# Neuburg Siliceous Earth
# in cathodic electrodeposition coatings

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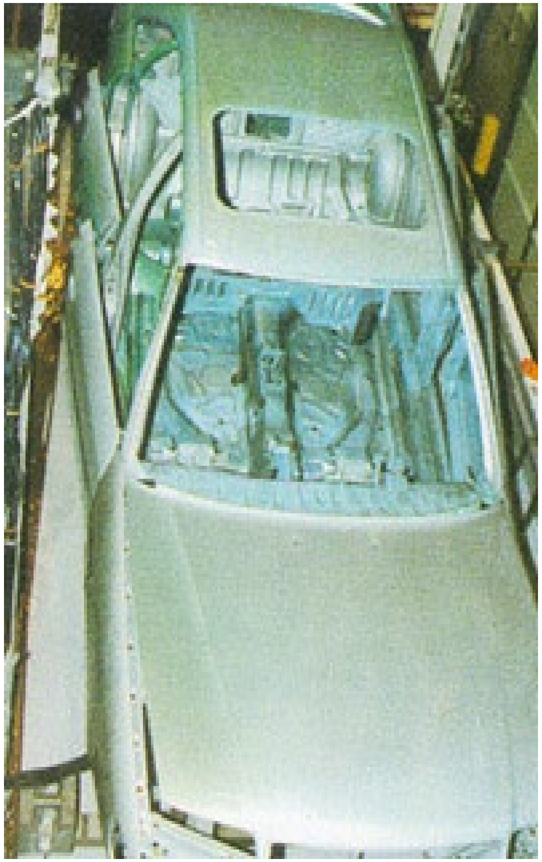
# Content

# Introduction





The project was carried out by the „Fachhochschule Niederrhein“ University of Applied Science) in cooperation with Dr. Kimpel, DuPont Performance Coatings GmbH (DPC), Wuppertal, between Juli 2001 and April 2003

# Introduction



**Objectives:**

- Evaluation of different Neuburg Siliceous Earth grades in bright automotive cathodic EDP formulations under conditions close to actual practice
- The effects of reducing the content of titanium dioxide
- The focus is on Low-Density

**Evaluation criteria:**

- Dip bath properties
- Coating performance

# Pigment Paste



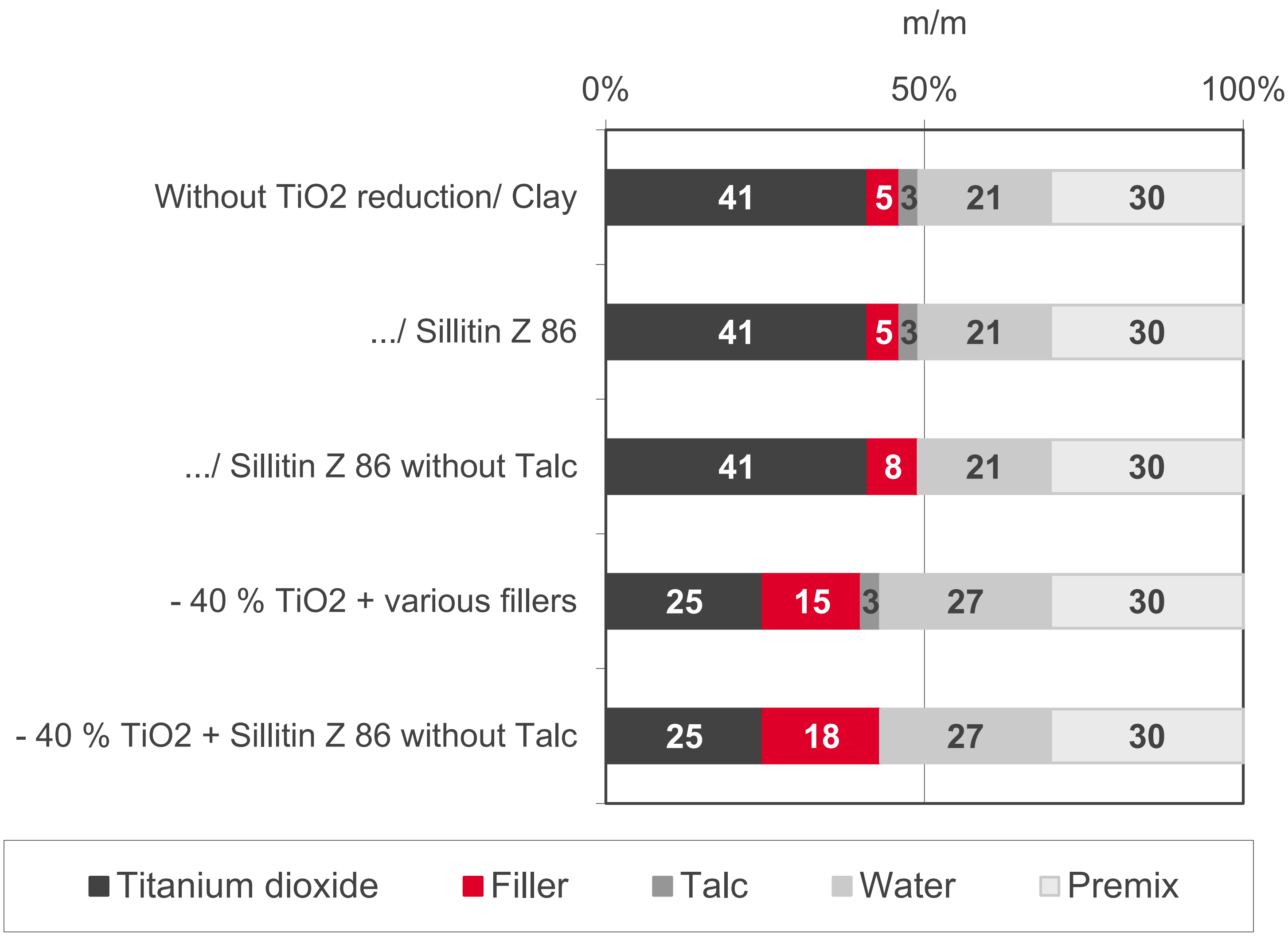
**Premix:**

- Mill base/binder: modified epoxy amine adduct
- Carbon black
- Non-ionic wetting agent
- Fumed silica
- Plasticizer
- Neutralizing agent:  acetic acid

# Pigment Paste



Variations of pigment paste (constant PVC)



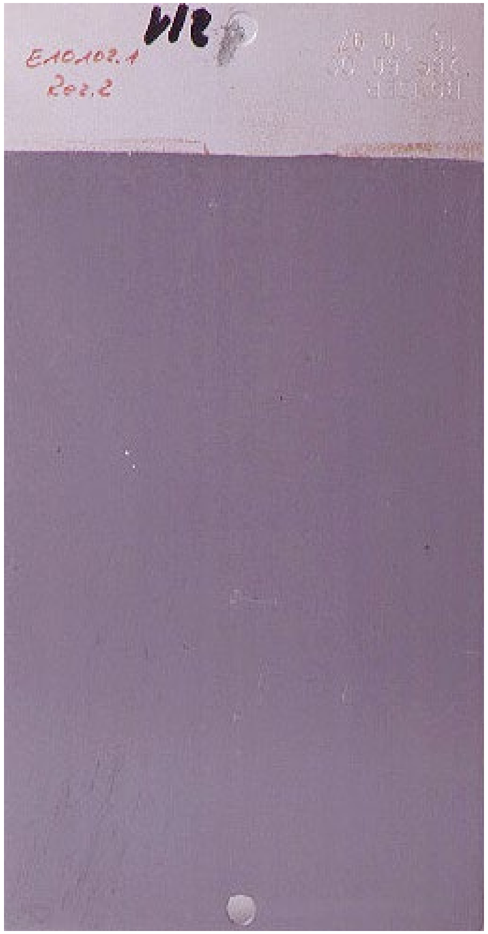
# Pigment Paste

## Pigment and fillers



- Titanium dioxide (standard grade)
- American Clay (standard clay)
- Sillitin Z 86 (Neuburg Siliceous Earth)
- Sillitin P 87 (finer particle size then Sillitin Z 86)
- Aktisil PF 777 (Sillitin Z 86, alkyl functionalized)
- Aktisil MM (Sillitin Z 86, mercapto functionalized)
- Talc (standard talc)

# Test Panels



Gardobond 2650T/6800/OC

(19 cm x 10.5 cm x 0.85 mm)

Material: steel

Surface pretreatment: zinc-manganese phosphatized

Rinsing: chromate free

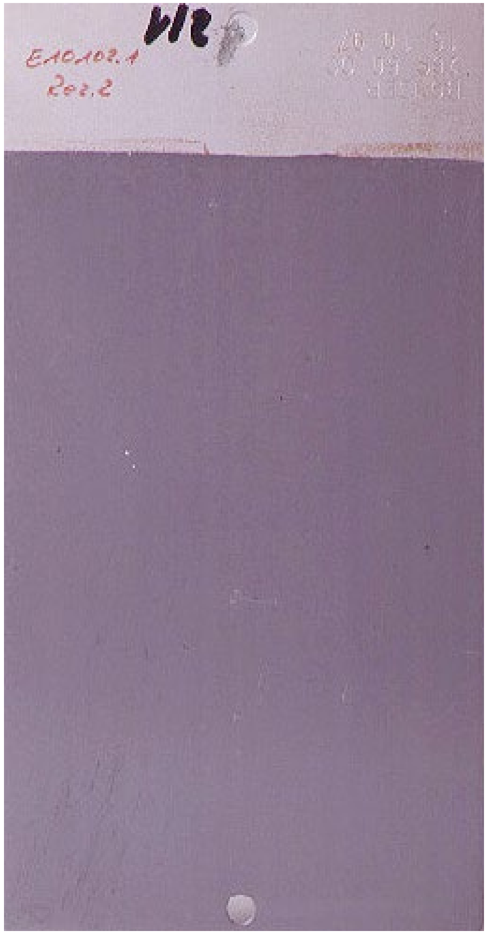
Film thickness: 20 - 25 µm

For testing:

- Impact Test
- Cupping Test

# Test Panels





Gardobond 2650T/6800/OG

(19 cm x 10.5 cm x 0.85 mm)

Material: steel, electrolytically zinc plated

Surface pretreatment: zinc-manganese phosphatized

Rinsing: chromate free

Film thickness: 20 - 25 µm

For testing:

- Impact Test
- VDA Test
- Adhesion (Cross Cut Test)

# Test Panels

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L – panels

Steel panel Bonder 2650T/6800/0C,

14 + 5 cm x 10.5 cm x 0.85 mm

Film thickness: 20 - 25 µm

For testing:

- L effect (dispersion performance and deposition behavior)

Parameter:

Panels were dipped into bath, 15 min quiescence, then deposition without stirring

# Test Panels

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Manschette „Ford Box“

Steel panel Bonder 2650T/6800/OC

30 cm x 10.5 cm x 0.9 mm

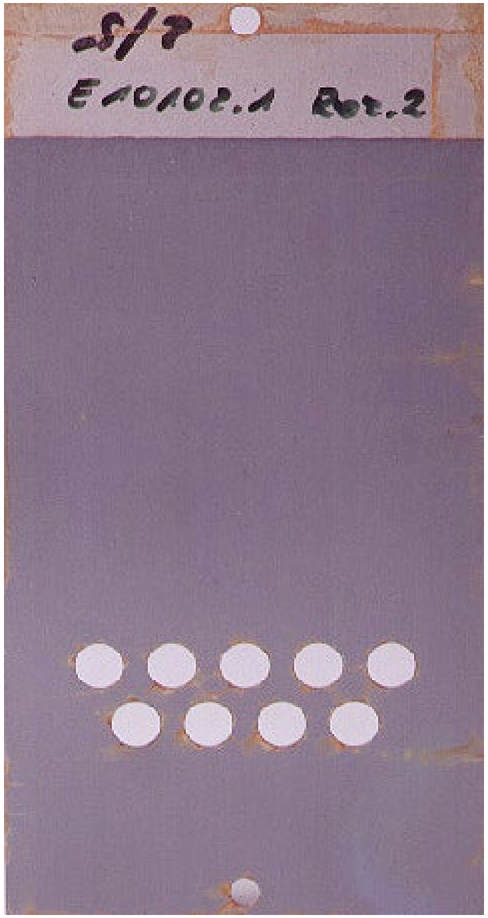
Distance between panels: 4 mm

For testing:

- Throwing Power

# Test Panels





Perforated panels, bonderized, 9 holes each (d = 1 cm)

Steel panel Bonder 2650T/6800/OC

20 cm x 10 cm x 0.9 mm

Film thickness: 21 - 25 µm

For testing:

- For determination of edge covering via degree of corrosion at sharp edges of holes

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# Test Panels

Cutter knives from Lutz Industria Solingen

No. AB 10, width 9mm

Film thickness: 28 - 34 µm

For testing:

- For determination of edge covering

# Deposition and Stoving

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Facility: Pilot plant EPV 20, Dürr company

Deposition pot: 24 - 30 cm high, glass. Temperature control by cooling hoses from bottom to top

Anode: Stainless steel, 20 x 4 cm² (small panels)
30 x 2 cm² (throwing power)

Electrode distance: 5,5 cm

Side distance
Cathode/vessel: minimum 2 cm

# Deposition and Stoving



| | |
|---|---|
| Deposition: | under continuous stirring with a magnetic stirrer; then rinse plates with demineralized water |
| Deposition data: | time: 3 min, voltage: 280 V |
| Stoving: | 180 °C, 30 min in forced ventilation oven |

# Bath Formulation

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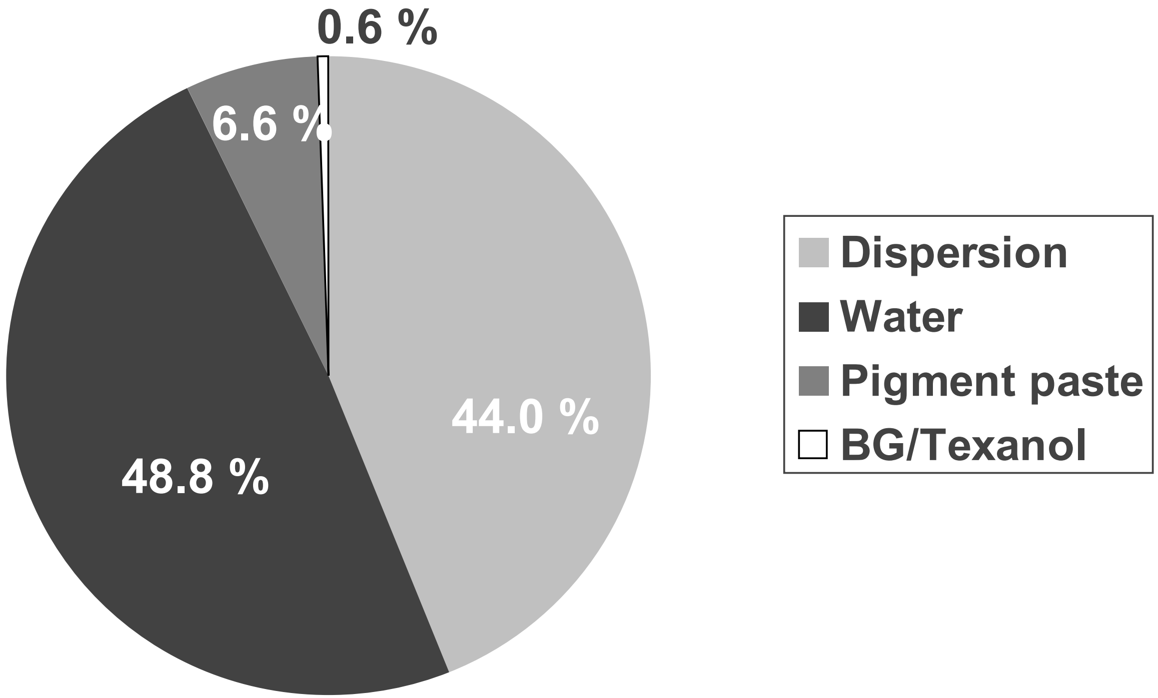


| Ratios m/m | Without $TiO_2$ reduction | - 40 % $TiO_2$ |
|---|---|---|
| Dispersion/pigment paste | 6.7 | 6.7 |
| Pigment (filler incl.)/ Binder solid | 0.20 | 0.18 |

# Bath Properties

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| | Unit | Intended bath properties | Attained bath properties |
|---|---|---|---|
| Solid content | % | 18 -19 | 17.5 – 18.5 |
| pH value | | 6.3 ± 0.2 | 5.7 – 6.0 |
| Electrical conductivity | µS/cm | 1300 ± 200 | 1200 - 1500 |

# Pigment Paste

Flow Times and Grain Fineness



- The pigment pastes without reduction of titanium dioxide had flow times between100 and 150 s and a grain fineness of 7 µm.

- The titanium dioxide substitution results in lower flow times between 23 und 56 s and a grain fineness between 6 and 12 µm.

# L effect / Gloss 60°

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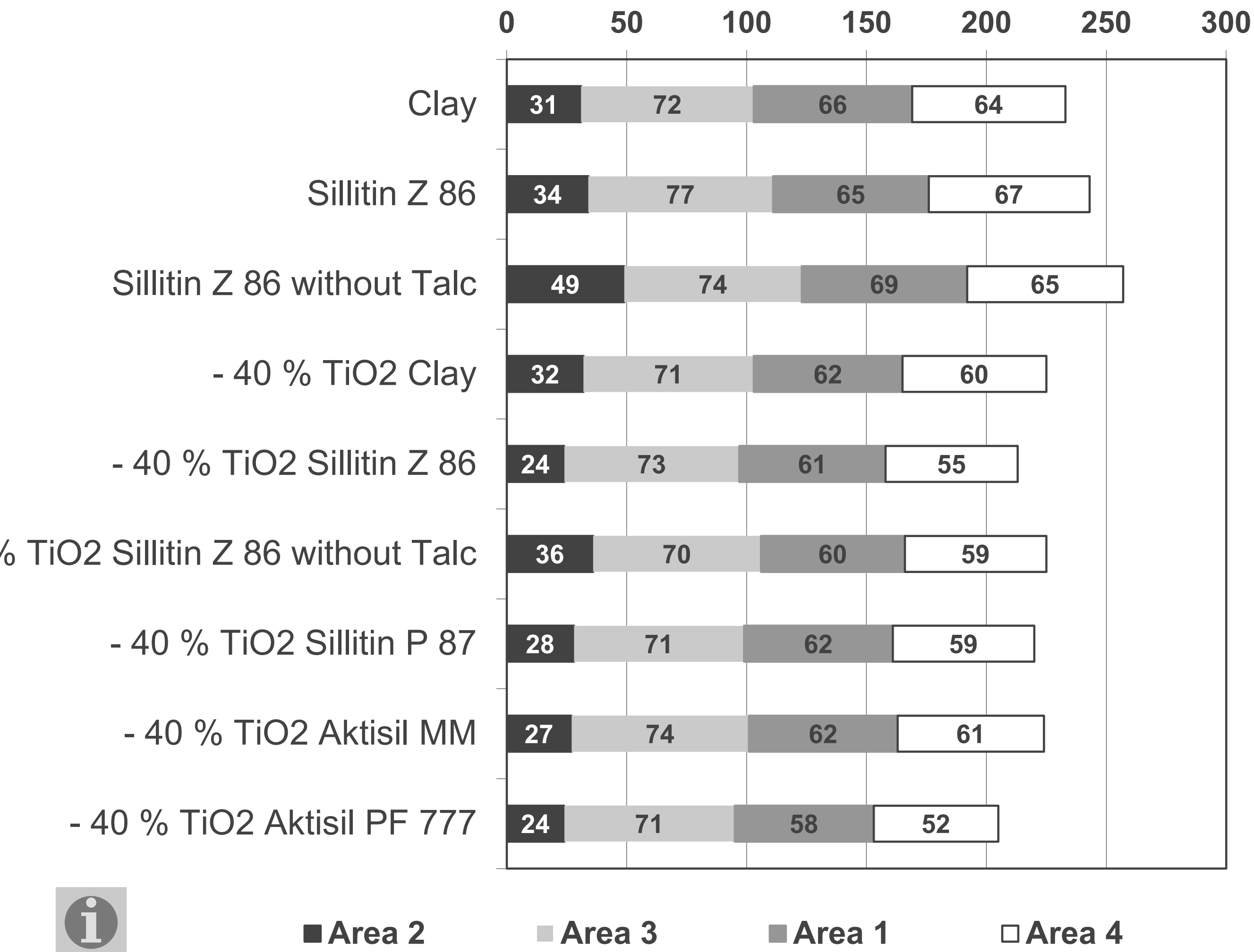


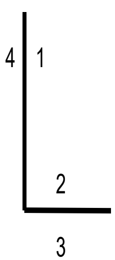

# Throwing Power

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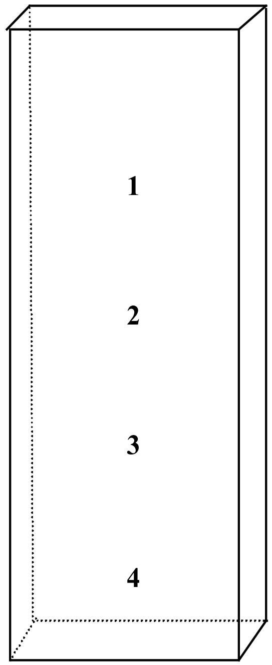
The figure below indicates the position of the film thickness measuring points 1 - 4.

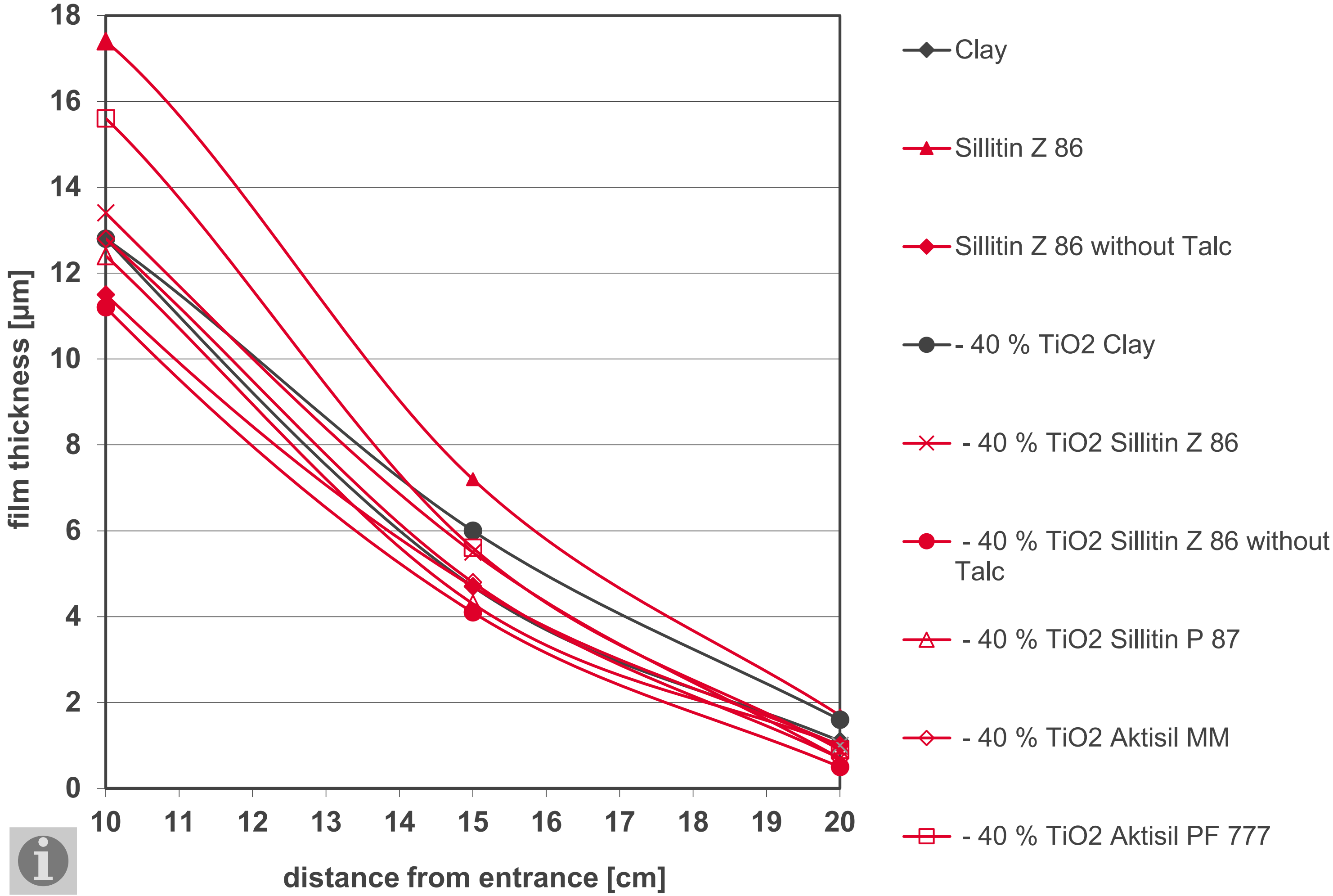



| | |
|---|---|
| Plate length: | 30 cm |
| Dip in to bath: | 22 cm |
| 1: | 20 cm |
| 2: | 15 cm |
| 3: | 10 cm |
| 4 : | 5 cm |

from entrance edge

# Throwing Power

## Film thickness vs distance from entrance

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# Throwing Power

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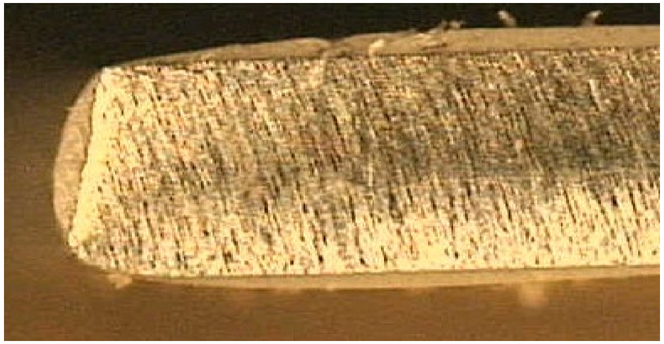
## Corrosion Protection Limit after 1000 h salt spray test

# Edge Covering

## Cutter knives

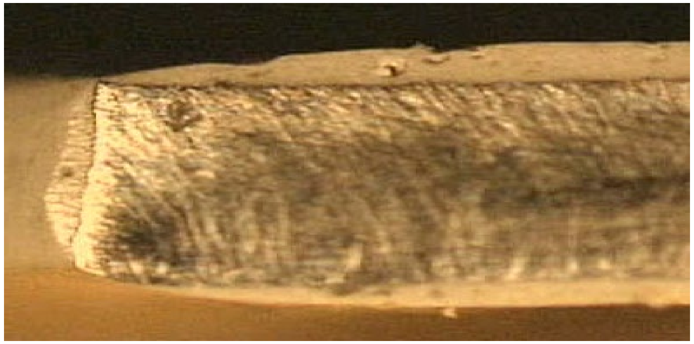


moderate



- - 40 % $TiO_2$ Clay
- - 40 % $TiO_2$ Sillitin Z 86
- - 40 % $TiO_2$ Aktisil MM

slightly improved



- Clay
- Sillitin Z 86
- - 40 % $TiO_2$ Aktisil PF 777

# Edge Covering

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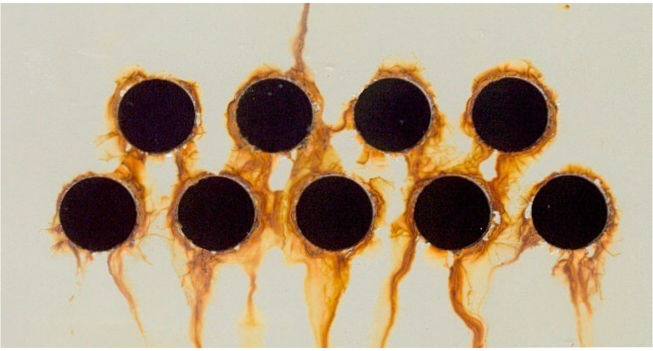
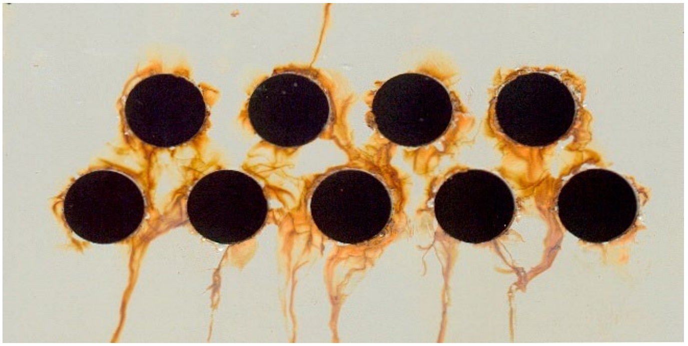
Perforated panels after 1000 h salt spray test

moderate



- Clay
- - 40 % $TiO_2$ Clay
- - 40 % $TiO_2$ Sillitin Z 86
- - 40 % $TiO_2$ Sillitin Z 86 without Talc
- - 40 % $TiO_2$ Sillitin P 87
- - 40 % $TiO_2$ Aktisil MM
- - 40 % $TiO_2$ Aktisil PF 777

slightly improved



- Sillitin Z 86
- Sillitin Z 86 without Talc

# Cupping Test

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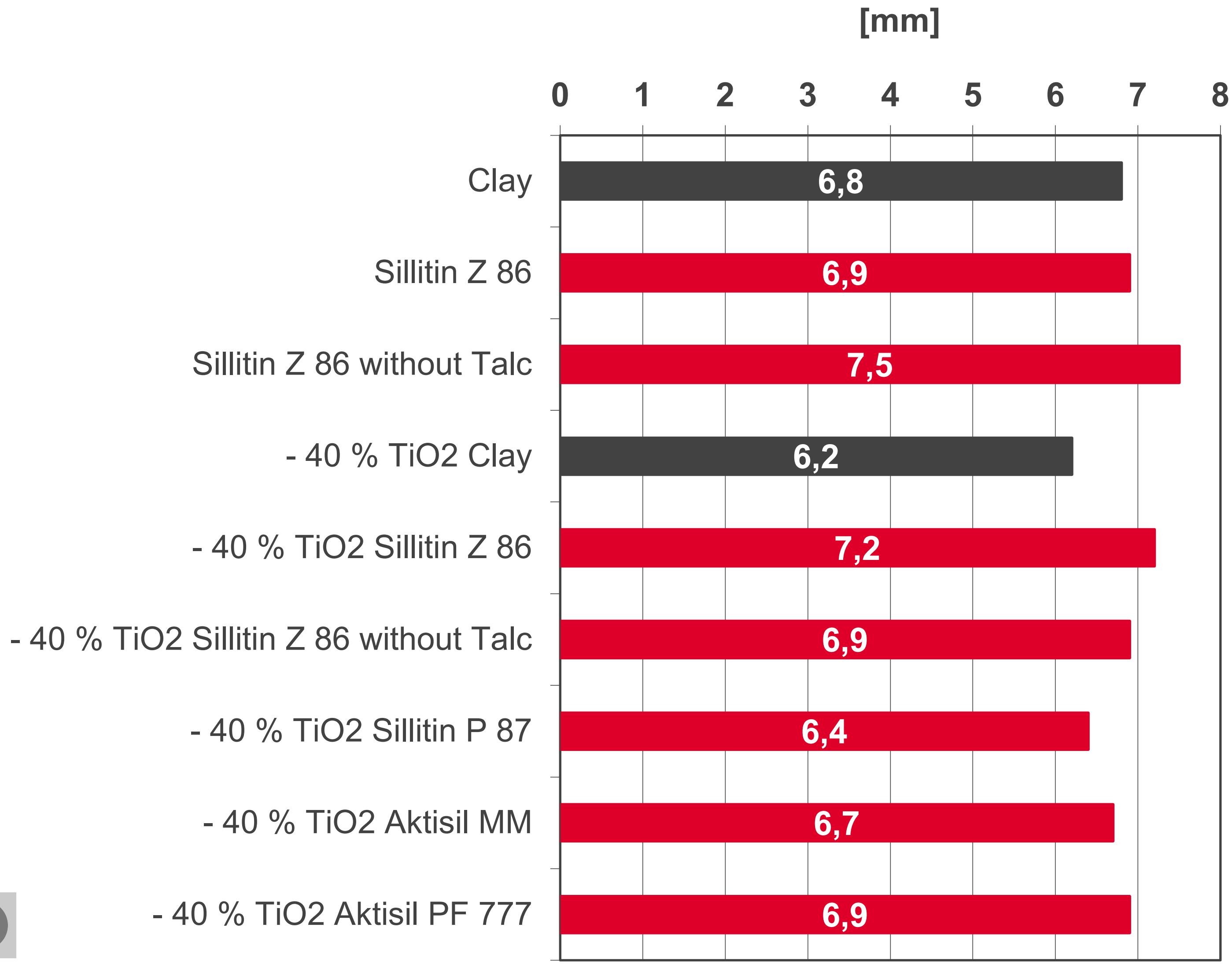

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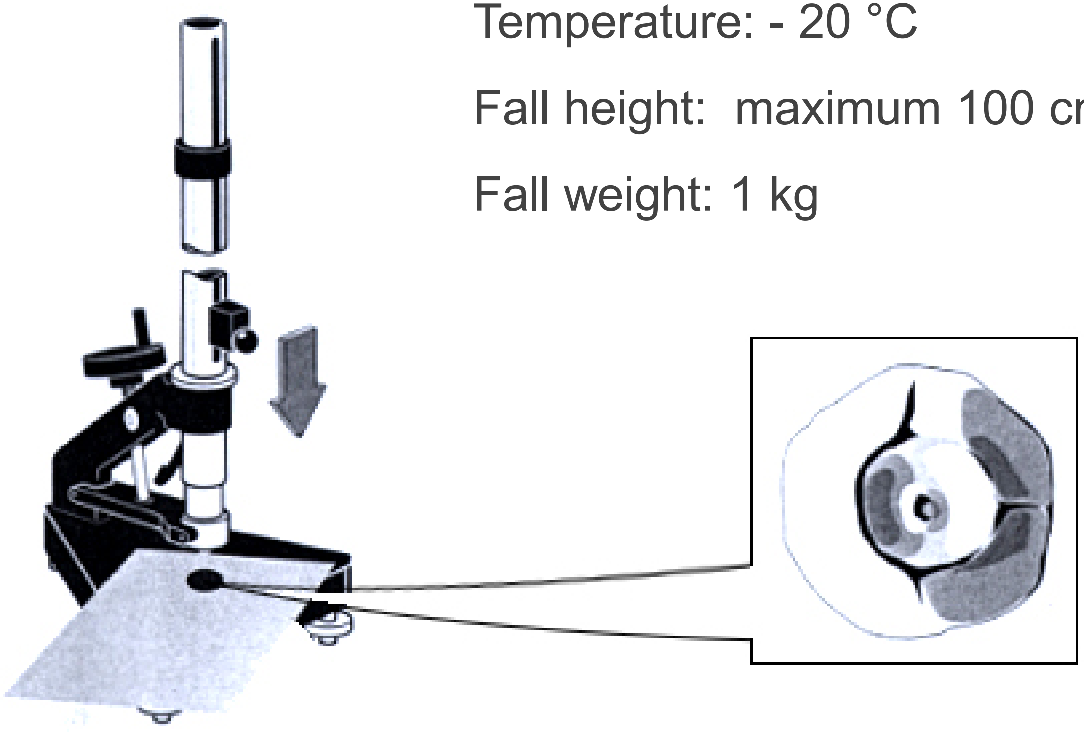
# Impact Test



Temperature: - 20 °C

Fall height: maximum 100 cm

Fall weight: 1 kg

# Impact Test at -20°C

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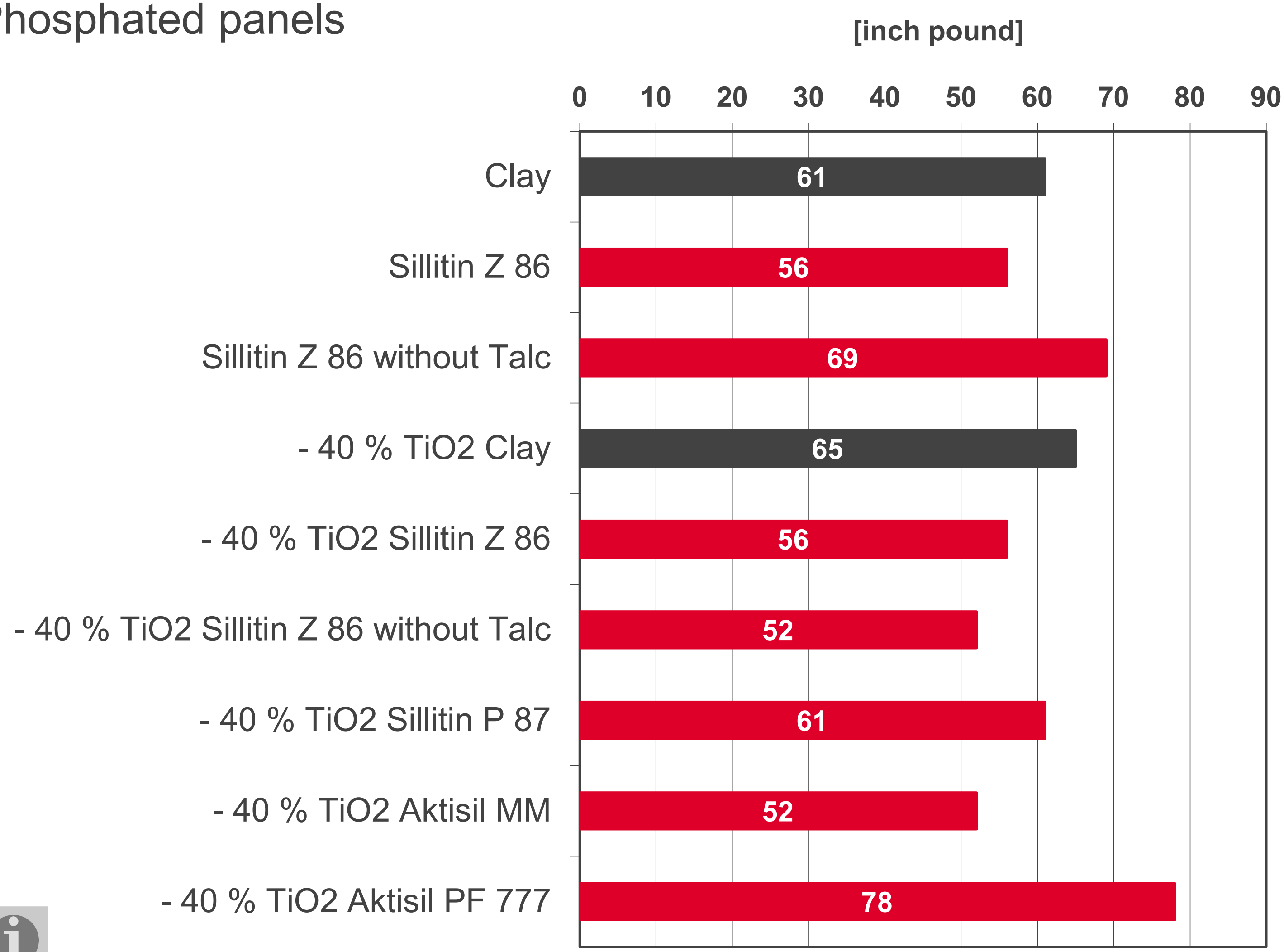
## Phosphated panels



# Impact Test at -20°C

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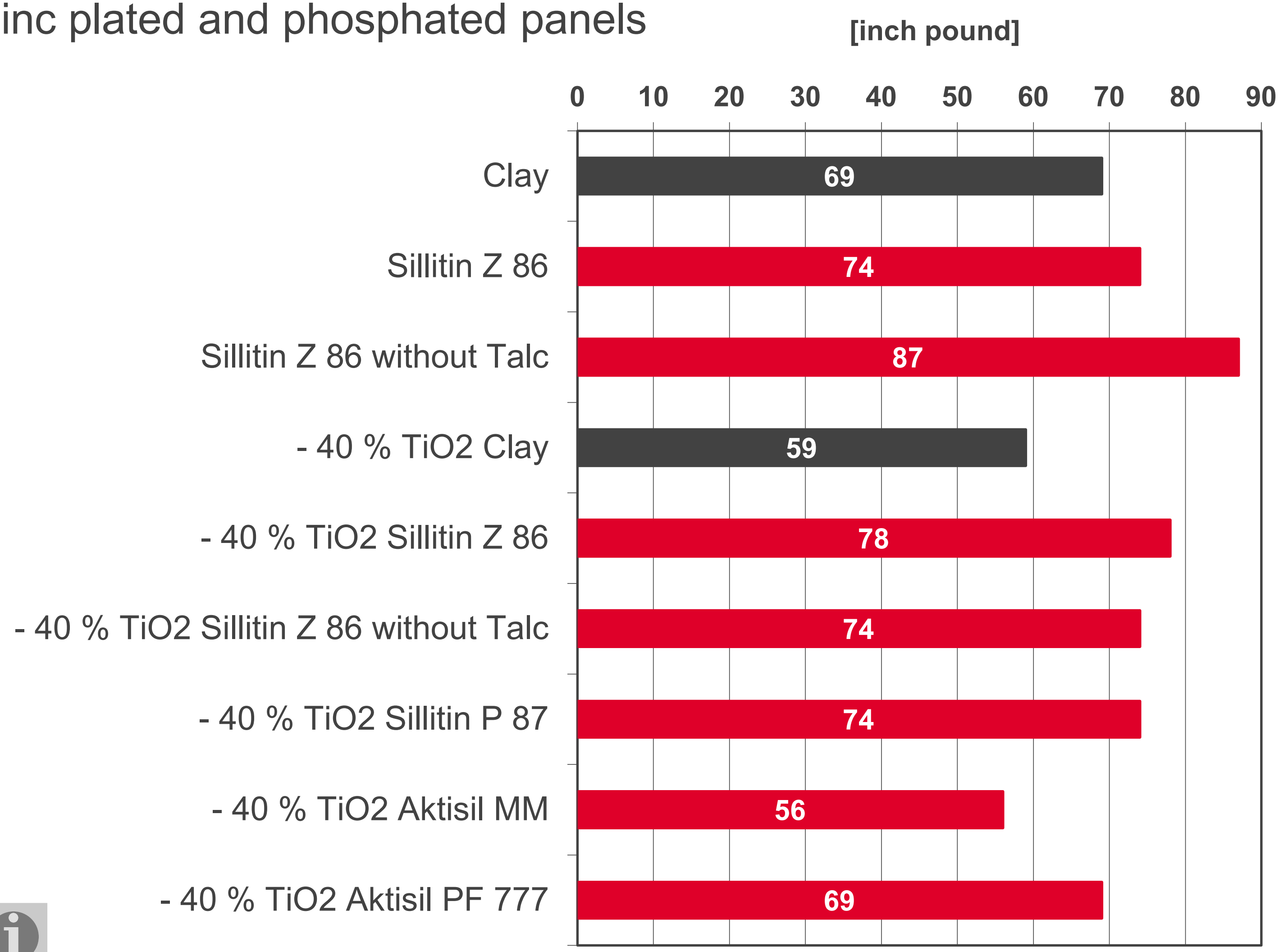
## Zinc plated and phosphated panels



# Reverse Impact Test at -20°C

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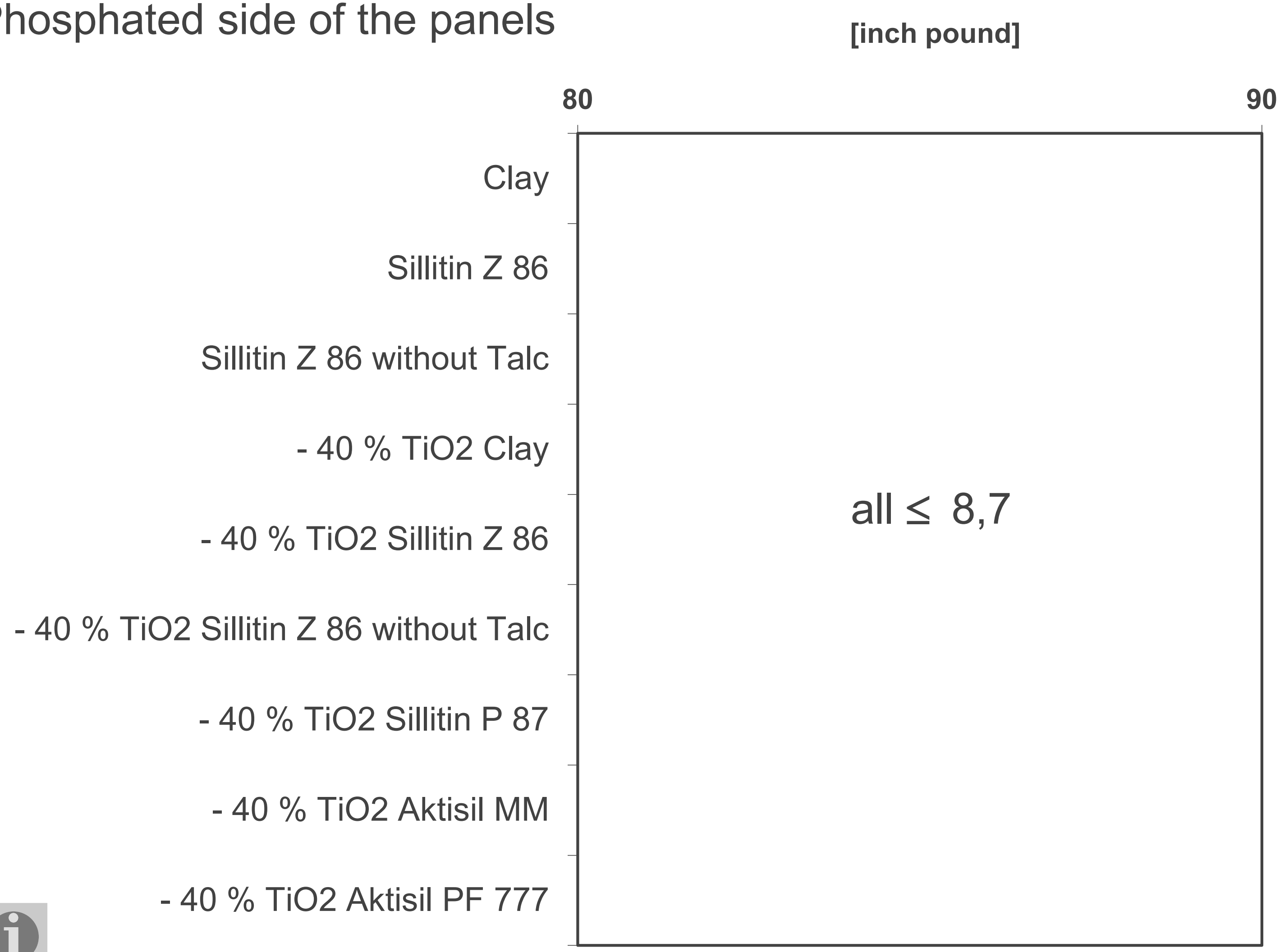
## Phosphated side of the panels



# Cross Cut Test

Adhesion after cross cut test and Tesa adhesive tape pull-off



- All results good, between 0 und 1
- No differentiation possible, as in three individual tests each formulation came off between 0 and 1

# VDA after 20 Cycles

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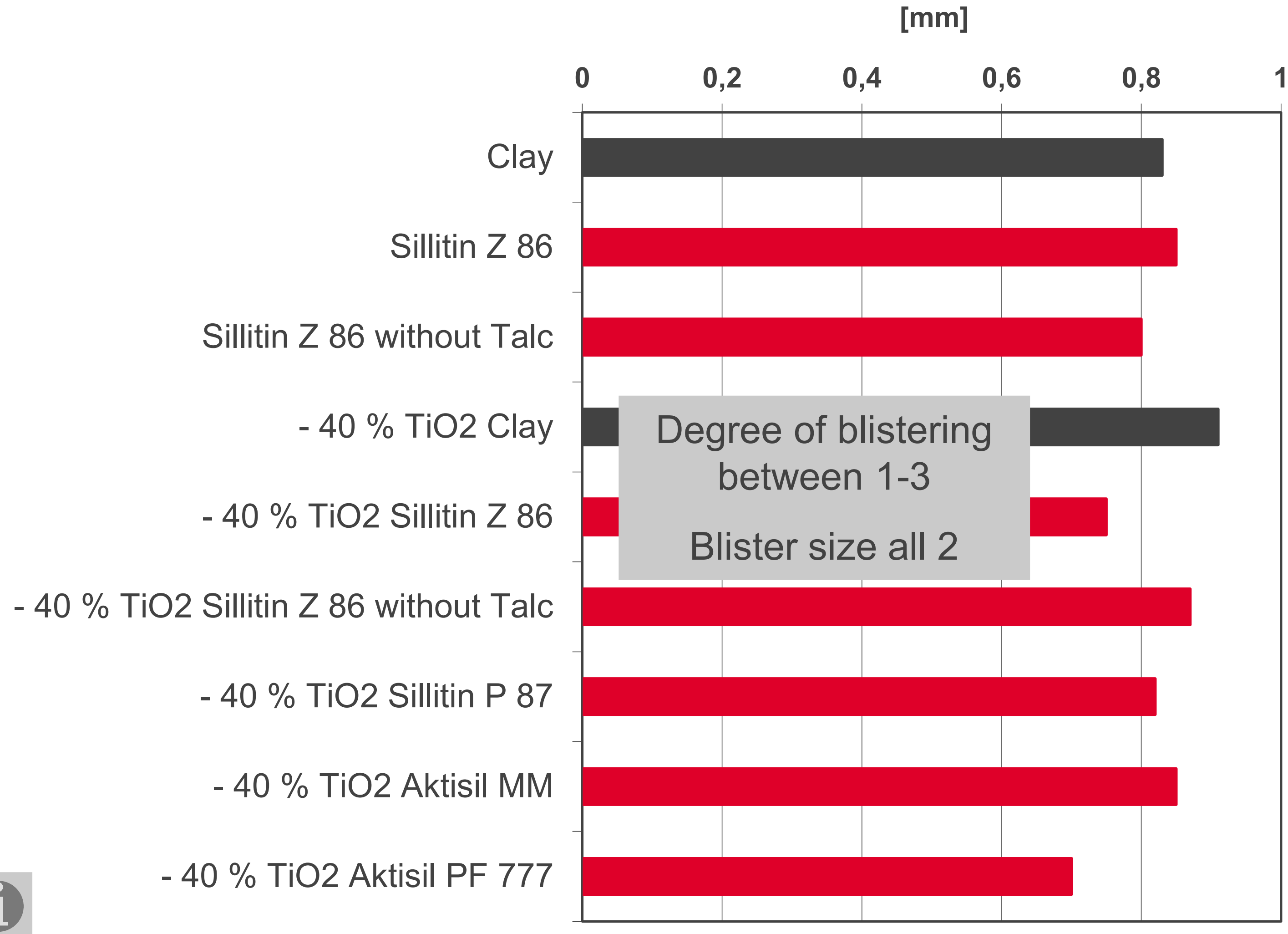
## Delamination at scribe



# Cross Cut Test
# after VDA Test

Adhesion after cross cut test and Tesa adhesive tape pull-off



- All results good, between 0 und 1
- No differentiation possible, as in three individual tests each formulation came off between 0 and 1

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# Summary

| Summary of the results "at a glance"<br><br>Specimen<br><br>Reference:<br>Standard formulation<br>(with Clay) | L effect, area 2 (gloss 60°) | Throwing powder (corrosion protection limit) | Perforated panels (edge covering) | Cutter knives (edge covering) | Cupping Test | Impact Test -20°C (phosphated panels) | Impact Test -20°C (zinc plated and phosphated panels) | Adhesion (Cross Cut Test) | VDA Test (after20 Cykles) Delamination at scribe |
|---|---|---|---|---|---|---|---|---|---|
| Sillitin Z 86 | 0 | 0 | + | 0 | 0 | 0 | 0 | 0 | 0 |
| Sillitin Z 86 without Talc | ++ | 0 | + | not tested | + | + | ++ | 0 | 0 |
| - 40 % TiO2 Clay | 0 | 0 | 0 | - | - | 0 | - | 0 | 0 |
| - 40 % TiO2 Sillitin Z 86 | - | 0 | 0 | - | + | 0 | + | 0 | 0 |
| - 40 % TiO2 Sillitin Z 86 without Talc | + | 0 | 0 | not tested | 0 | 0 | 0 | 0 | 0 |
| - 40 % TiO2 Sillitin P 87 | 0 | 0 | 0 | not tested | - | 0 | 0 | 0 | 0 |
| - 40 % TiO2 Aktisil MM | 0 | 0 | 0 | - | 0 | 0 | - | 0 | 0 |
| - 40 % TiO2 Aktisil PF 777 | - | 0 | 0 | 0 | 0 | ++ | 0 | 0 | 0 |

Compared to the standard Clay:

+ Advantage

+ + Significant advantage

- Disadvantage

- - Significant Disadvantage

0 Without any remarkable difference to the standard

# Summary

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- Compared with the clay, Sillitin Z 86 without talc imparts advantages in L effect with respect to a glossy surface on the critical side.

  Benefits of Sillitin Z 86 are evident also in edge covering, Cupping Test and Impact Test at -20°C. Last not least, the price/ performance ratio speaks in favour of Sillitin Z 86.

- Aktisil PF 777 with substitution of 40 % titanium dioxide shows comparable results to the clay, but better results at Impact Test at -20 °C on phosphated panels.

# We supply material for good ideas!

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# Data



## Titanium dioxide

| Properties | | Unit | Result |
|---|---|---|---|
| Composition | | | Rutile, surface treated |
| Particle size distribution | d10 | µm | 0.1 |
| | d50 | µm | 0.3 |
| | d97 | µm | 0.9 |
| Residue | 40 µm | ppm | 23 |
| | 200 µm | ppm | 4 |
| Loss on ignition | | % | 1.2 |
| Volatile matter | | % | 0.5 |
| Electrical conductivity | | µS / cm | 57 |
| Oil absorption | | g /100g | 26 |
| pH value | | | 7.4 |
| | | | |
| | | | |

# Data

## American Clay



| Properties | | Unit | Result |
|---|---|---|---|
| Composition | | | Aluminum silicate |
| Particle size distribution | d10 | µm | 0.3 |
| | d50 | µm | 1.9 |
| | d97 | µm | 8.4 |
| Residue | 40 µm | ppm | 3 |
| | 200 µm | ppm | - |
| Loss on ignition | | % | 14.4 |
| Volatile matter | | % | 1.0 |
| Electrical conductivity | | µS / cm | 154 |
| Oil absorption | | g /100g | 56 |
| pH value | | | 4.7 |
| Brightness | Y | | 82.7 |
| | Z | | 82.5 |

## Sillitin Z 86

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| Properties | | Unit | Result |
|---|---|---|---|
| Composition | | | Silica / Kaolinite |
| Particle size distribution | d10 | µm | 0.6 |
| | d50 | µm | 1.9 |
| | d97 | µm | 9 |
| Residue | 40 µm | ppm | 3 |
| | 200 µm | ppm | 2 |
| Loss on ignition | | % | 4.5 |
| Volatile matter | | % | 0.5 |
| Electrical conductivity | | µS / cm | 78 |
| Oil absorption | | g /100g | 50 |
| pH value | | | 8.1 |
| Brightness | Y | | 81.8 |
| | Z | | 74.5 |

# Data

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## Sillitin P 87

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| Properties | | Unit | Result |
|---|---|---|---|
| Composition | | | Silica / Kaolinite |
| Particle size distribution | d10 | µm | 0.5 |
| | d50 | µm | 1.5 |
| | d97 | µm | 6 |
| Residue | 40 µm | ppm | 4 |
| | 200 µm | ppm | 1 |
| Loss on ignition | | % | 5.4 |
| Volatile matter | | % | 0.4 |
| Electrical conductivity | | µS / cm | 49 |
| Oil absorption | | g /100g | 50 |
| pH value | | | 7.3 |
| Brightness | Y | | 81.9 |
| | Z | | 74.9 |

# Data

## Aktisil MM

| Properties | | Unit | Result |
|---|---|---|---|
| Composition | | | Sillitin Z 86<br>mercapto functionalized |
| Particle size distribution | d10 | µm | 0.7 |
| | d50 | µm | 2.2 |
| | d97 | µm | 10 |
| Residue | 40 µm | ppm | 7 |
| Loss on ignition | | % | 5.4 |
| Volatile matter | | % | 0.4 |
| Electrical conductivity | | µS / cm | 37 |
| Oil absorption | | g /100g | 49 |
| pH value | | | 7.2 |
| Brightness | Y | | 80.9 |
| | Z | | 74.7 |

# Data

## Aktisil PF 777



| Properties | | Unit | Result |
|---|---|---|---|
| Composition | | | Sillitin Z 86 alkyl functionalized |
| Particle size distribution | d10 | µm | 0.8 |
| | d50 | µm | 2.2 |
| | d97 | µm | 10 |
| Residue | 40 µm | ppm | 6 |
| Loss on ignition | | % | 5.4 |
| Volatile matter | | % | 0.2 |
| Electrical conductivity | | µS / cm | - |
| Oil absorption | | g /100g | 35 |
| pH value | | | 7.1 |
| Brightness | Y | | 79.6 |
| | Z | | 74.6 |

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## Talc

| Properties | | Unit | Result |
|---|---|---|---|
| Composition | | | Magnesium silicate hydrate |
| Particle size distribution | d10 | µm | 1.8 |
| | d50 | µm | 5.2 |
| | d97 | µm | 17 |
| Residue | 40 µm | ppm | 5 |
| | 200 µm | ppm | - |
| Loss on ignition | | % | 3.7 |
| Volatile matter | | % | 0.2 |
| Electrical conductivity | | µS / cm | 78 |
| Oil absorption | | g /100g | 55 |
| pH value | | | 9.2 |
| Brightness | Y | | 89.0 |
| | Z | | 93.3 |

# Tests and Standards

## Wet lacquer tests



| Test / measurement / rating | Norm |
|---|---|
| Solid content (non-volatile matter) | DIN EN ISO 3251 |
| pH value, by pH Meter 620, Metrohm | DIN 53785 |
| Electrical conductivity, Conductometer LF 2000, WTW | DIN 53779 |
| Fineness of grind (Grindometer) | DIN EN ISO 1524 |
| Flow time, DIN 4 mm cup | DIN 53211-4 |
| U/t and I/t curves (voltage behavior, current flow) at deposition | |

# Tests and Standards

## Mechanical tests

| Test / measurement / rating | Norm |
|---|---|
| Film thickness (Surfix, Phynix)<br>Determination of throwing power with „Ford Box“ | DIN EN ISO 2178 |
| Impact Test, 1 kg from max. height 100 cm | DIN EN ISO 6272 |
| Cupping Test | DIN EN ISO 1520 |
| Gloss, Multi Gloss, Byk Gardner (at all 4 areas of L-panels) | DIN 67530 |
| Cross Cut Test | DIN EN ISO 2409 |

# Tests and Standards

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## Corrosion protection tests

| Test / measurement / rating | Norm |
|---|---|
| Testing of corrosion protection of auto-mobile finishing at cyclic changing stress (20 cycles with cut, 1 cycle: 24 h SST, 4 d AHT, 48 h 23 °C / 50 % rel. humidity) | VDA 621-415 |
| Determination of resistance to humidity | DIN EN ISO 6270-2 |
| Salt spray test (1000 h) on perforated and throwing power specimen, evaluation of corrosion behavior | DIN EN ISO 9227 |
| Assessment of degree of rusting | DIN EN ISO 4628-3 |
| Assessment of degree of cracking | DIN EN ISO 4628-4 |