Electrophoretic deposition -

Neuburg Siliceous Earth in black

cathodic electro deposition paints

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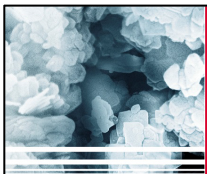
1 Introduction

In the field of electrodeposition coating, the traditional types of Neuburg Siliceous Earth have been successfully using for many years. With their well-known property profile, such as the good storage stability of the pigment paste, as well as the advantageous edge coverage and excellent flexibility of the coating, Sillitin Z 86 and Sillikolloid P 87 are ideally suited for this application.
The new product line of Calcined Neuburg Siliceous Earth is also suitable for this application as well as the with a functional group surface treated products from Hoffmann Mineral. The property profile of electrodeposition coatings can be further improved by the low sieve residues, excellent dispersing properties and high color neutrality as well as other positive effects due to functionalization, such as rheology control or hydrophobicity and corrosion protection.
Consequently, in this study the traditional and new types of (calcined) Neuburg Siliceous Earth in the current binder generation were tested in comparison with competitors available on the market.
In cooperation with the company Allnex (Graz) a classical binder system for automotive add-on and spare parts was selected and the fillers were tested for their effects in the black pigment paste as well as in the finished e-coat.

2 Experimental

2.1 Pigment paste and used fillers

The components of the black pigment paste are listed in *Fig. 1*. Resydrol EM 6642/55 BG is the grinding resin which, after appropriate neutralization and dilution with water, is the grinding component for producing the pigment paste. Surfynol 104/50 BG is a wetting and dispersing agent and is added to the dispersion and mixed until the liquid is clear. Afterwards the solid mixture consisting carbon black and filler is added. The pigment paste was produced on the dissolver with an adapted bead mill and glass beads for 10 minutes at a peripheral speed of 7.9 m/s.



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Pigment Paste
Base Formulation

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Percent

	Pigment paste
Deionized water	38.075
Acetic acid 30%	2.00
Resydrol EM 6642/55 BG	18.175
Surfynol 104/50 BG	1.75
Special black 4	3.65
Filler	36.35
Total	**100.0**

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Fig. 1

The following fillers were selected for the pigment pastes, the characteristic values can be found in the appendix:

Competitors:

- Clay 1
- Clay 2 (slightly finer than clay 1)
- Calcined Clay

Neuburg Siliceous Earth:

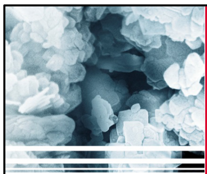
- Sillitin Z 86 (standard product)
- Sillikolloid P 87 (finer than Sillitin Z 86, another standard recommendation)
- Aktisil PF 777 (Sillitin Z 86 alkyl functionalized, hydrophobic)

Calcined Neuburg Siliceous Earth:

- Silfit Z 91 (based on the standard product Sillitin Z 86)
- Aktifit PF 111 (Silfit Z 91 alkyl functionalized, hydrophobic)
- Aktifit PF 115 (Silfit Z 91 amino functionalized, hydrophobic)
- Aktifit PF 111 (Silfit Z 91 vinyl functionalized, hydrophobic)

2.2 Bath formulation

Fig. 2 shows the bath formulation for the production of the e-coat. From each of the above mentioned and prepared pigment paste 6.25 % were added to the diluted binder dispersion and mixed for some time with a paddle mixer. After a stirring time of approx. two hours, the now finished bath formulation was transferred to the later separating vessel. The pigment/binder ratio of 0.2 corresponds to a "low-density" formulation.



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E-Coat
Base Formulation

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Percent

	E-Coat
Resydrol EZ 6635WCAT/35WA	33.92
Deionized water	59.82
Pigment paste	6.25
Total	**100.0**

Pigment/binder ratio: 0.2
PVC: 7.8 %

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Fig. 2

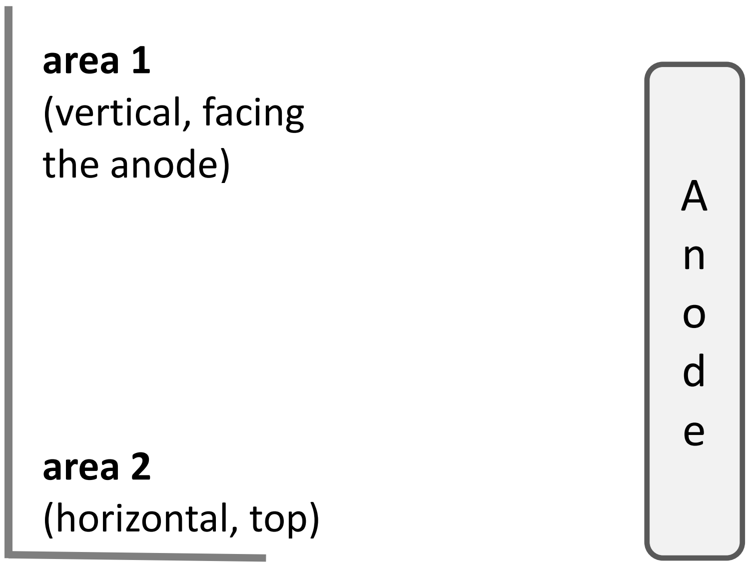
2.3 Parameter preparation / application / curing

Deposition:
In a voltage series with 260, 280 and 300 V the individual charge quantity for each formulation was determined for a dry film thickness of 30 µm. The charge quantity was between 50 and 54 Coulomb.

Typical bath values:
pH value according to DIN ISO 976: 5.3 – 5.6
Specific conductivity DIN 53779: 1100 – 1350 µS/cm

Curing conditions:
Oven temperature 180 °C, dwelling time 25 minutes in the oven

Substrate:
Gardobond 26S/6800/OC (steel, zinc phosphated) for optical and mechanical properties. In addition, to assess the L-effect (differences in gloss and roughness on horizontal and vertical surfaces), a panel was bent by hand for this test. The following draft shows the arrangement of the L-panels in the bath.



The substrate is the cathode and is negatively charged so that the positively charged paint components can move there, be deposited and form an insoluble structure.

3 Results pigment paste

3.1 Viscosity

The viscosity was measured on the rheometer one day after the pigment pastes were produced. *Fig. 3* shows the viscosity at a shear rate of 1 and 100 s^{-1}. All pigment pastes are largely comparable with each other, the only exception being Aktisil PF 777, which is clearly higher in the low shear range. This relativizes again at higher shear rates, and at 100 s^{-1} is again comparable with the others. Aktifit PF 115 shows a similar behavior at a markedly lower level.

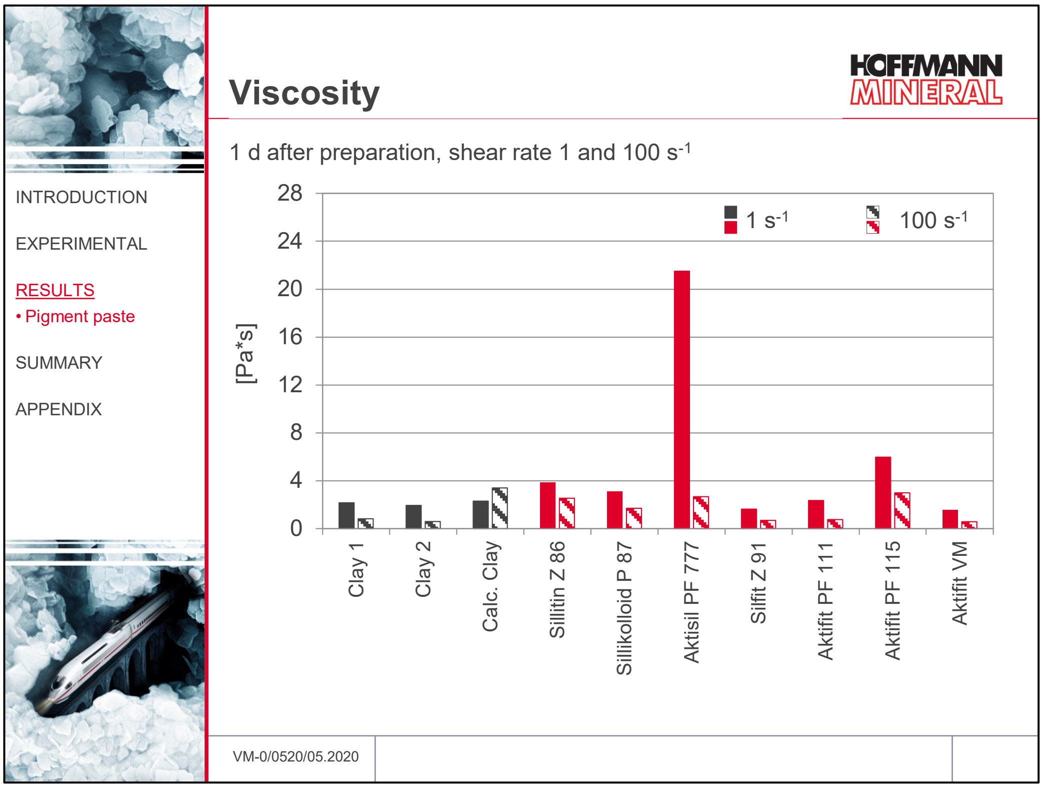


Fig. 3

3.2 Storage stability at 23 °C

The pigment pastes were stored at room temperature 23 °C to check the storage stability. Here, a clear disadvantage of the calcined Clay can be observed. Already after 7 days, it had some sediment. After 2 months, the sediment was so solid that it could not be homogenized.
All other Clays and (calcined) Neuburg Siliceous Earth grades had no or hardly any sediment or gelation and therefore have a very good storage stability (*Fig. 4*).

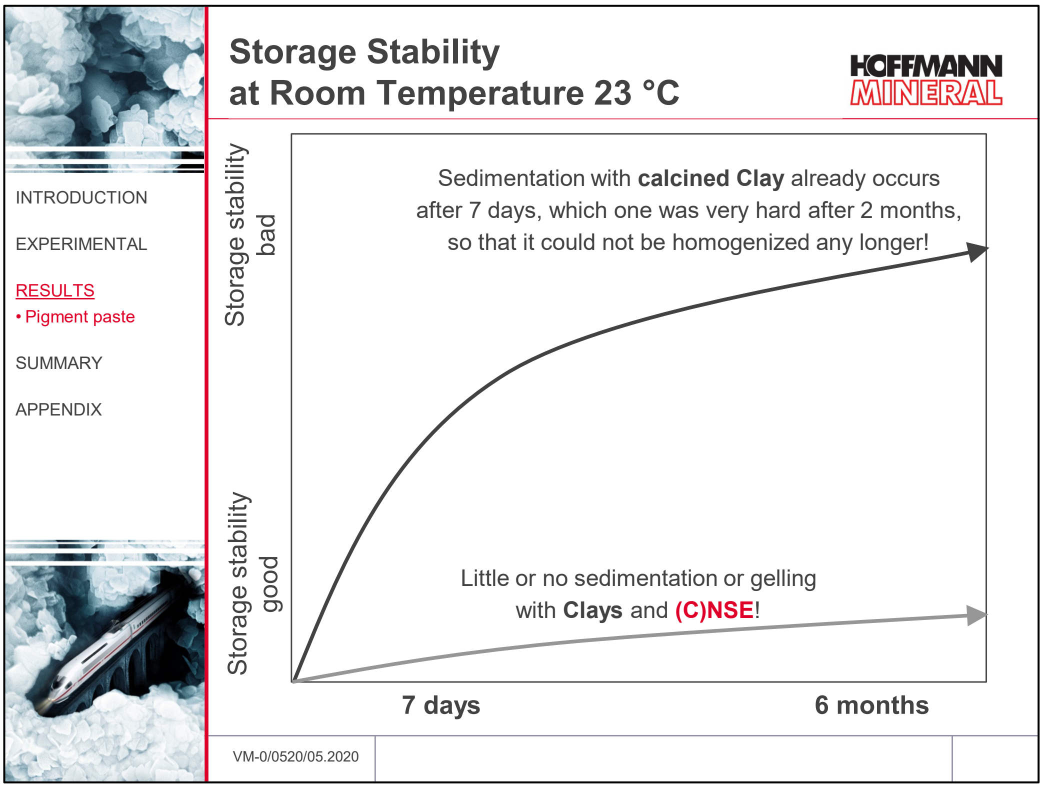


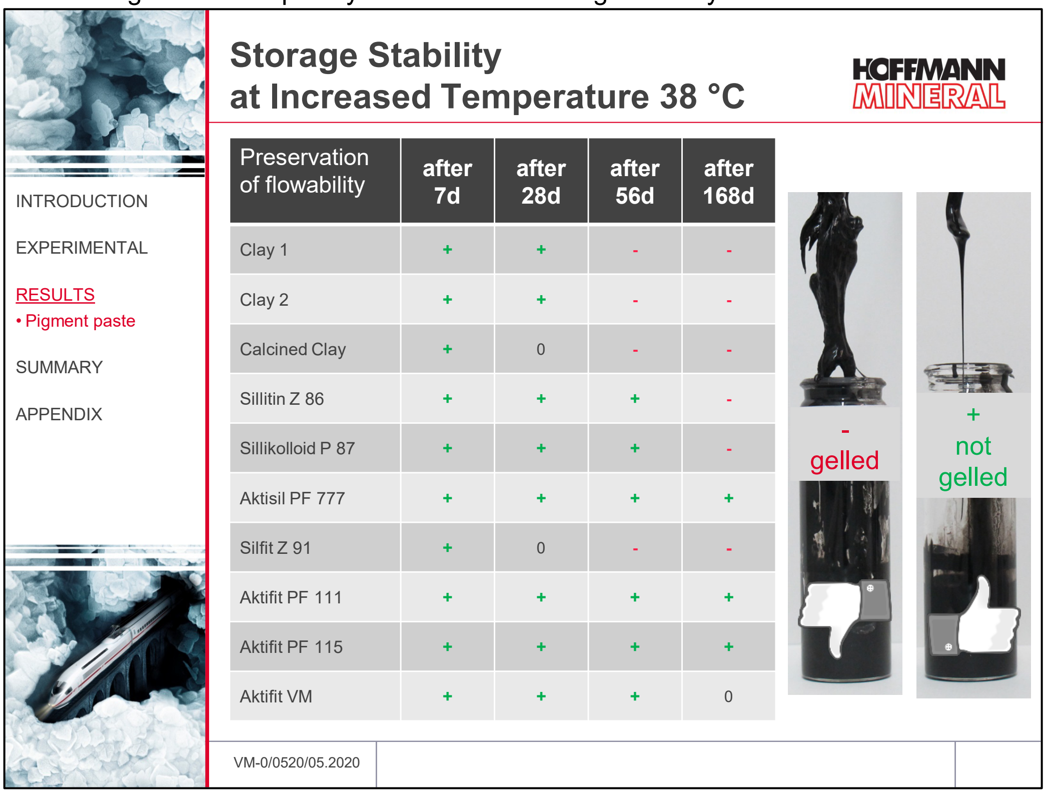
Fig. 4

After a storage period of 6 months, which corresponds to the shelf life of the binder, the pigment paste was additionally gelled with the calcined Clay, all others were free flowing, as shown in *Fig. 5*. A bent spatula was pressed down to the bottom of the glass and pulled up again. The left picture shows the formulation with calcined Clay, which could no longer flow freely due to the sediment and gelation, while all other pigment pastes could flow freely from the spatula.

Fig. 5

3.3 Storage stability at 38 °C

In order to test the storage stability at increased temperature, the pigment pastes were stored in the heat chamber at 38 °C and the flowability was assessed. After 28 days, the pigment pastes with the calcined Clay and Silfit Z 91 had already become a little bit more pasty, and therefore in *Fig. 6* they were rated only with 0. After 56 days (= 2 months), all competitors of (C)NSE and Silfit Z 91 were coagulated, i.e. no longer flowable. After 168 days (= 6 months = shelf life of binder), the Aktifit VM was somewhat pasty. Only the pastes with Aktisil PF 777, Aktifit PF 111 and 115 were not gelled after this time, and thus free flowing and consequently with excellent storage stability.



Preservation of flowability	after 7d	after 28d	after 56d	after 168d
Clay 1	+	+	-	-
Clay 2	+	+	-	-
Calcined Clay	+	0	-	-
Sillitin Z 86	+	+	+	-
Sillikolloid P 87	+	+	+	-
Aktisil PF 777	+	+	+	+
Silfit Z 91	+	0	-	-
Aktifit PF 111	+	+	+	+
Aktifit PF 115	+	+	+	+
Aktifit VM	+	+	+	0

Fig. 6

4 Results E-Coat

4.1 Gloss 60°

Uniform optical properties of the E-coat are of elementary importance for the subsequent paint layers, as differences in gloss or irregularities in roughness can otherwise show up to the surface. *Fig. 7* shows the gloss at an angle of 60°, the side facing the anode was optically assessed. The finer fillers such as Clay 2 and Sillikolloid P 87 achieve the highest gloss values of 68 to 70 GU due to the smaller particle size, followed by Clay 1 and Sillitin Z 86 with 60 GU. All calcined fillers are slightly less glossy with about 50 GU.

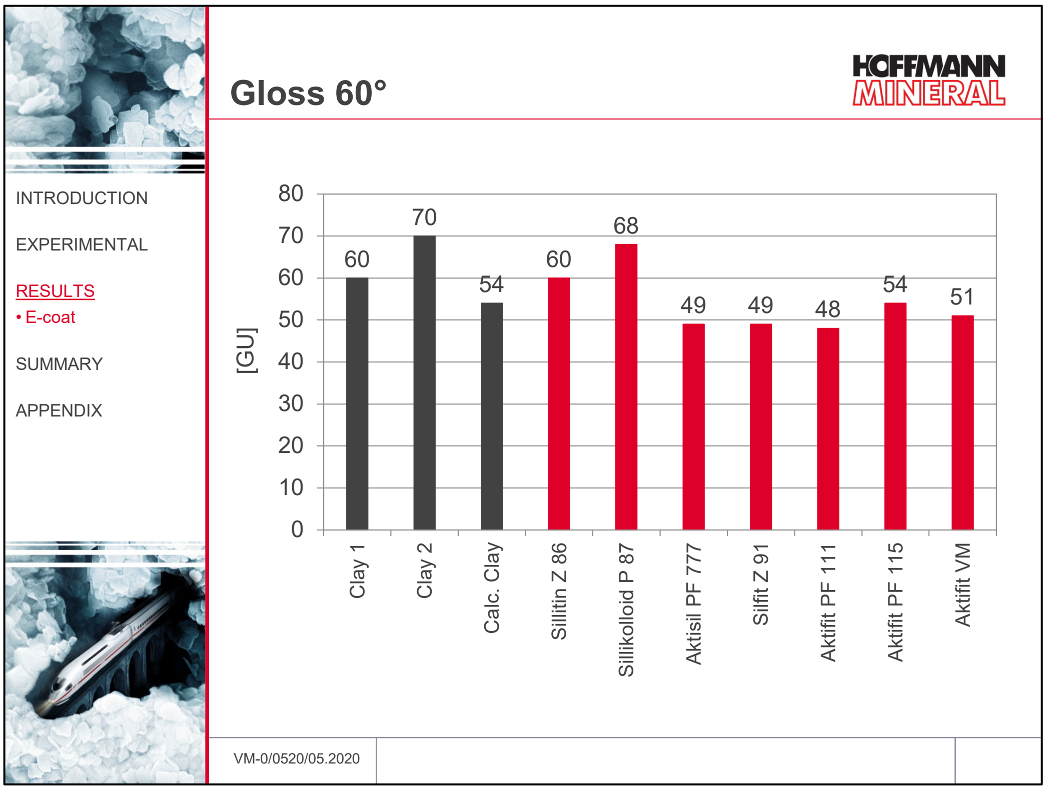


Fig. 7

Gloss deviations are often visible on the vertical and horizontal areas of the coated objects. Therefore, the gloss was measured on the four different sides of the L-panel. Here, the horizontal and facing upwards side 2 is most problematic in terms of optical losses, so only this side was used for evaluation (*Fig. 8*). Here too, the positive influence of the finer fillers Clay 2 and Sillikolloid P 87 with the highest gloss of 46 to 50 GU is shown on the critical side 2. The gloss level is clearly lower with all fillers than on the vertical side.

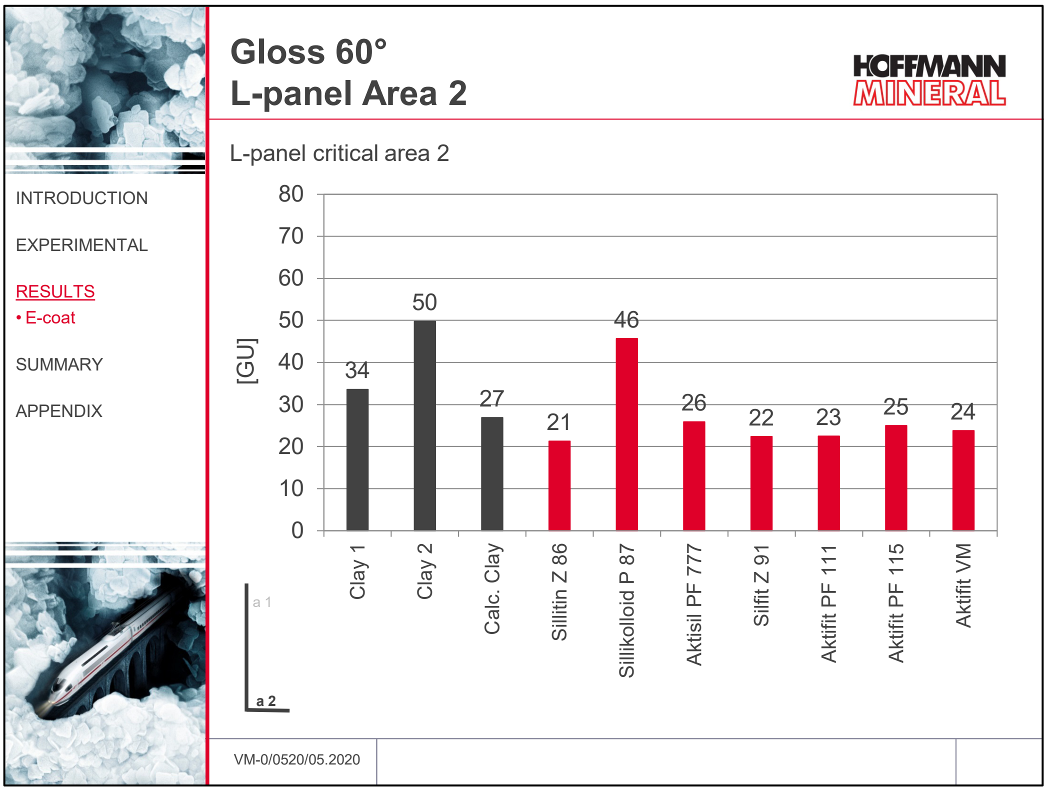


Fig. 8

Therefore, to assess the difference in gloss horizontally to vertically, the difference from side 1 to side 2 was calculated (*Fig. 9*). The smaller this difference is, the less variation in gloss on the two sides, the more advantageous is this for the object to be coated. Aktisil PF 777 shows here with a difference of 17 GU the most positive starting point.

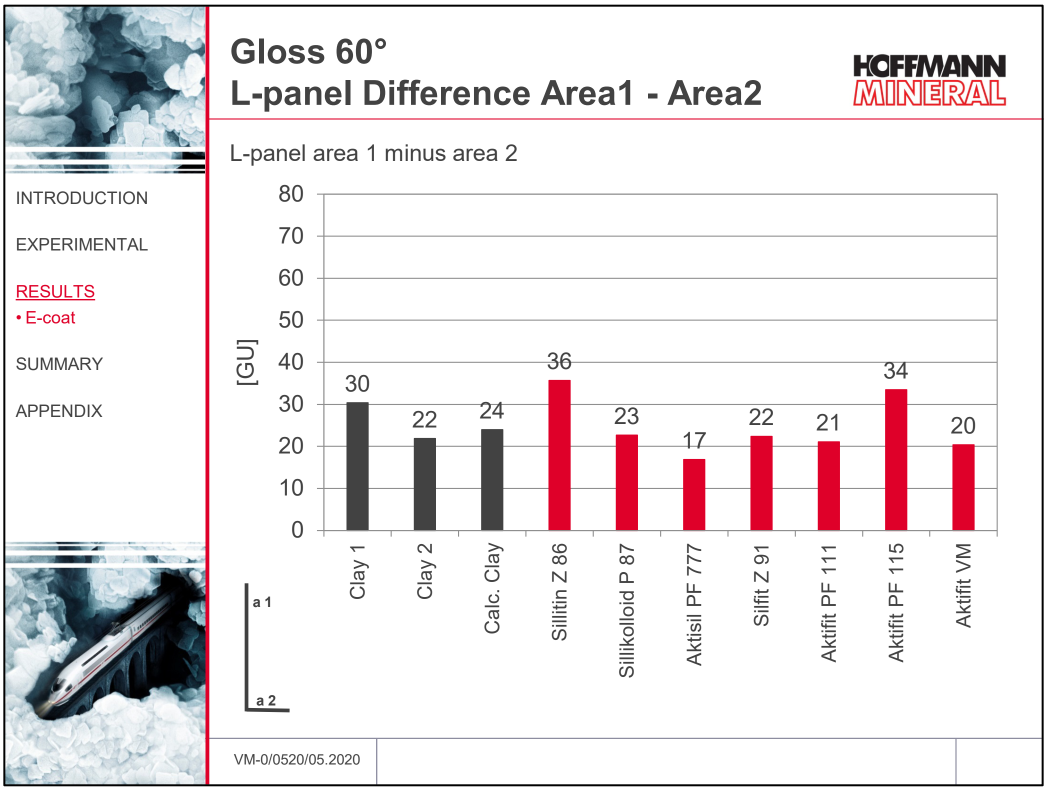


Fig. 9

4.2 Roughness

The roughness was determined with a perthometer. *Fig. 10* shows the arithmetic mean value Ra (absolute values of all profile figures of the roughness profile), which was determined on the vertical side facing the anode. The Clay 1 causes the highest roughness of the coating with slightly more than 0.6, whereas the calcined Clay reaches the lowest roughness with slightly more than 0.3. All other formulations are in between.

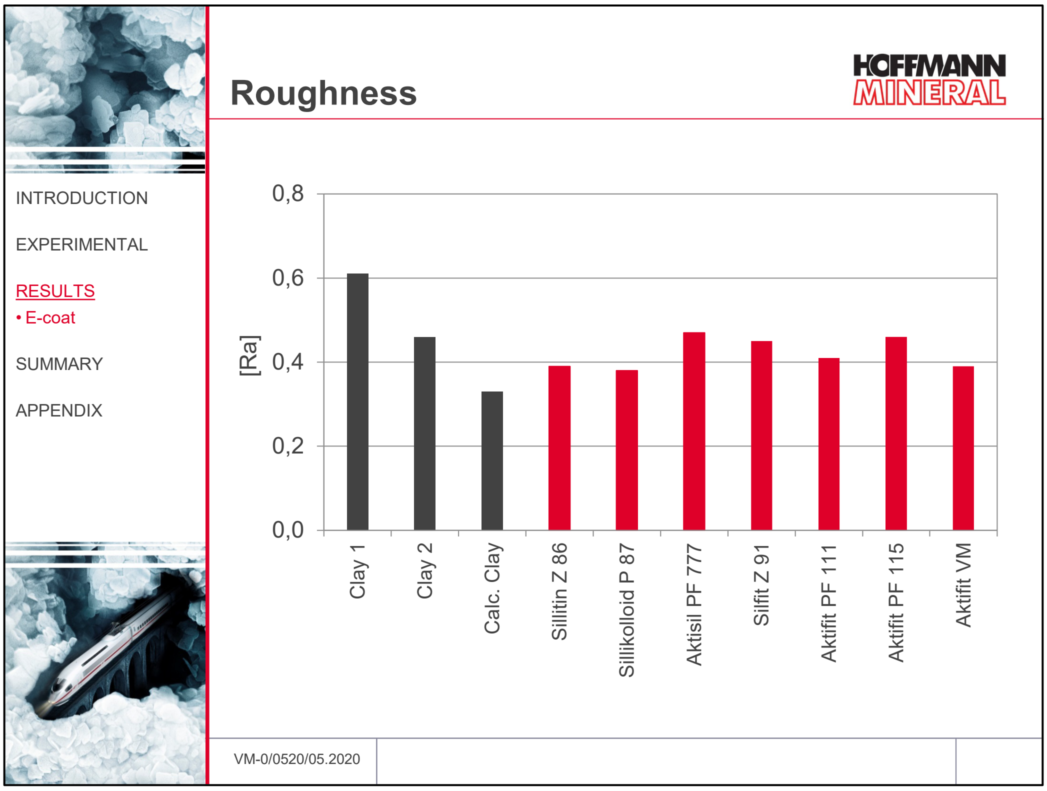


Fig. 10

Analogous to the gloss measurement, the horizontal, upward facing and problematical side 2 was also measured (*Fig. 11*). This again shows the positive influence of the fine fillers Clay 2 and especially Sillikolloid P 87 with the lowest roughness Ra of 0.4 on the critical side 2. With the exception of calcined Clay, all other fillers result in higher roughness.

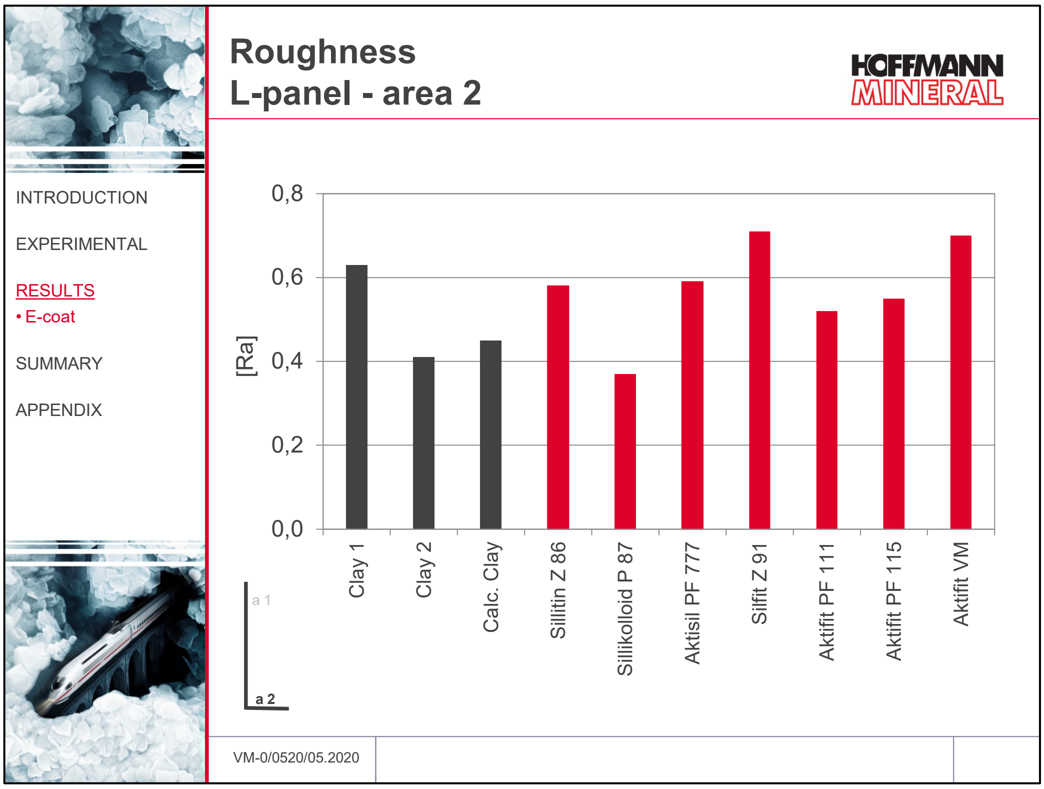


Fig. 11

Conclusion optics:

The highest gloss on all areas is achieved with the two fine fillers Clay 2 and Sillikolloid P 87. The lowest roughness can be achieved with Sillikolloid P 87. Aktisil PF 777 is a little bit more matt, but has got the best gloss maintenance as difference between vertical and horizontal side.

4.3 Cupping Test

The mechanical resistance by slow deformation with a hemisphere was determined by the Cupping Test according to DIN EN ISO 1520 and is shown in *Fig. 12*. Most fillers reach values between 5 and 6 mm, only Aktisil PF 777 and Aktifit PF 111 are slightly below. Silfit Z 91 and Aktifit VM achieve somewhat above 6 mm, Aktifit PF 115 marks the best cupping value with 6.6 mm.

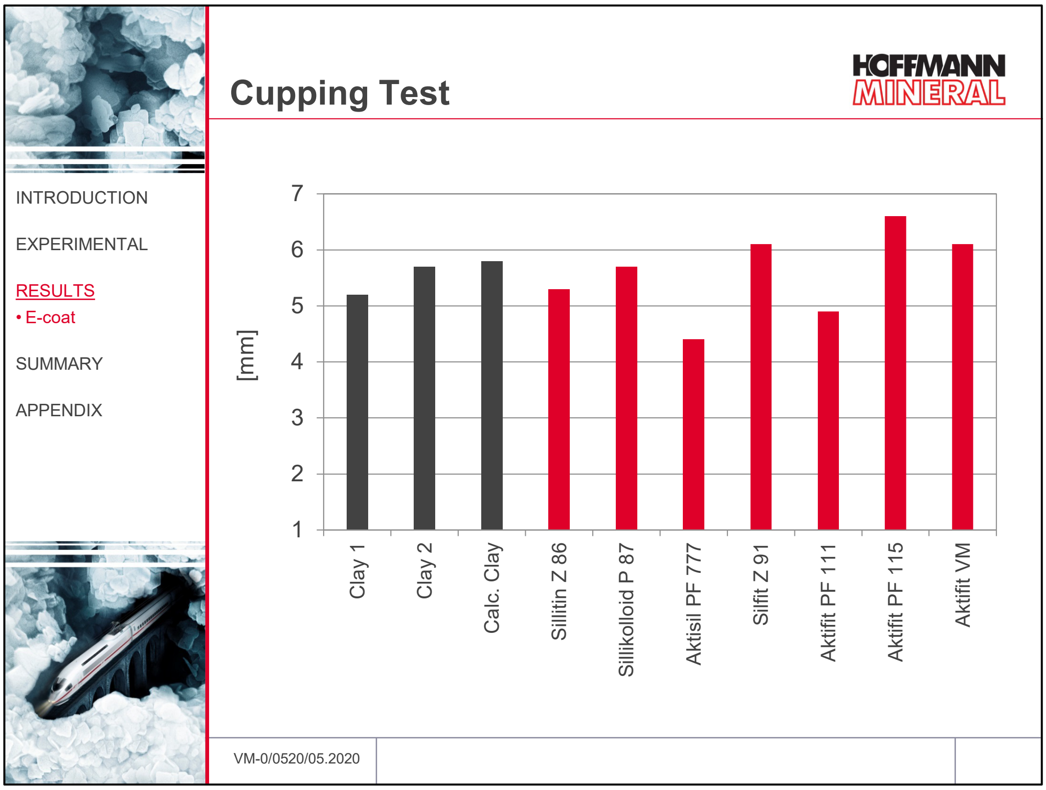


Fig. 12

4.4 Impact Test

The mechanical resistance by rapid deformation with a hemisphere was determined with the Impact Test according to DIN EN ISO 6272-2 and is shown in *Fig. 13*. The two Neuburg Siliceous Earth grades Sillitin Z 86 and Sillikolloid P 87 have slightly better impact values compared to the corresponding Clays. The two alkyl functionalized treated products Aktisil PF 777 and Aktifit PF 111 are at the same level of about 15 inchpound. However, if a calcined Clay, Silfit Z 91 or Aktifit VM is used, the flexibility can be markedly improved, the impact is 24 inchpound. An additional significant improvement can be achieved with Aktifit PF 115, with the highest impact of 32 inchpound.

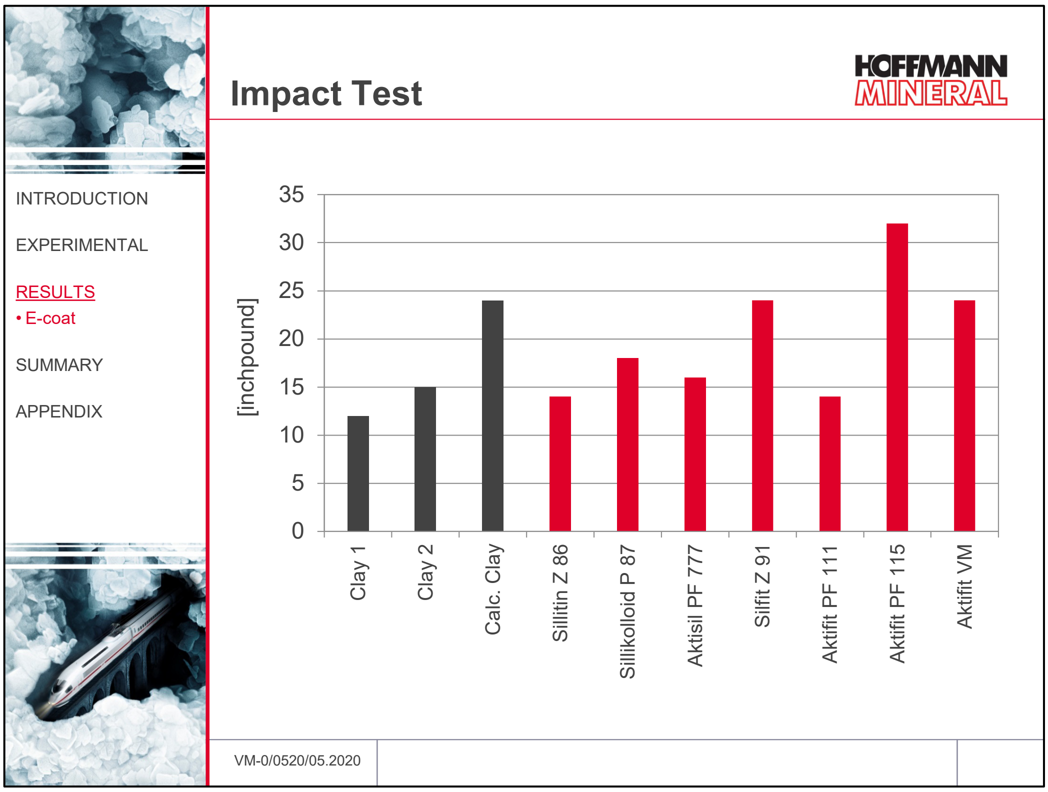


Fig. 13

Conclusion mechanical resistance/flexibility:

Sillitin Z 86 and Sillikolloid P 87 achieve slightly better impact values than the corresponding Clays. A treatment of the fillers with alkyle does not improve the mechanical properties. The calcined products, if Aktifit PF 111 is excluded, are at a considerably higher level than the non-calcined ones. For the best mechanical properties, Aktifit PF 115 with a special amino functional group surface modification is recommended.

4.5 Salt Spray Test 1000 hours

The actually most important purpose of the E-coat, the corrosion protection, was checked by the neutral Salt Spray Test according to DIN EN ISO 9227. The coated panels (double determination per formulation) were damaged before testing in a defined manner with a longitudinal scribe according to Sikkens (1 mm), so that the scribe penetrates the zinc phosphate layer and reaches completely down to the steel substrate. *Fig. 14* depicts the test specimens, the left picture shows a still unstressed panel before the Salt Spray Test, the middle picture shows a plate after 1000 hours of loading. On the surface, no blisters were visible, in and on the scribe some rust formation is visible. The right picture shows a panel after delamination. The evaluation was carried out according to DIN EN ISO 4628-8, whereby hardly any corrosion or delamination could be detected at the scribe and the evaluation was therefore grade 0-1 for all fillers.
However, a differentiation of the fillers could be made on the basis of the pitting corrosion size. As can be seen in the small section on the right in *Fig. 14*, as well as in the microscopic image enlarged using the example of calcined Clay in *Fig. 15*, the panels were rusted through in the scribed area, so that small holes were arised at these points. These holes were measured under the microscope and the average area in mm² was calculated and graphically displayed as the average value of the two specimens in *Fig. 16*. The calcined Clay had relatively many and large holes, so that the average pitting size was almost 3 mm². The Clays, Sillitin Z 86, Sillikolloid P 87, Aktisil PF 777 and Aktifit PF 115, on the other hand, already had considerably fewer and much smaller holes and thus an area of minimum 0.1 to maximum 0.7 mm². However, there were also fillers that had no holes and thus no pitting at all, such as Silfit Z 91, Aktifit PF 111 and Aktifit VM.

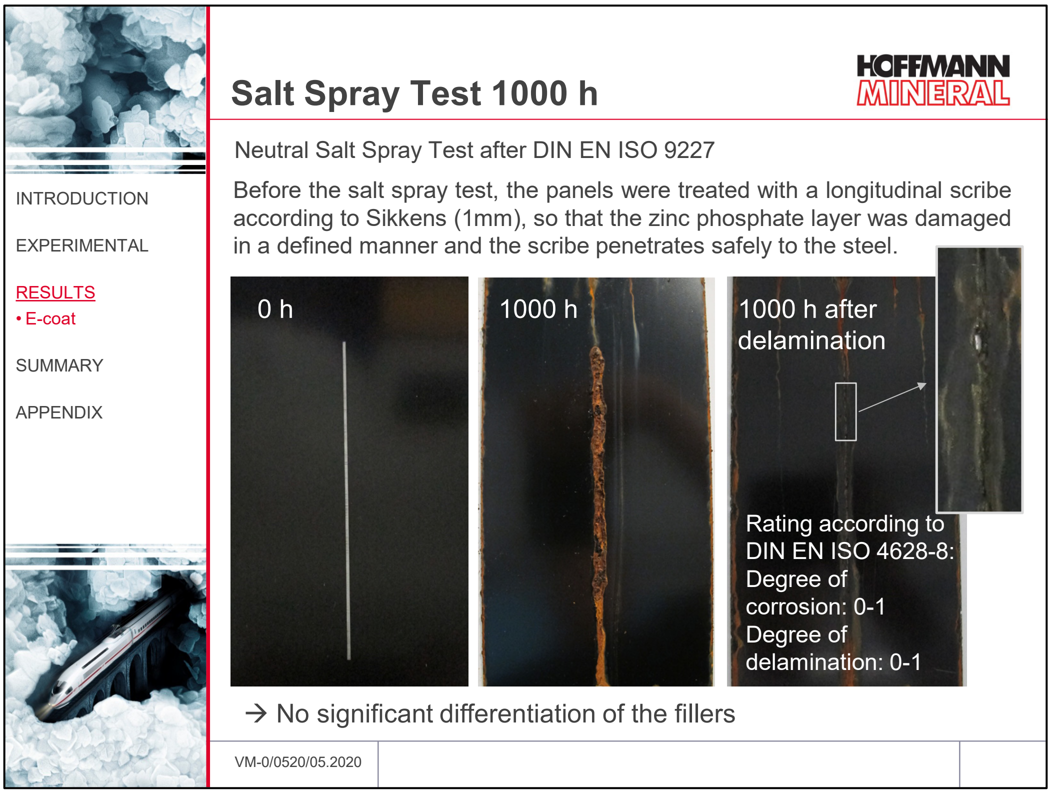


Fig.14

Salt Spray Test 1000 h

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Microscopic view: example of pitting corrosion with calcined Clay

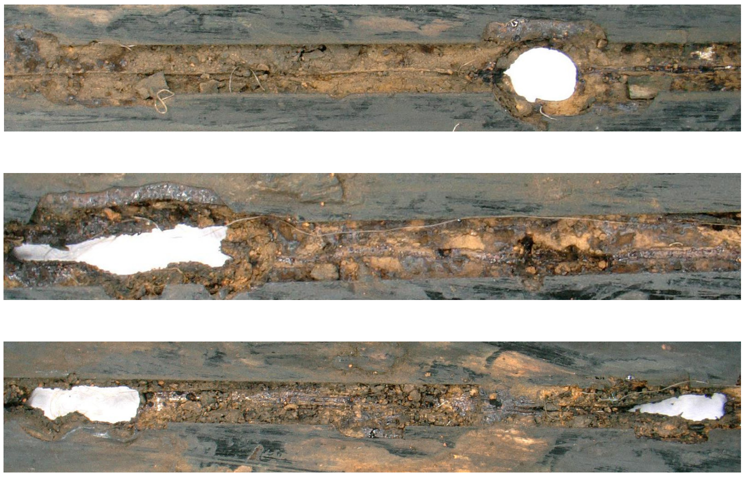

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Fig.15

Salt Spray Test 1000 h

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Area of the holes in the scribe, average value of two panels

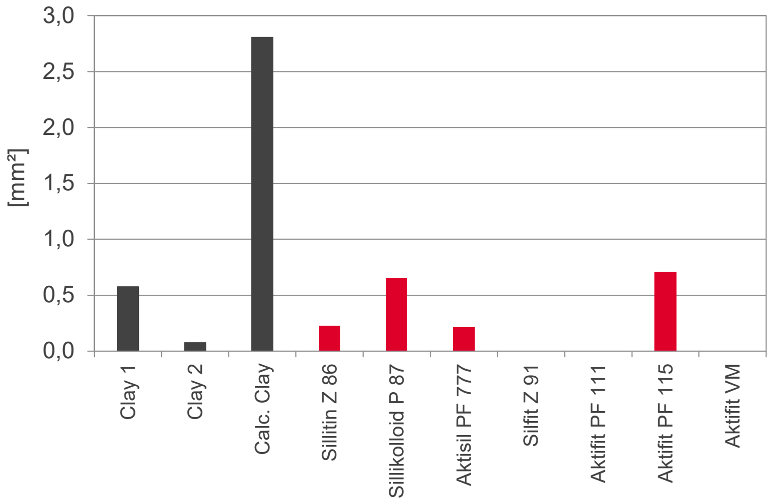

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Fig. 16

5 Summary

- Compared to the Clays, Sillitin Z 86 and Sillikolloid P 87 have a comparably good storage stability at room temperature, but an improved shelf life at raised temperatures.

  Aktisil PF 777 becomes more viscous when stored at 38 °C, but is stable over a considerably longer period of time (at least 6 months) and does not gel. It is also recommended for a visual uniform appearance on the different geometric parts (L-effect).

- Compared to calcined Clay, Silfit Z 91, Aktifit PF 111, Aktifit PF 115 and Aktifit VM offer improved storage stability even at room temperature, all Aktifit grades achieve this even at raised temperatures.

  In addition, Aktifit PF 115 achieves better mechanical values (cupping and impact test).

  All calcined Neuburg Siliceous Earth products show a significant improvement in corrosion protection.

6 Appendix filler characteristics

		Clay 1	Clay 2	Calcined Clay	Sillitin Z 86	Sillikolloid P 87	Aktisil PF 777	Silfit Z 91	Aktifit PF 111	Aktifit PF 115	Aktifit VM
Particle size d50	µm	3.3	2.0	2.0	1.9	1.5	2.2	2.0	2.0	2.0	2.0
d97	µm	15	10	11	9	6	10	10	10	10	10
Residue > 40µm	ppm	23	94	35	20	20	20	10	10	10	10
Electrical conductivity	µS / cm	177	166	12	80	80	n.a. (hydrophobic)	20	n.a. (hydrophobic)	n.a. (hydrophobic)	n.a. (hydrophobic)
Oil absorption	g / 100g	53	50	106	55	55	35	65	60	60	65
Specific surface area BET	m²/g	17	18	15	12	13	9	10	9	9	9
Surface treatment		-	-	-	-	-	alkyl functionalized	-	alkyl functionalized	Special amino functionalized	vinyl functionalized