Non-black fillers

in peroxide cured EPDM cable

insulation compounds

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VM-4/0699/04.2010

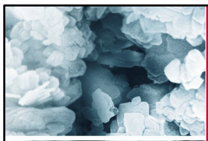
Content

ABSTRACT

Among the untreated fillers, the American hard clay came off, straight or in the blend with whiting, as the weakest filler. The English calcined clay and Sillitin Z 86, when used straight, give very similar results to each other, however, in the blend with whiting, Sillitin Z 86 proved superior. Including cost considerations, **Sillitin Z 86 results as the best suited filler.**

When looking at the total property profile of the two surface treated fillers, Aktisil VM 56 has to be confirmed on equal level with the calcined clay. Including cost considerations, **Aktisil VM 56 must be judged the best suited product in this comparison.**

Summary at a Glance



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At a Glance

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	untreated						surface treated			
	American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Incorporation	-	0	++	++	++	++	++	++	++	++
Processing (Extrusion)	0	--	++	+	++	++	++	++	++	++
Cure behavior	+	0	-	-	+	+	+	+	+	+
Mechanical properties	0	-	+	+	++	++	+	+	++	++
- Hot air aging	--	0	++	++	0	++	++	+	+	+
Electrical properties dry	0	+	++	++	+	+	++	++	++	++
- After water immersion	0	+	--	+	-	+	++	++	+	+
Cost	+	+	0	0	++	++	0	0	++	++
Total assessment	-	0	+	+	+	++	+	+	++	++

++ = very good; + = good; 0 = satisfactory; - = poor; -- = very poor

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Table 1

1 Introduction

Cable insulation compounds are subject to many different requirements, as for instance listed in DIN VDE 0207 Part 20 EI4.

The profile required includes good mechanical properties, excellent extrusion characteristics as well as high electrical resistivity also after water immersion.

Required properties – taken from parts of this standard:

	Tensile strength	Elongation at break	Volume resistivity[1)]
Before Aging	> 5.0 MPa	> 200 %	> 10^{12} W x cm
After hot air aging 168 h / 100 °C	> 4.2 MPa < +/- 25 % Change	> 200 % < +/- 25 % Change	

[1]) Only valid for national constuctions

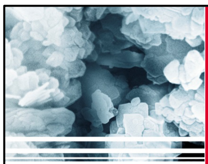
Properties were also studied which are not included in cable standards, but which how-ever give the compounder valuable indications about the processing properties and the quality of the final product.

The test program included potentially suitable fillers for this application, as summarized in Table 3.

Also blends with whiting, as common in the industry, were considered in appropriate variations (see Table 2).

2 Experimental

2.1 Compound formulations



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Base Formulation

EPDM – 70 Shore A

	phr	
Buna AP 258 (Buna EP G 3963)	130.0	130.0
Stearic acid	1.0	1.0
Zinkoxyd aktiv	5.0	5.0
Paraffin 54/56	4.0	4.0
Filler	225.0	125.0
Whiting	-	100.0
Sunpar 2280	15.0	15.0
Vulkanox HS/LG	1.0	1.0
Vulkanox MB/MG	0.5	0.5
TAC GR 50 %	2.0	2.0
Perkadox 14/40 pd	8.0	8.0
Total	391.5	391.5

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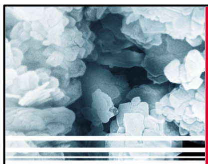
Table 2

The raw materials used were the following:

Buna AP 258 (Buna EP G 3963):	crystalline, medium green strength ML (1+4) 125°C: 34 ENB-Content: 10 % Ethylene content corrected: 66 %-Gew. Ethylene content uncorrected: 73 %-Gew. Oil type: paraffinic Oil content: 30 phr
Zinkoxyd aktiv:	Zinc oxide
Stearic acid :	Processing aid
Paraffin 54/56:	Paraffin wax
Sunpar 2280:	Paraffinic mineral oil
Vulkanox HS/LG:	2.2.4-Trimethyl-1.2-dihydroquinoline (TMQ)
Vulkanox MB/MG:	2-Mercapto-benzimidazole (MBI)
TAC GR 50 %:	Triallylcyanurate (50 %)
Perkadox 14/40 pd:	Bis(tert-butylperoxyisopropyl)benzene (40 %)



Fillers Selected

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Characteristics

	Particle size [µm]		Oil Absorption [g/100g]	Specific Surface area BET [m²/g]	Functiona-lization
	d_{50}	d_{97}			
American hard clay	3.7	31	50	25	none
English calcined clay	3.6	19	60	6.5	none
Sillitin Z 86	1.9	8	55	11	none
Surface treated American calcined clay	3.0	18	61	7.5	Vinyl silane
Aktisil VM 56	2.2	10	45	7.0	Vinyl
Whiting	2.4	13	28	4.9	none

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Table 3

Appropriate EPDM compounds are made up with fillers which can markedly affect the processing and final performance properties.

The American hard clay has the highest BET surface area and a high particle size d_{97}. Sillitin Z 86 by comparison offers a markedly lower BET surface area and lower figures for the particle size distribution along with a slightly higher oil absorption.

As different from the untreated fillers, Aktisil VM 56 is an activated Sillitin Z 86, produced by modifying the surface with an amino functional group and the American calcined clay has been subject to a surface treatment with vinylsilane (Table 3).

2.2 Compounding and Curing

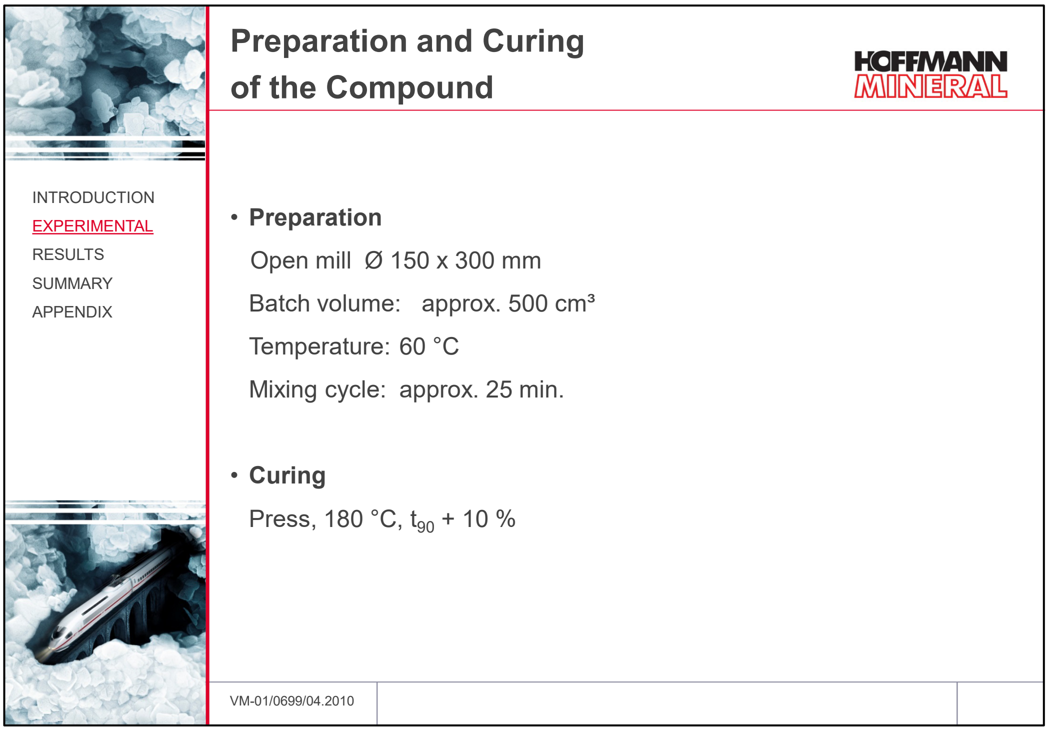

Fig. 1

All compounds were mixed on a laboratory roll mill (Ø 150 x 300 mm) at 20 rpm with a batch size of about 500 cm^3. The mixing time was adjusted according to the incorporation characteristics of the fillers, and each time registered.

The curing time was always t_{90} + 10 % at 180 °C in an electrically heated press (Fig. 1).

2.3 Extrusion

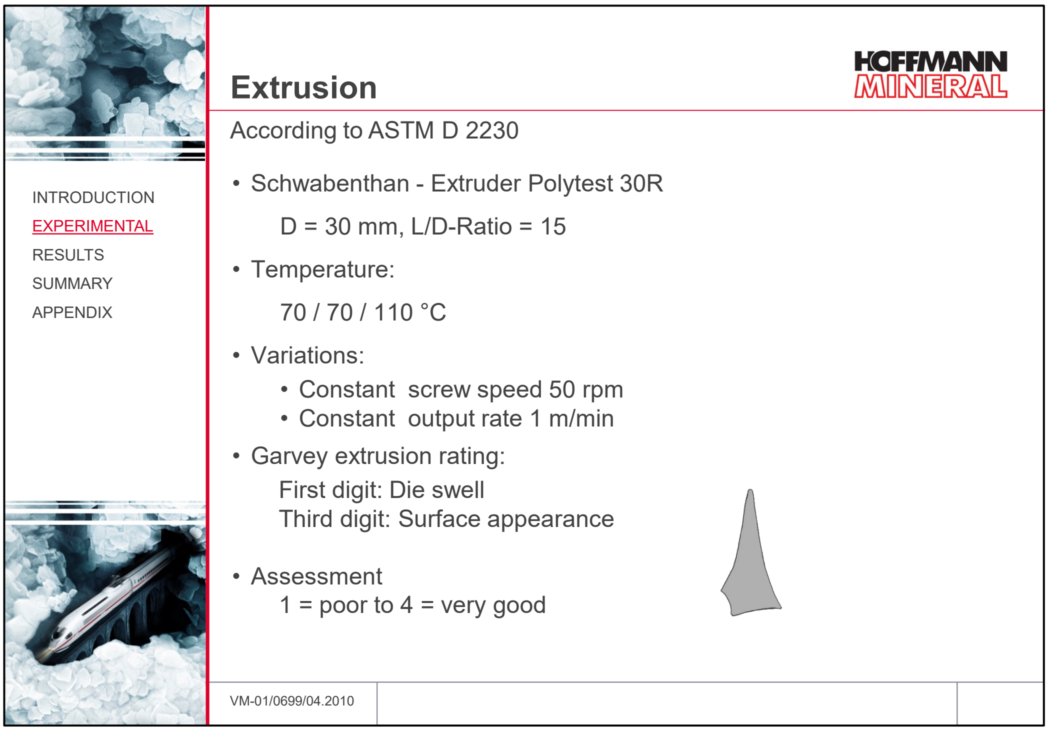

Fig. 2

Garvey extrusion tests were carried out in accordance with ASTM D2230.

For assessing the extrusion characteristics of the compounds just the first and the third digit in Method A were used, because these are most relevant for cable extrusions. In fact, these digits reflect the die swell (first digit) and the surface quality (third digit) of the profiles.

The tests with a screw speed of 50 rpm served for the determination of the throughput and the corresponding extrudate quality. By contrast, at constant output rate only the surface quality can be assessed (Fig. 2).

2.4 Volume Resistivity

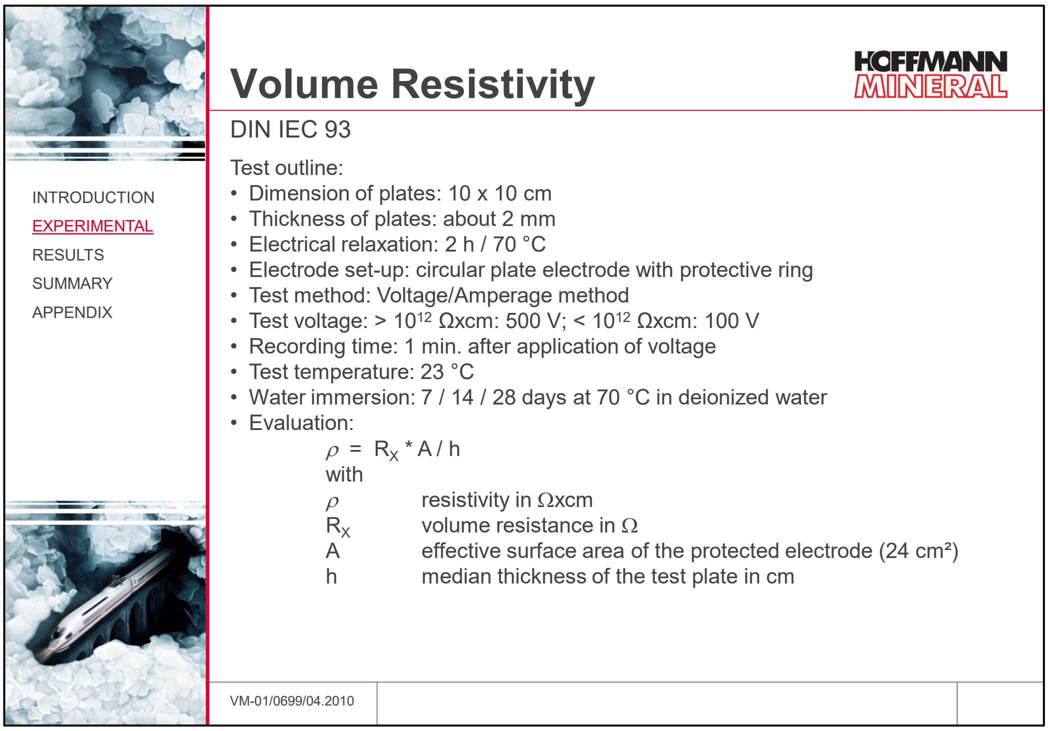

Fig. 3

All important test parameters are listed in Fig. 3.

The water immersion test, while not part of the cable standard, helps towards a better differentiation of the fillers (Fig. 3).

3 Results

3.1 Mooney viscosity and Mooney scorch

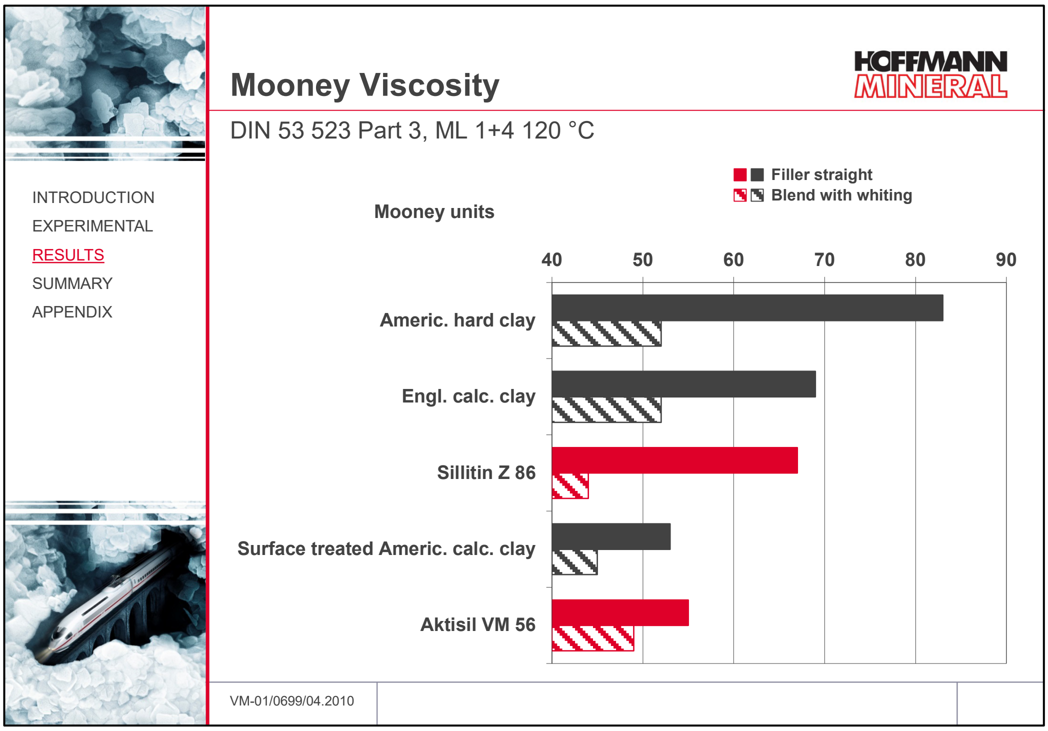

Fig. 4

Sillitin Z 86 gives a lower Mooney viscosity compared to the other non-treated fillers.

The surface treated fillers lead to a lower viscosity compared with the untreated pro-ducts, and Aktisil VM 56 hardly differs from the surface treated American calcined clay.

In blends with whiting, the Mooney viscosity will be markedly decreased, while the differences between the fillers are also minimized (Fig. 4).

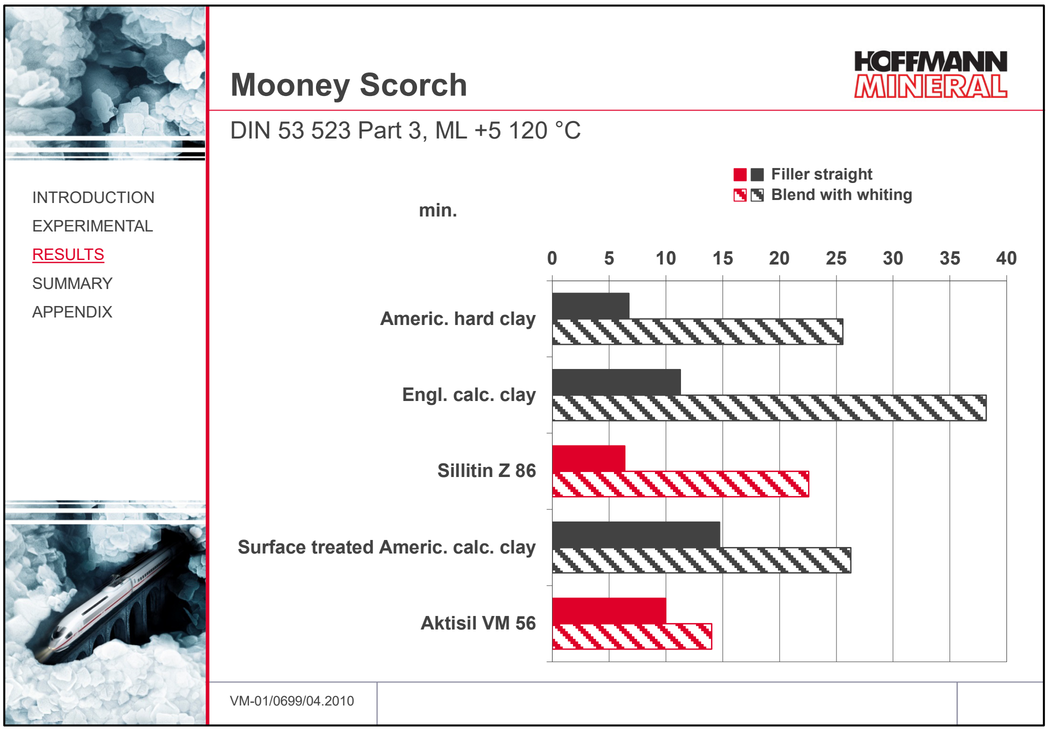

Fig. 5

Mooney scorch time as an index of onset of cure during processing only changes moderately with the different fillers. Sillitin Z 86 comes out at the same level with the hard clay, while the calcined clay reaches somewhat higher figures. The surface treated grades attain directionally slightly longer scorch times. In the blends with whiting, the scorch time generally comes off markedly longer, with this effect particularly pronounced with the non-treated fillers (Fig. 5).

3.2 Curing properties

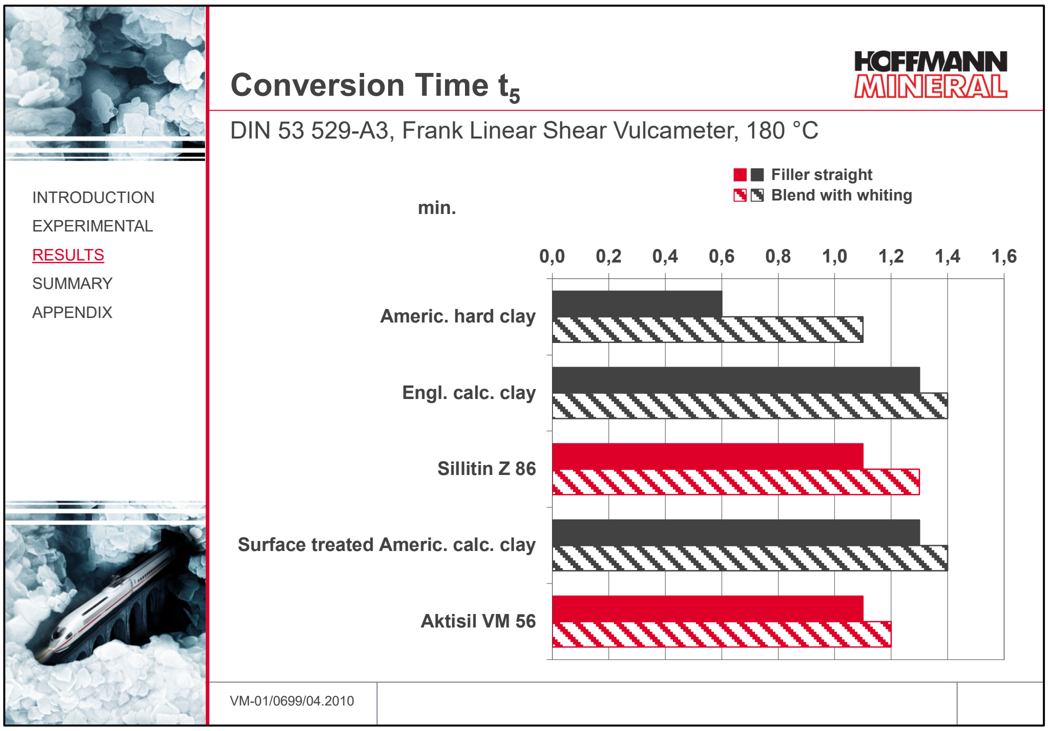

Fig. 6

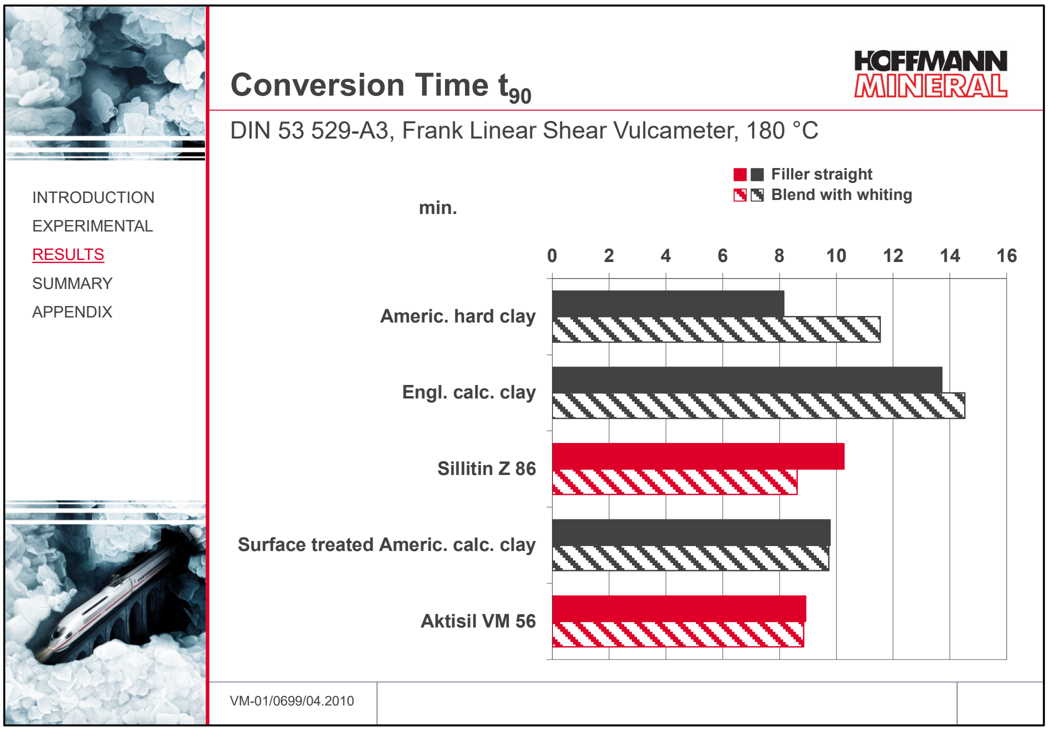

Fig. 7

Sillitin Z 86 and Aktisil VM 56 generate the shortest conversion times t_{90}, which indicates the required curing time, coupled with a long conversion time t_5.

The surface treated calcined clay offers a similarly long conversion time t_5, but needs a longer time to full cure.

The American hard clay straight also gives a short conversion time t_{90}, but also a shorter t_5. In the blend with whiting the cure time, however, comes out definitely longer. The calcined clay without surface treatment requires very long cure times (Figs. 6 and 7).

3.3 Extrusion

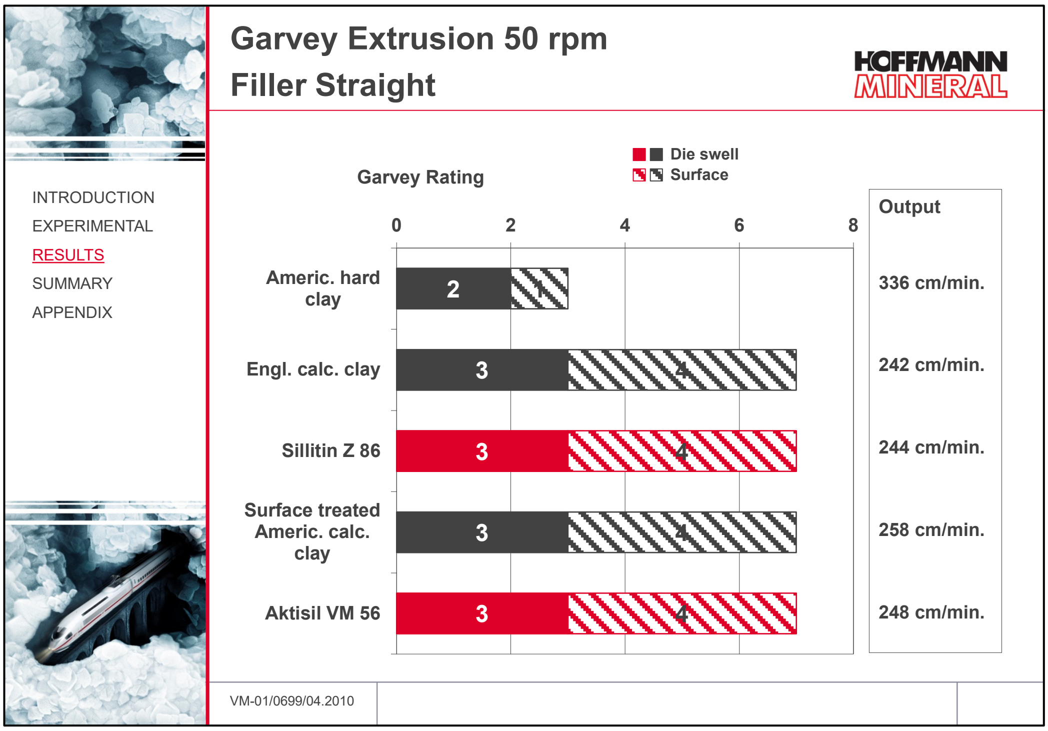

Fig. 8

Sillitin Z 86 and Aktisil VM 56, along with the calcined clays, lead to excellent profile surface appearance as well as a high throughput. The American hard clay offers a still higher output, but at the cost of a much poorer surface quality. Also the die swell is higher (Fig. 8).

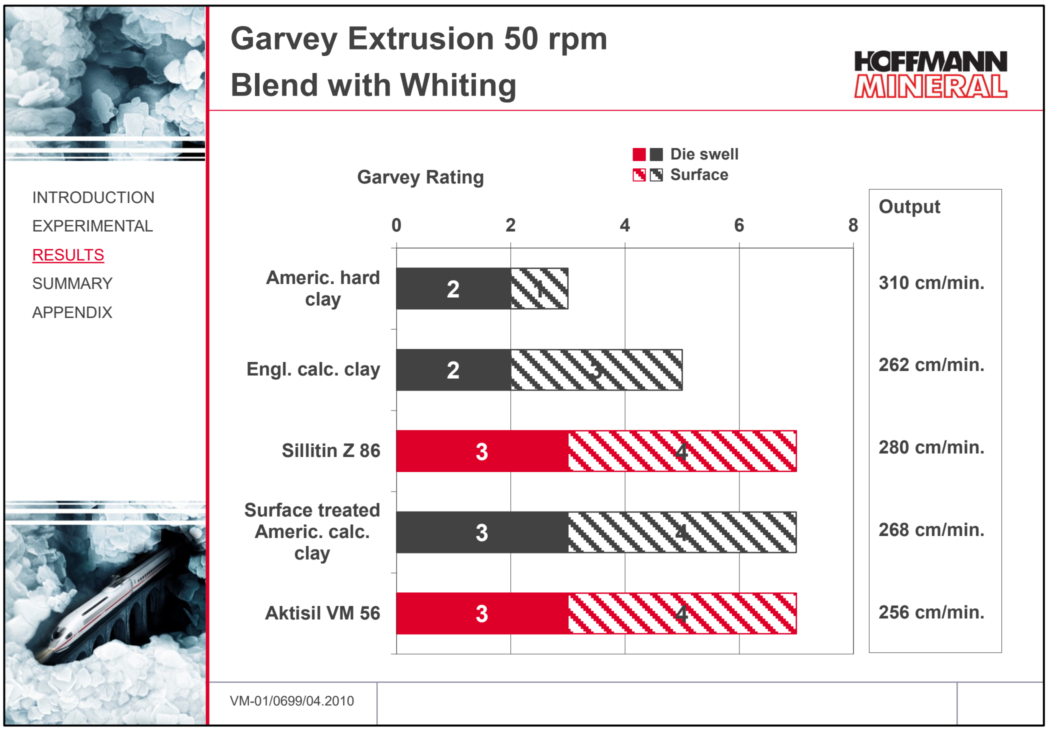

Fig. 9

In blend with whiting, Sillitin Z 86 and Aktisil VM 56 give a high output rate along with good surface appearance. Only the surface treated calcined clay reaches the same level, while this grade without treatment brings about higher die swell and a rough surface. With the exception of the hard clay, the output of the blends with whiting generally is somewhat increased (Fig. 9).

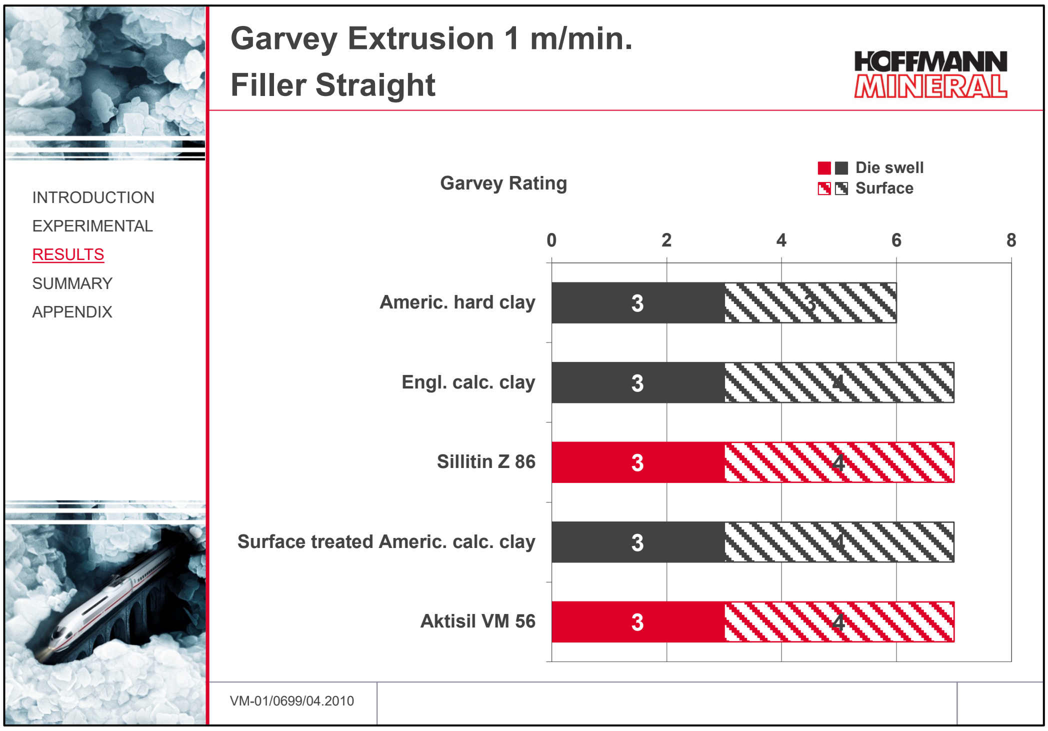

Fig. 10

At a constant output rate of 1 m/min similar conditions are found as for the extrusion at 50 rpm. The calcined clays and the two Neuburg Siliceous Earth grades lead to attractive surfaces and low die swell. Only the hard clay disappoints with a rough surface (Fig. 10).

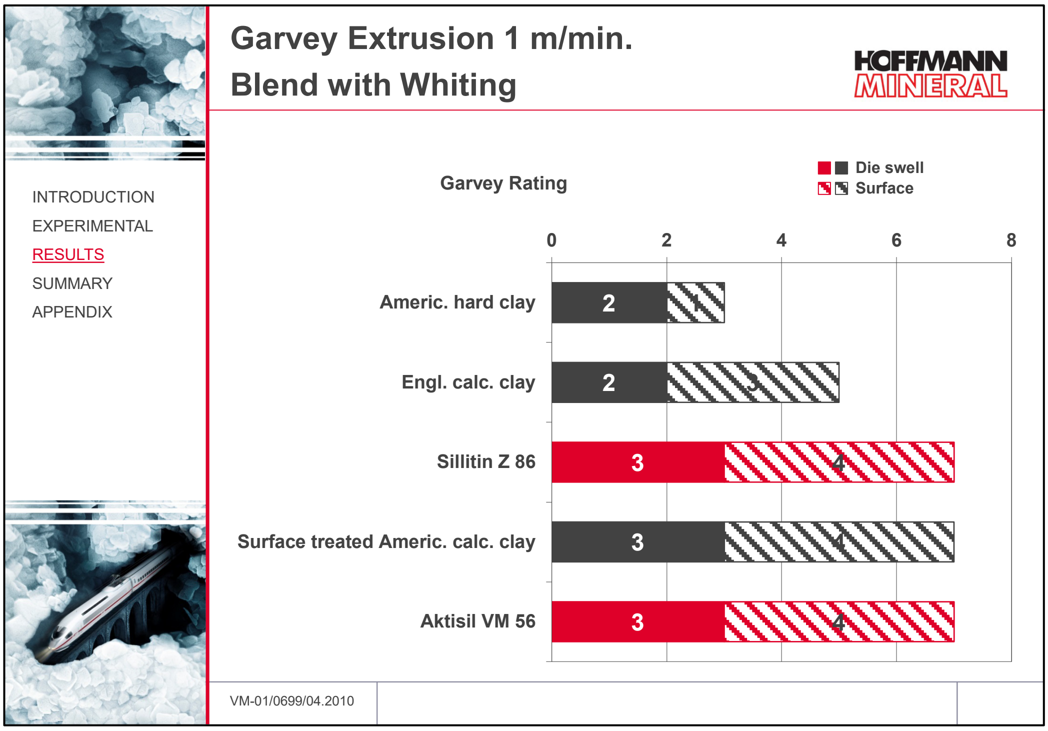

Fig. 11

The blends with whiting obey the same assessment as at 50 rpm. Sillitin Z 86 and Aktisil VM 56, along with the surface treated calcined clay, offer the best results.

The hard clay, once again, comes out last with the lowest results (Fig. 11).

3.4 Mechanical properties

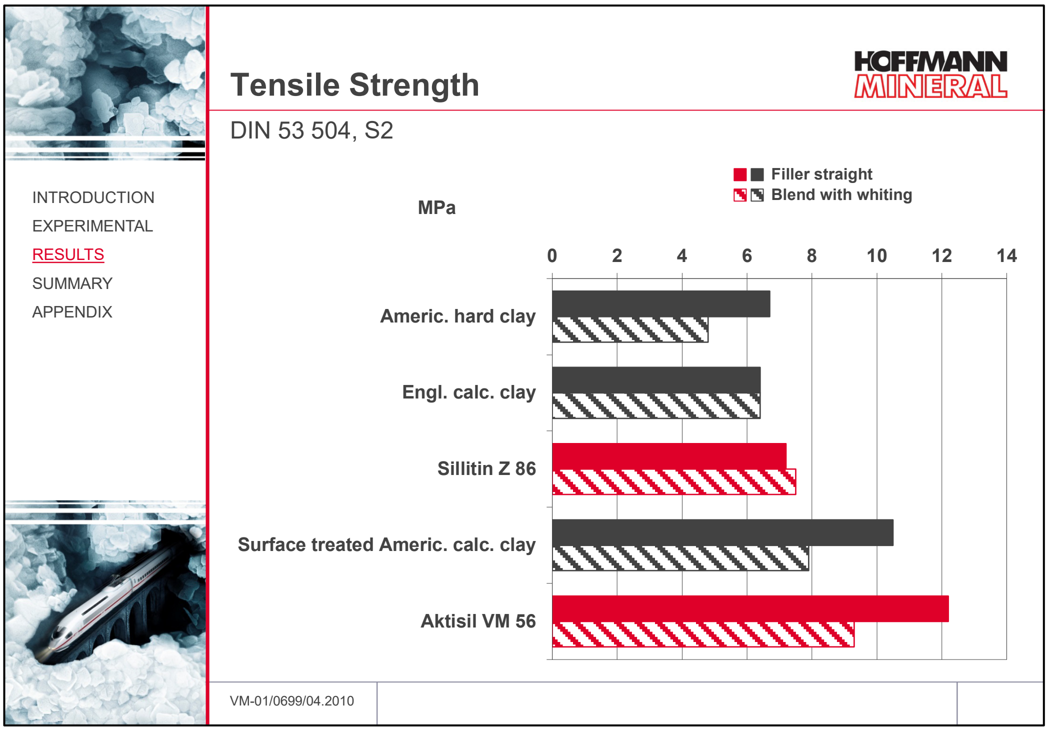

Fig. 12

Sillitin Z 86 imparts the highest tensile strength of the non-treated fillers. This level remains valid also in the blend with whiting, while the hard clay here suffers from a decrease. Aktisil VM 56 reaches the highest tensile strength of all the fillers tested, including the surface treated clay. In the blends with whiting, however, the tensile strength with surface treated fillers tends to decrease, but in particular the combination with Aktisil VM 56 still remains well above the straight non-treated grades (Fig. 12).

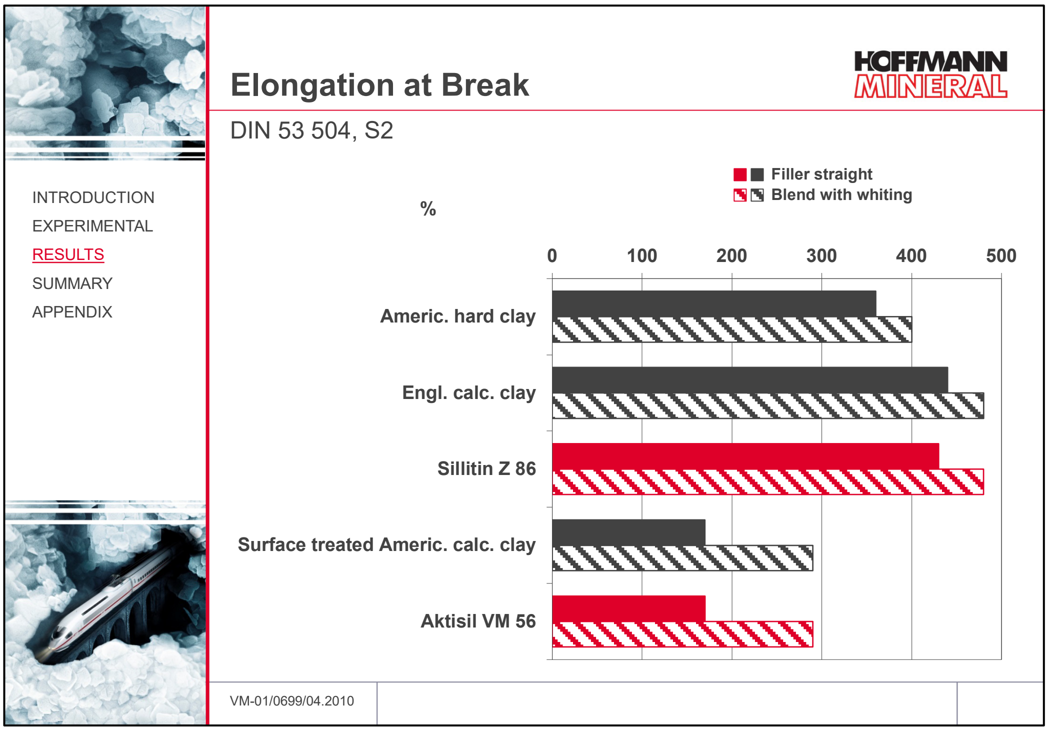

Fig. 13

Among the non-treated fillers, Sillitin Z 86 comes off comparable with the calcined clay, while the hard clay shows much lower figures. The combination with whiting for all non-treated fillers results in a similar increase of the elongation. The surface treated fillers straight only lead to relatively low elongations at break, which however can be improved by additions of whiting. Another way to achieve this is the reduction of the peroxide concentration, which also has positive effects on the cost side (Fig. 13) .

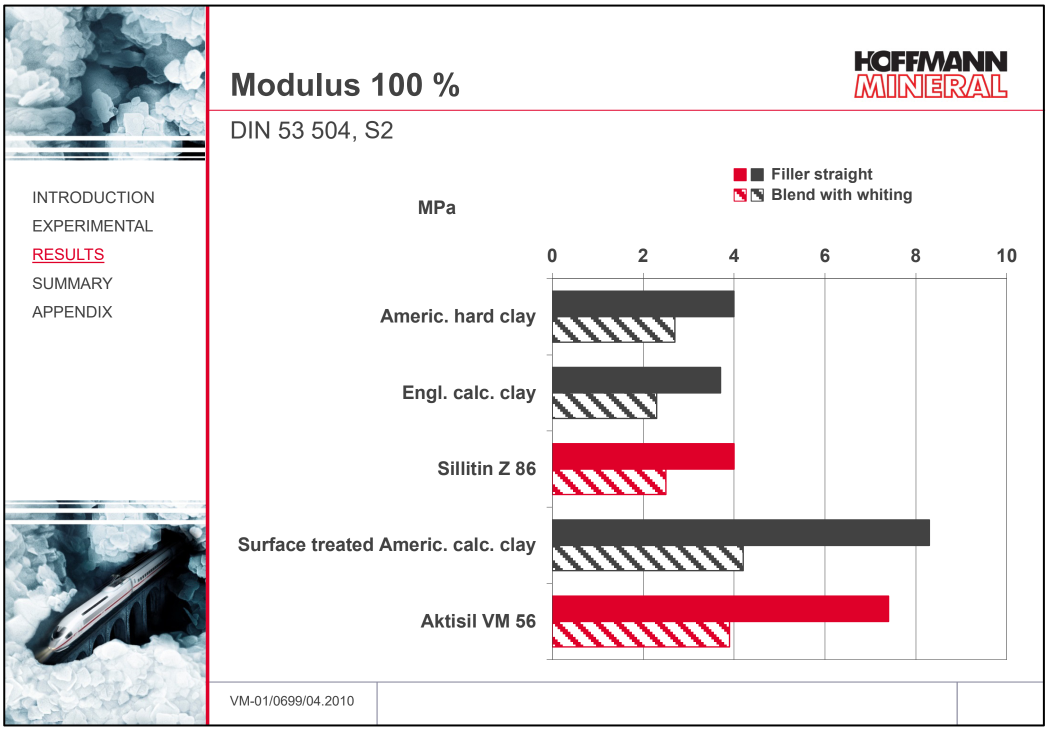

Fig. 14

Differences are only observed between the two groups without respectively with surface treatment, but there is an increase by the factor of two.

In the blends with whiting, the modulus generally is decreased, so that with the surface treated fillers similar levels come out as with the straight non-treated grades.

Moduli along with compression set figures should indicate a correlation with the hot set as well as with the high temperature pressure resistance. The higher the modulus in combination with a low compression set, the better characteristics should result.

The surface treated grades including Aktisil VM 56 meet such a property profile in an excellent way (Fig. 14).

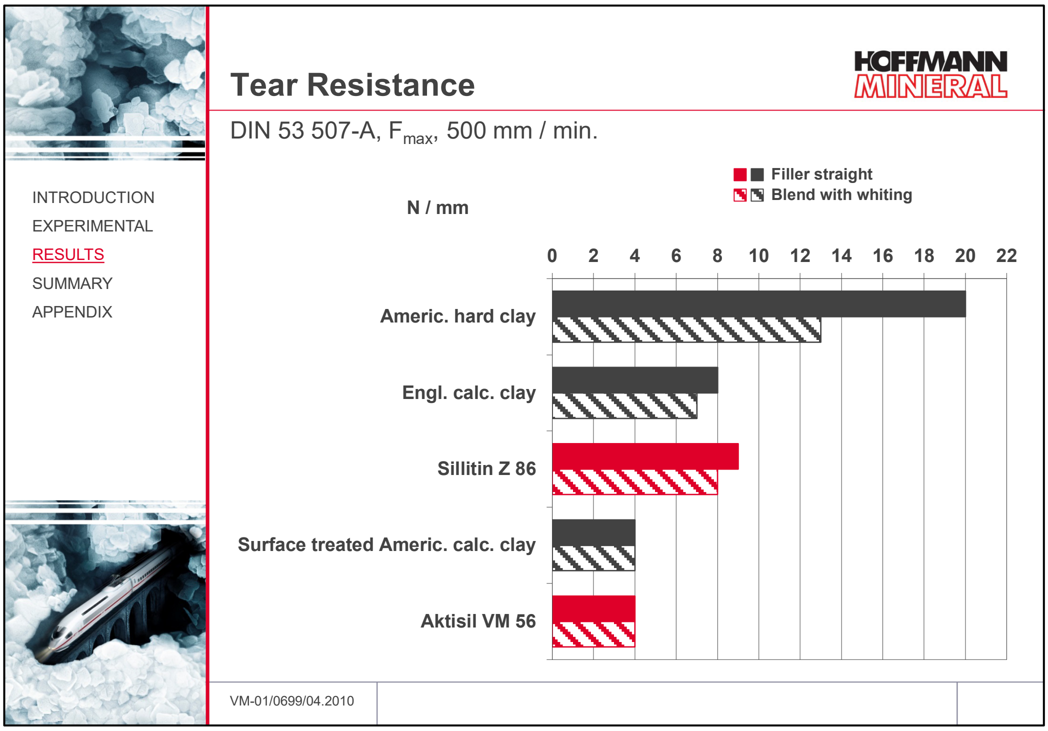

Fig. 15

Among the fillers without surface treatment, Sillitin Z 86 arrives at a slightly higher tear strength compared with the calcined clay, while the hard clay offers by far the highest level of all fillers tested. Combinations with whiting, by contrast, give lower figures throughout.

The surface treated grades attain only lowish tear strength levels, which are not further modified by blending with whiting (Fig. 15).

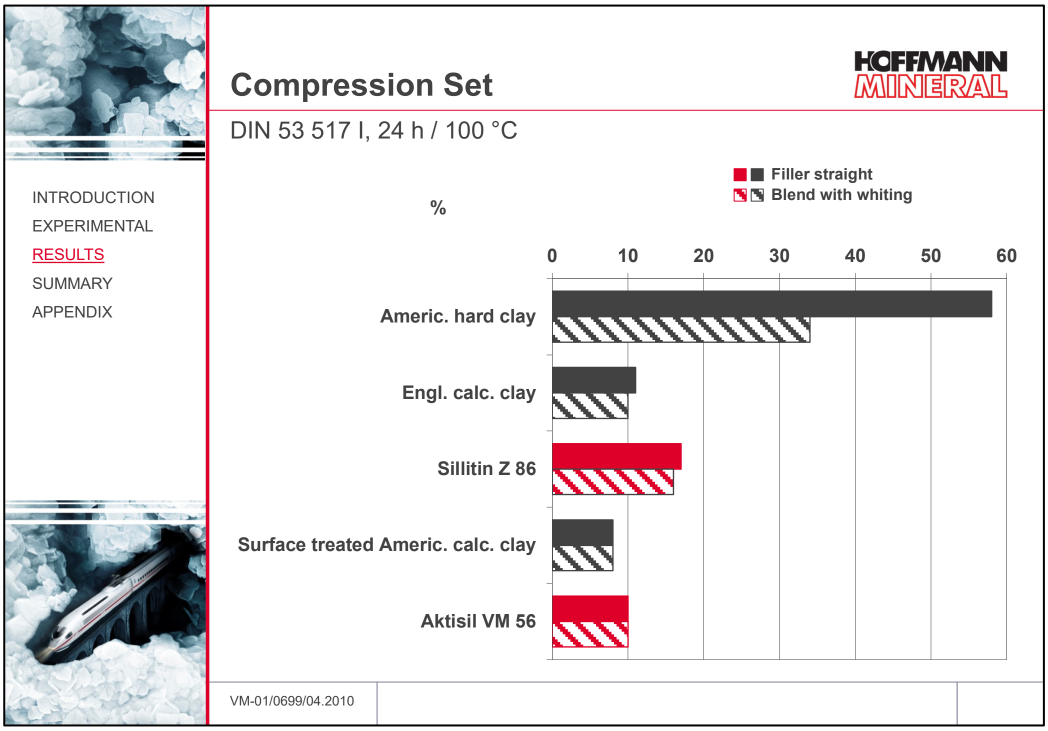

Fig. 16

The hard clay by far imparts the highest compression set of all fillers tested, but the figures are improved by blending with whiting.

Otherwise within the groups without respectively with surface treatment hardly any significant differences can be observed. Blending with whiting hardly affects the compression set results or not at all, while with the surface treated fillers similar results are obtained as with the straight non-treated grades.

In line with the low compression set along with high moduli the hot set test as well as the high temperature compression resistance should be optimum with the surface treated fillers (Fig. 16).

3.5 Volume resistivity

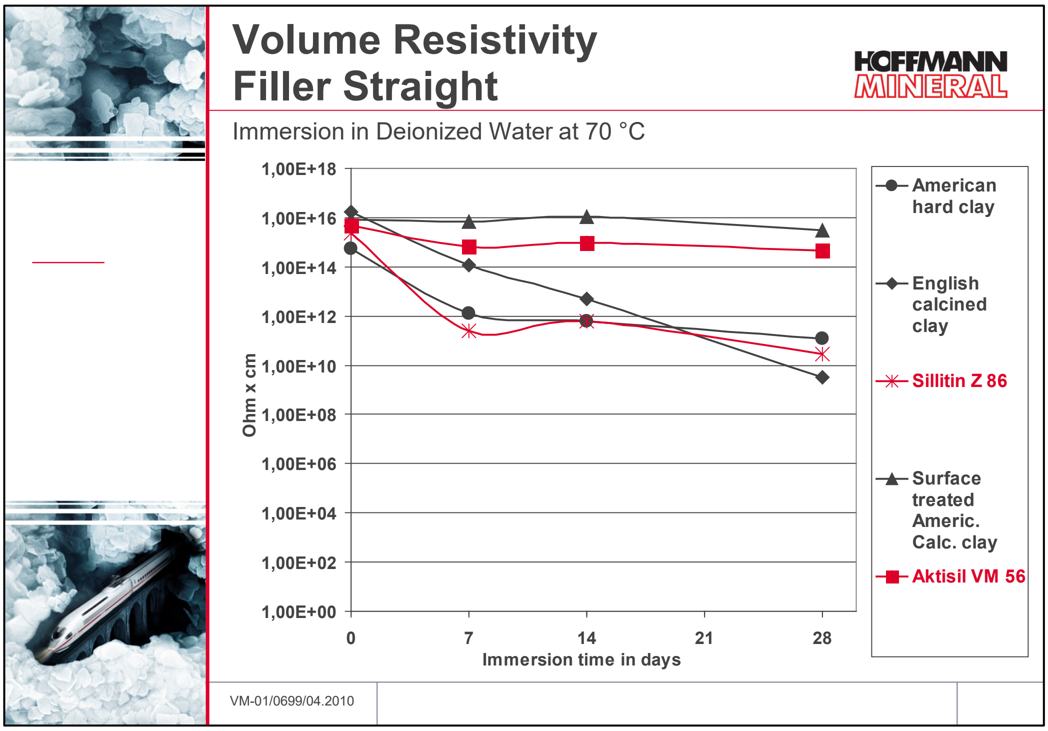

Fig. 17

In the DIN VDE 0207 standard Part 20 no requirements are listed with regard to the electrical resistance after immersion in water, but this test allows an assessment of the emergency properties of a cable insulation. In order to ensure a sufficiently high resistivity also after water immersion, the use of a surface treated grade such as Aktisil VM 56 must be recommended, as there exists only a minimum initial change of the resistivity which then remains on a stable high level. The volume resistivity with the non-treated fillers dramatically goes down during immersion in water, and this without reaching a stable final level (Fig. 17).

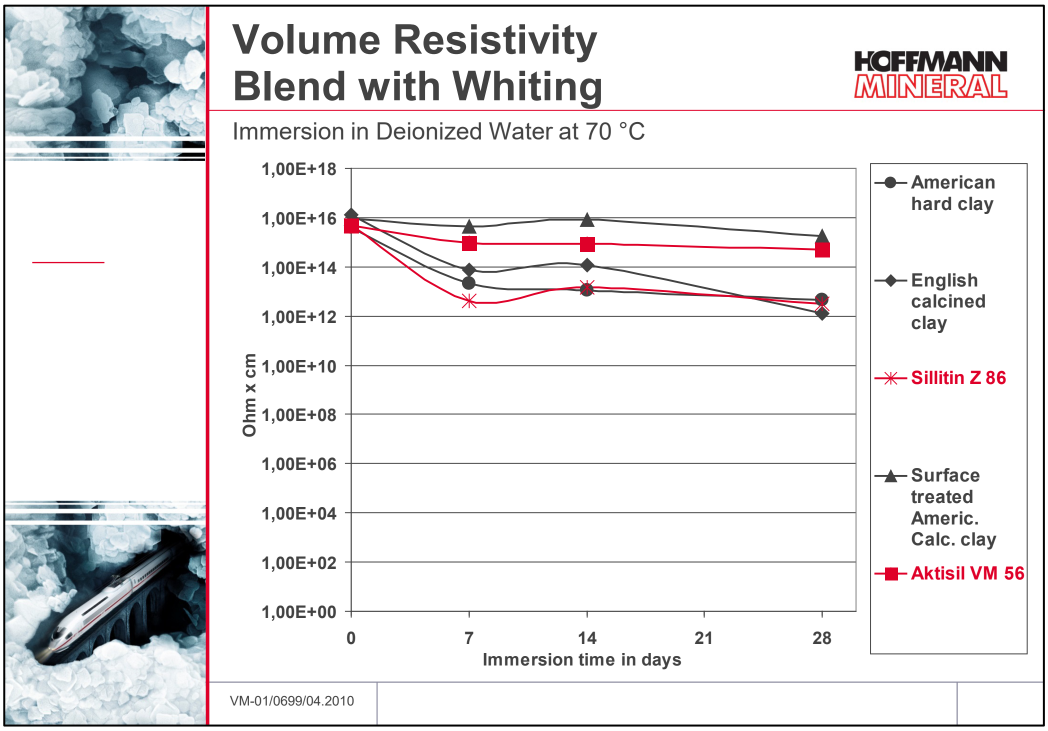

Fig. 18

The combination with whiting results in an improvement of the figures for the non-treated fillers, but the excellent high level of the surface treated grades will still not be matched (Fig. 18).

3.6 Hot air aging 168 h / 100 °C

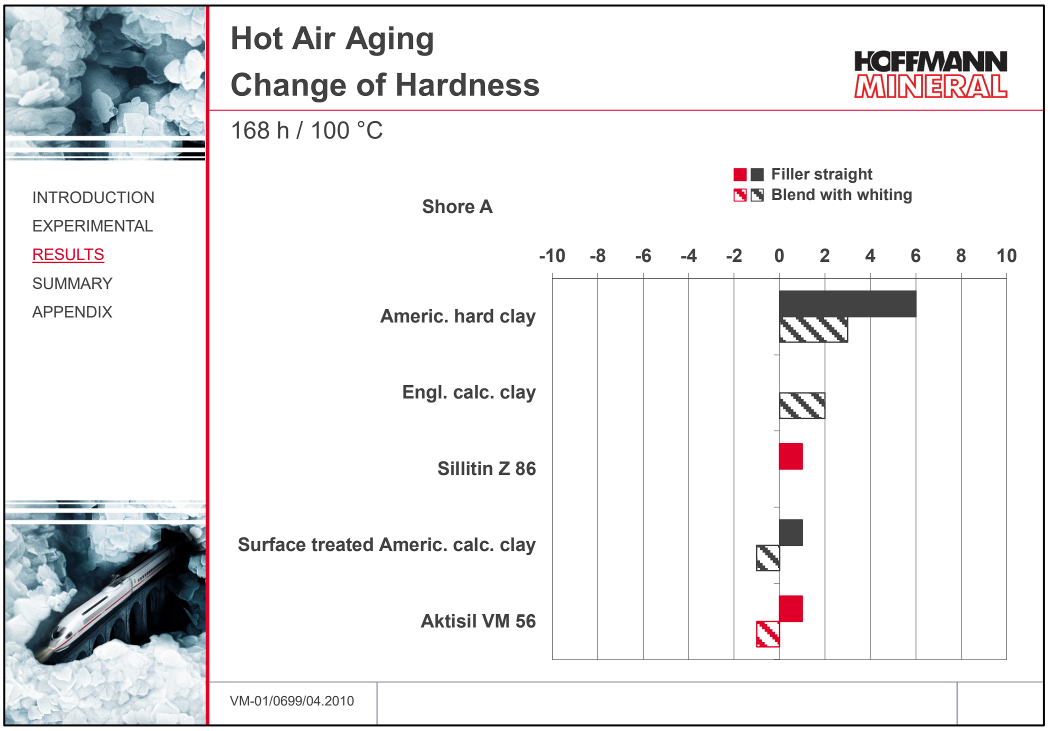

Fig. 19

Within the group without but also with surface treatment, excepting the hard clay hardly any significant differences can be observed. The combination with whiting also shows no mentionable effects (Fig. 19).

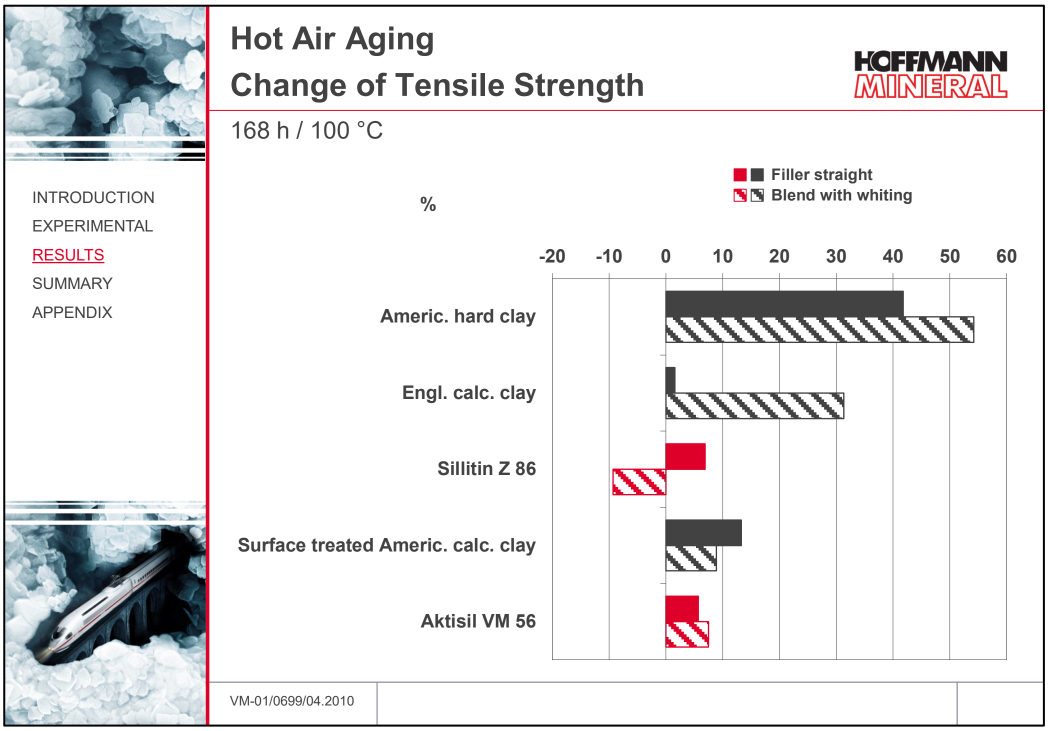

Fig. 20

Similar to the situation for hardness, within the groups without respectivly with surface treatment, and with the exception of the hard clay and the calcined clay/whiting blend, there are hardly any significant differences to be found. The combination with whiting does not significantly affect the results (Fig. 20).

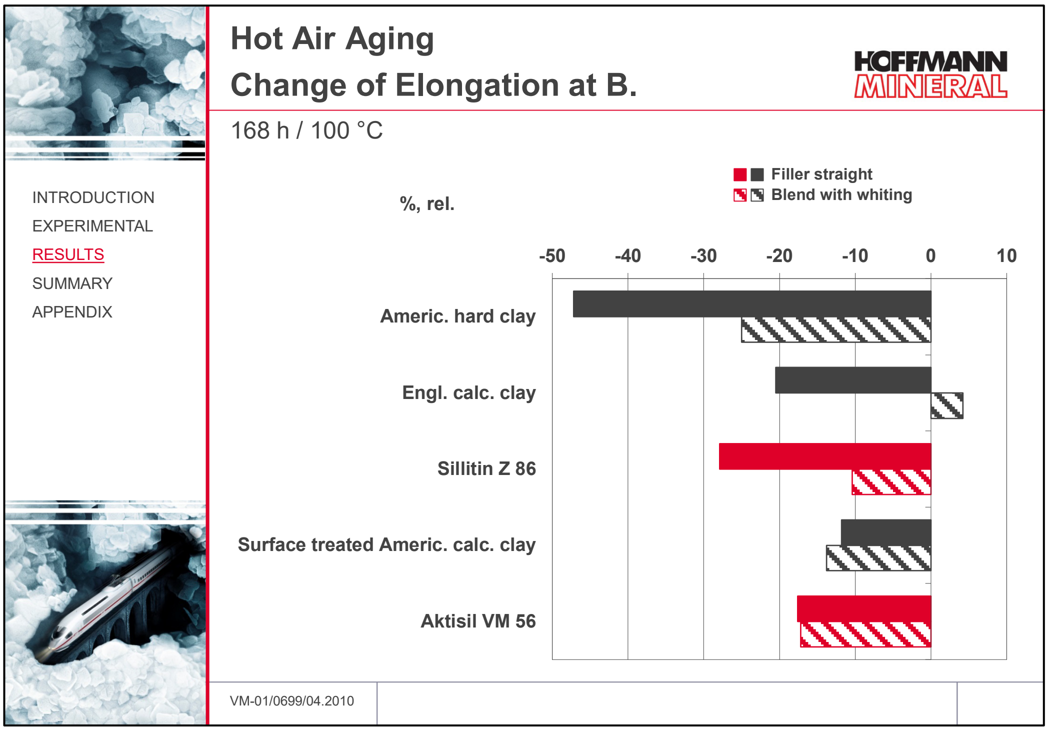

Fig. 21

The hard clay shows the largest change of elongation at break of all the fillers tested, followed by Sillitin Z 86. Combinations with whiting give only little changes. The surface treated fillers straight respectively in blends with whiting lead to comparable level of elongation change (Fig. 21).

3.7 Compound raw material cost indices

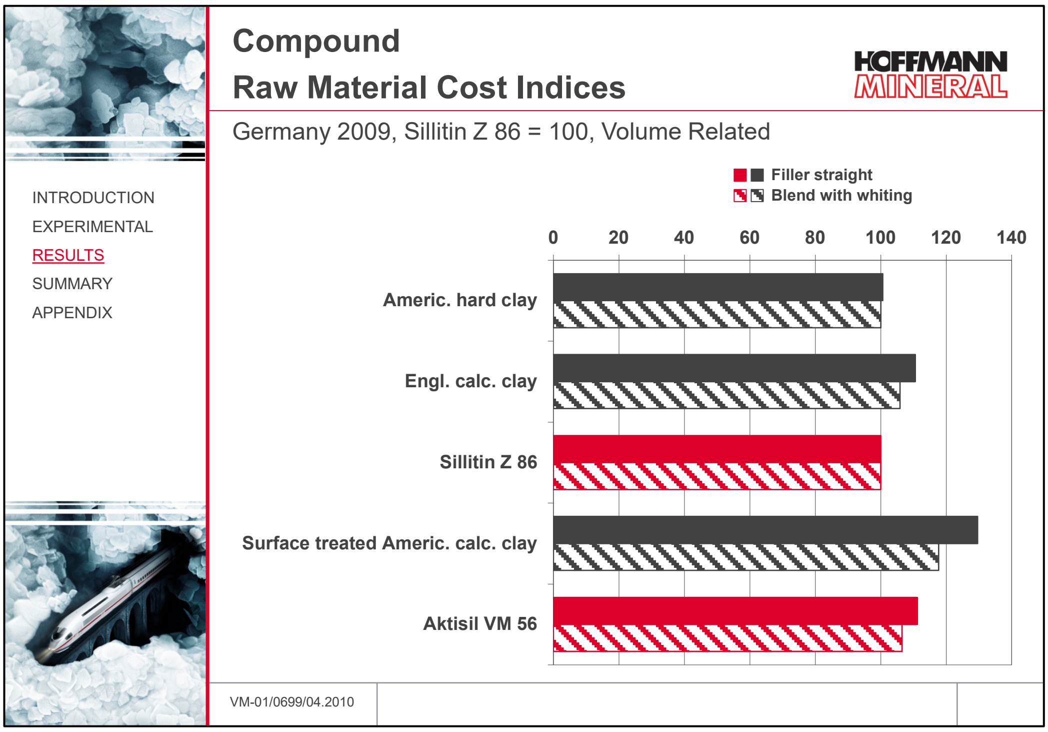

Fig. 22

The costs of the compound with Sillitin Z 86 was deliberately set at 100 index points. The hard clay compound comes off comparably, while the calcined clay calls for higher expenses. Still more pronounced is the difference towards the surface treated fillers, where the treated version of the calcined clay brings about the highest compound costs. Aktisil VM 56 in comparison is situated clearly lower, and in the blend with whiting is able to even go below the costs of the non-treated calcined clay (Fig. 22).

4 Summary

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Untreated Fillers

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- American hard clay, straight as well as in blend with whiting, comes out very unsatisfactory in mixing and processing, leads to high compression set, high tear strength, low volume resistance, poor extrusions and high changes of properties upon aging.
- English calcined clay is easy to mix and process, gives very good compression set, good extrusion properties, but suffers from a sharp decrease of the volume resistance upon water immersion.
- Sillitin Z 86 too is easy to mix and process and largely comes close to the calcined clay. With respect to extrusion, however, Sillitin Z 86 is markedly superior, in particular in the blend with whiting. Also cost aspects should speak for the Neuburg Siliceous Earth grade.

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Fig. 23

Summary

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Surface Treated Fillers

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- Surface treated American calcined clay provides a very good property profile with respect to incorporation, processing, mechanical and electrical properties as well as extrusion characteristics. However, the costs here present themselves very high.
- Aktisil VM 56 too comes off with a very good property profile which regard to incorporation, processing, mechanical and electrical properties as well as extrusion characteristics. The price/performance ratio without doubt speaks in favor of Aktisil VM 56.

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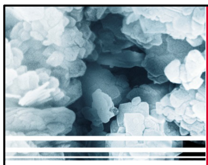
Fig. 24



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- Among the untreated fillers, the American hard clay came off, straight or in the blend with whiting, as the weakest filler. The English calcined clay and Sillitin Z 86, when used straight, give very similar results to each other, however, in the blend with whiting, Sillitin Z 86 proved superior. Including cost considerations, **Sillitin Z 86 results as the best suited filler.**
- When looking at the total property profile of the two surface treated fillers, Aktisil VM 56 has to be confirmed on equal level with the calcined clay. Including cost considerations, **Aktisil VM 56 must be judged the best suited product in this comparison.**

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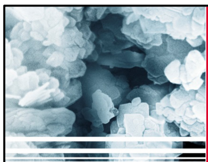
Fig. 25

4.1 Appendix



Results

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Raw Compound Properties

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M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Mixing time	min.	30	25	19	20	21	19	20	20	25	17
Mooney viscosity DIN 53 523, Part 3 ML (1+4), 120 °C	ME	83	52	69	52	67	44	53	45	55	49
Mooney scorch DIN 53 523, Part 3 ML +5, 120 °C	min.	6.7	25.6	11.3	38.2	6.4	22.6	14.7	26.3	10.0	14.0
Linear shear vulcameter (Frank) DIN 53 529, A3 180 °C											
t_5	min.	0.6	1.1	1.3	1.4	1.1	1.3	1.3	1.4	1.1	1.2
t_{90}	min.	8.2	11.6	13.7	14.5	10.3	8.6	9.8	9.7	8.9	8.9
t_{90} + 10 % (Cure time)	min.	9	13	15	16	11	10	11	11	10	10

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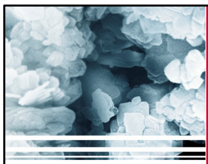
Fig. 26



Results

HOFFMANN MINERAL

Cured Rubber Properties

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Hardness DIN 53505-A	Shore A	71	67	73	66	72	67	73	69	74	69
Tensile strength DIN 53 504, S2	MPa	6.7	4.8	6.4	6.4	7.2	7.5	10.5	7.9	12.2	9.3
Modulus 100 % DIN 53 504, S2	MPa	4.0	2.7	3.7	2.3	4.0	2.5	8.3	4.2	7.4	3.9
Modulus 300 % DIN 53 504, S2	MPa	6.3	4.2	4.7	3.2	5.2	3.6	-	-	-	-
Elongation at break DIN 53 504, S2	%	360	400	440	480	430	480	170	290	170	290
Rebound DIN 53 512	%	43	51	54	57	55	56	52	55	53	57
Tear resistance DIN 53 507 A, Fmax 500 mm/min	N/mm	20	13	8	7	9	8	4	4	4	4
Compression set DIN 513 517 I 24 h/100°C	%	58	34	11	10	17	16	8	8	10	10
Density DIN 53 479	g/cm³	1.47	1.48	1.48	1.48	1.48	1.48	1.48	1.49	1.47	1.48

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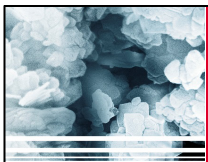
Fig. 27



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HOFFMANN MINERAL

Extrusion ASTM D 2230

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Output rate 1m/min Rating Torque	Nm	3131 70	2111 60	3142 80	2132 70	31436 0	3142 80	3444 70	3142 80	3143 60	3142 80
Screw speed 50 rpm Rating Output Torque	cm/min. g/min. Nm	2111 336 232 80	2111 310 228 80	3142 242 204 100	2132 262 216 80	3142 244 206 90	3142 280 238 90	3142 258 218 80	3142 268 234 80	3142 248 212 85	3142 256 224 90

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Fig. 28

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Volume Resistivity, DIN IEC 93

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
unaged	Ωcm	5.6x 10^{14}	4.1x 10^{15}	1.7x 10^{16}	1.3x 10^{16}	2.3x 10^{15}	4.9x 10^{15}	8.0x 10^{15}	9.3x 10^{15}	5.0x 10^{15}	4.6x 10^{15}
after aging in deionized water at 70 °C											
7 days	Ωcm	1.3x 10^{12}	2.1x 10^{13}	1.2x 10^{14}	7.2x 10^{13}	2.5x 10^{11}	4.2x 10^{12}	6.6x 10^{15}	4.3x 10^{15}	6.3x 10^{14}	9.8x 10^{14}
14 days	Ωcm	5.9x 10^{11}	1.1x 10^{13}	4.8x 10^{12}	1.2x 10^{14}	6.3x 10^{11}	1.5x 10^{13}	1.1x 10^{16}	8.0x 10^{15}	9.6x 10^{14}	8.7x 10^{14}
28 days	Ωcm	1.2x 10^{11}	4.4x 10^{12}	3.2x 10^{9}	1.3x 10^{12}	2.9x 10^{10}	3.1x 10^{12}	3.1x 10^{15}	1.8x 10^{15}	4.5x 10^{14}	5.2x 10^{14}

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Fig. 29

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Properties after Aging in Hot Air 168 h / 100 °C

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Hardness Change	Shore A Shore A	77 + 6	70 + 3	73 ± 0	68 + 2	73 + 1	67 ± 0	74 + 1	68 - 1	75 + 1	68 - 1
Tensile strength Change	MPa %	9.5 + 42	7.4 + 54	6.5 + 2	8.4 + 31	7.7 + 7	6.8 - 9	11.9 + 13	8.6 + 9	12.9 + 6	10.0 + 8
Modulus 100 % Change	MPa %	7.2 + 80	4.6 + 70	4.5 + 22	3.0 + 30	5.6 + 40	3.1 + 24	9.4 + 13	4.8 + 14	8.4 + 14	4.7 + 21
Elongation at break change	% %, rel.	190 - 47	300 - 25	350 - 21	500 + 4	310 - 28	430 - 10	150 - 12	250 -14	140 - 18	240 - 17

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Fig. 30

Our technical service suggestions and the information contained in this report are based on experience and are made to the best of our knowledge and belief, but must nevertheless be regarded as non-binding advice subject to no guarantee. Working and employment conditions over which we have no control exclude any damage claims arising from the use of our data and recommendations. Furthermore, we cannot assume any responsibility for any patent infringements which might result from the use of our information.