Electrophoretic deposition - Neuburg Siliceous Earth in black cathodic deposition paints

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Status Quo

Sillitin Z 86 and Sillitin P 87 have been successfully used for many years in the field of electrodeposition coatings by a number of major corporation.

Traditionally, these products achieve an excellent property profile. They are characterized by very good storage stability of the pigment paste as well as bath stability. In addition to advantageous edge covering, the Neuburg Silicous Earth grades achieve good coating flexibility (impact and cupping test), even in "low density" formulations with low titanium dioxide content.

Status Quo

The new product line of Calcined Neuburg Siliceous Earth is suitable for electrodeposition applications due to lowest possible sieve residues, excellent dispersion properties, highest brightness and color neutrality, and very good results in other applications such as powder coatings.

Furthermore, the question of additional performance is raised by the with a functional group surface-treated products Aktisil and Aktifit which, depending on the functionality selected, can achieve hydrophobicity, rheology control and covalent bonding.

Objective

In this study, the traditional and new types of (Calcined) Neuburg Siliceous Earth in the current binder generation are tested in comparison with competitors on the market.

In cooperation with the company Allnex (Graz, Austria), a standard binder system for automotive add-on and spare parts was selected, in which the fillers were tested for their effects in

- a black pigment paste
- and the complete e-coat

Overview of the selected fillers

Clays:
Clay 1
Clay 2 (slightly finer than clay 1)
Calcined Clay

Neuburg Siliceous Earth (NSE):
Sillitin Z 86, standard product
Sillitin P 87, finer, standard recommendation after Z 86
Aktisil PF 777, Sillitin Z 86 alkyl functionalized, hydrophobic

Calcined Neuburg Siliceous Earth (CNSE):
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 VM, Silfit Z 91 vinyl functionalized, hydrophobic

Characteristics in appendix

Pigment Paste
Base Formulation

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**

E-Coat
Base Formulation

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 %

Preparation / Application / Curing

Preparation Pigment paste:

Dissolver with adapted bead mill, teflon disc and glass beads, 10 minutes at 7.9 m/s.

Preparation E-Coat:

Mix pigment paste, water and binder dispersion with blade agitator and fill into the deposition vessel, stir for about 2 hours, then deposit.

Deposition:

Voltage series with 260, 280 and 300 V and note down the corresponding charge, determine the analog film thickness and individual setting of the charge (50-54 Coulomb) for each individual recipe so that the film thickness is ± 30 µm

Typical bath values:

pH value according to DIN ISO 976: 5.3 – 5.6

Specific conductivity DIN 53779: 1100 – 1350 µS/cm

Curing conditions:

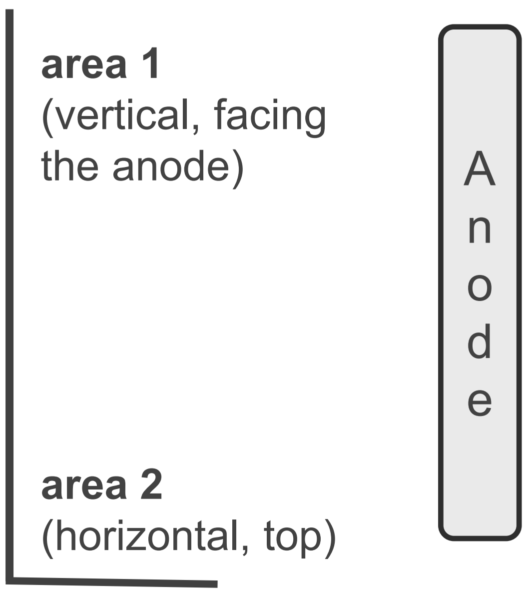
Oven temperature 180 °C, dwelling time 25 minutes

Substrate

Gardobond 26S/6800/OC (Steel, zinc phosphated)

Optical and mechanical testings as well as L-effect (gloss and roughness on horizontal and vertical surface areas)

Arrangement of the L-panels in the bath; the substrate is the cathode



Deposition at 300 V, 120 s, stirrer on

Viscosity

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• Pigment paste

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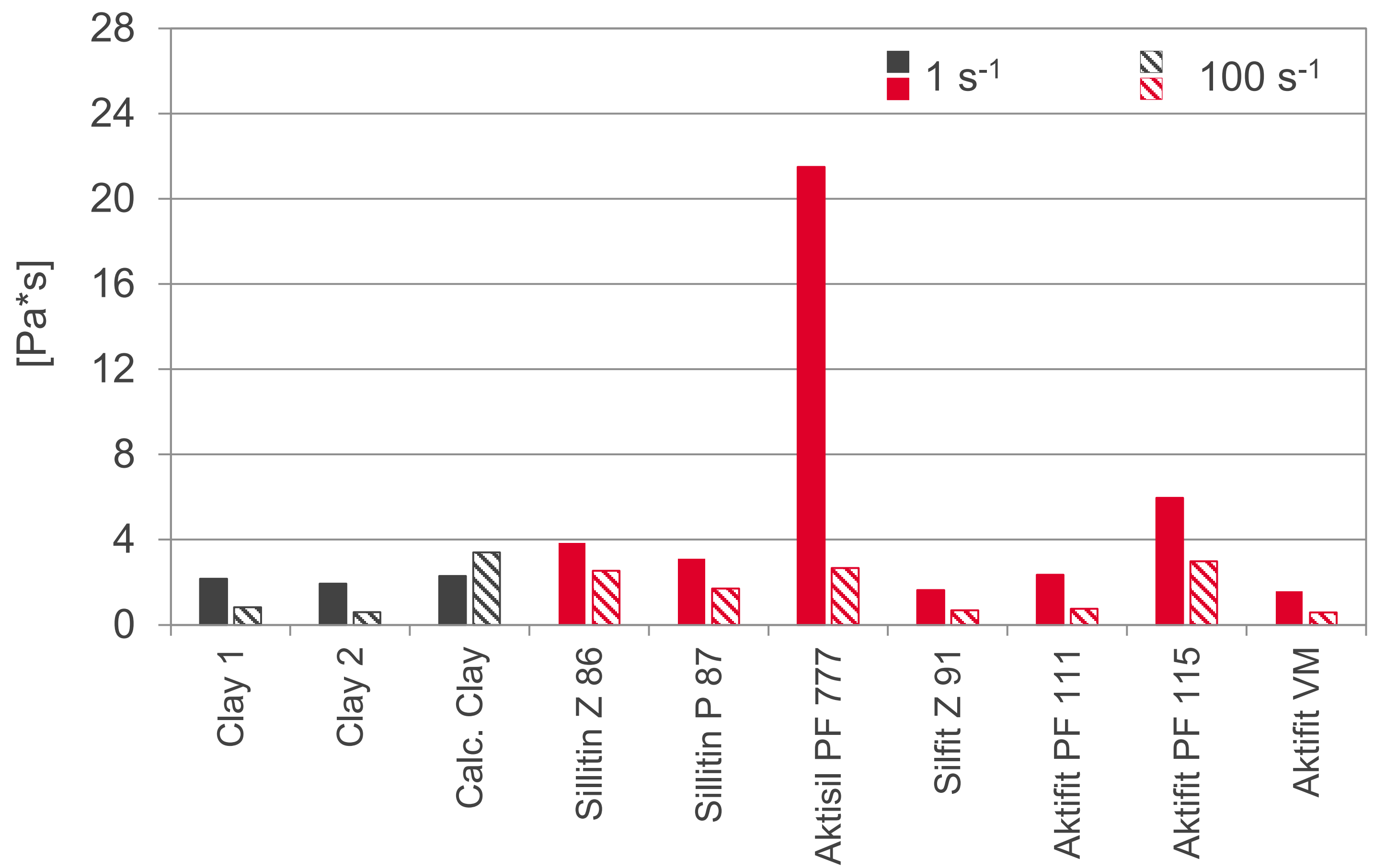
1 d after preparation, shear rate 1 and 100 s^{-1}



Storage Stability
at Room Temperature 23 °C

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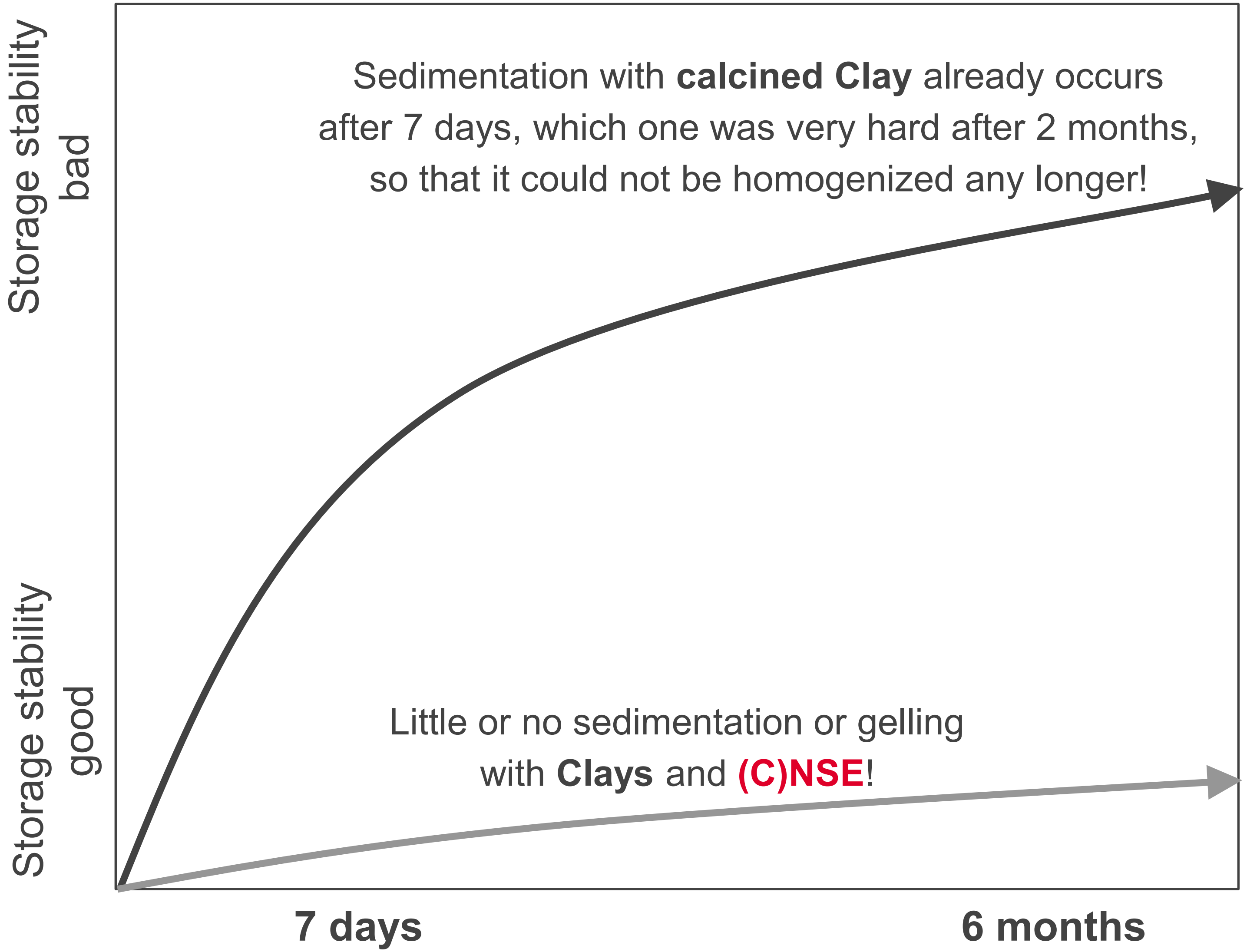

Storage Stability
at Room Temperature 23 °C

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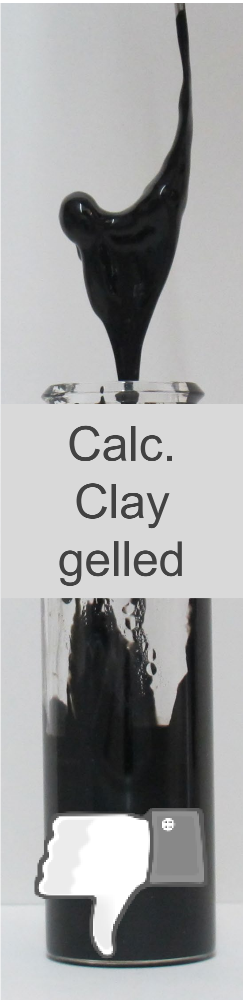
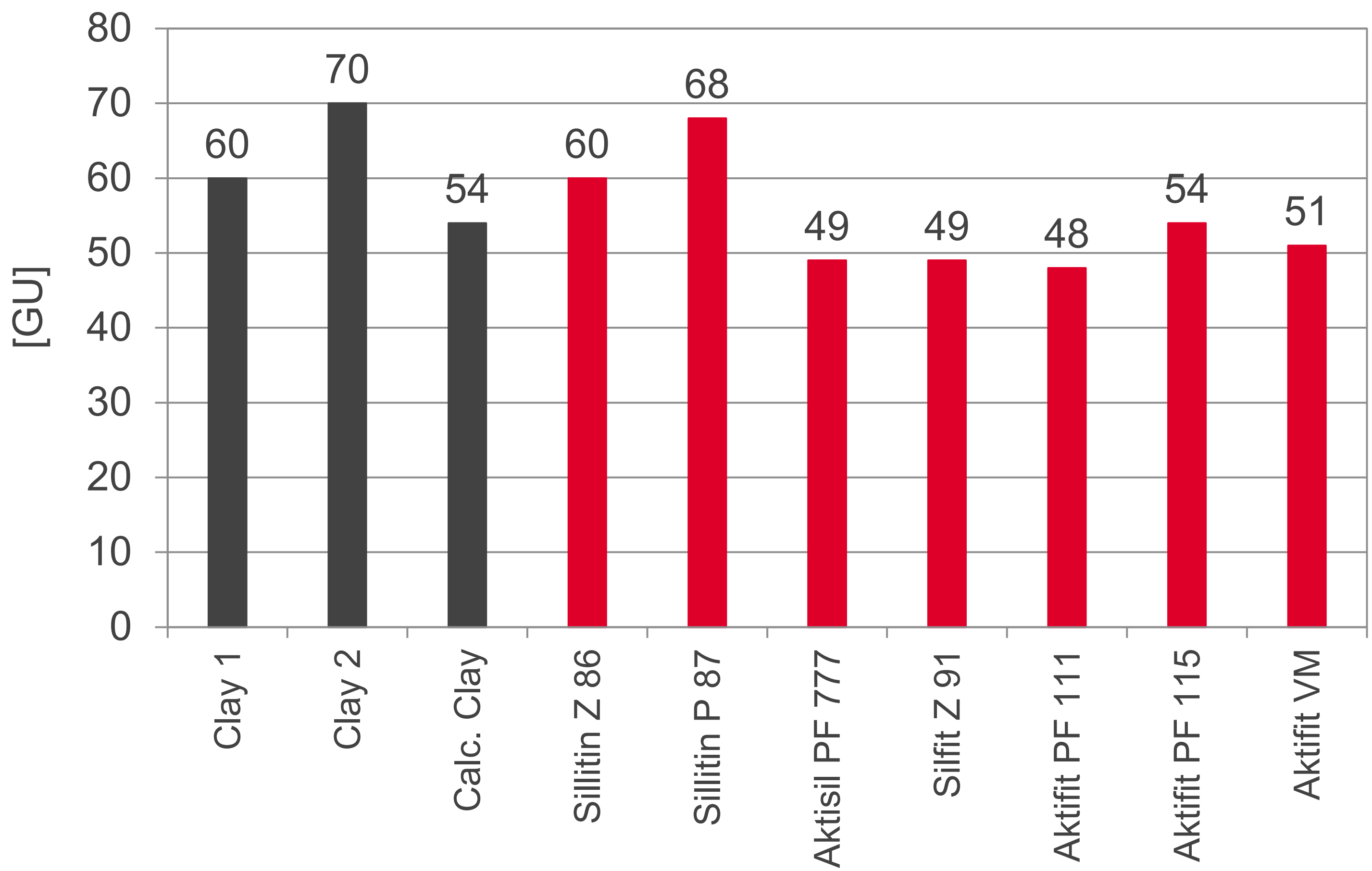
after 6 months



Storage Stability
at Increased Temperature 38 °C

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

Gloss 60°



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68
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49
48
54
51
Clay 1
Clay 2
Calc. Clay
Sillitin Z 86
Sillitin P 87
Aktisil PF 777
Silfit Z 91
Aktifit PF 111
Aktifit PF 115
Aktifit VM

Gloss 60°
L-panel Area 2

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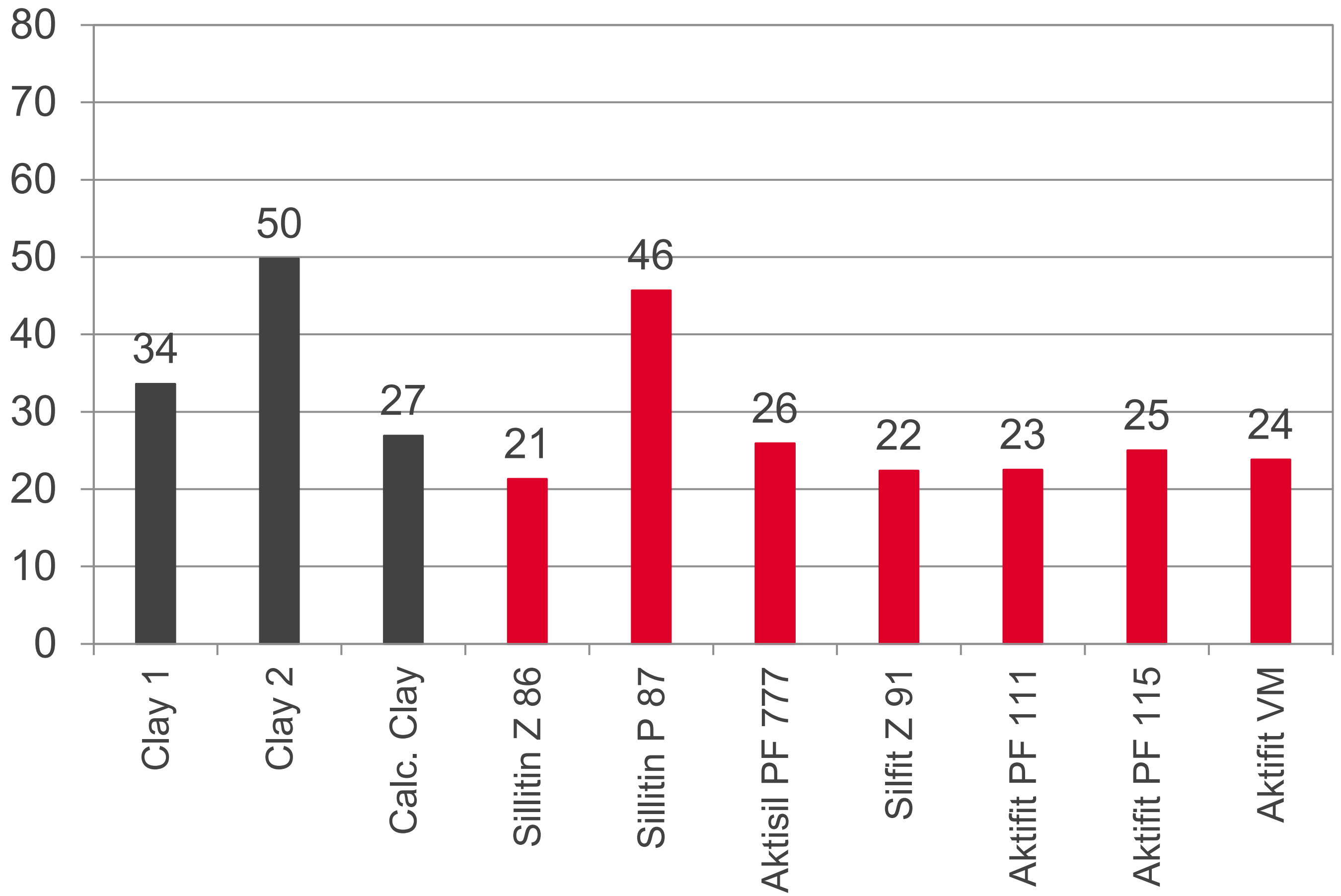
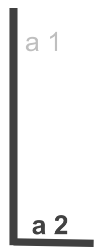
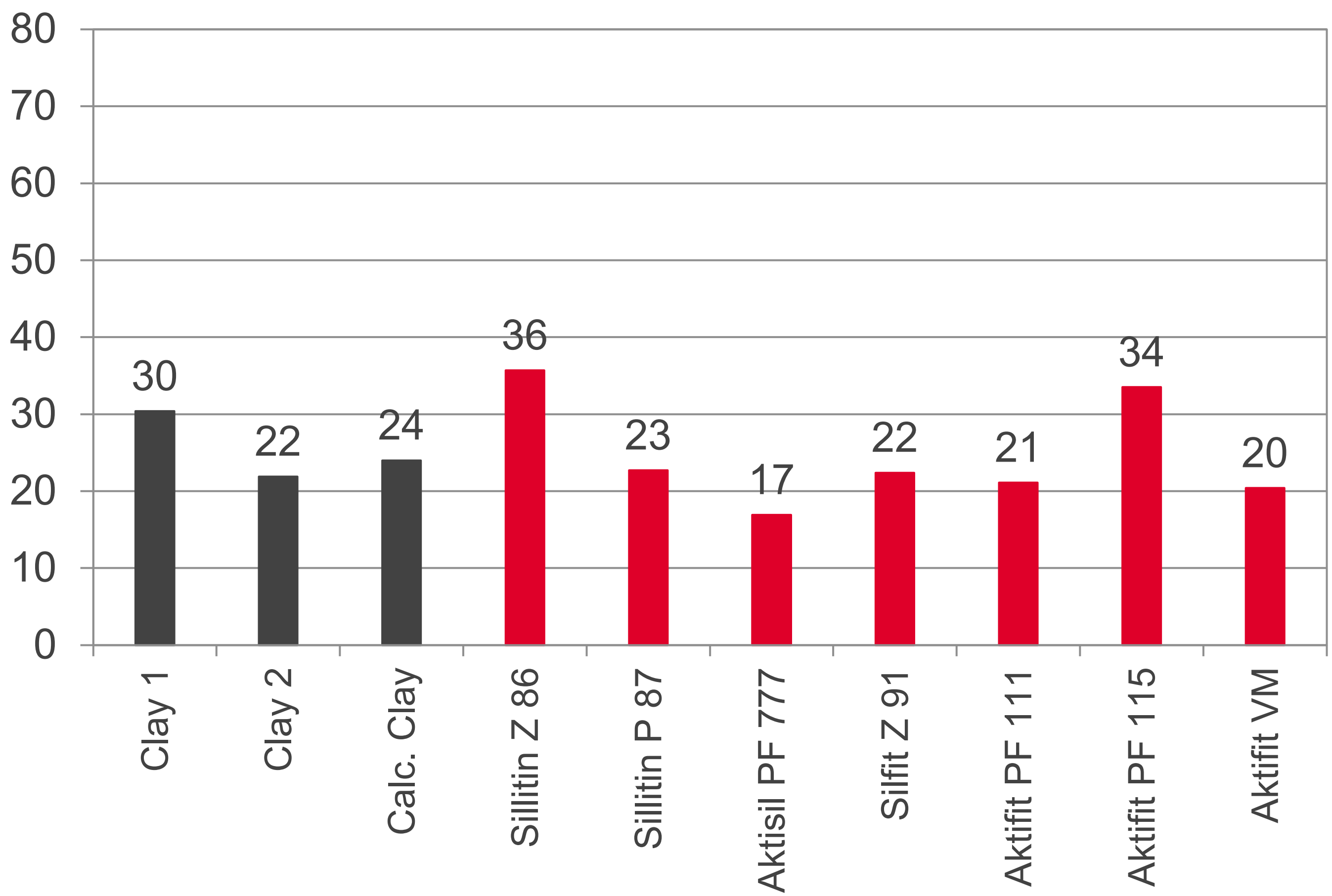
L-panel critical area 2

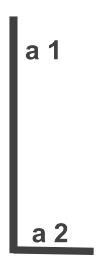




Gloss 60°
L-panel Difference Area1 - Area2

L-panel area 1 minus area 2





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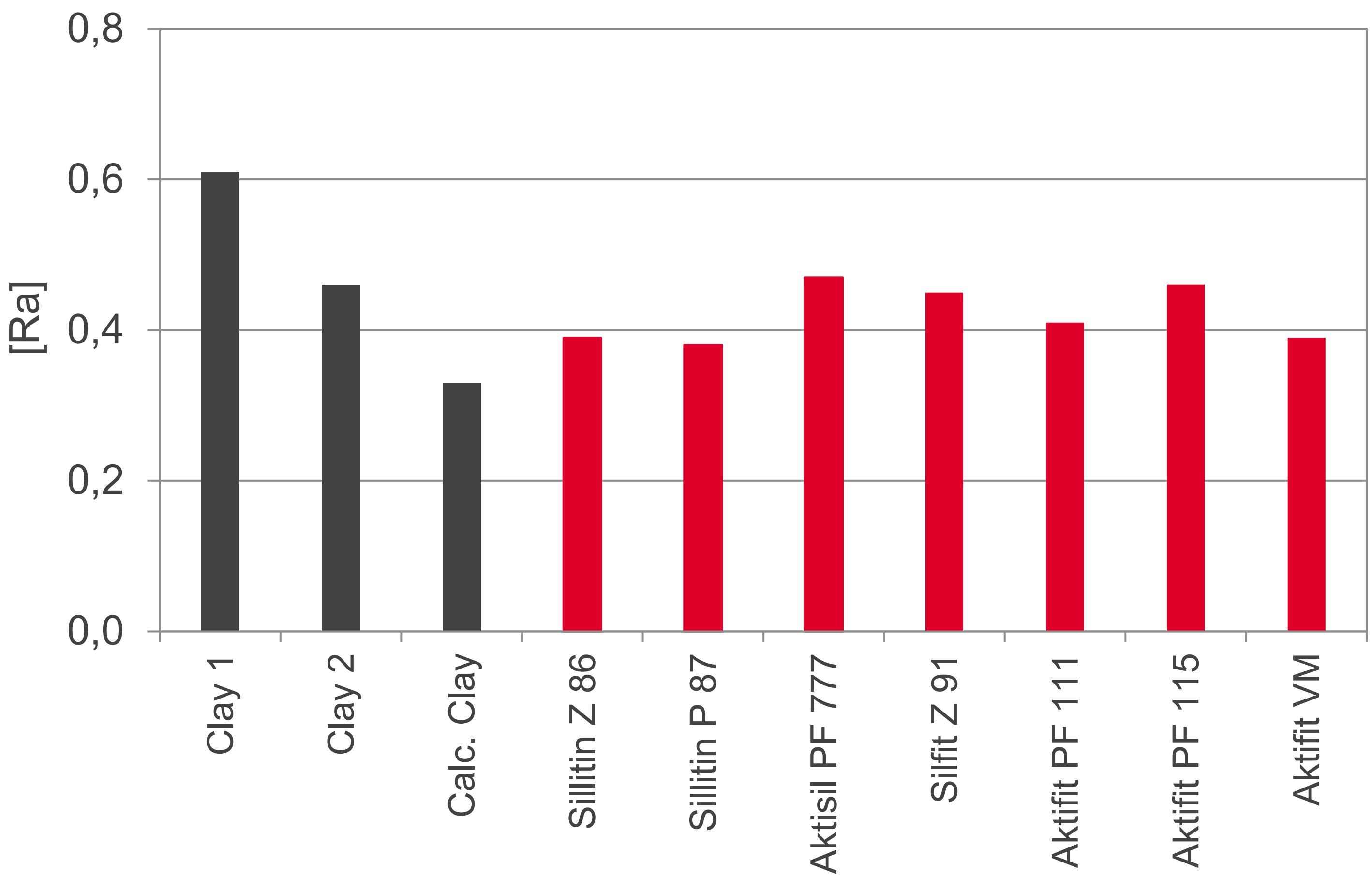
Roughness



Roughness
L-panel - area 2

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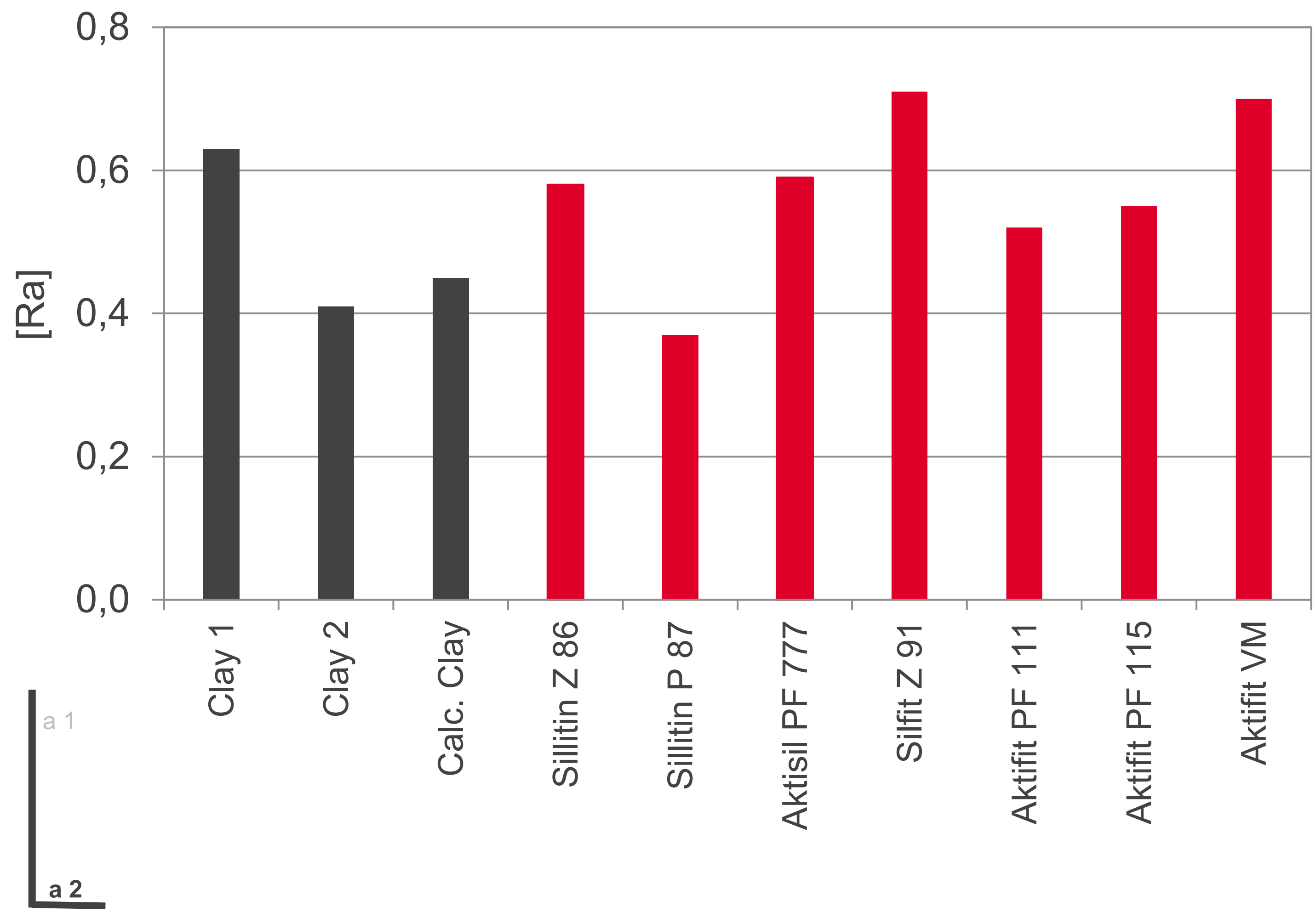
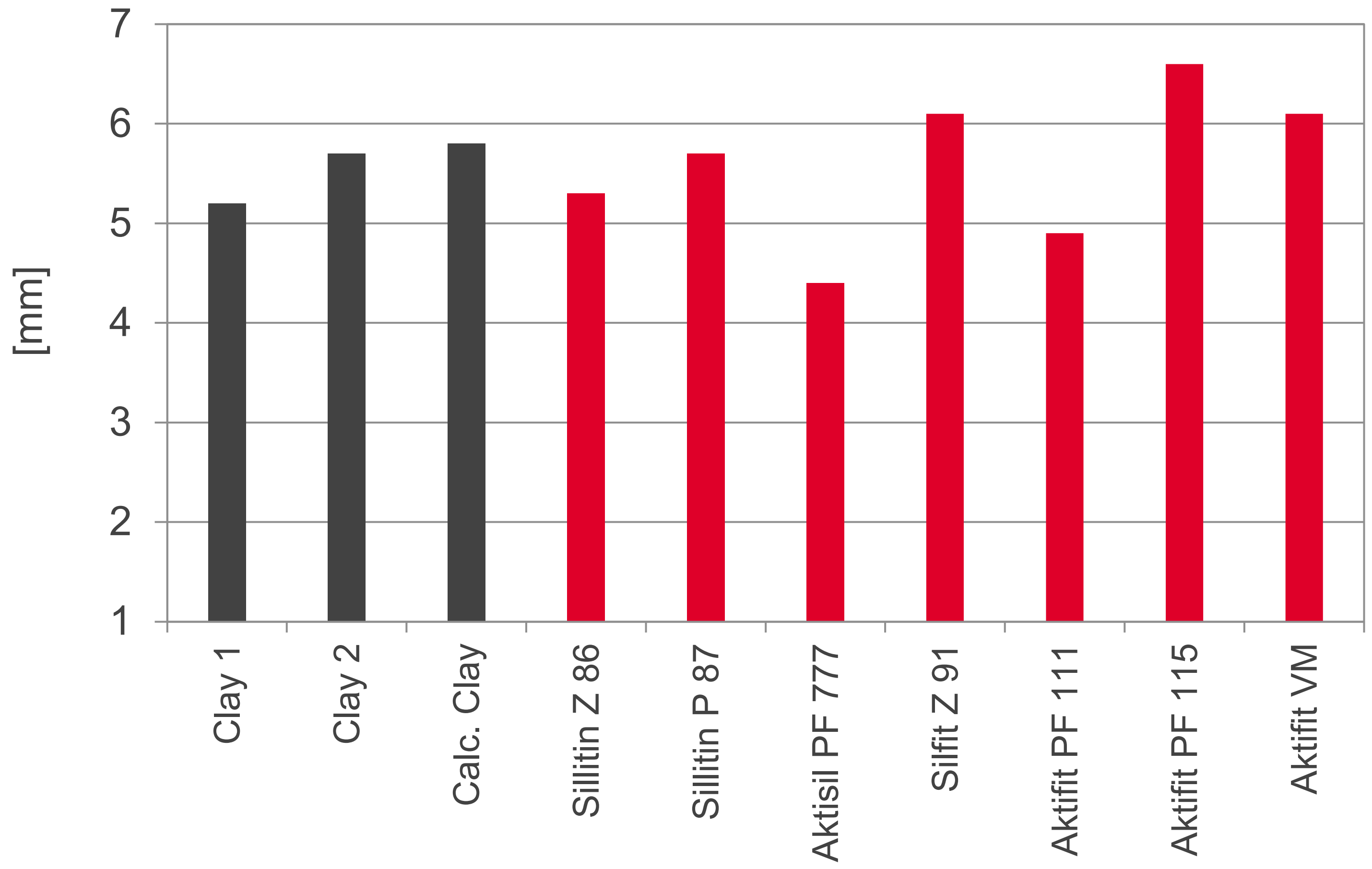
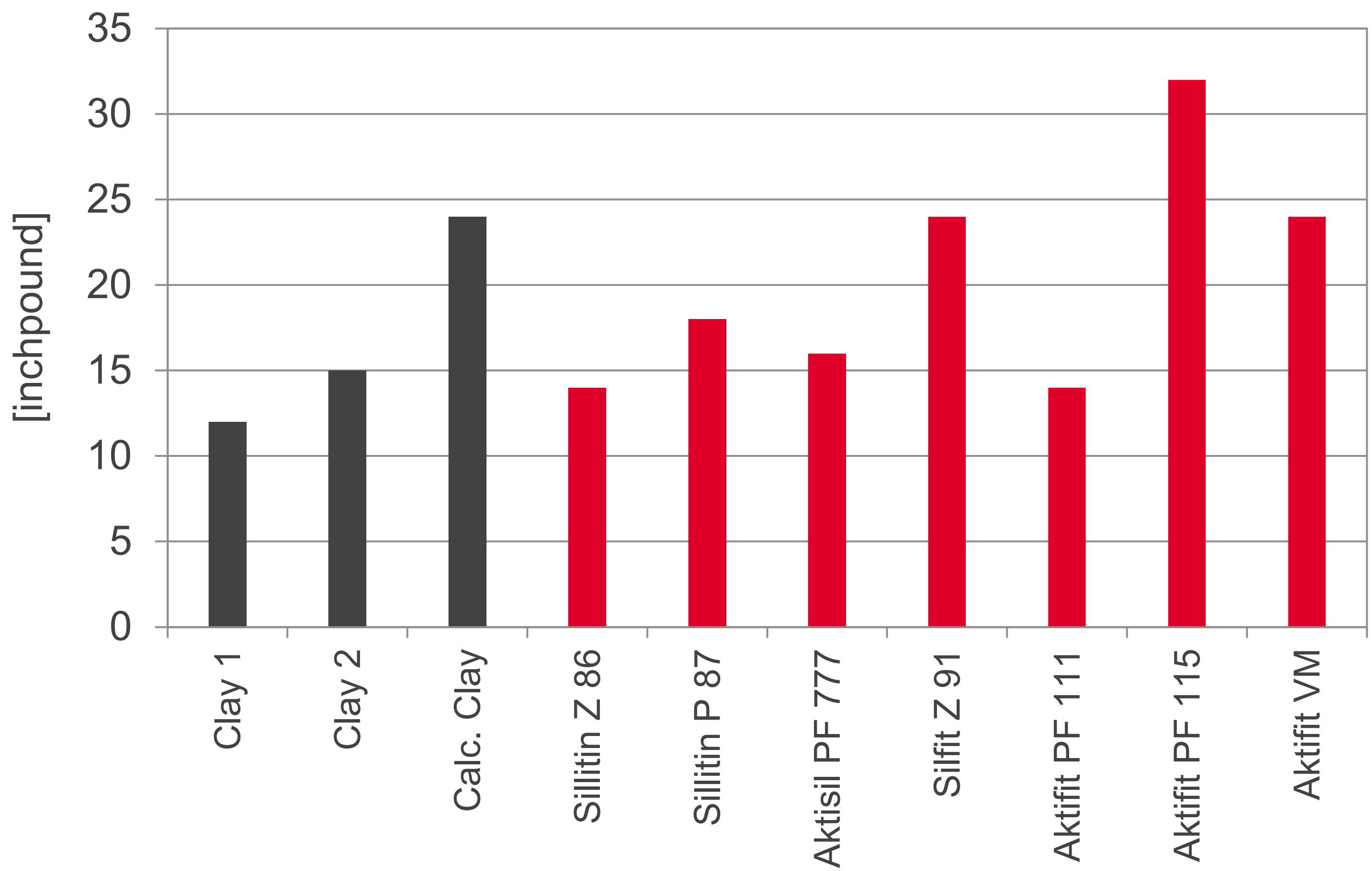


Cupping Test



Impact Test


35
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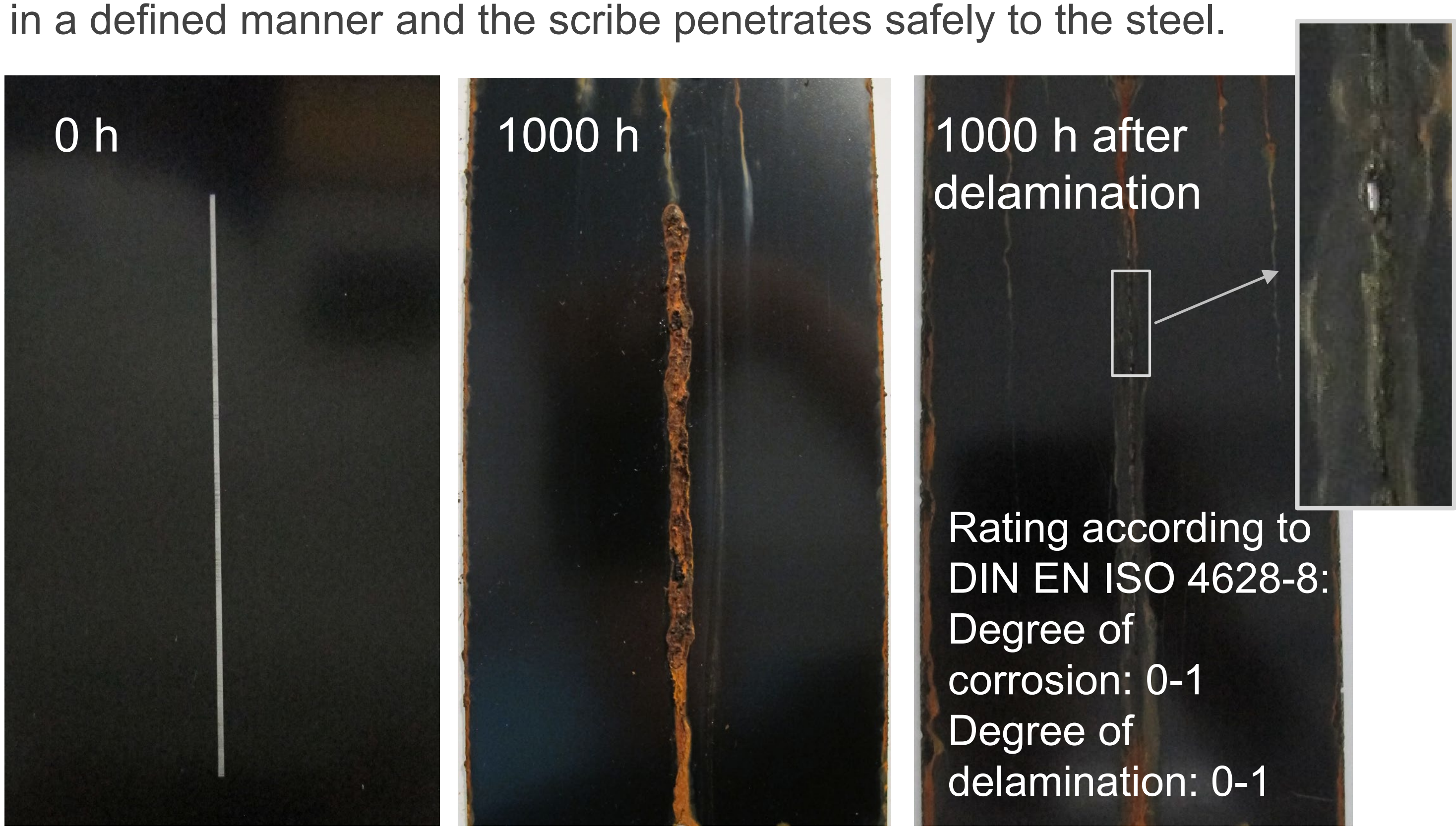
[inchpound]
Clay 1
Clay 2
Calc. Clay
Sillitin Z 86
Sillitin P 87
Aktisil PF 777
Silfit Z 91
Aktifit PF 111
Aktifit PF 115
Aktifit VM

Salt Spray Test 1000 h

Neutral Salt Spray Test after DIN EN ISO 9227

Before the salt spray test, the panels were treated with a longitudinal scribe according to Sikkens (1mm), so that the zinc phosphate layer was damaged in a defined manner and the scribe penetrates safely to the steel.



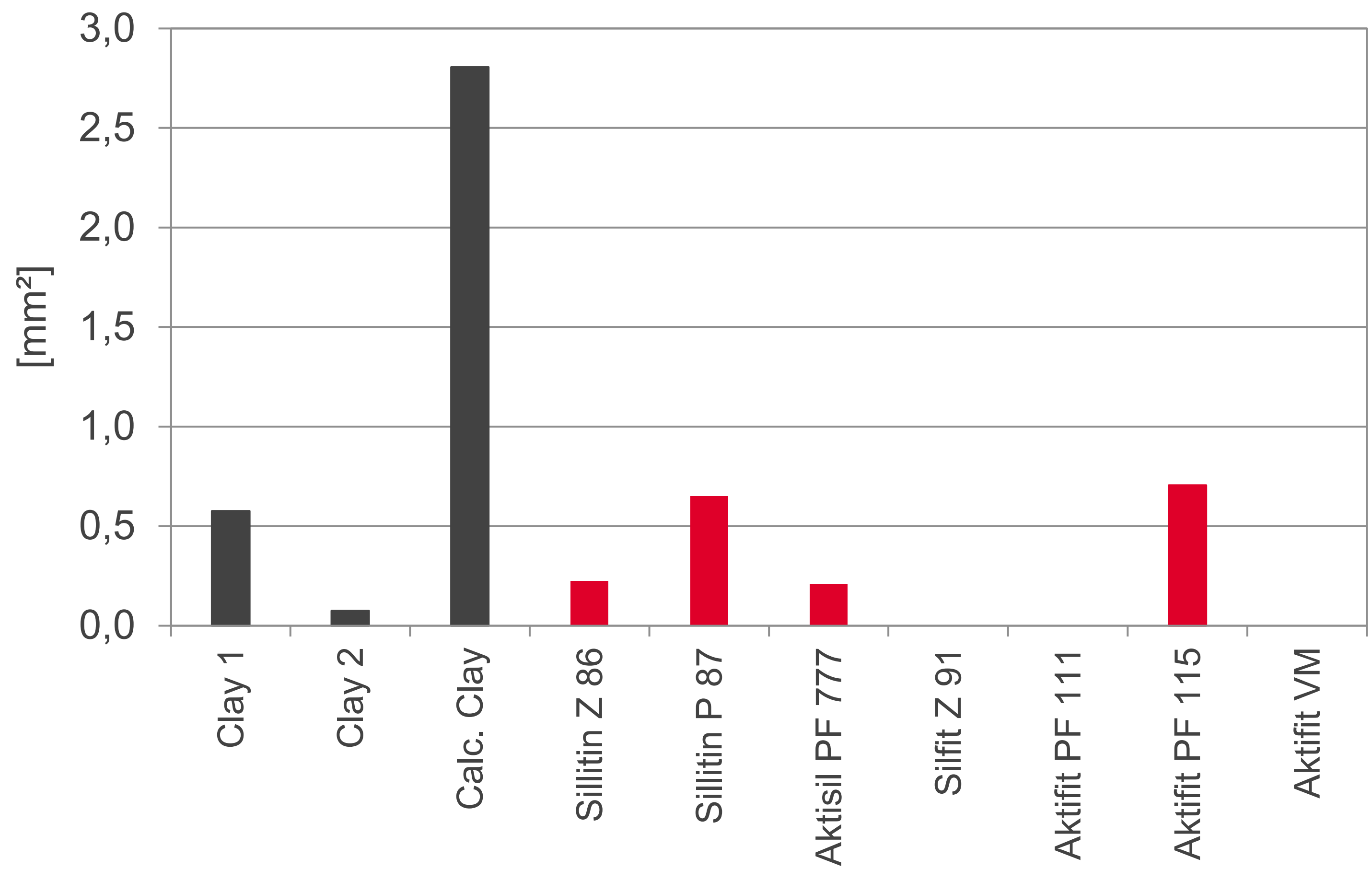
→ No significant differentiation of the fillers

Salt Spray Test 1000 h

Microscopic view: example of pitting corrosion with calcined Clay

Salt Spray Test 1000 h

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



Sillitin Z 86 and Aktisil PF 777 vs. Clay 1

Clay 1
Reference base

Sillitin Z 86

- improved storage stability of pigment paste at 38°C
- reduced roughness vertical area
- slightly higher Impact

Aktisil PF 777

- best storage stability of pigment paste at 38°C
- matting, but in return best maintaining of gloss L-panel, horizontal area
- slightly higher Impact

Sillitin P 87
vs. Clay 2

Clay 2
Reference base

Sillitin P 87

- improved storage stability of pigment paste at 38°C
- slightly reduced roughness vertical area and
  L-panel horizontal area
- slightly higher Impact

Silfit Z 91 and Aktifit Types vs. Calcined Clay

Calcined Clay
Reference base

Silfit Z 91

- improved storage stability of pigment paste at 23°C
- markedly improved corrosion resistance, no pitting corrosion

Aktifit

- best storage stability of pigment paste at 38°C with all Aktifit types, and over a long period of time with Aktifit PF 111 and Aktifit PF 115
- highest Impact with Aktifit PF 115
- markedly improved corrosion resistance

Summary

- Compared to the Clays, Sillitin Z 86 and Sillitin 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 by storage 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 with the calcined Clay, Silfit Z 91, Aktifit PF 111, Aktifit PF 115 und Aktifit VM offer improved storage stability even at room temperature. All Aktifit types achieve this even at raised temperatures.
  In addition, the Aktifit PF 115 achieves better mechanical values (cupping and Impact Test).
  All Calcined Neuburg Siliceous Earth products show a significant improvement in corrosion protection.

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Filler Characteristics

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	Clay 1
Particle size d_{50} [µm]	3.3
Particle size d_{97} [µm]	14.7
Residue > 40µm [mg/kg]	23
Electrical conductivity [µS/cm]	177
Oil absorption [g/100g]	53
Spec. surface area BET [m²/g]	17
Surface treatment	-

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Filler Characteristics

	Clay 2
Particle size d_{50} [µm]	2
Particle size d_{97} [µm]	10
Residue > 40µm [mg/kg]	94
Electrical conductivity [µS/cm]	166
Oil absorption [g/100g]	50
Spec. surface area BET [m²/g]	18
Surface treatment	-

Filler Characteristics

	Calcined Clay
Particle size d_{50} [µm]	2
Particle size d_{97} [µm]	11
Residue > 40µm [mg/kg]	35
Electrical conductivity [µS/cm]	12
Oil absorption [g/100g]	106
Spec. surface area BET [m²/g]	15
Surface treatment	-

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Filler Characteristics

Neuburg Siliceous Earth	Sillitin Z 86
Particle size d_{50} [µm]	1.9
Particle size d_{97} [µm]	9
Residue > 40µm [mg/kg]	20
Electrical conductivity [µS/cm]	80
Oil absorption [g/100g]	55
Spec. surface area BET [m²/g]	12
Surface treatment	-

Filler Characteristics

Neuburg Siliceous Earth	Sillitin P 87
Particle size d_{50} [µm]	1.5
Particle size d_{97} [µm]	6.0
Residue > 40µm [mg/kg]	20
Electrical conductivity [µS/cm]	80
Oil absorption [g/100g]	55
Spec. surface area BET [m²/g]	13
Surface treatment	-

Filler Characteristics

Neuburg Siliceous Earth	Aktisil PF 777
Particle size d_{50} [µm]	2.2
Particle size d_{97} [µm]	10
Residue > 40µm [mg/kg]	20
Electrical conductivity [µS/cm]	n. a. (hydrophobic)
Oil absorption [g/100g]	35
Spec. surface area BET [m²/g]	9
Surface treatment	alkyl functionalized

Filler Characteristics

Calcined Neuburg Siliceous Earth	Silfit Z 91
Particle size d_{50} [µm]	2
Particle size d_{97} [µm]	10
Residue > 40µm [mg/kg]	10
Electrical conductivity [µS/cm]	20
Oil absorption [g/100g]	65
Spec. surface area BET [m²/g]	10
Surface treatment	-

Filler Characteristics

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Calcined Neuburg Siliceous Earth	Aktifit PF 111
Particle size d_{50} [µm]	2
Particle size d_{97} [µm]	10
Residue > 40µm [mg/kg]	10
Electrical conductivity [µS/cm]	n. a. (hydrophobic)
Oil absorption [g/100g]	60
Spec. surface area BET [m²/g]	9
Surface treatment	alkyl functionalized

Filler Characteristics

Calcined Neuburg Siliceous Earth	Aktifit PF 115
Particle size d_{50} [µm]	2
Particle size d_{97} [µm]	10
Residue > 40µm [mg/kg]	10
Electrical conductivity [µS/cm]	n. a. (hydrophobic)
Oil absorption [g/100g]	60
Spec. surface area BET [m²/g]	9
Surface treatment	special amino functionalized

Filler Characteristics

Calcined Neuburg Siliceous Earth	Aktifit VM
Particle size d_{50} [µm]	2
Particle size d_{97} [µm]	10
Residue > 40µm [mg/kg]	10
Electrical conductivity [µS/cm]	n. a. (hydrophobic)
Oil absorption [g/100g]	65
Spec. surface area BET [m²/g]	9
Surface treatment	vinyl functionalized