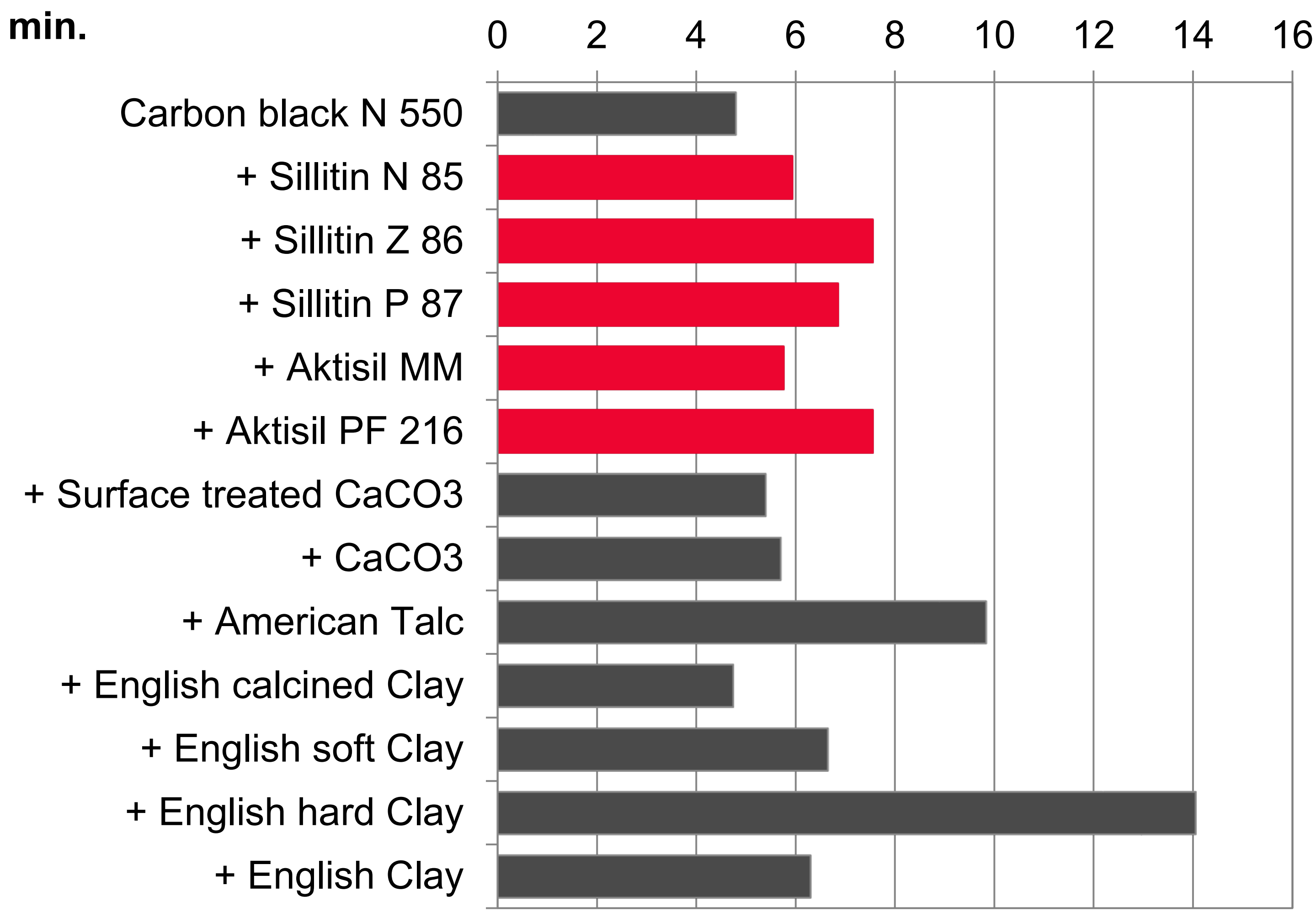
Mooney Viscosity

DIN 53 523 Part 3, ML 1+4 120 °C



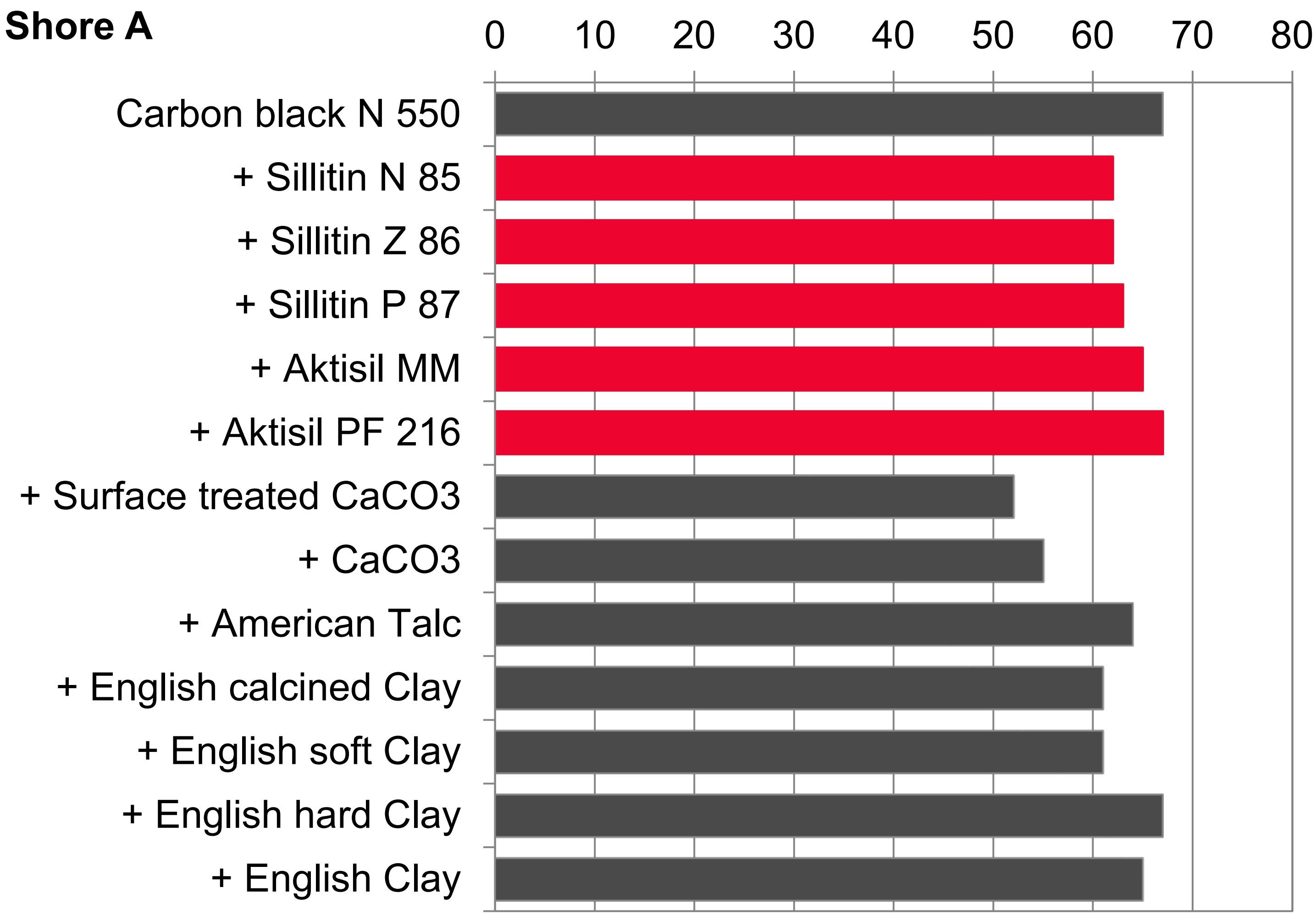
Conversion Time t_{90}

DIN 53 529-A3, 170 °C, 0.2° deflection – Göttfert Elastograph



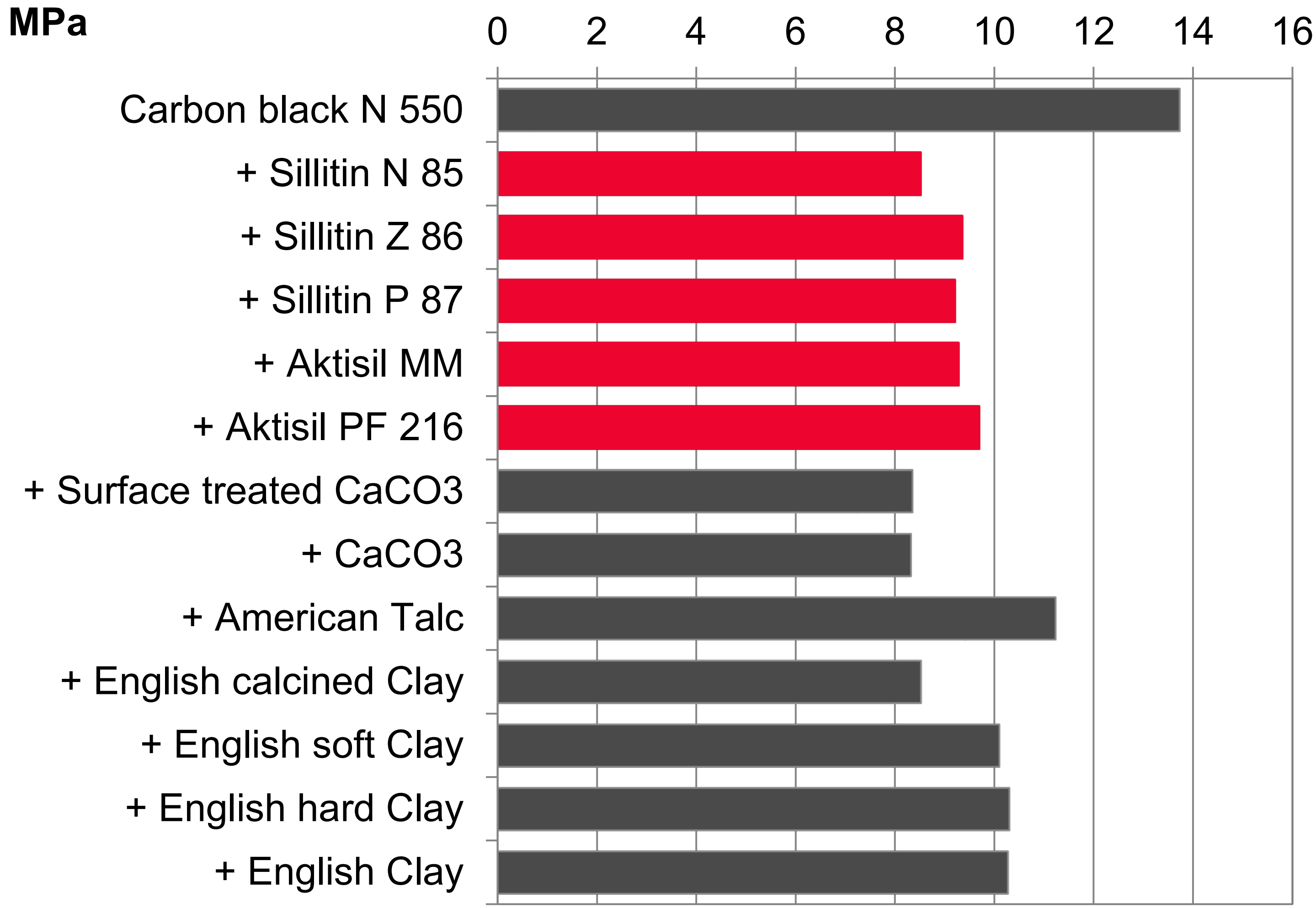
Hardness

DIN 53 505-A, piled-up S2 dumbbells



Tensile Strength

DIN 53 504, S2



Elongation at Break

INTRODUCTION

LAB TESTS

• EXPERIMENTAL

• RESULTS

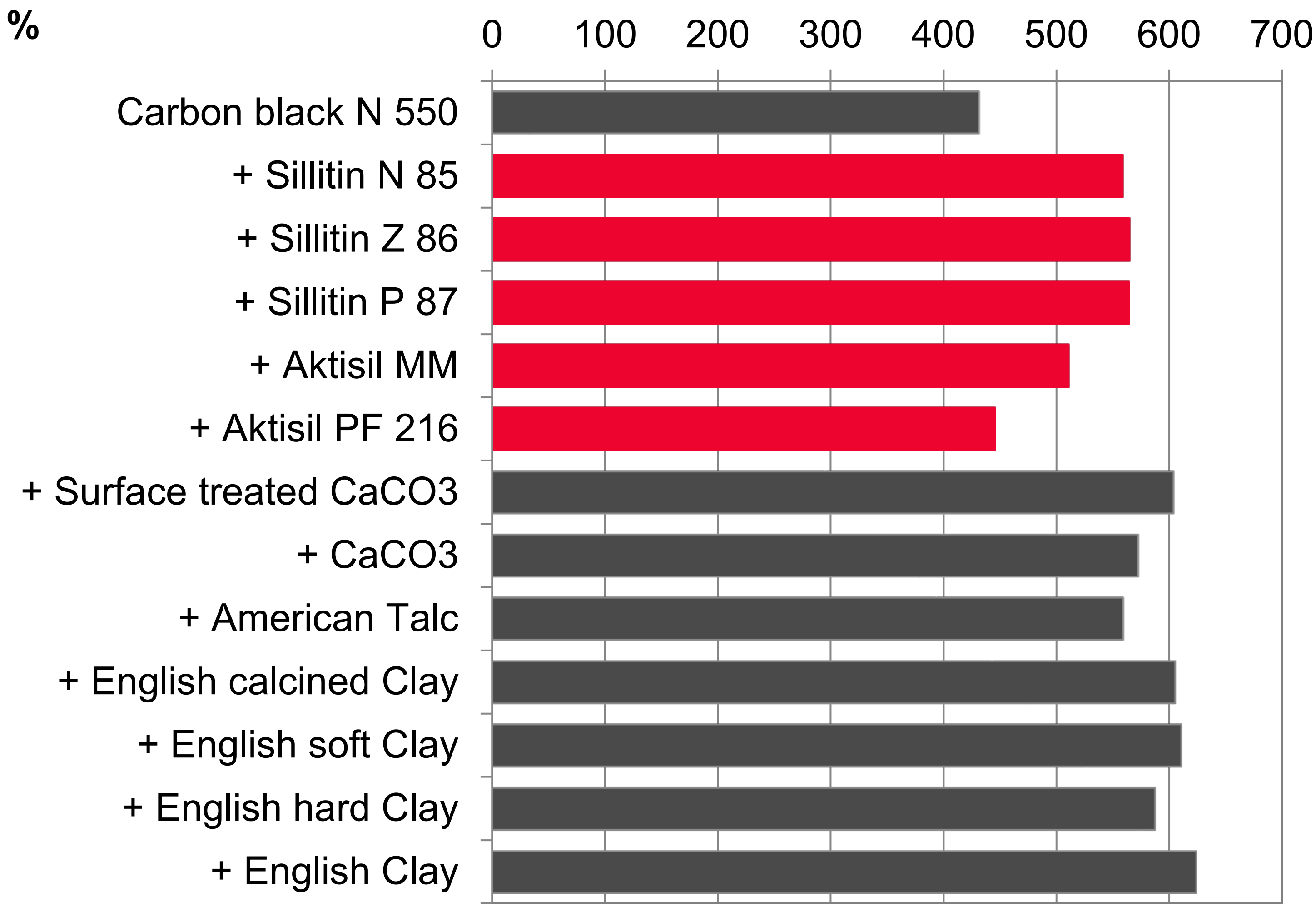
• SUMMARY

PILOT PLANT TRIALS

SUMMARY

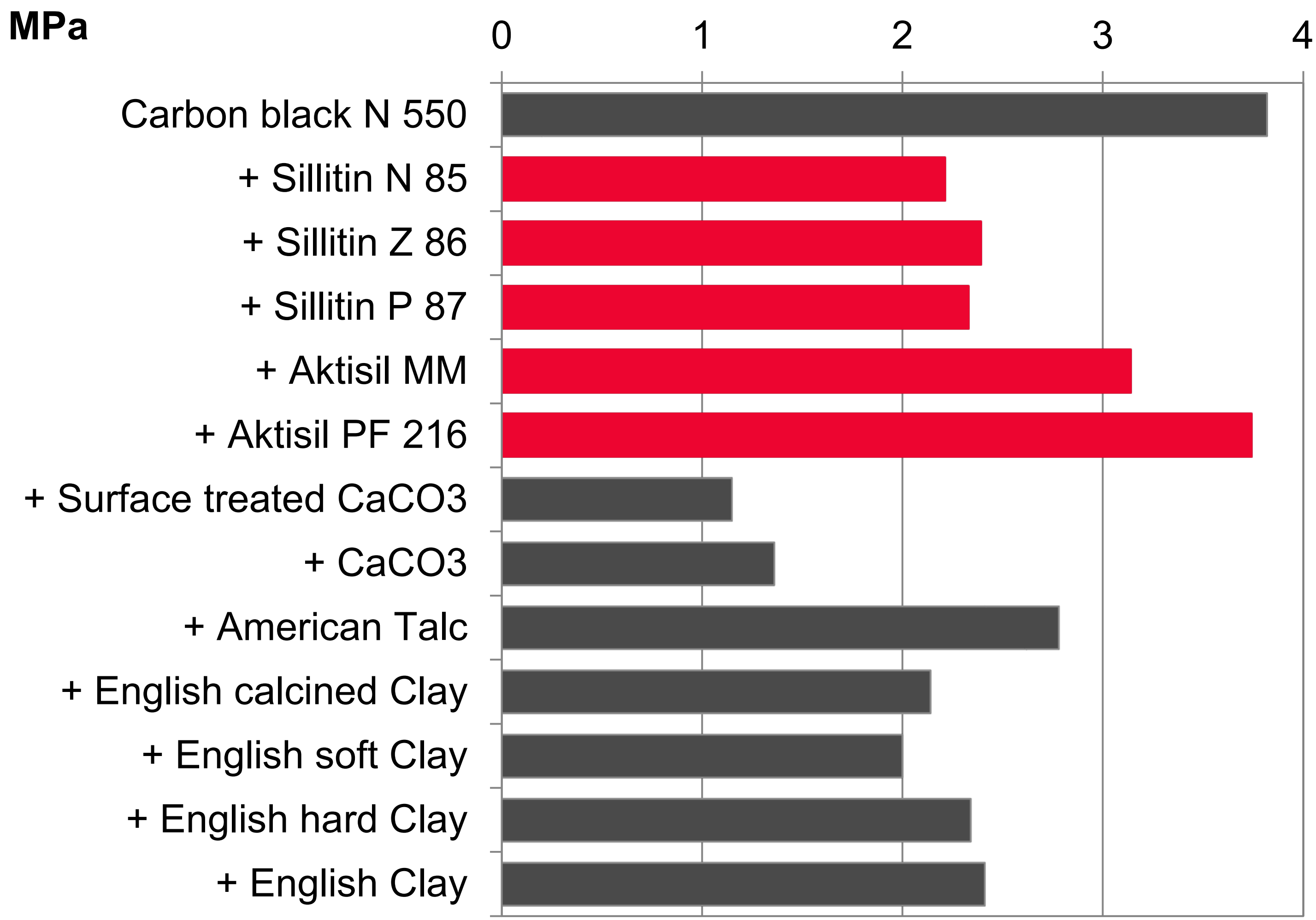
APPENDIX

DIN 53 504, S2



Modulus 100 %

DIN 53 504, S2



Tear Resistance

HOFFMANN MINERAL

INTRODUCTION

LAB TESTS

• EXPERIMENTAL

• RESULTS

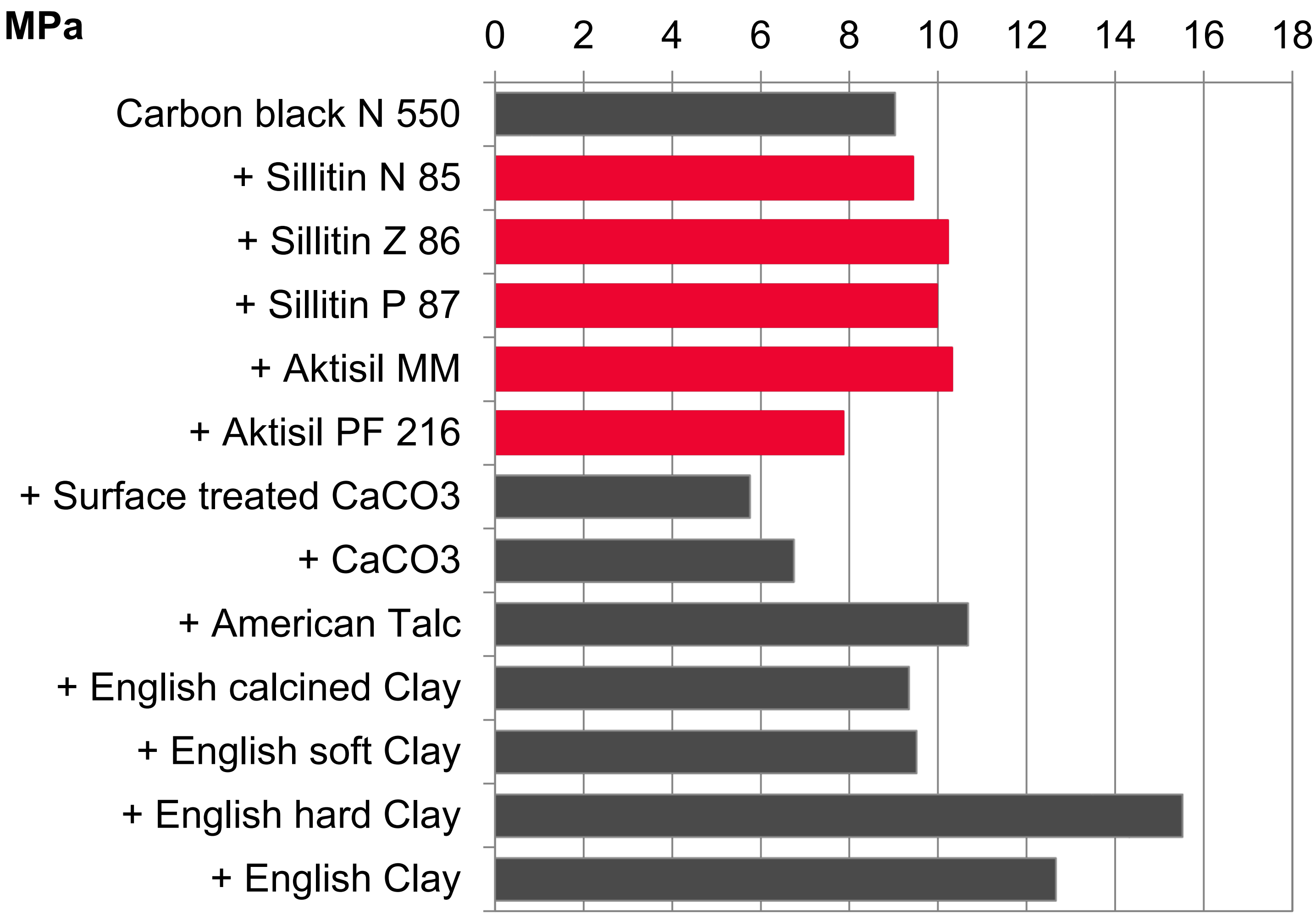
• SUMMARY

PILOT PLANT TRIALS

SUMMARY

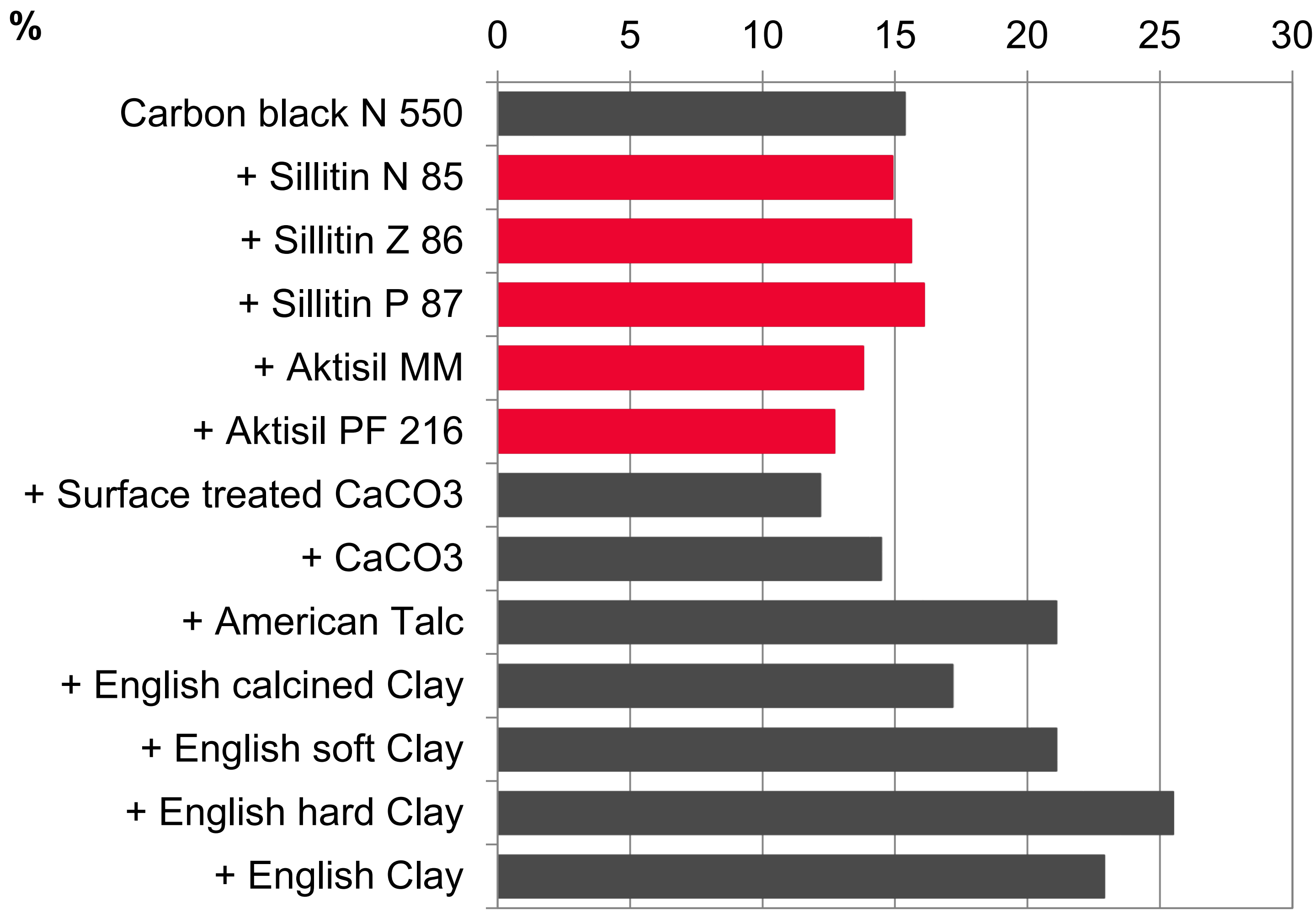
APPENDIX

DIN 53 507-A, Fmax 500 mm/min



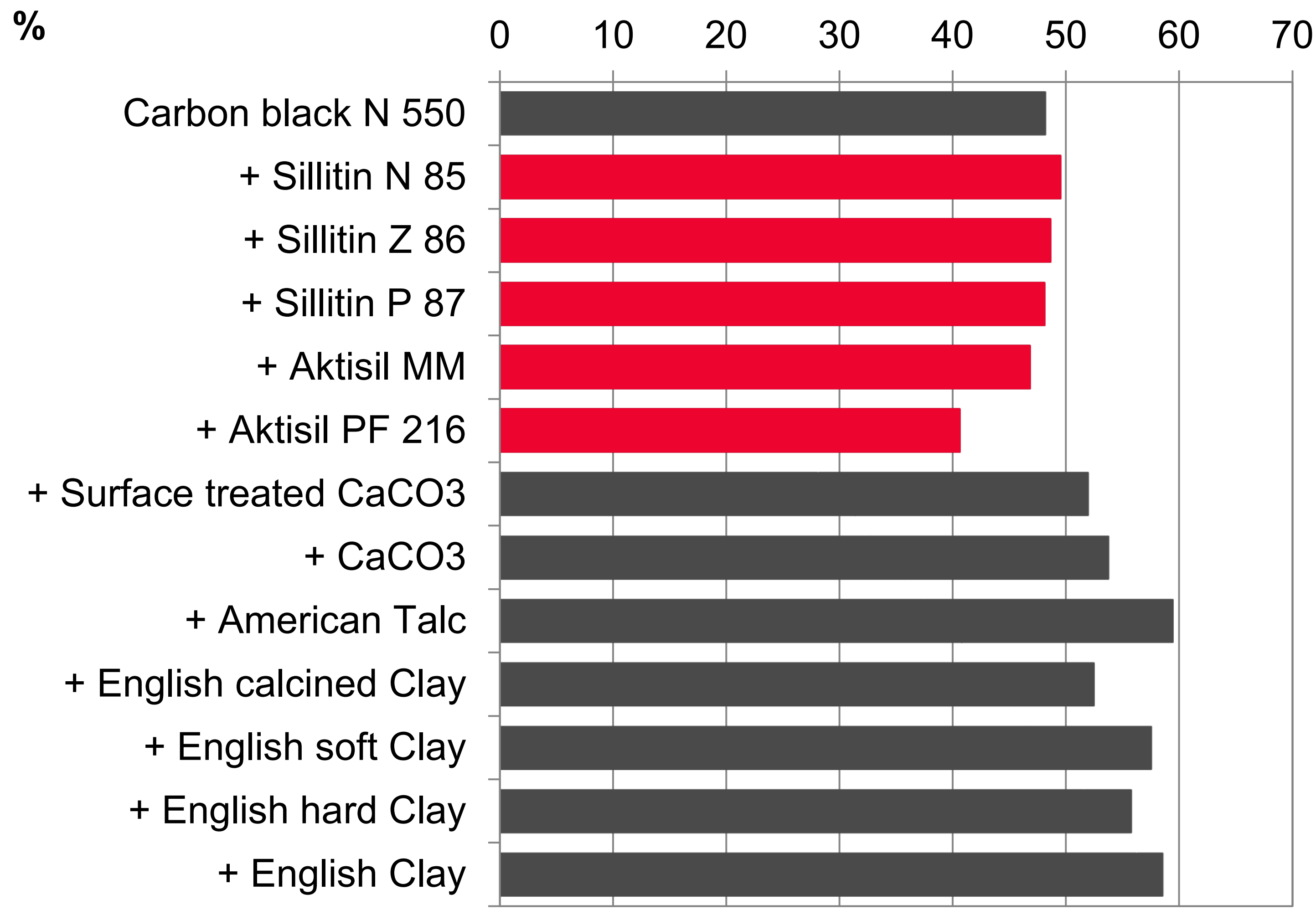
Compression Set

DIN ISO 815-1 B, cooling method A, 24 h / 70 °C



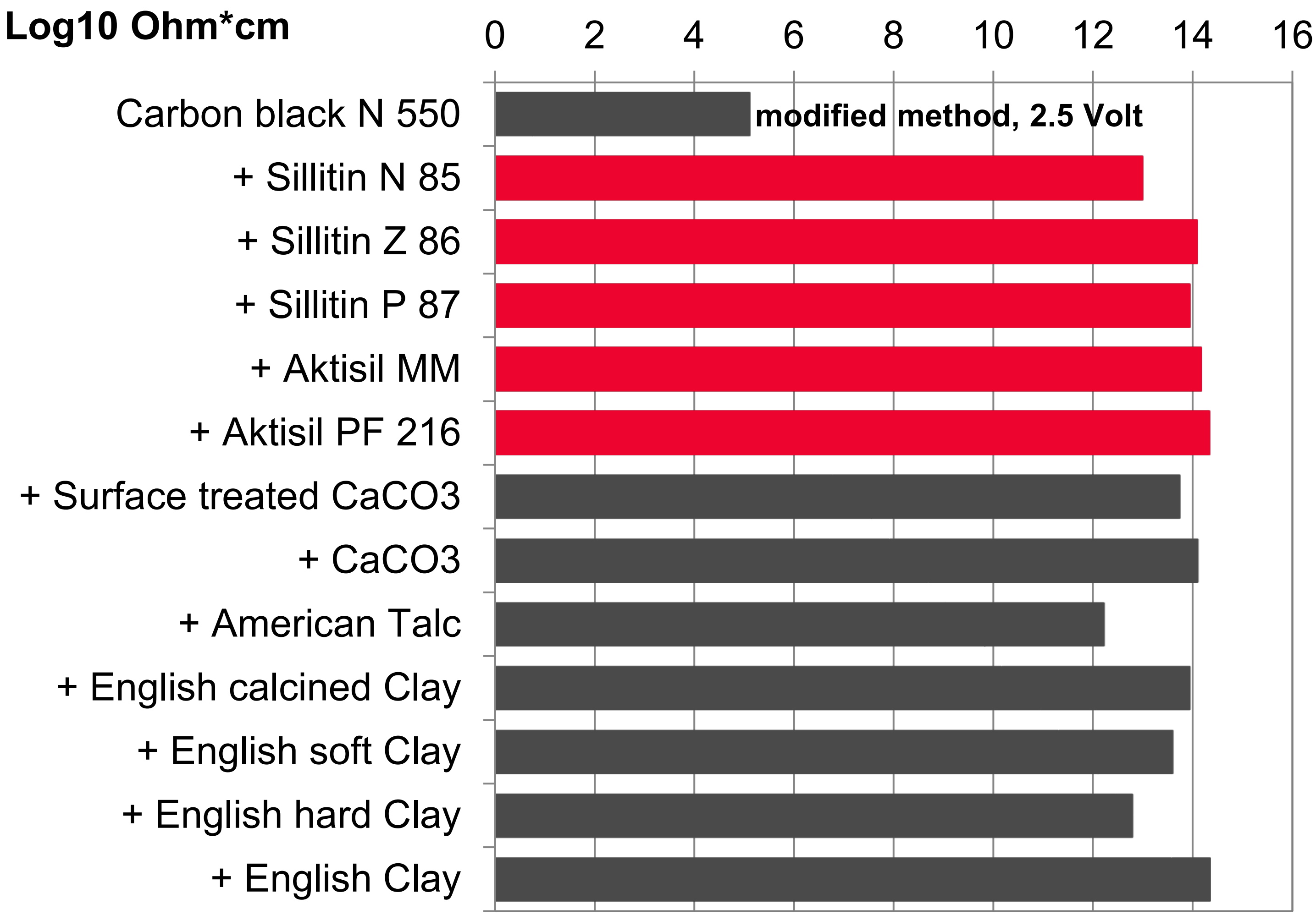
Compression Set

VW PV 3307, 50 % deformation, 5 s Relaxation, 100 h / 70 °C



Volume Resistivity

DIN IEC 93, 100 Volt, 1 min.



Garvey-Extrusion
Haul-off Speed

ASTM D 2230, 50 U/min.

INTRODUCTION

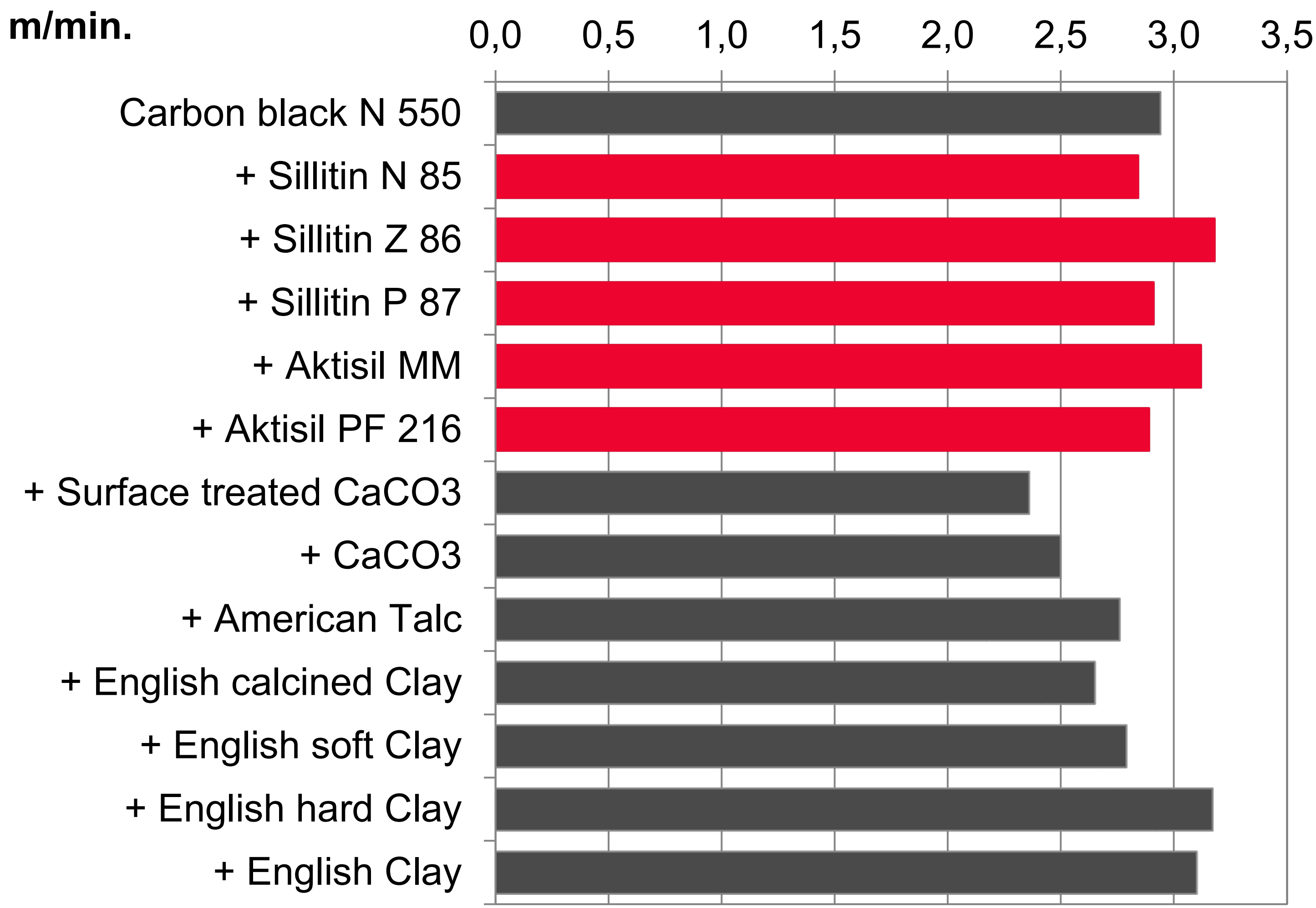
LAB TESTS

- EXPERIMENTAL
- RESULTS
- SUMMARY

PILOT PLANT TRIALS

SUMMARY

APPENDIX



Garvey-Extrusion
Profile Quality

INTRODUCTION

LAB TESTS

• EXPERIMENTAL

• RESULTS

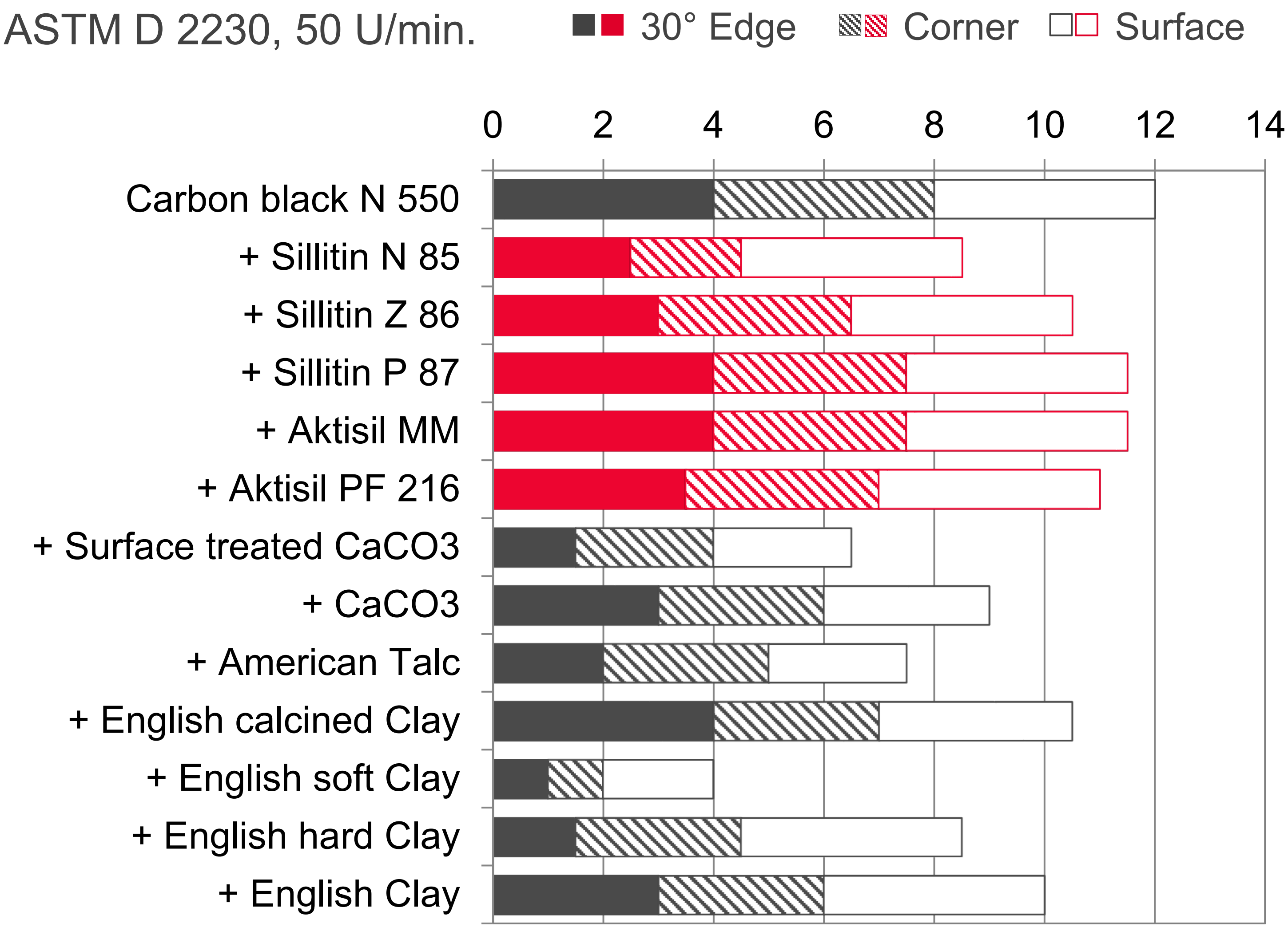
• SUMMARY

PILOT PLANT TRIALS

SUMMARY

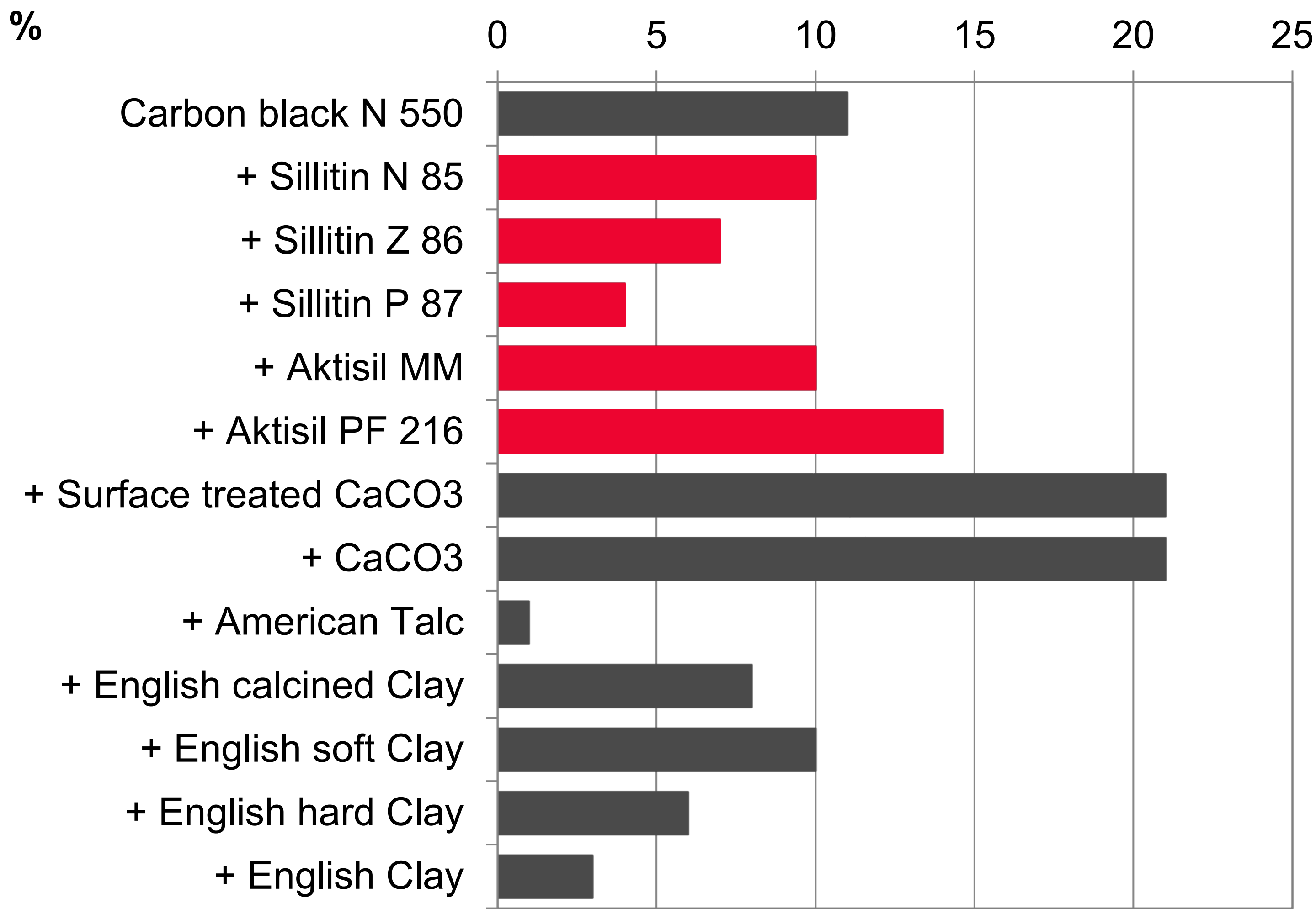
APPENDIX

ASTM D 2230, 50 U/min.



Garvey-Extrusion
Die Swell

ASTM D 2230, 50 U/min.



Garvey-Extrusion
Profile Quality vs. Haul-off Speed

INTRODUCTION

LAB TESTS

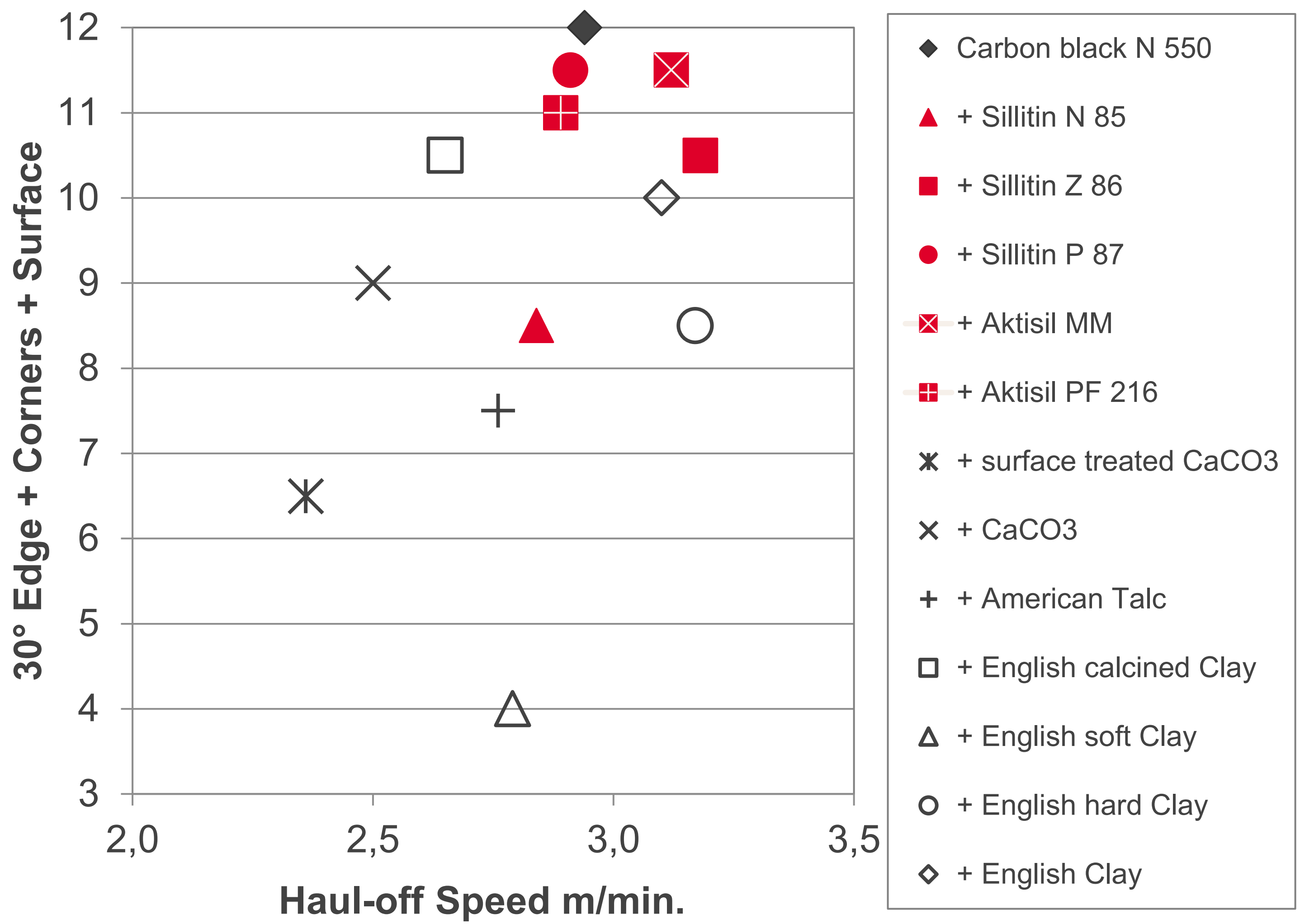
- EXPERIMENTAL
- RESULTS
- SUMMARY

PILOT PLANT TRIALS

SUMMARY

APPENDIX

ASTM D 2230, 50 U/min.



Laboratory Trials
Summary (1)

HOFFMANN MINERAL

With mineral fillers non-conductive car body seals can be produced which – with the only exception of tensile strength – do not give evidence of diminished performance properties.

- The calcium carbonates show their main deficiency in the mechanical and extrusion properties, but at short cure times they give good compression set results.
- Talc imparts good tensile strength levels, but even at long cure times compression set comes out poor, and extrusion properties are just moderate.
- With clays, excepted the calcined version, good mechanical properties are obtained, but they show weak points in extrusion properties and particularly in compression set results. For the calcined clay, more or less the reverse is true.

Laboratory Trials

Summary (2)

- The Neuburg Siliceous Earth grades are distinguished above all by their outstanding extrusion properties and low compression set.
- The most suitable grades are Aktisil MM and Aktisil PF 216. They impart very good extrusion properties along with high tensile moduli and excellent compression set.

INTRODUCTION

LAB TESTS

PILOT PLANT TRIALS

• EXPERIMENTAL

• RESULTS

• SUMMARY

SUMMARY

APPENDIX

Part 2:

Pilot plant trials

Part 2:
Pilot Plant Trials

The starting point was, with minor adjustments, the same formulation as was used for the laboratory trials. The following changes were applied:

- Calcium oxide was increased to 10 phr, in order to ensure blister-free extrusions.
- Because of availability, Lipoxol 3000 was replaced by Breax 3400.
- Use of Rhenogran CBS-80 instead of Santocure CBS, however same dosage.

Base Formulation

HOFFMANN MINERAL

EPDM – 65 Shore A

	phr	phr
Keltan 8340 A	100.00	100.00
Zinc Oxyde active	5.00	5.00
Stearic acid	1.00	1.00
Breax 3400	2.00	2.00
Kezadol GR	10.00	10.00
Carbon black N 550	135.00	60.00
Mineral Filler	-	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
Rhenodure S/G	1.00	1.00
Rhenocure TP/G	2.00	2.00
Vulkalent E/C	0.50	0.50
Rhenogran CBS-80 %	0.50	0.50
Total	**326.55**	**406.55**

Preparation of the Compound

Mixing parameters

Internal mixer Farrel 3D, tangential, volume 70 liters

Rotational speed: 35 rpm

Fill factor: 72 % by volume

Starting temperature (at wall): 50 °C

Mixing time: 6 min

Final mix temperature:	Carbon black	Carbon black + Mineral Filler
	135 °C	100 – 120 °C

Mixing cycle

0 - 1 min	Polymer
1 - 2 min	All others except accelerator and sulfur
2 - 4 min	Mixing
4 - 4.5 min	Sweep down
4.5 - 6.0 min	Mixing

Dump on open mill (30 °C), cool, and add accelerator and sufur

Extrusion

Vacuum Extruder, Diameter$_D$: 90 mm, Length: 16 D

Temperatures °C	Straight carbon black	Carbon black + Mineral Filler
Zone 1 (screw)	75	50
Zone 2	75	40
Zone 3	80	50
Zone 4	90	60
Zone 5 (head)	110	70

Rational speed: 15 to 18 rpm

Output rate: 7.5 m/min constant

The extrusion of the straight carbon black compound was not possible with the temperature profile of the carbon black + mineral filler compounds!

Curing

UHF channel:
2 x 6 kW, length 6 m, air temperature 200 °C,
typical discharge temperature 185 °C

Hot air tunnel:
length 3 x 9 m, air temperature 270 °C

Cooling basin:
length 2 x 9 m, water temperature 10 °C

Preparation of Test Specimens

INTRODUCTION

LAB TESTS

PILOT PLANT TRIALS

• EXPERIMENTAL

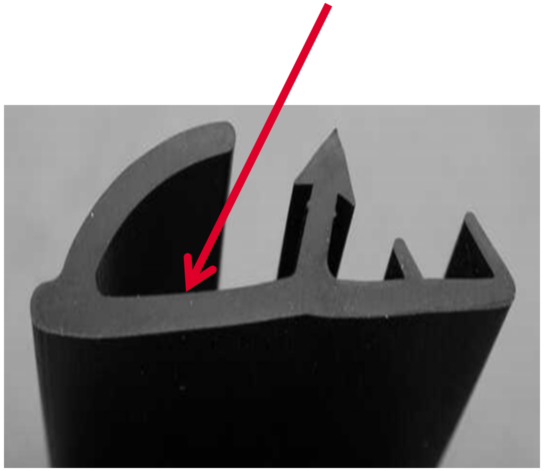
• RESULTS

• SUMMARY

SUMMARY

APPENDIX

- The optical and mechanical properties were evaluated on samples taken from the bottom of the extruded profiles.



- The sheets for the determination of volume resistance were cured from the compound mixed in the internal mixer.

INTRODUCTION

LAB TESTS

PILOT PLANT TRIALS

• EXPERIMENTAL

• RESULTS

• SUMMARY

SUMMARY

APPENDIX

Measurement of Color

ISO 7724

- **Parameter**

  Spectral photometer (Luci 100, Dr. Lange)

  Light D 65

  Geometry d/8°, without gloss trap

  Observation angle 10°

- **Definition**

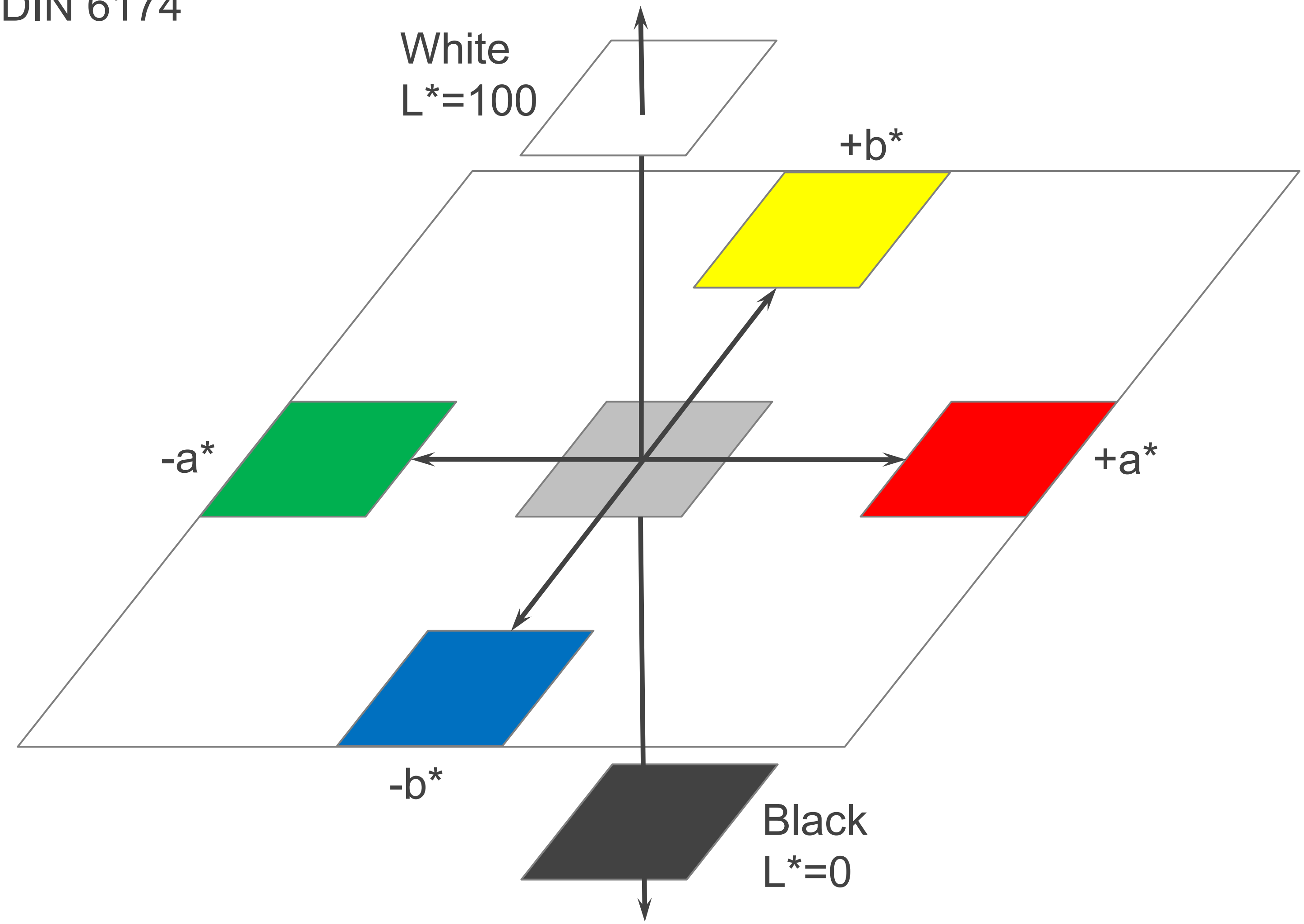
  L*: brightness (0: ideal black; 100: ideal white)

  a*: red / green (positive values: red tints; negative values: green tints)

  b*: yellow / blue (positive values: yellow tints; negative values: blue tints)

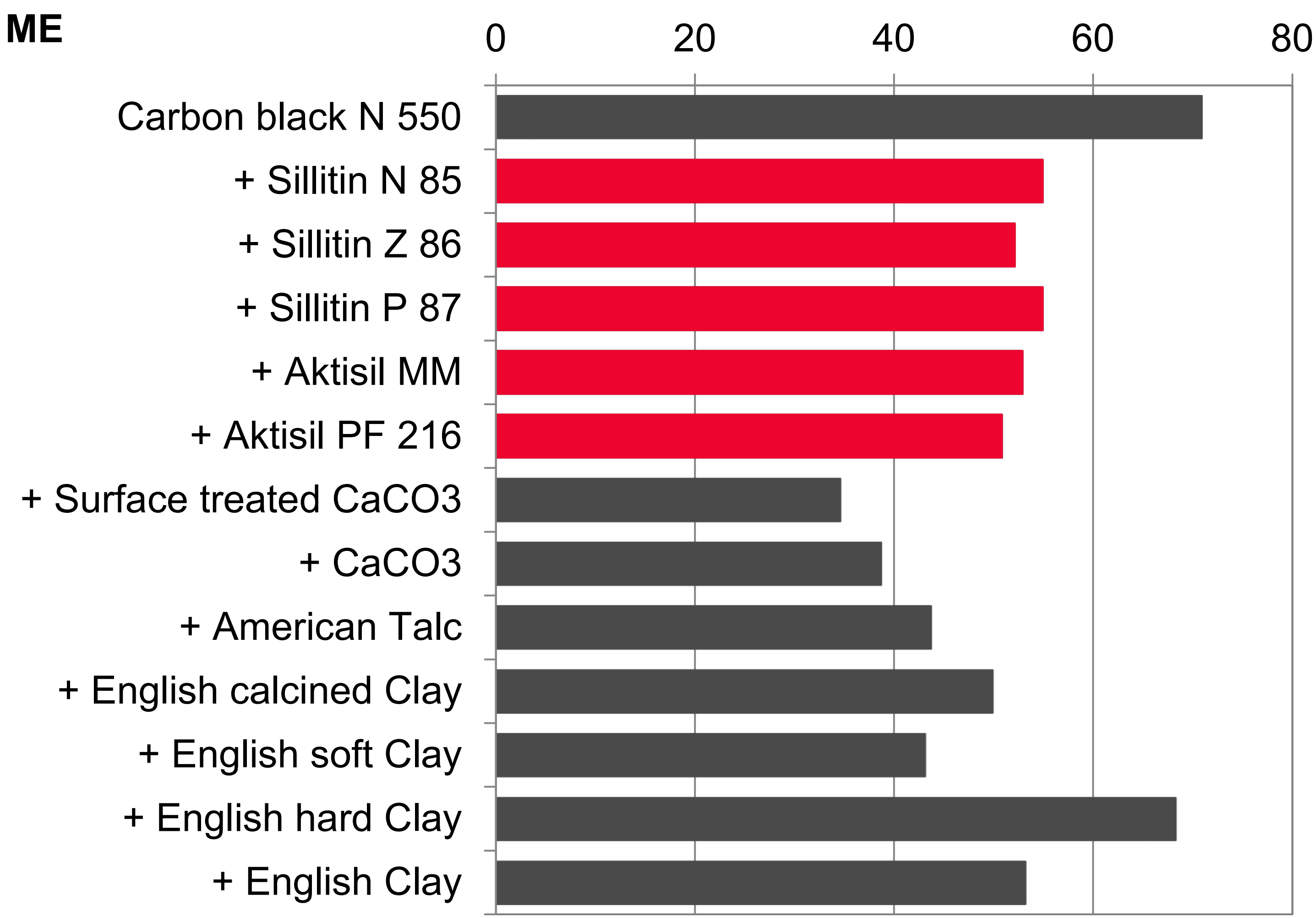
CIE-LAB-System

DIN 6174



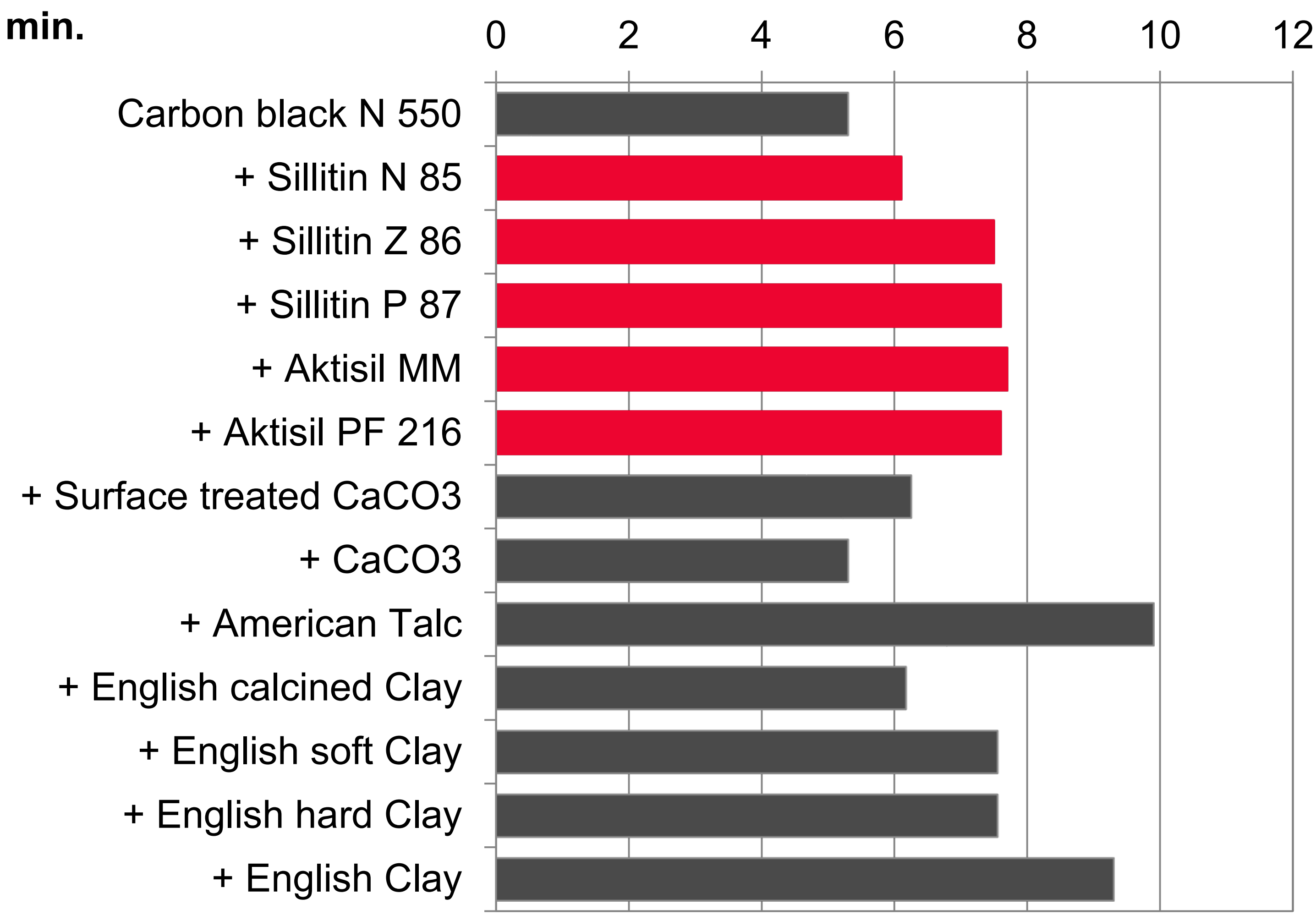
Mooney Viscosity

DIN 53 523 Part 3, ML 1+4 120 °C



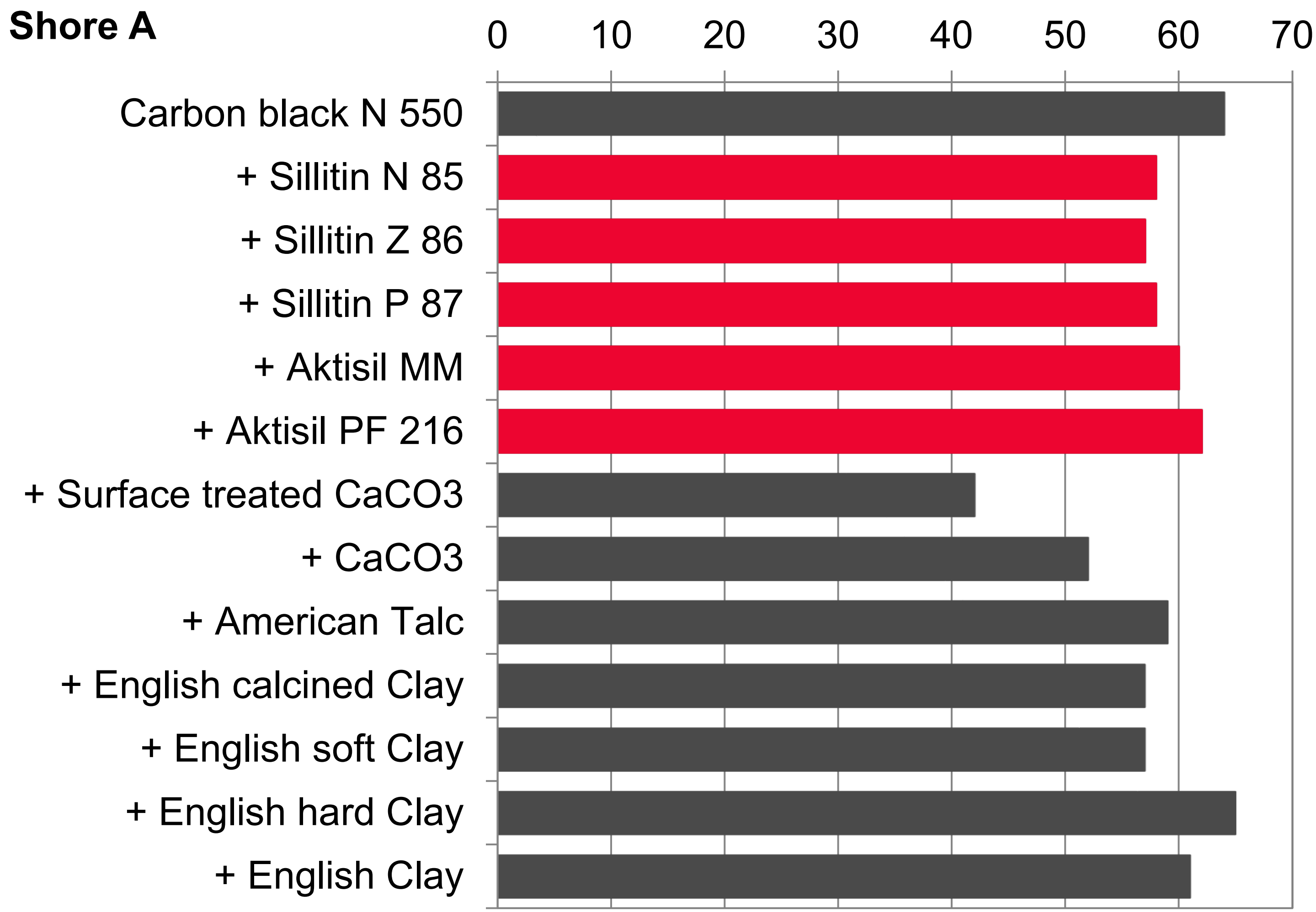
Conversion Time t_{90}

DIN 53 529-A3, 170 °C, 0.2° deflection – Göttfert Elastograph



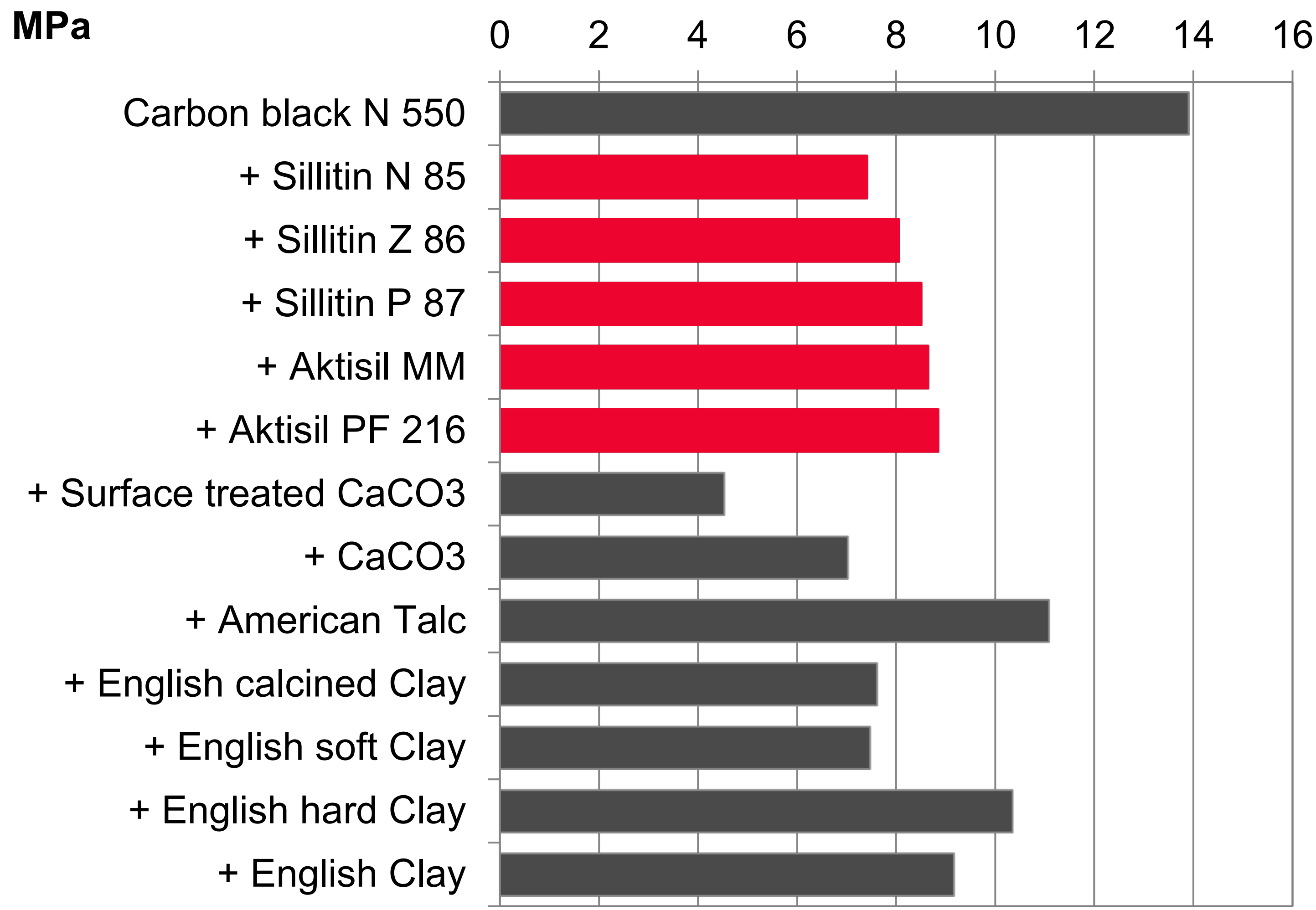
Hardness

DIN 53 505-A, piled-up S2 dumbbells



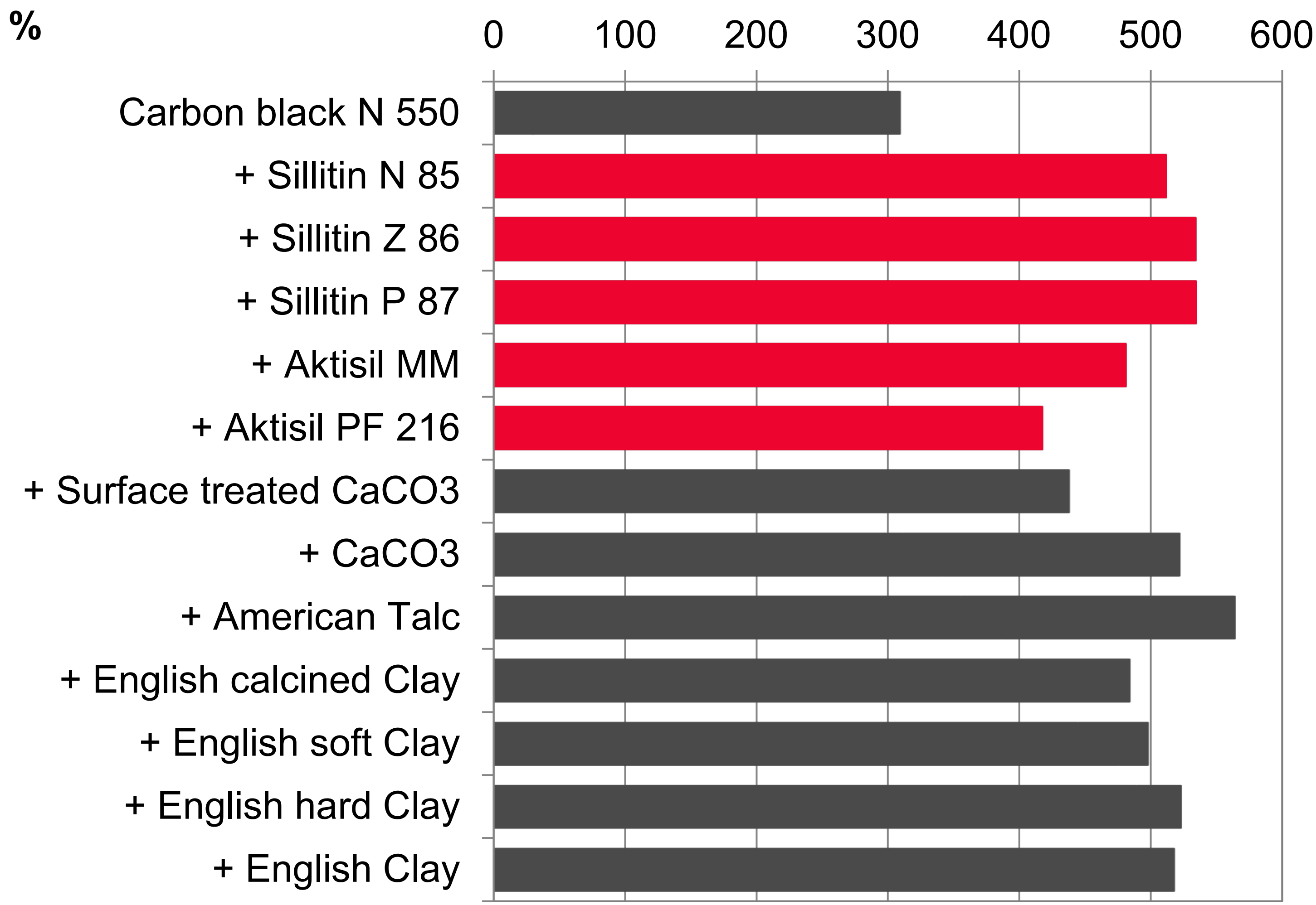
Tensile Strength

DIN 53 504, S2



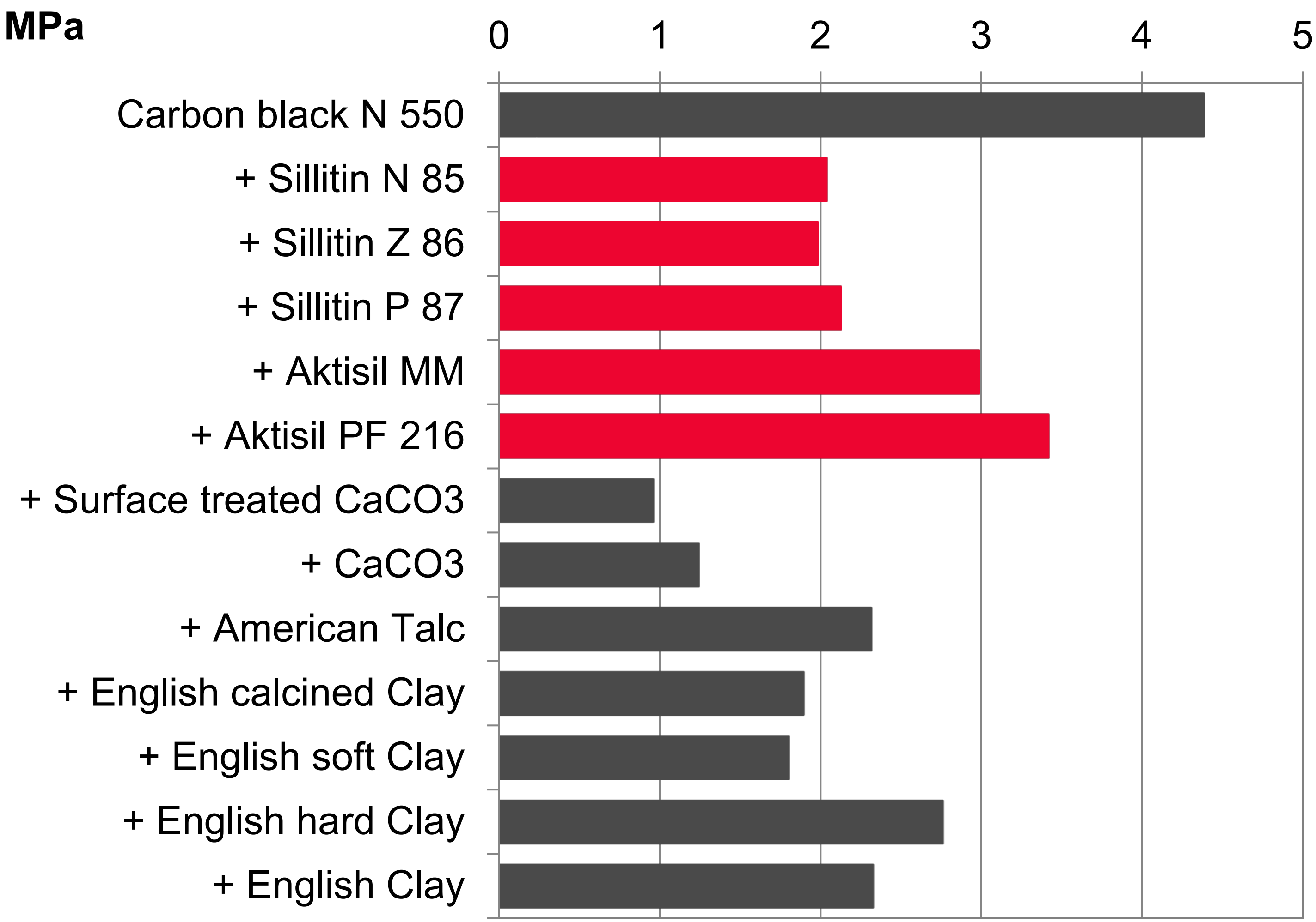
Elongation at Break

DIN 53 504, S2



Modulus 100 %

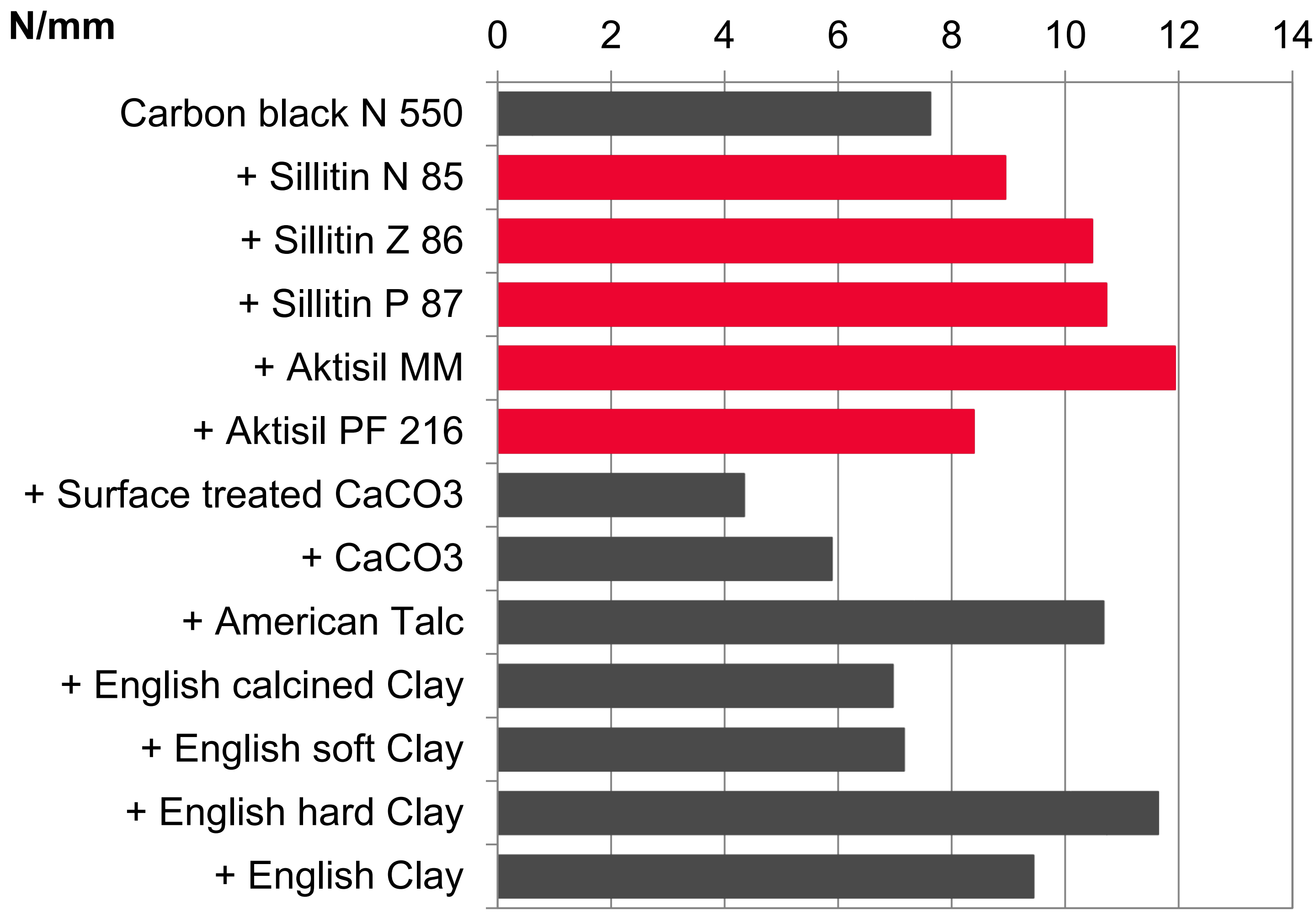
DIN 53 504, S2



Tear Resistance

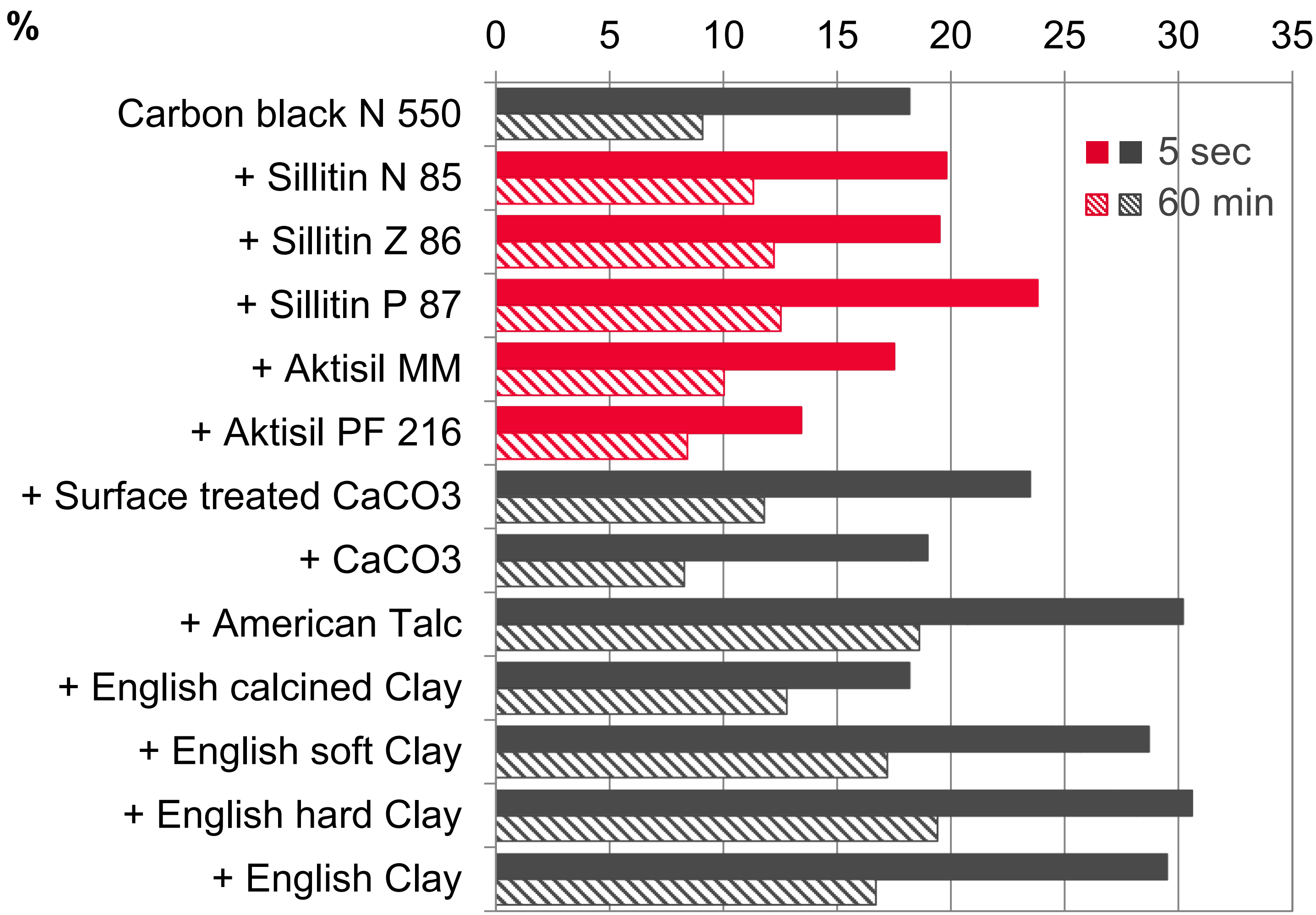
HOFFMANN MINERAL

DIN 53 507-A, Fmax 500 mm/min



Compression Set

VW PV 3307, 50 % deformation, 5 s/60 min. Relaxation, 72 h/23 °C



INTRODUCTION

LAB TESTS

PILOT PLANT TRIALS

• EXPERIMENTAL

• RESULTS

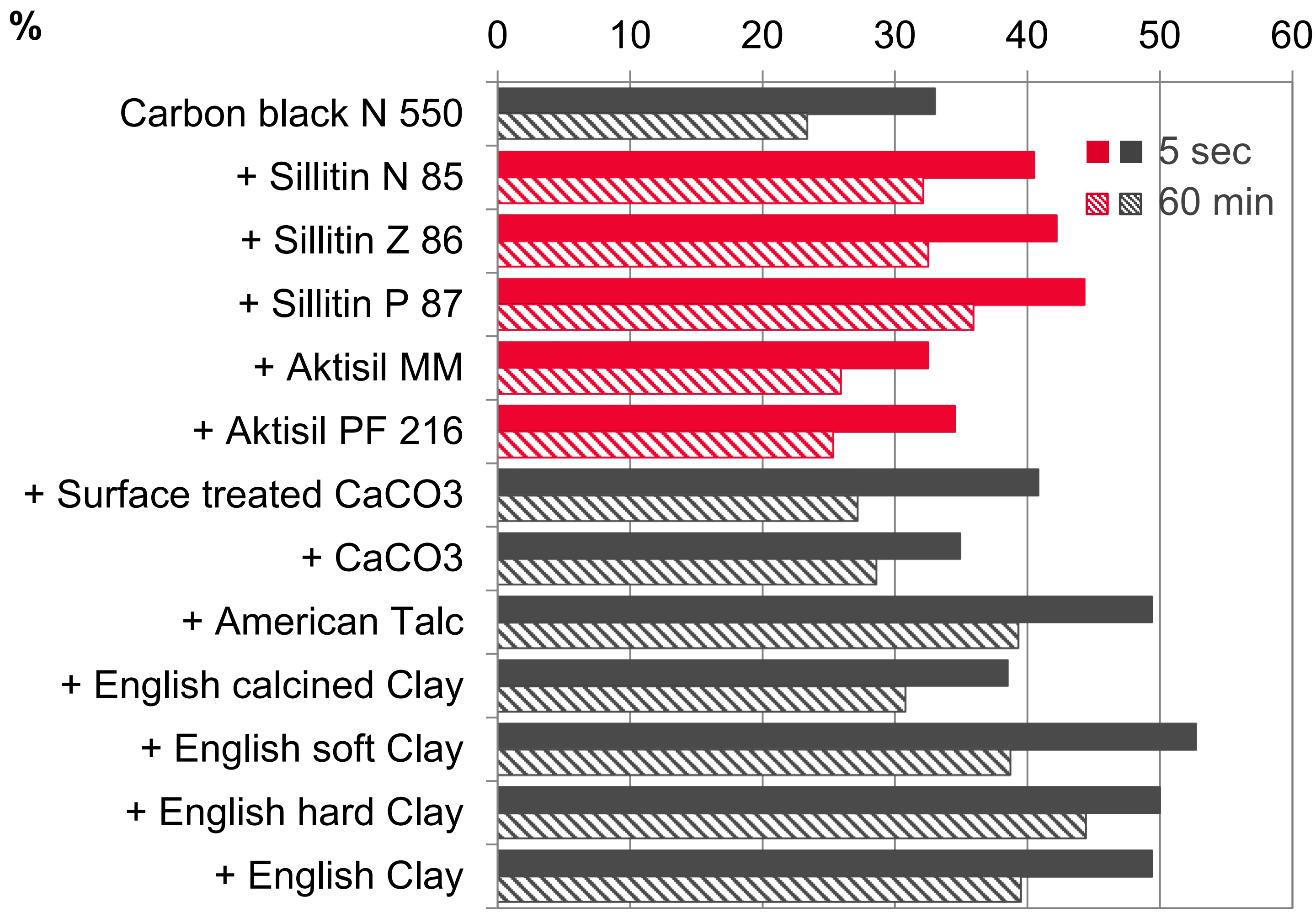
• SUMMARY

SUMMARY

APPENDIX

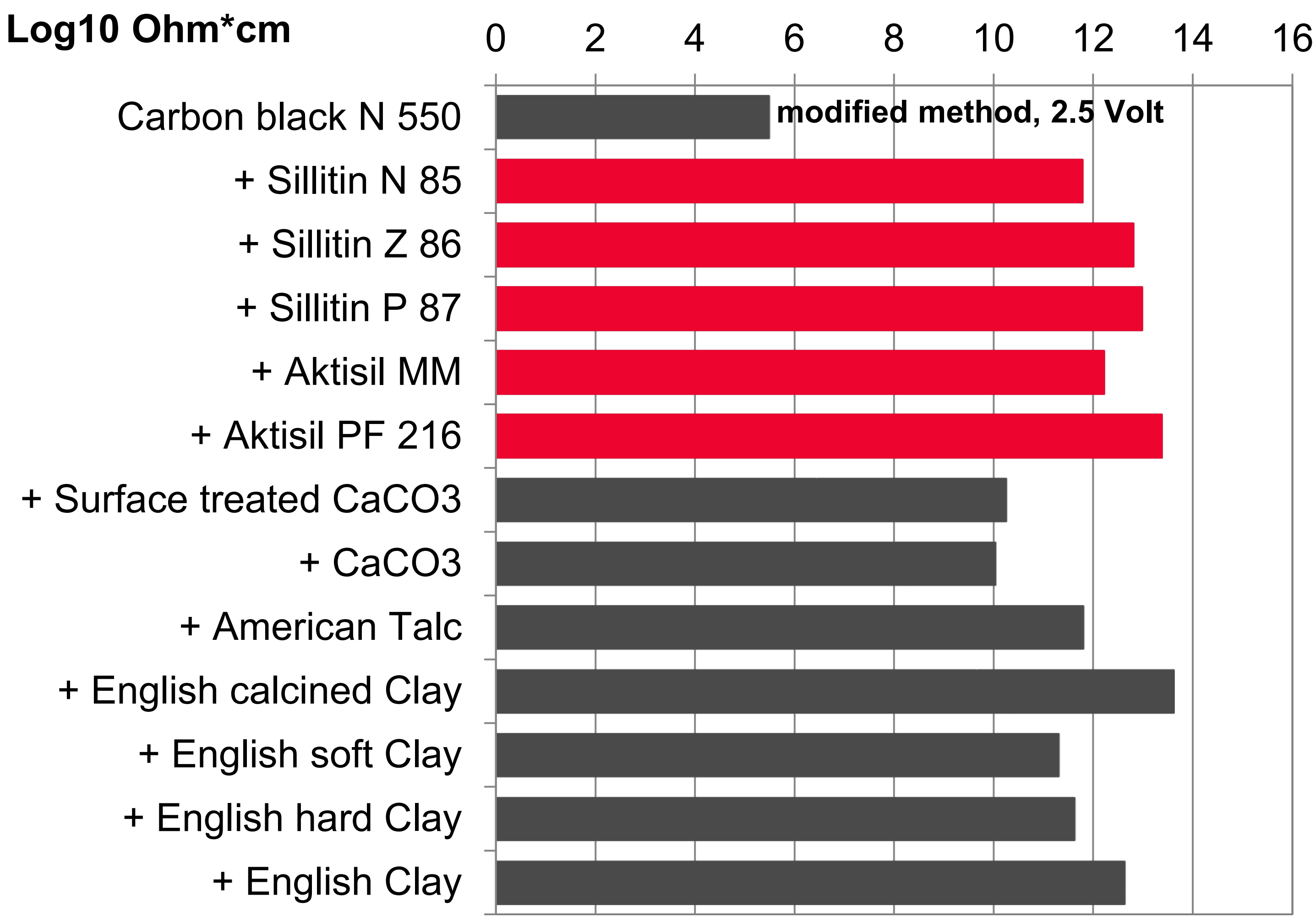
Compression Set

VW PV 3307, 50 % deformation, 5 s/60 min. Relaxation, 22 h/70 °C

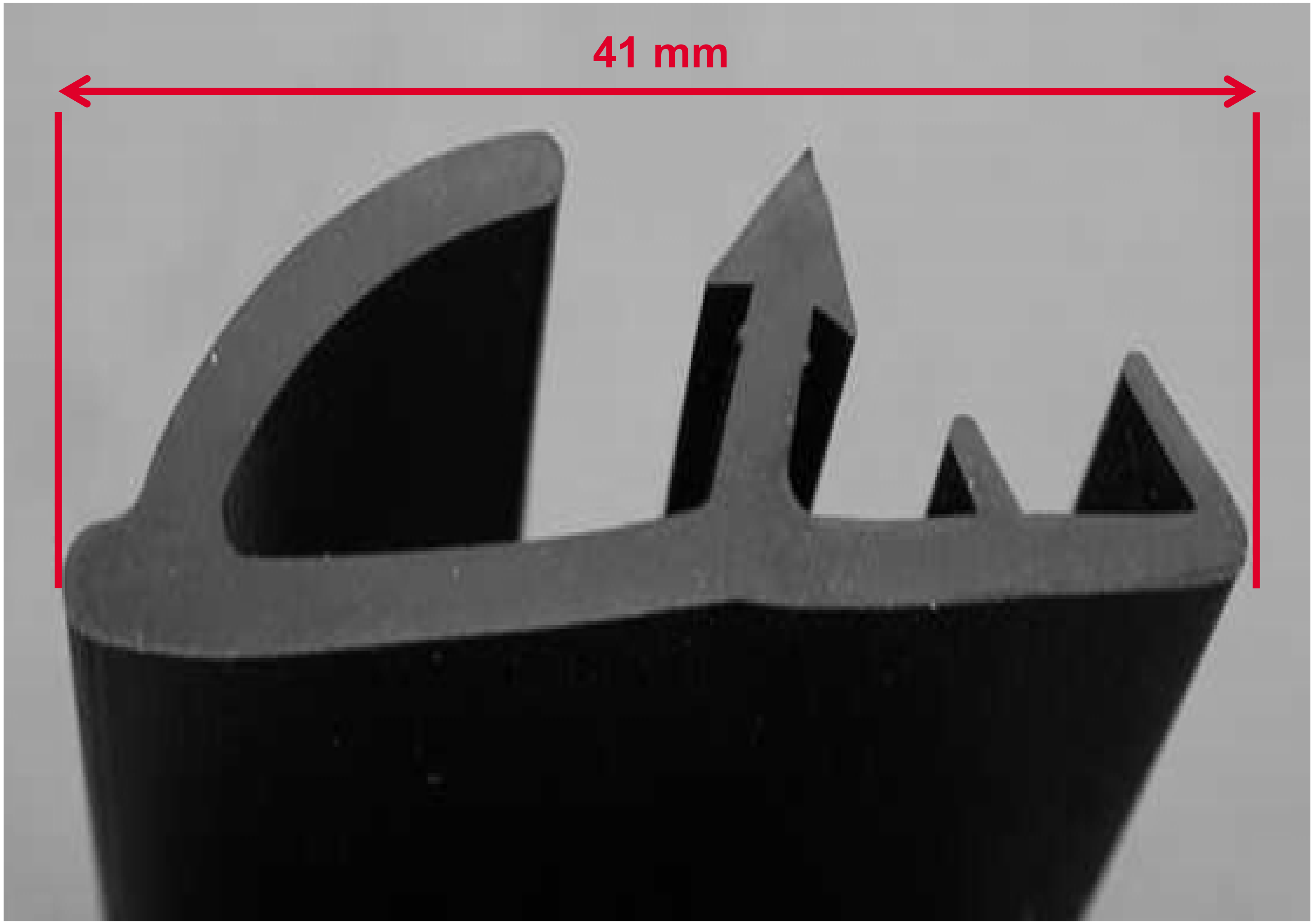


Volume Resistivity

DIN IEC 93, 100 Volt, 1 min., press-cured slab



Profile Geometry

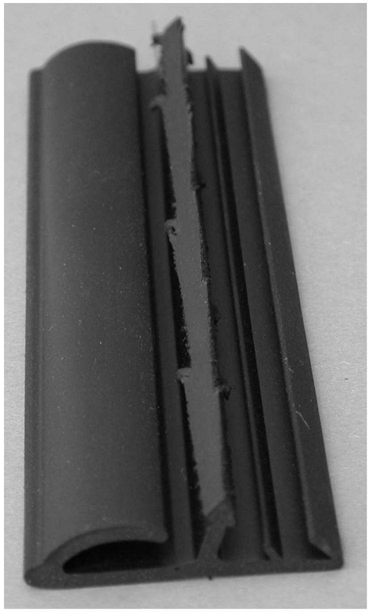


Shape of Profiles (1)

Magnifications of all profile images are found in the appendix. Click on the profile.

Carbon black N 550

+ Sillitin N 85



+ Sillitin Z 86

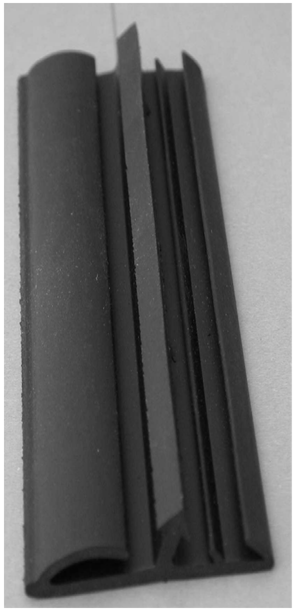
+ Sillitin P 87

Shape of Profiles (2)

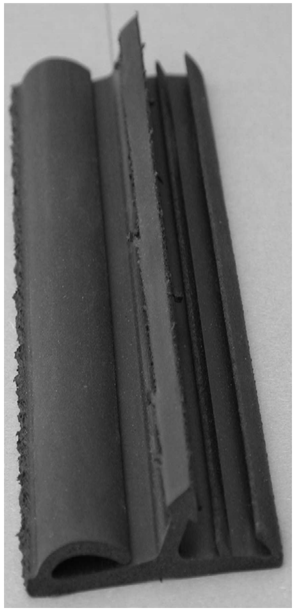
Magnifications of all profile images are found in the appendix. Click on the profile.

+ Aktisil MM

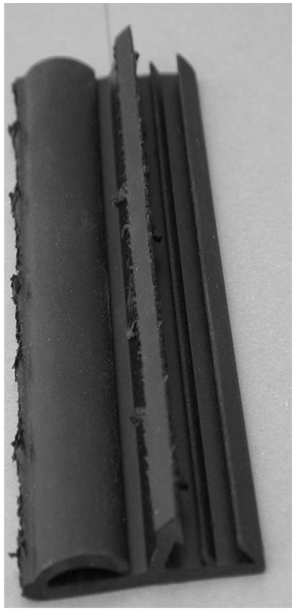
+ Aktisil PF 216



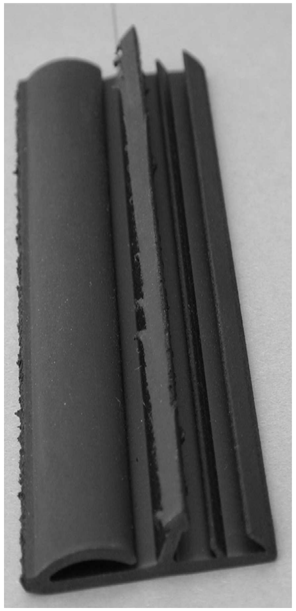
+ Surface treated $CaCO_3$



+ $CaCO_3$



+ Talc

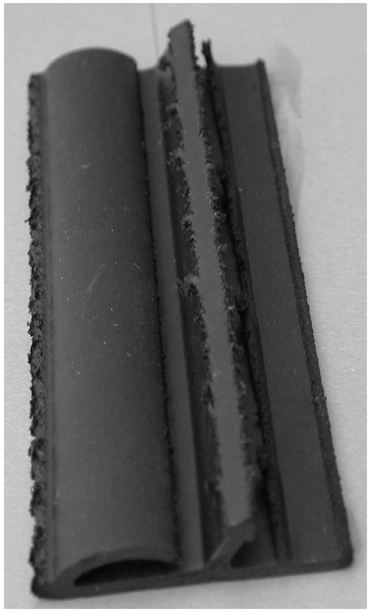


Shape of Profiles (3)

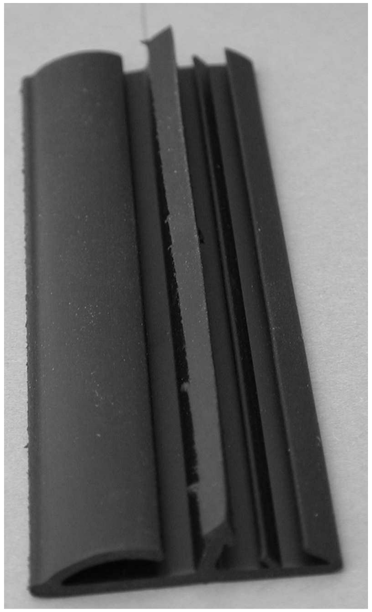
Magnifications of all profile images are found in the appendix. Click on the profile.

+ Calcined Clay

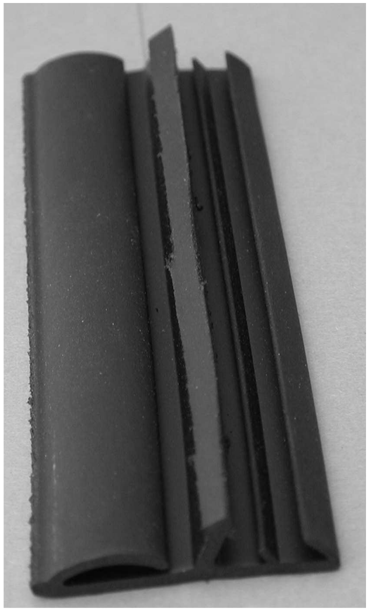
+ Soft Clay



+ Hard Clay



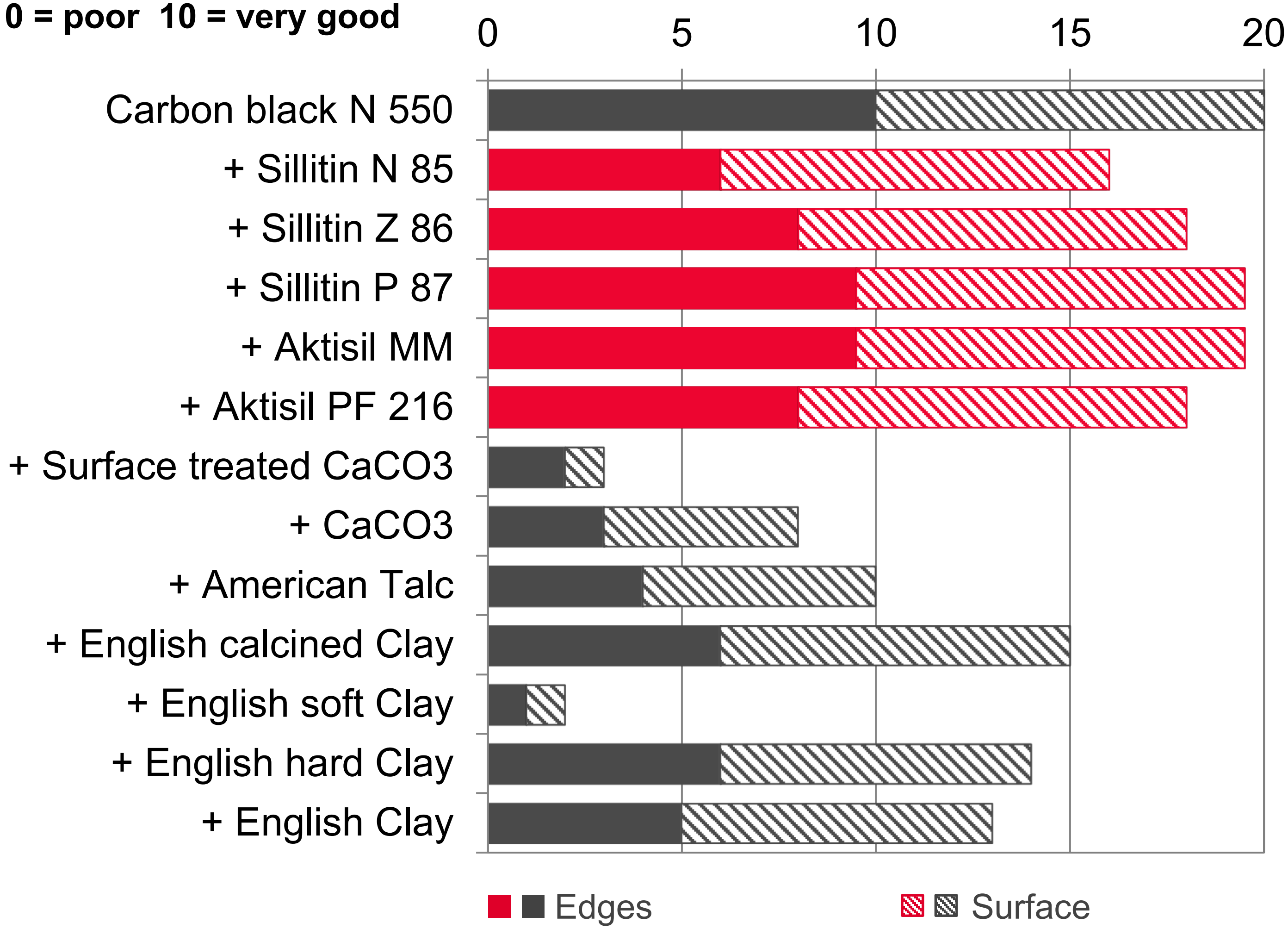
+ Clay



Extrusion
Profile Quality

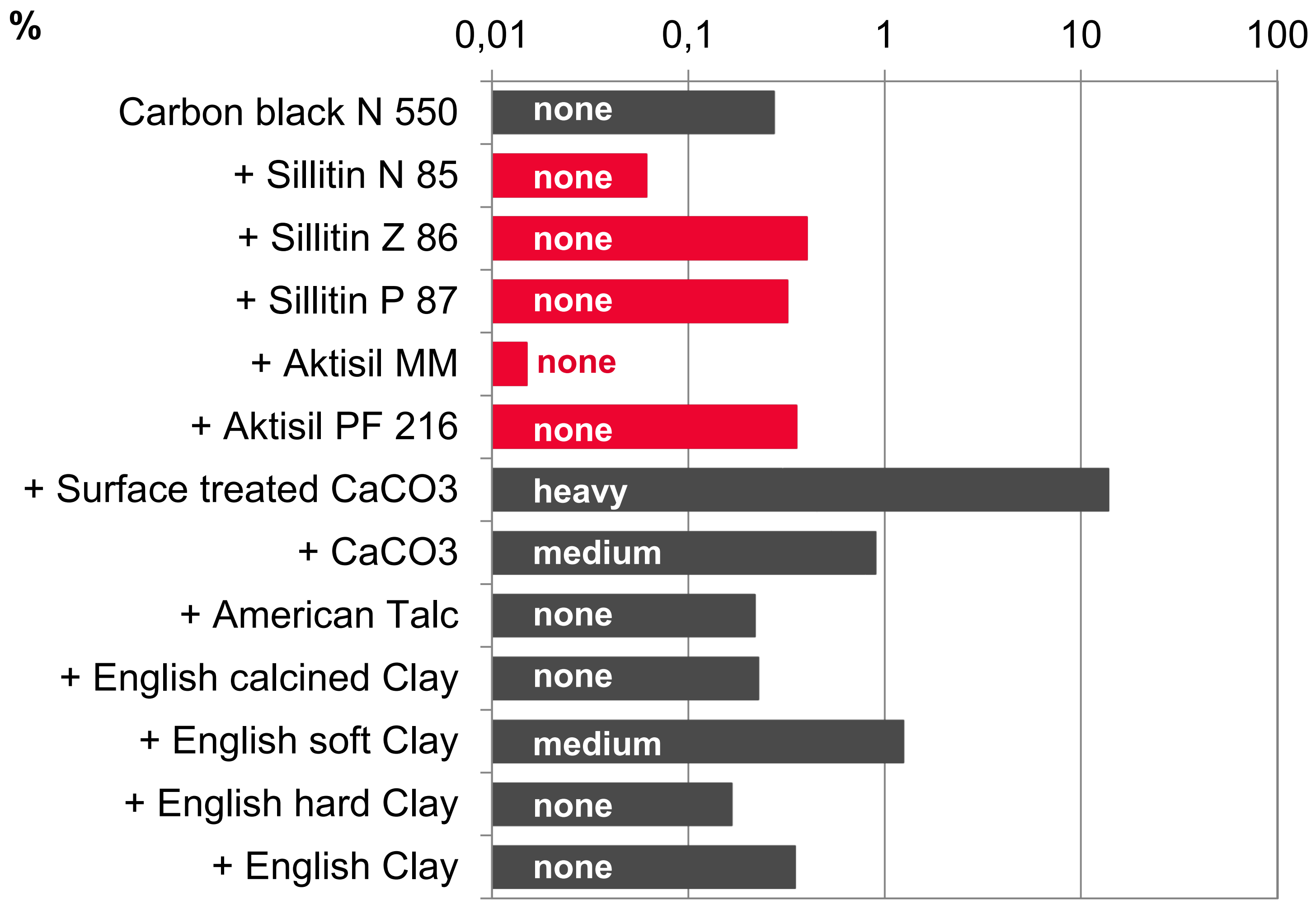
HOFFMANN MINERAL

0 = poor 10 = very good



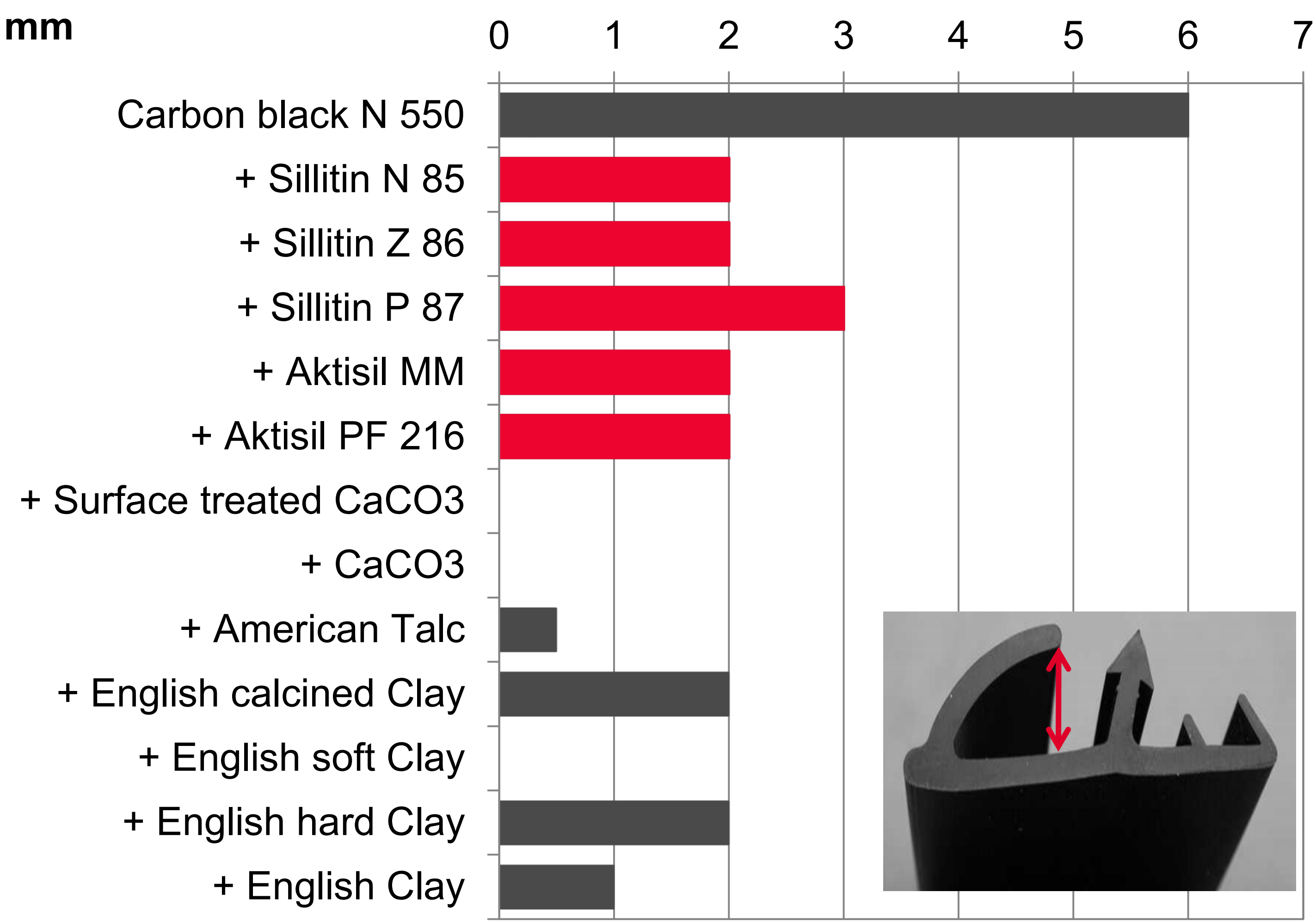
Porosity

Difference in density slab/profile, bar captions: visual assessment



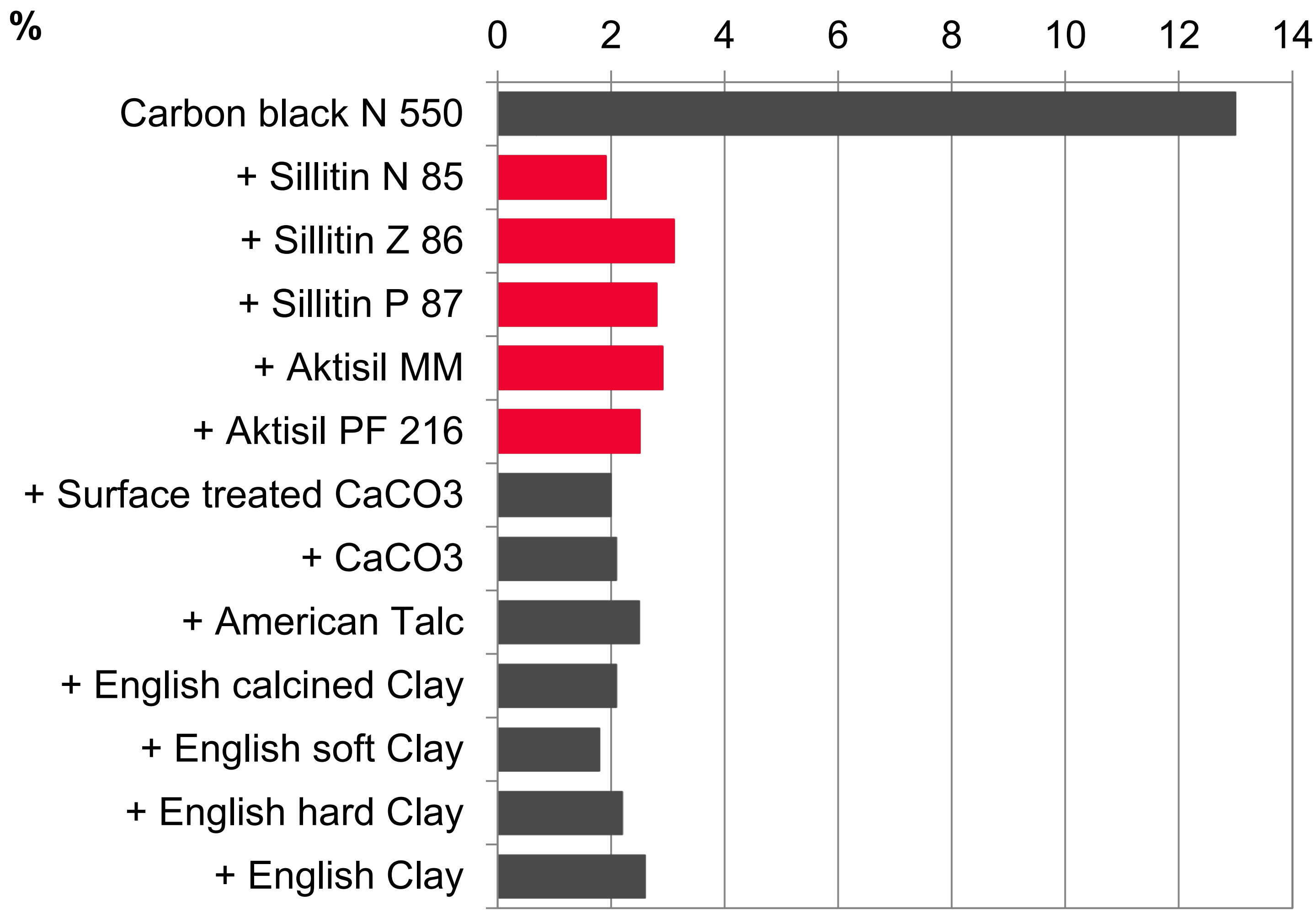
Dimension Stability

Determined as distance of profile leg



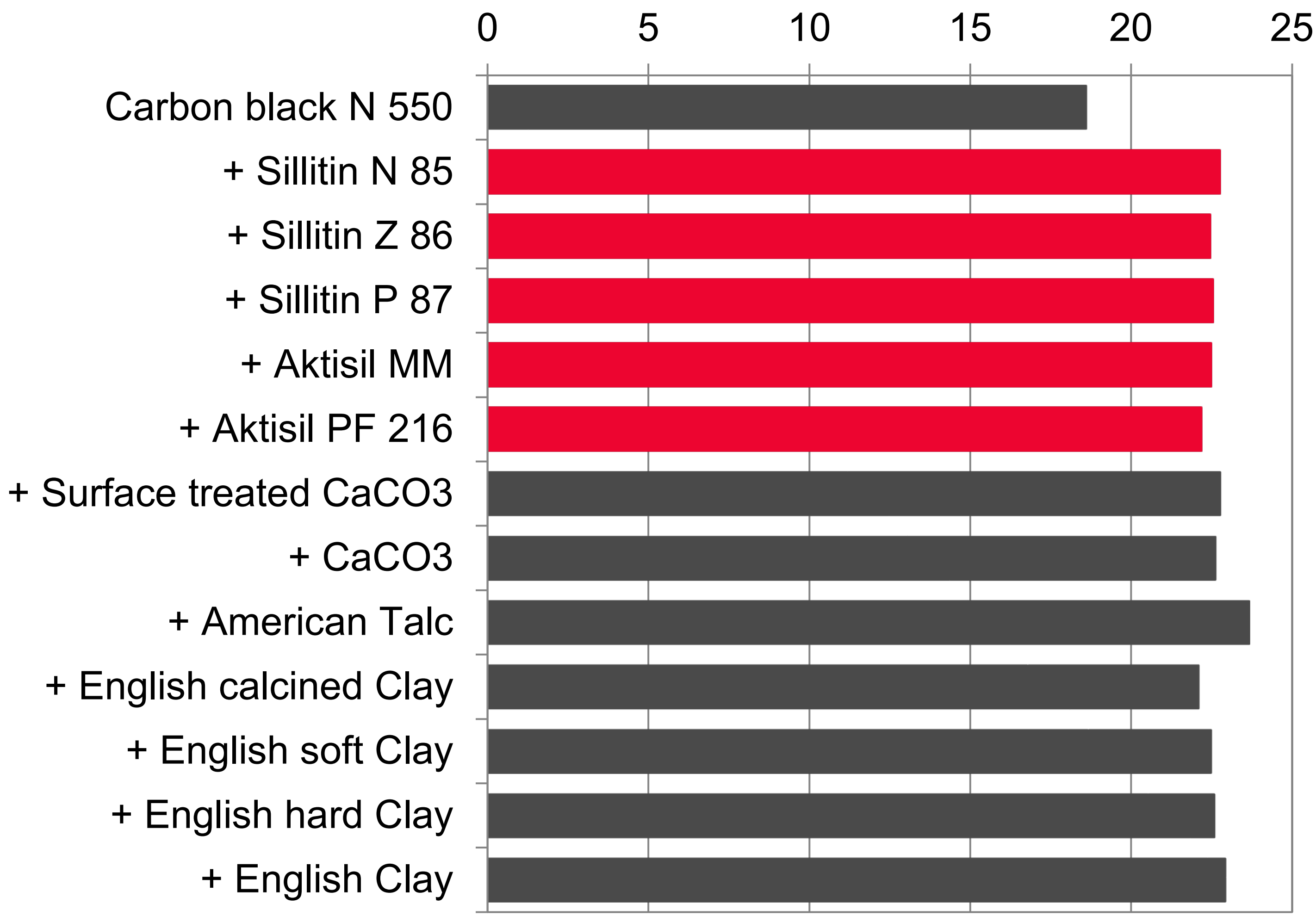
Gloss

DIN 67 530, 60°



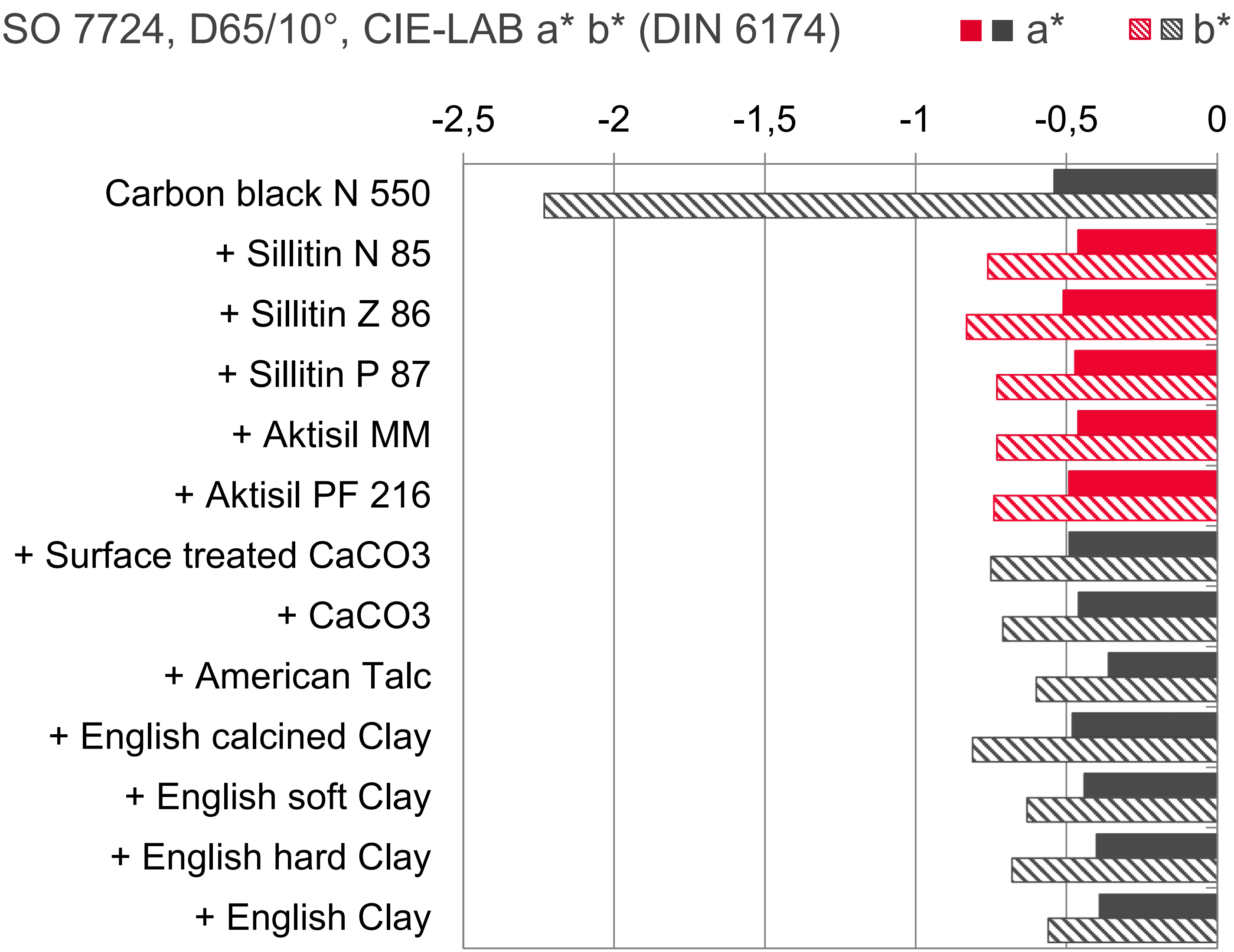
Color Values after 49 days

ISO 7724, D65/10°, CIE-LAB L* (DIN 6174)



Color Values after 49 days

ISO 7724, D65/10°, CIE-LAB a* b* (DIN 6174)



Pilot Plant Trials
Summary (1)

HOFFMANN MINERAL

- The calcium carbonates exhibit their main weak points in the mechanical properties as well as during extrusion and in electrical resistivity, however they impart good compression set resistance.
- Talc gives good mechanical properties, but unsatisfactory compression set and moderate extrusion properties.
- Calcined clay is characterized by moderate mechanical properties, medium extrusion properties and good compression set along with high electrical resistivity.
- Soft clay comes off with very poor extrusion properties and moderate mechanical properties und also poor compression set resistance.

Pilot Plant Trials
Summary (2)

HOFFMANN MINERAL

- Hard clay imparts good mechanical properties und moderate extrusion properties, but there are definite weak points relative to compression set.
- Medium activity clay comes close to the hard clay, but only reaches moderate mechanical properties along with higher electrical resistivity.
- The Neuburg Siliceous Earth grades distinguish themselves above all by their excellent extrusion properties, high electrical resistivity and good compression set along with high tear resistance.
- Particularly recommended are Aktisil MM and Aktisil PF 216. These grades impart very good extrusion properties in combination with high tensile moduli and excellent compression set results.

Conclusion

The basic statement from the laboratory tests largely also apply to the pilot plant trials which were close to production conditions.

- With mineral fillers electrically insulating car body seals can be produced, which with the exception of lower tensile strength and partly less optimum extrusion properties do not give evidence of poorer performance levels. Some of the compounds do already meet the requirements of pertinent specifications.
- A further optimization can be visualized via the loading ratio of carbon black to mineral filler, as in view of the partly very high resistivity there is still room for a higher carbon black loading. In this context, also the volume resistivity after water immersion should be taken into account.

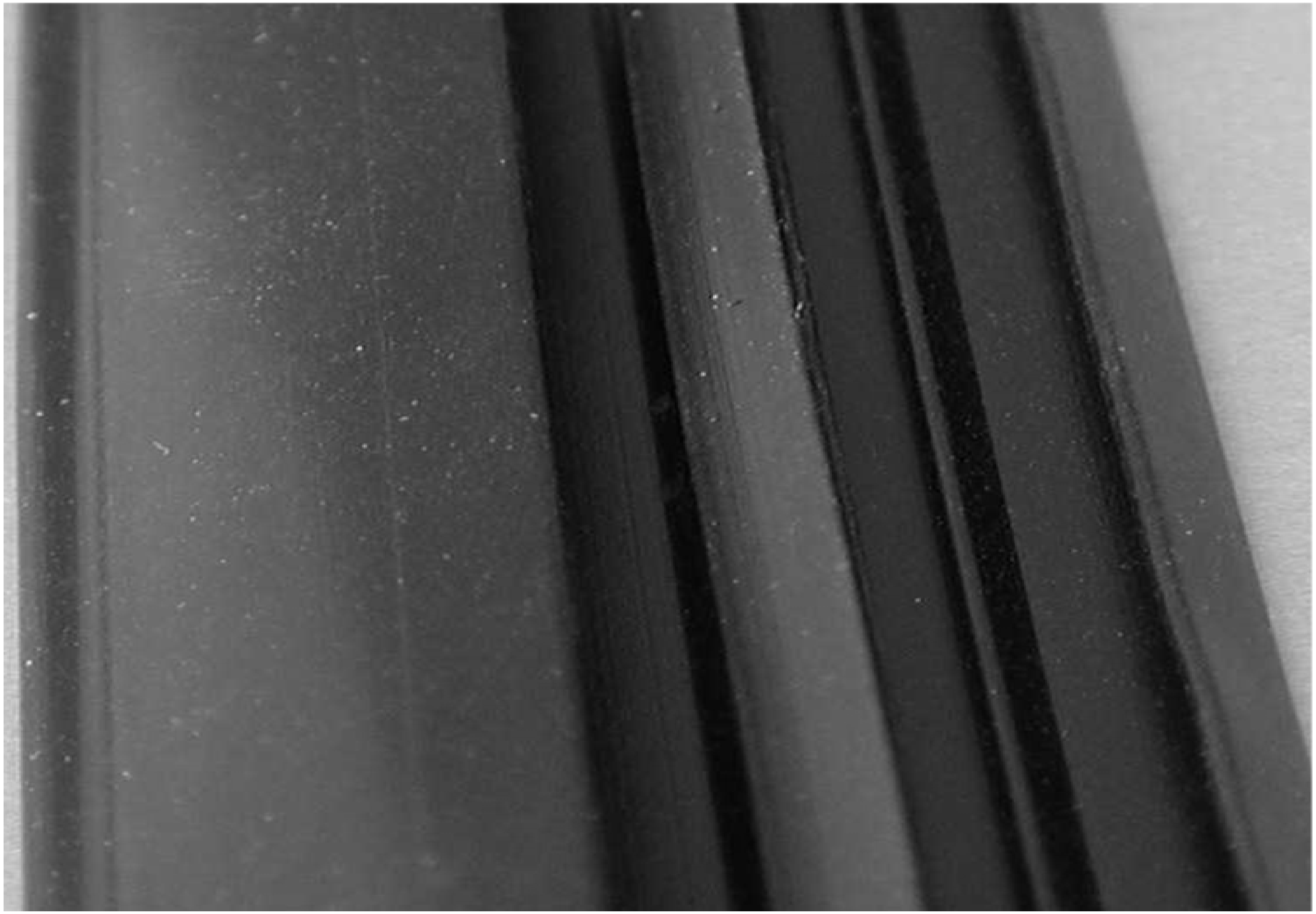
We supply material for good ideas!

HOFFMANN MINERAL GmbH
Muenchener Straße 75
DE-86633 Neuburg (Donau)

Phone: +49 8431 53-0
Internet: www.hoffmann-mineral.de
E-mail: info@hoffmann-mineral.com

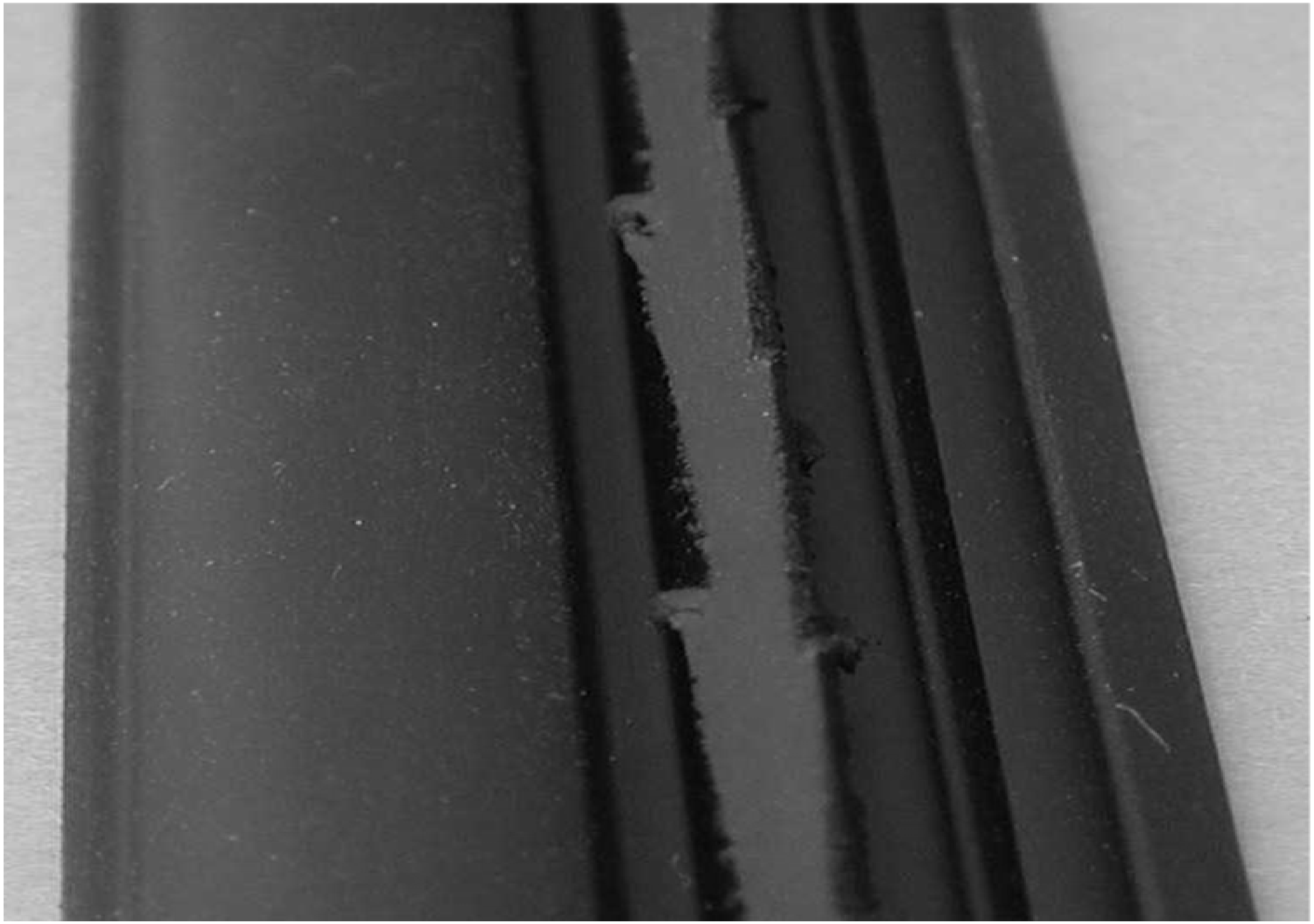
Profile Detail

Carbon Black N 550



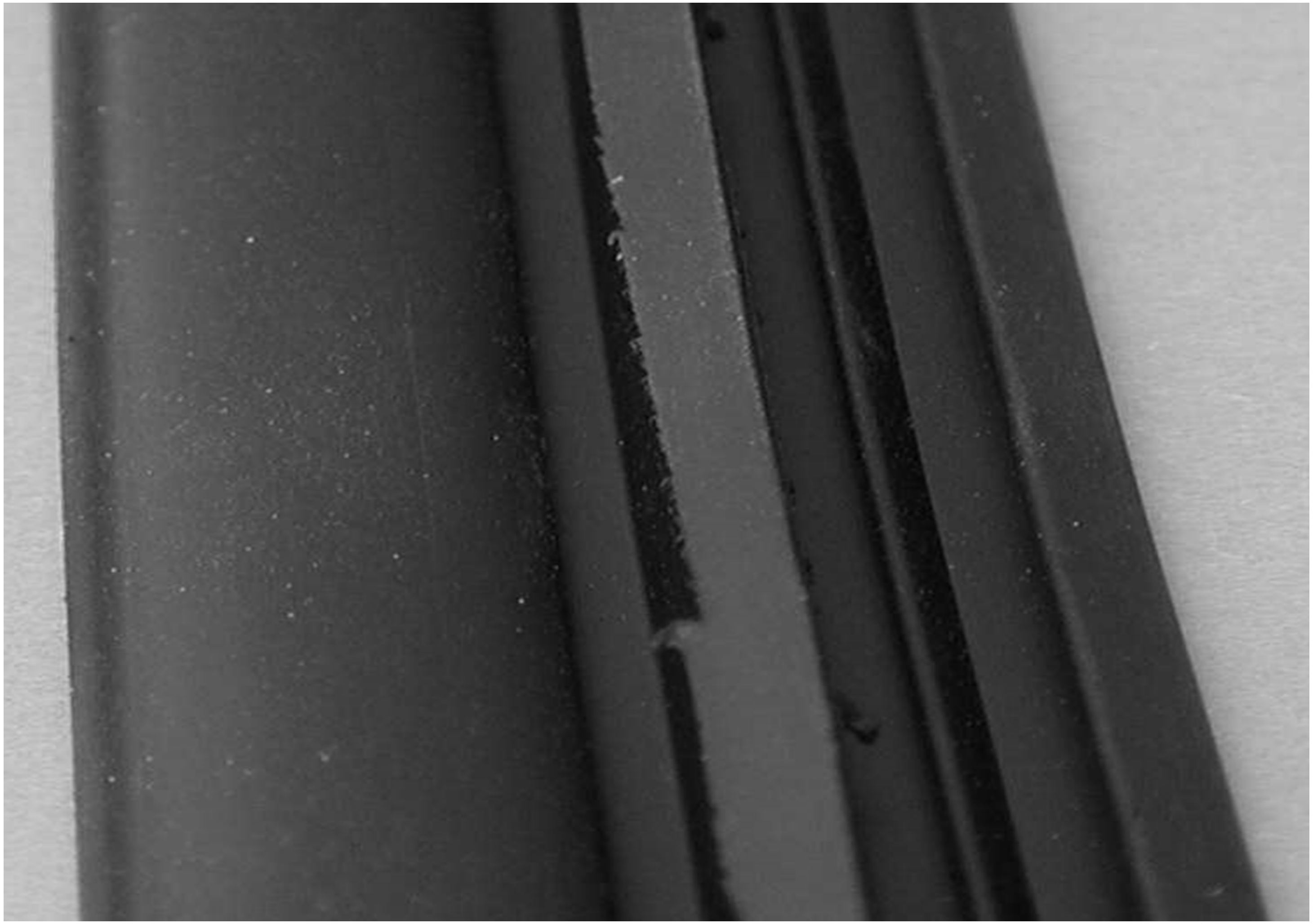
Profile Detail

+ Sillitin N 85



Profile Detail

+ Sillitin Z 86

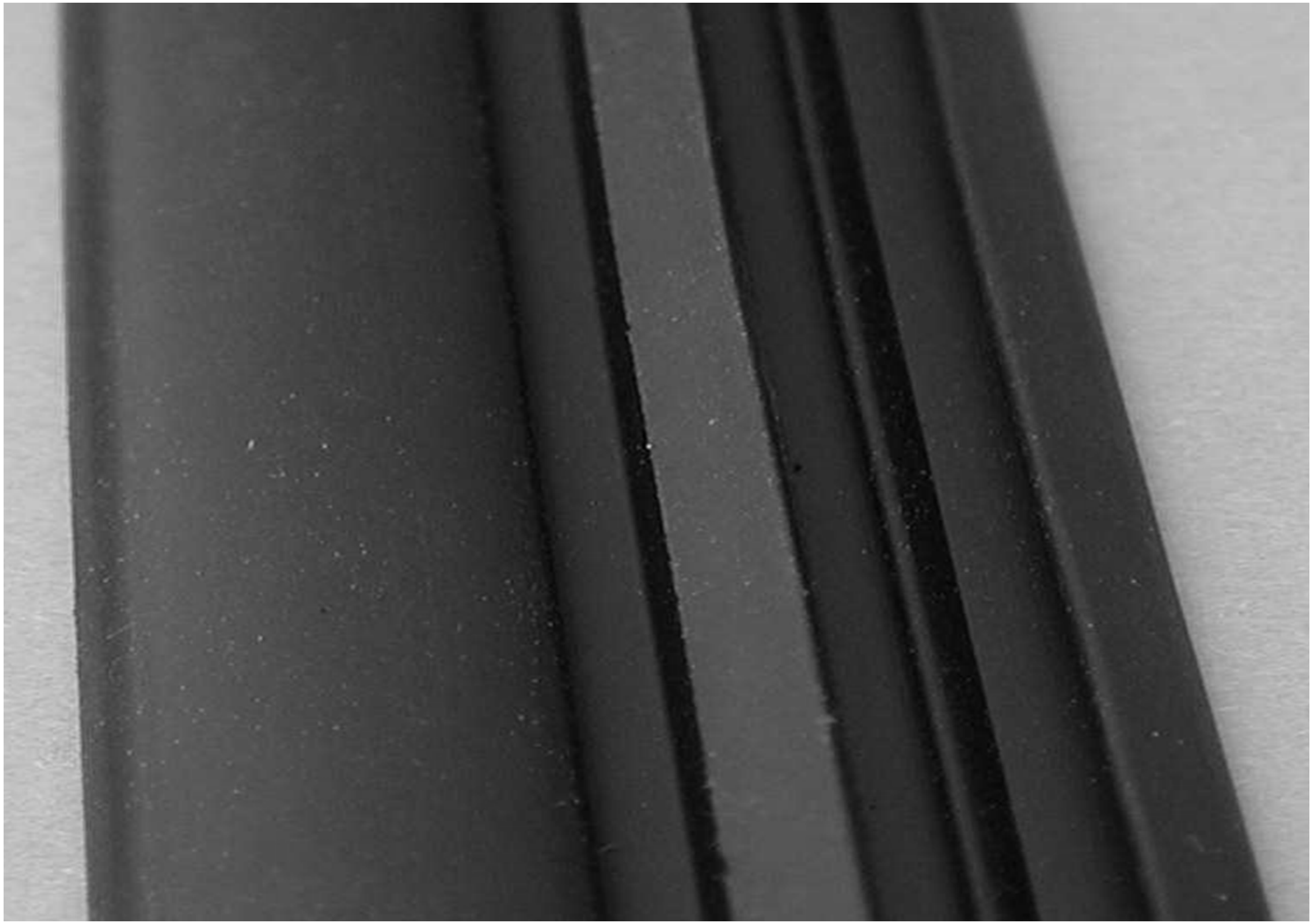


Profile Detail

+ Sillitin P 87

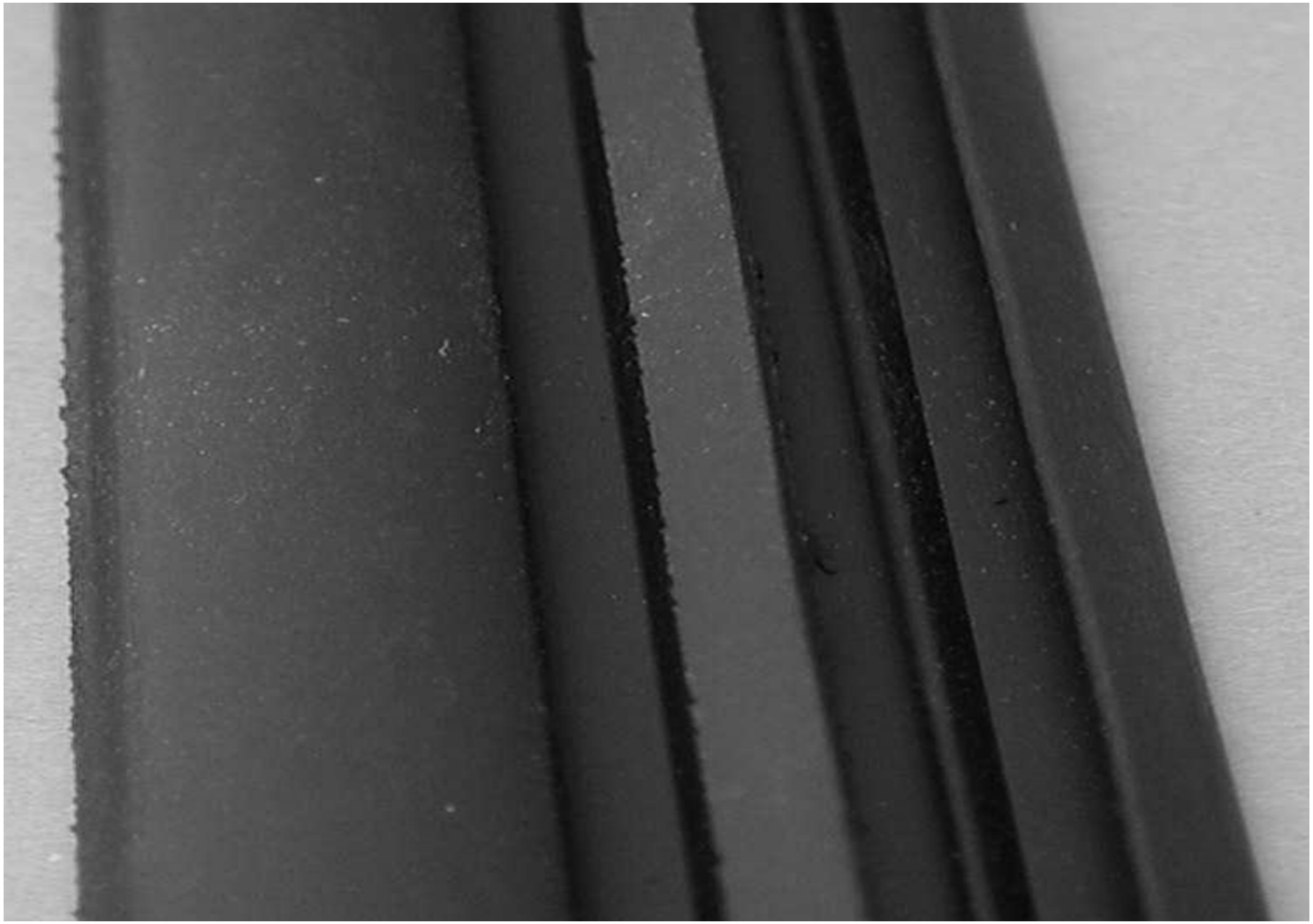
Profile Detail

+ Aktisil MM



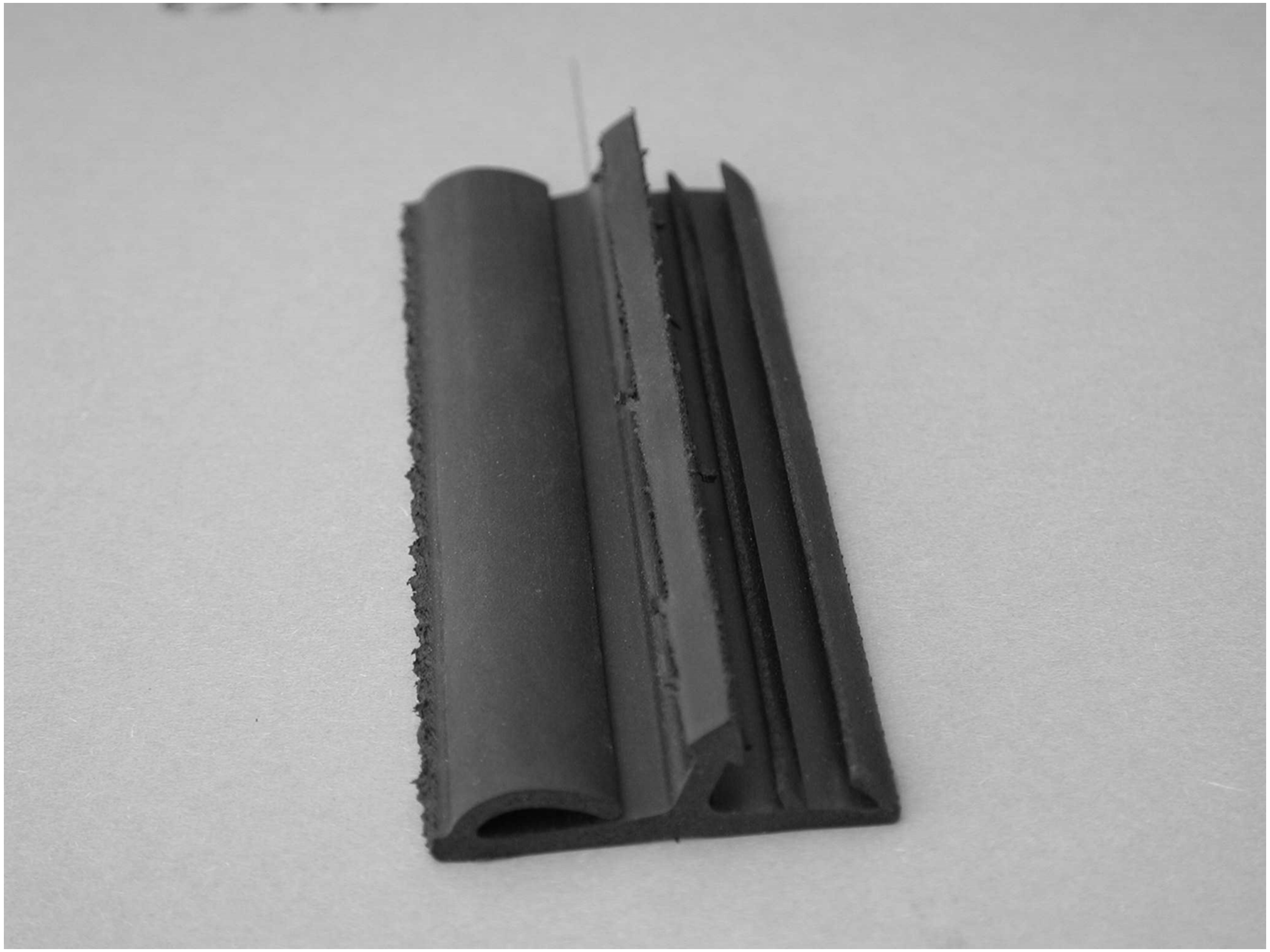
Profile Detail

+ Aktisil PF 216



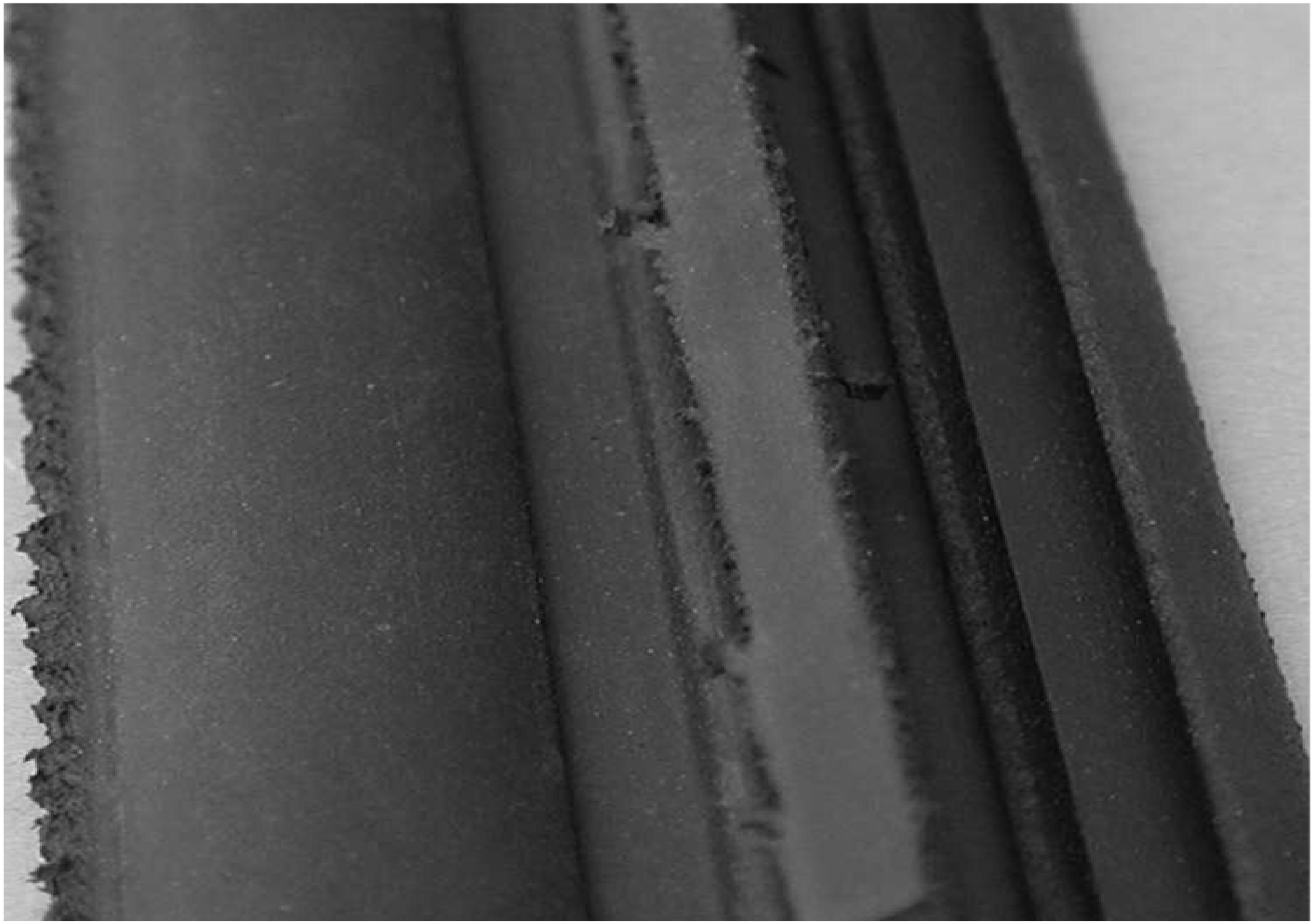
Profile Detail

\+ Surface Treated Calcium Carbonate



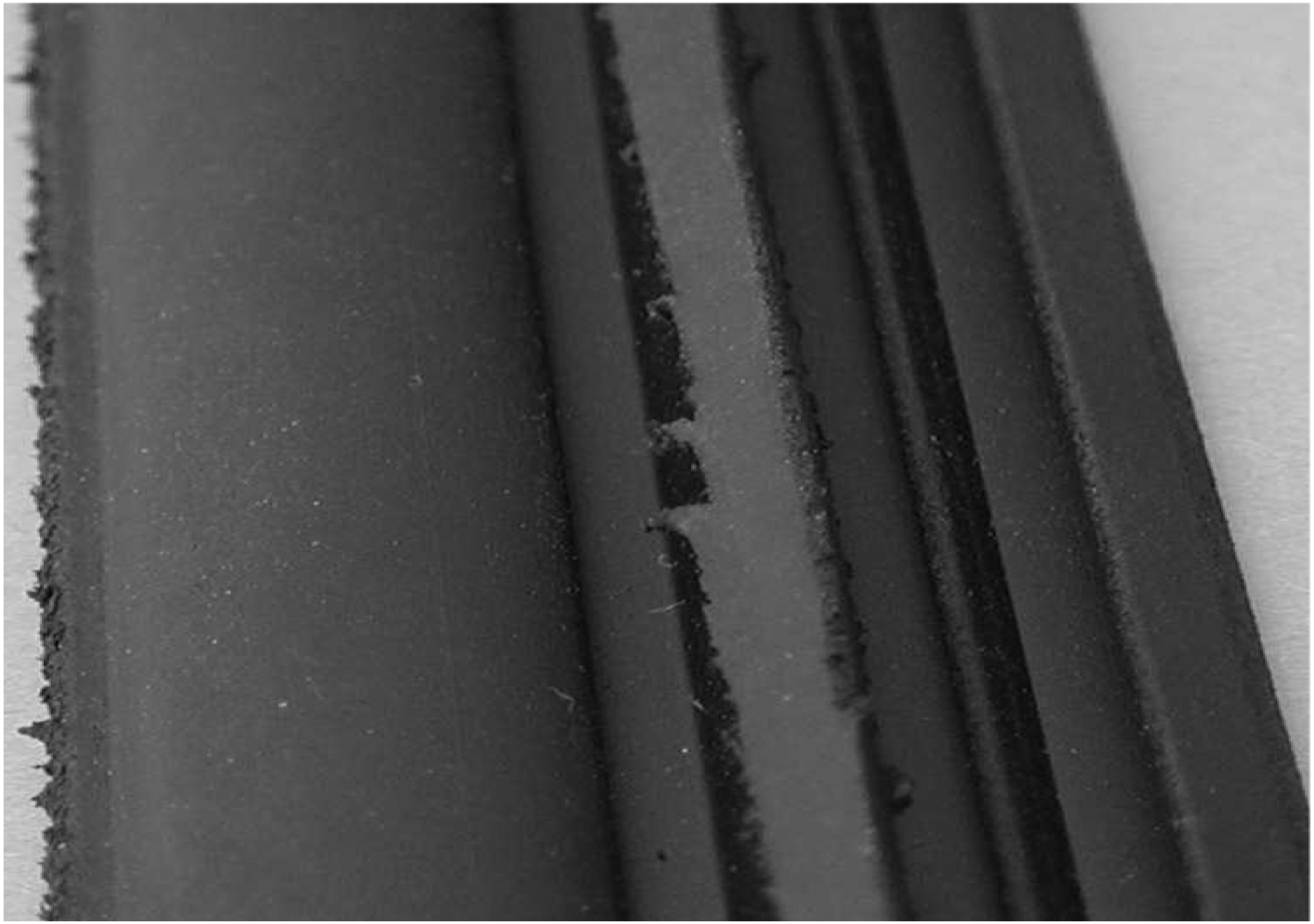
Profile Detail

+ Calcium Carbonate



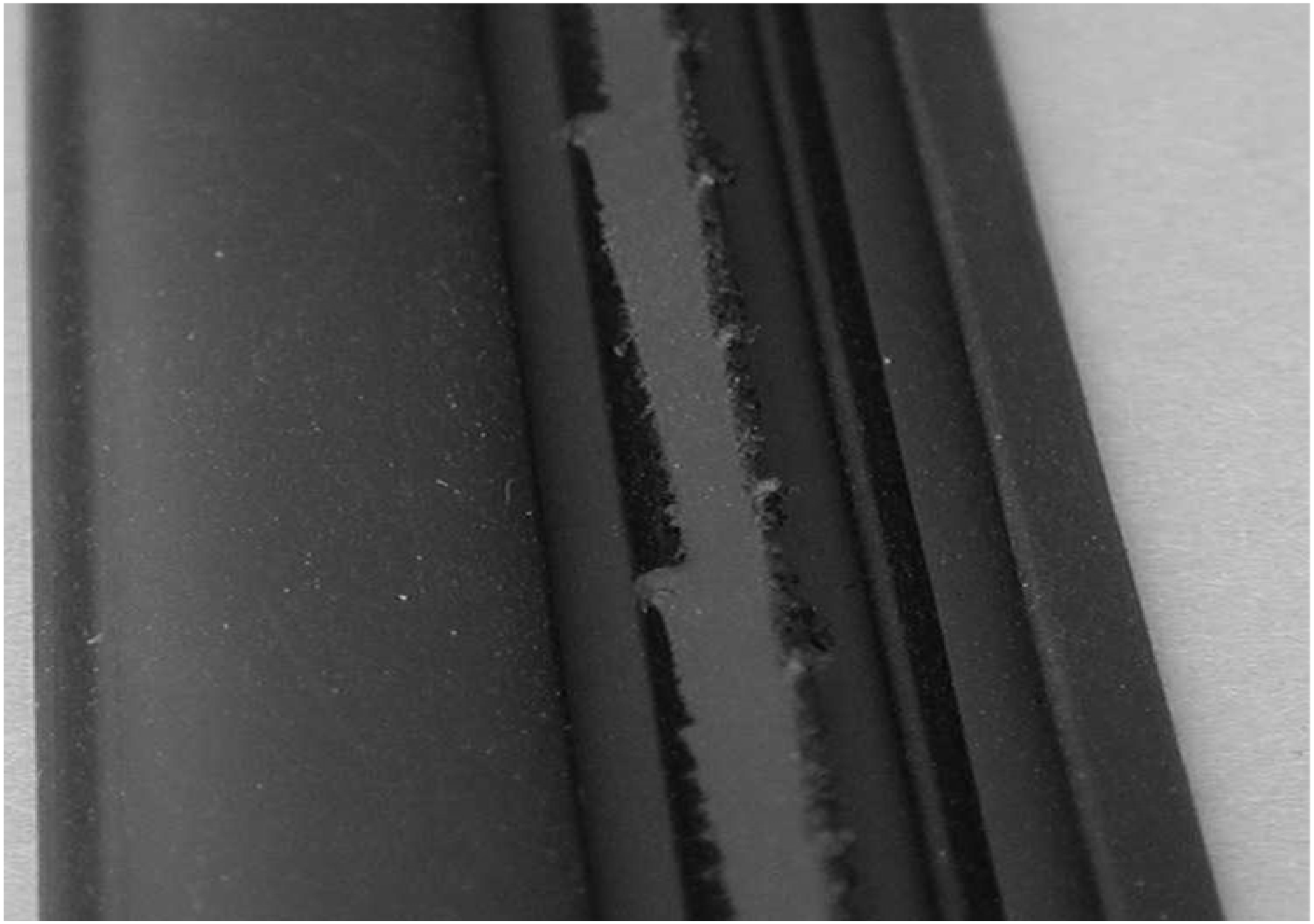
Profile Detail

+ American Talc



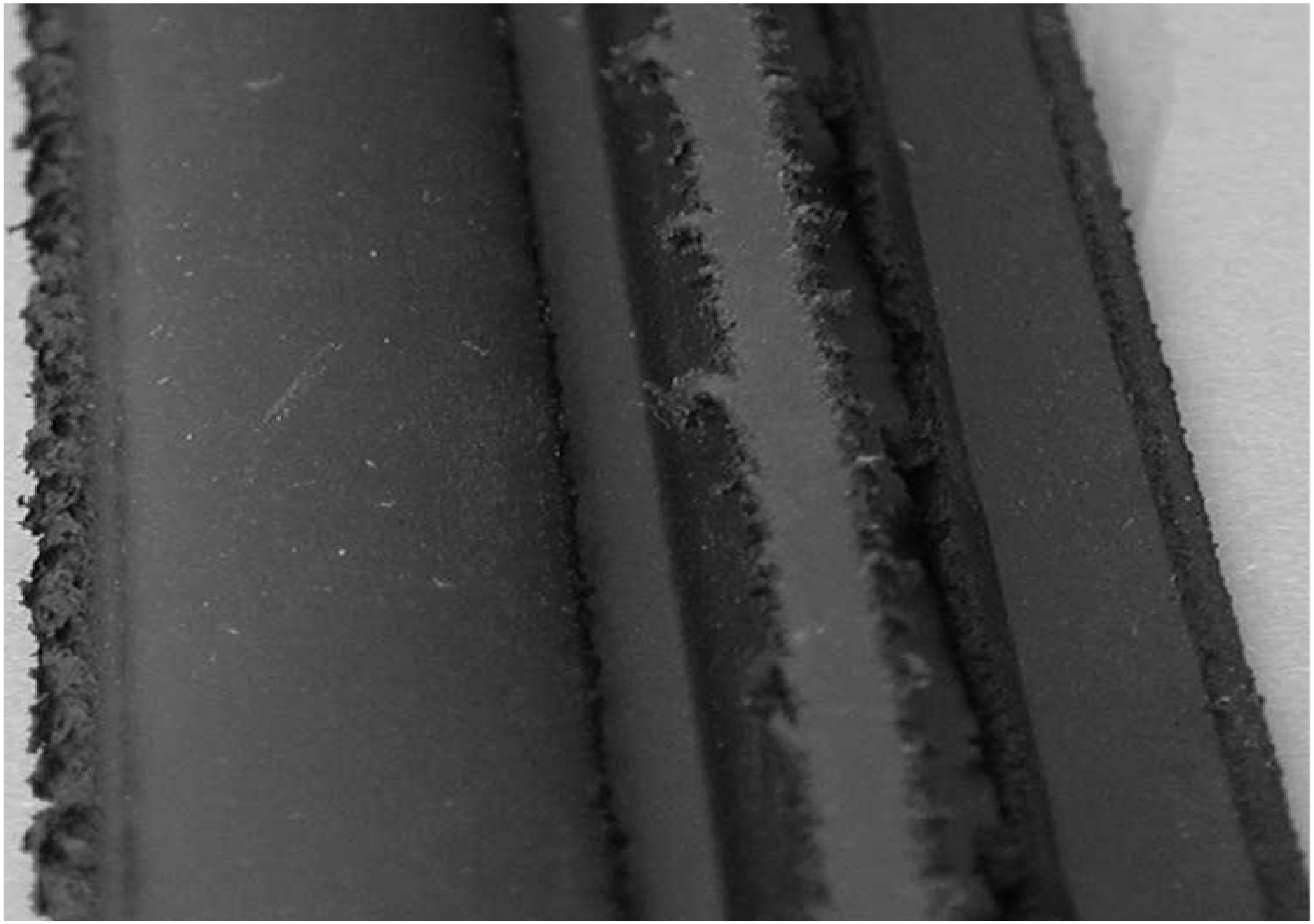
Profile Detail

+ English Calcined Clay



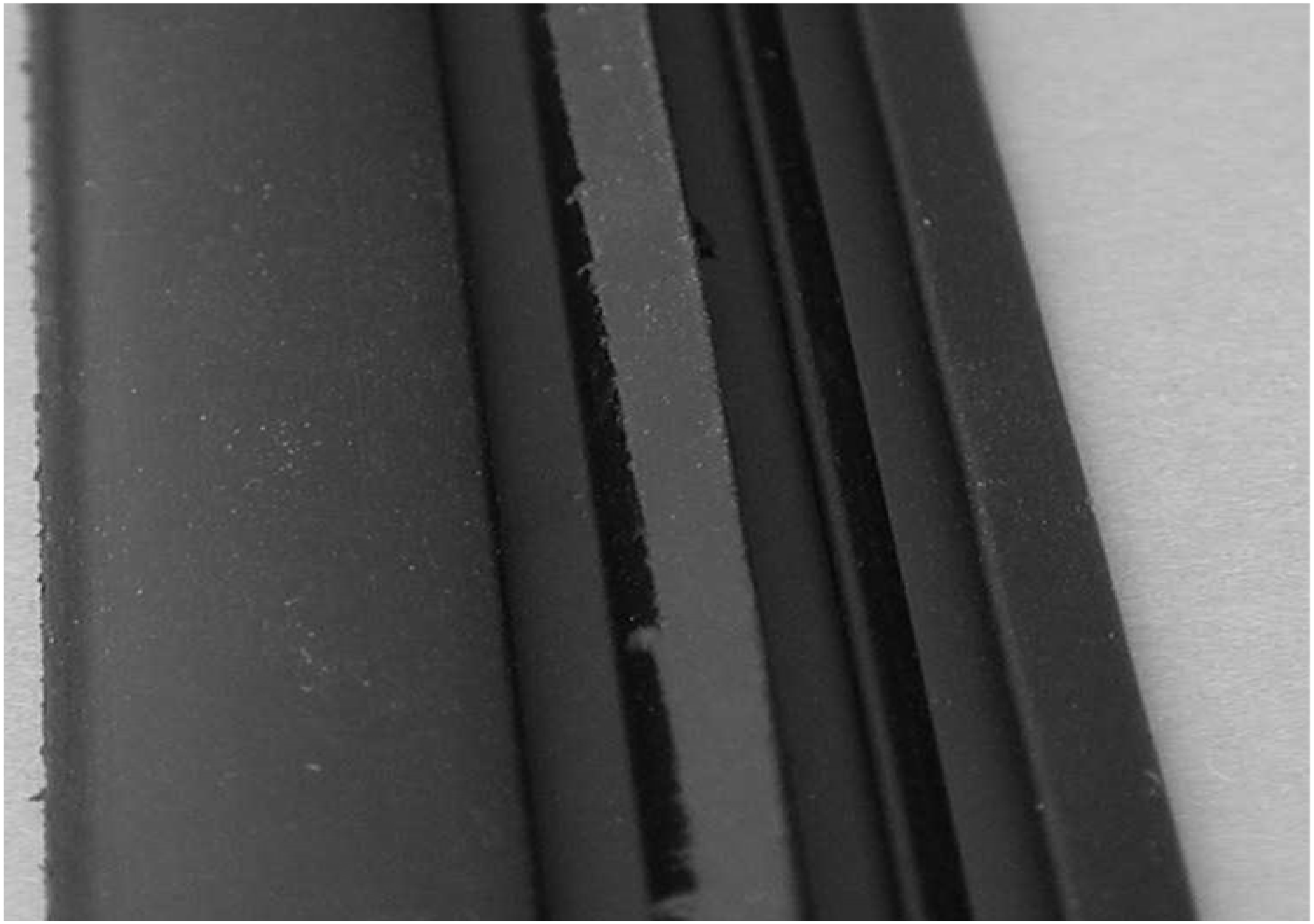
Profile Detail

+ English Soft Clay



Profile Detail

+ English Hard Clay



Profile Detail

+ English Clay