Neuburg Siliceous Earth

in heavy-cuty 2K PU coatings,

e.g. for pipelines

Authorship: Hubert Oggermüller
Petra Zehnder

VM-0/0521/05.2021

Contents

1 Introduction

2K-PU coatings are used as thick-layer up to millimeter scale, hard coatings for buried pipelines, predominantly for complex shaped parts such as bends or fittings and also as repair coatings and for transitions of pipes.

Compared with 2K epoxy systems, a comparable area can be coated with a higher layer thickness in a shorter time. The drying process and thus the usability or recoatability is much shorter (a few minutes to hours as opposed to several days). Possible defects can be detected earlier due to the rapid curing, and the temperature window for application is also larger.

Thus, if one considers not only the pure material costs, but also takes into account the application time, maintenance costs and other hidden costs, the use of 100 % PU systems is ultimately significantly more cost-effective.

The application is usually carried out in a 2K airless process. In addition to good deaeration and storage stability, important properties include good corrosion protection, a fast reaction (pot life < 5 min) and high requirements for mechanical properties such as strength, toughness and flexibility.

Sillitin Z 86 puriss is traditionally used in such systems.

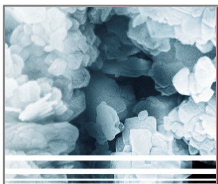
The study shows the possibilities of using Neuburg Siliceous Earth as a mineral filler in a hard 2K polyurethane coating and looks at the differentiation of the individual siliceous earth grades.

Besides rheology and storage stability of the A-component, the mechanical properties of the cured formulations were also considered.

2 Experimental

2.1 Base formulation and filler combinations

The table gives a description of the structure of the base formulation. The A-component contains two different polyol types as binders, zeolite paste as molecular sieve for moisture absorption, some additives for defoaming/deaerating as well as wetting/dispersing agents and the catalyst. Also included is a combination of several fillers.
The B-component (hardener) is an isocyanate based on MDI prepolymer.
The mixing ratio of the two components is 1:1 by volume. This corresponds to an isocyanate excess of 25 %.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

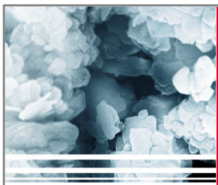
Base Formulation

HOFFMANN MINERAL

Component A		parts by weight
Desmophen BT 1400	*Binder, polyol*	13.14
Desmophen T 460	*Binder, polyol*	13.14
Combination of fillers		21.90
Finma Sorb 430 PR	*Molecular sieve*	5.21
Ethacure 100 Plus	*Crosslinking aid*	1.26
Byk-A 530	*Defoamer*	0.26
Disperbyk 163	*Wetting/dispersing agent*	0.26
Dabco LV 33	*Catalyst*	0.24
Total Component A		**55.41**
Component B		
Desmodur E 29	*Hardener, isocyanate (prepolymer based on MDI)*	approx. 44
Total Formulation A + B		**approx. 99.4**
Mixing ratio		
Component A:B by volume		1:1
Stoichiometric, isocyanate/polyol		approx. 1.25

VM-0/0321/03.2021

The filler combination in the base formulation consists of barite, a natural mica-chlorite-quartz intergrowth (leucophyllite) and a quartz flour surface treated with epoxy silane. In the tests, the leucophyllite and the quartz flour were replaced by products of Neuburg Siliceous Earth in equal weights. The barite remained present in all formulations and was dosed unchanged.



INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Filler Combinations

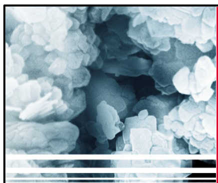
HOFFMANN MINERAL

	Control [pbw]		Variation with Neuburg Siliceous Earth [pbw]
Barite	8.87		8.87
Coalescence of mica, chlorite and quartz	**6.69**	replaced by weight with **Neuburg Siliceous Earth**	13.03
Quartz flour surface treated	**6.34**		

VM-0/0321/03.2021

2.2 Filler characteristics

The table summarizes the fillers used and shows their most important characteristic properties.



INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Filler Characteristics

HOFFMANN MINERAL

	Particle size		Oil absorp-tion	Density	Specific surfacce BET	Surface treatment
	d_{50} [µm]	d_{97} [µm]	[g/100g]	[g/cm³]	[m²/g]	
Coalescence of mica, chlorite and quartz	9	30	29	2.78	4.2	---
Quartz flour surface treated	4	11	24	2.65	3.0	Epoxy silane
Sillitin Z 86 puriss	1.9	9	55	2.6	12	---
Silfit Z 91	2.0	10	65	2.6	10	---
Aktifit PF 115	2.0	10	60	2.6	9	amino functionalized
Other fillers in the formulation (only for comparison)						
Barite	2.9	14	14	4,4	1,7	---

VM-0/0321/03.2021

Sillitin Z 86 puriss is a classic Neuburg Siliceous Earth grade and is already used by various customers as a cost-effective filler in such systems.

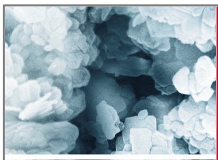
Other products used are Silfit Z 91 and Aktifit PF 115. Both are calcined grades, Silfit Z 91 being the untreated base grade. Aktifit PF 115 is surface treated with an amino functional group and has a hydrophobic surface character.
All Neuburg Siliceous Earth grades show clearly finer particles, which is consistently true for the mean particle diameter d_{50} as well as for the topcut d_{97} in the case of the mica-chlorite-quartz intergrowth. Also, Neuburg Siliceous Earth offers a significantly larger surface area as well as oil number and thus more interaction and anchoring potential for the polymer matrix. In contrast, the difference in density is negligible.

2.3 Preparation of A-component

2.4 Preparation of test specimens

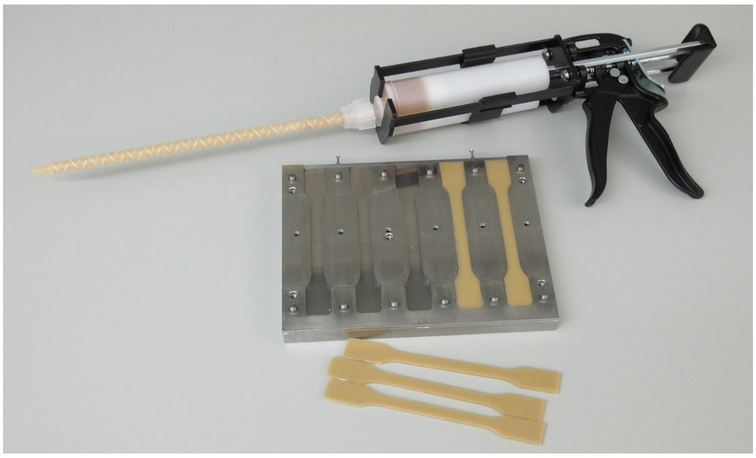
Tensile specimens type 1A according to DIN EN ISO 527 were produced for testing tensile properties, as well as standard bars measuring 80 x 10 x 4 mm for assessing impact strength.

The stainless steel molds were pretreated with “Wax release agent GP” from Gößl & Pfaff. By means of a 2-component cartridge with a volume ratio of 1:1, the formulations were injected into the corresponding molds. The mixing of the two components took place in a helix mixing tube with a diameter of 8 mm and 32 mixing segments (see also the following figure). Immediately afterwards, the surface of the test specimens was smoothed with a metal blade. After curing for at least 3 hours or on the following day, the specimens could be demolded. The mechanical tests were performed after a total curing time of 14 to 16 days. Before testing, the edges of the specimens were deburred with fine sandpaper.



Preparation of Test Specimens

- manual application with 2K cartridges at 23 °C
- mixing tube: Ø 8 mm, 32 mixing segments, helix type
- injection into a metal mold pre-treated with release agent
- demolding after 3 hours at the earliest or the next day
- tests were carried out after 14 to 16 days curing time

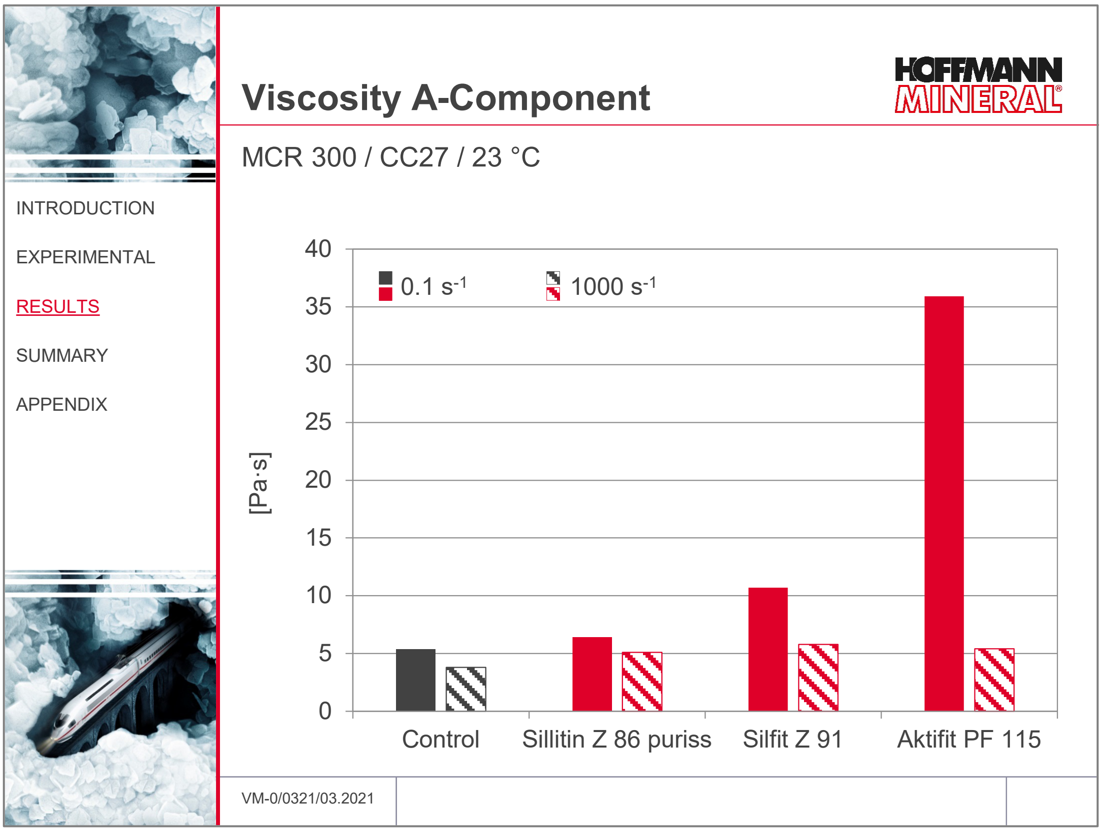


3 Results

3.1 Properties A-component

3.1.1 Viscosity

7 days after preparation of the A-component, a flow curve from 0.1 to 1000 s^{-1} was measured by means of logarithmically increased measuring points and the viscosity at 0.1 and 1000 s^{-1} was evaluated.



The high shear rate (shaded columns) represents the behavior during pumping processes as well as the behavior during application. Here, hardly any difference between the formulations is detectable.

The low shear rate (filled columns) represents the behavior of the formulations after application, quasi at rest, and provides information on important properties such as stability and sagging tendency.
The formulation with Sillitin Z 86 puriss remains almost at the level of the control formulation, Silfit Z 91 tends to a somewhat stronger thickening effect. Aktifit PF 115 shows a marked increase in viscosity in the low shear range, corresponding to a higher stability or reduced sagging tendency.

In the graph, only the rheology of the A component is shown, since due to the very high reaction rate when the hardener is added, a measurement of the mixture is not accessible. If the low viscosity hardener (approx. 220 mPa·s) is added to the formulations in a volume ratio of 1:1, the viscosity level will be more than halved.
The formulation with Aktifit PF 115 nevertheless still shows a comparatively clearly higher low shear viscosity, which allows the application of higher film thicknesses without sagging tendency in one pass. This was found during the application into the mold.

3.1.2 Storage stability

The samples were stored at 40 °C for 3 months. The height of the supernatant and the solid sediment formed were assessed.

INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

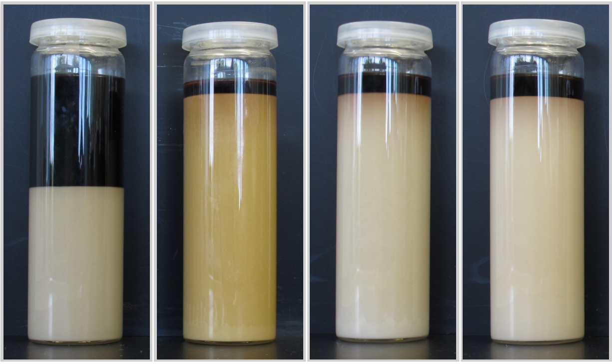
APPENDIX

Storage Stability A-Component

HOFFMANN MINERAL

3 months at 40 °C

	Control	Sillitin Z 86 puriss	Silfit Z 91	Aktifit PF 115
Supernatant [%]	44	6	8	9
Sediment [%]	5	3	5	none



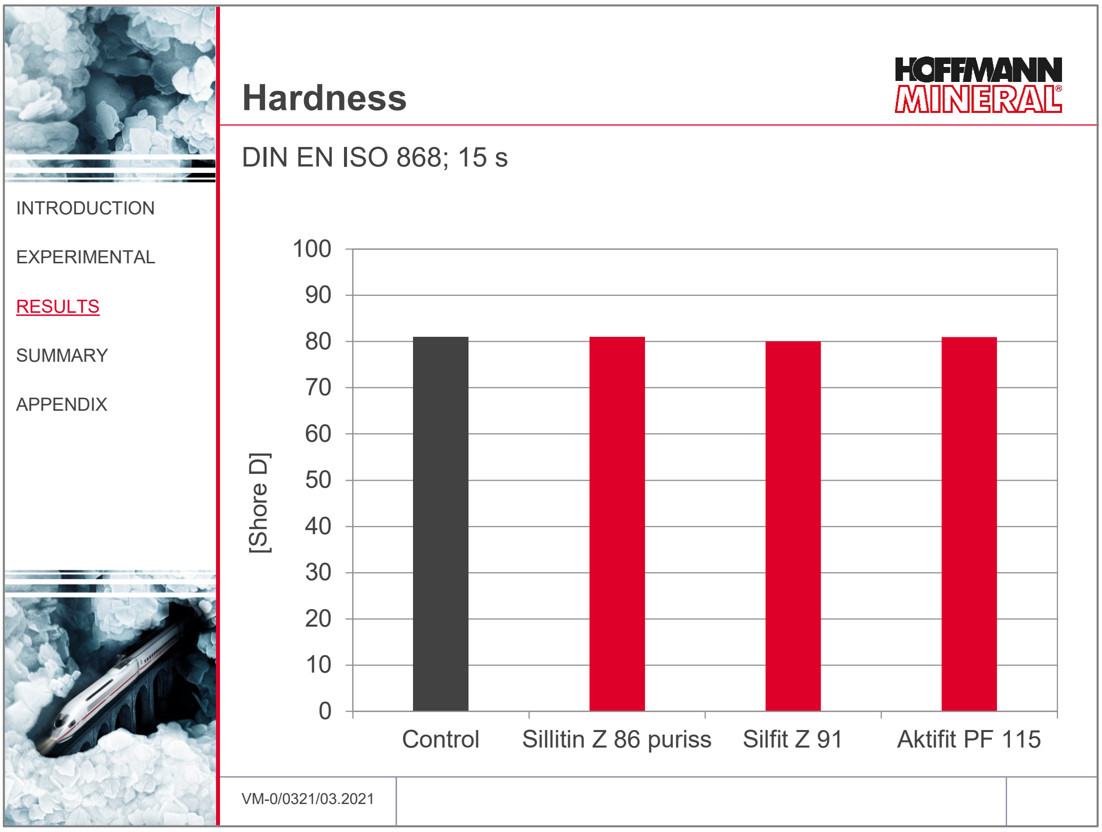
VM-0/0321/03.2021

Compared with the control formulation, the phase separation with Neuburg Siliceous Earth is clearly reduced. As with the control formulation, however, also with Sillitin Z 86 puriss and Silfit Z 91 a relatively solid sediment is formed over the storage time. With Aktifit PF 115, sediment formation can be completely prevented. The formulation is thus much easier to homogenize and thus perfectly storage stable.

3.2 Mechanical properties

3.2.1 Hardness

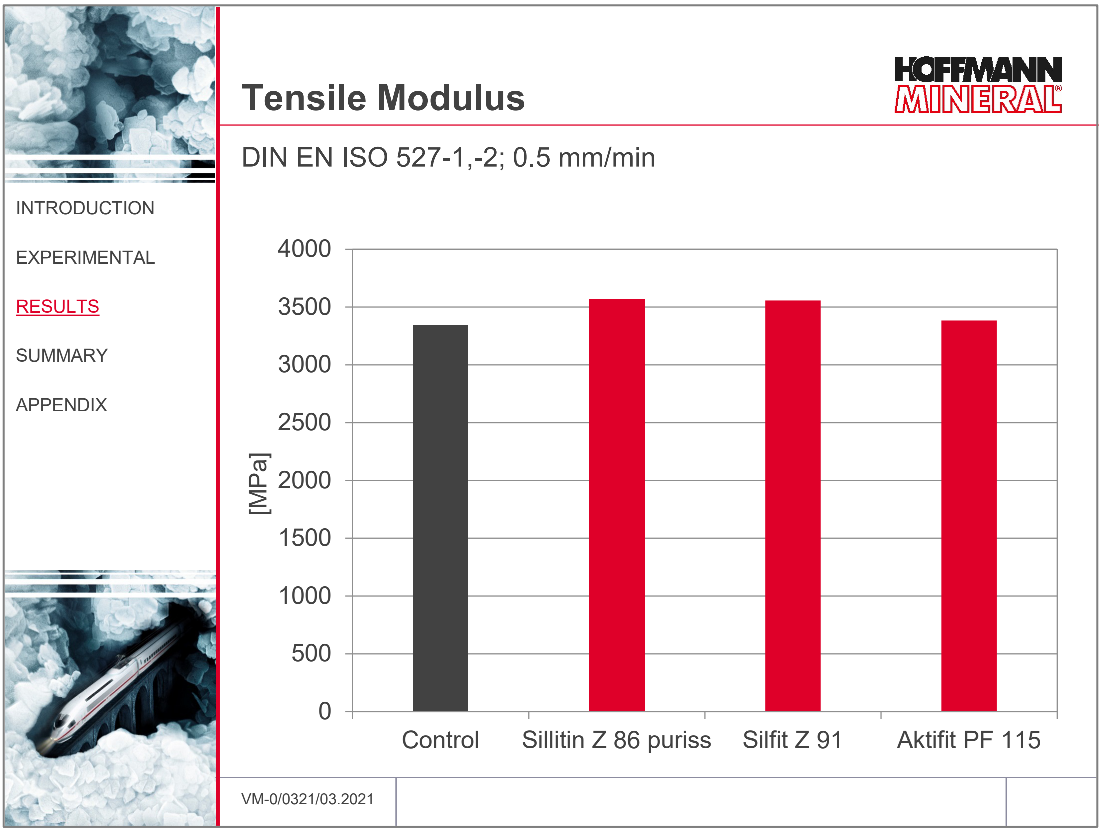
The Shore D hardness test was carried out according to DIN EN ISO 868 on the shoulders of the tensile specimens with a penetration time of the indenter of 15 s.



No difference can be detected between the formulations.

3.2.2 Tensile modulus

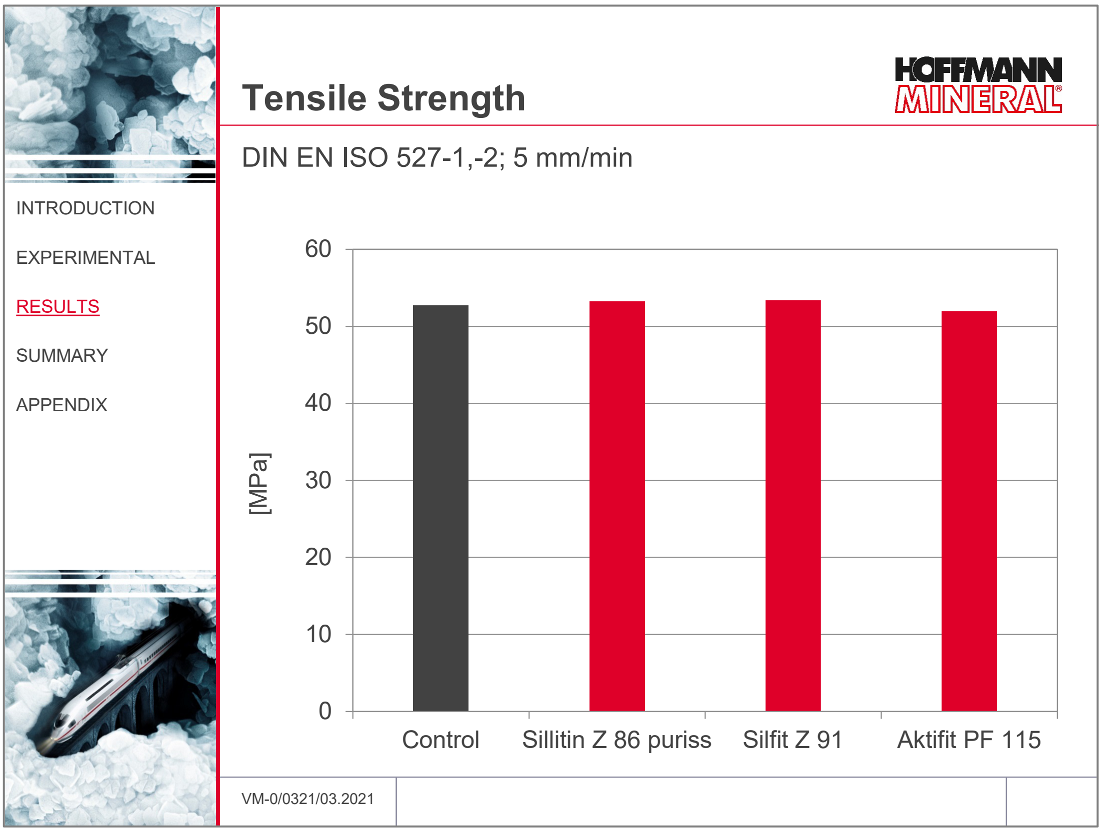
Representing the stiffness of the material, the tensile modulus was determined according to DIN EN ISO 527 at a test speed of 0.5 mm/min.



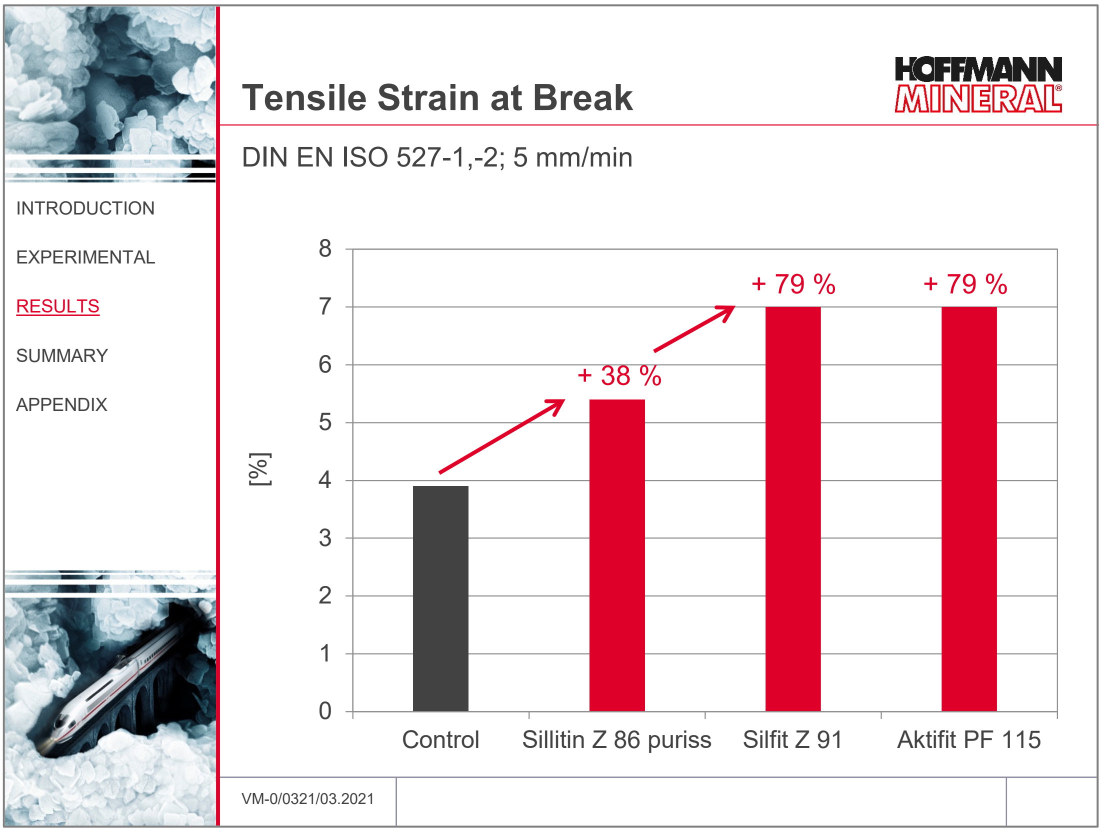
All formulations show about the same stiffness.

3.2.3 Tensile strength and tensile strain at break

The test was carried out according to DIN EN ISO 527 with a test speed of 5 mm/min until the specimens break.



Also with regard to tensile strength, no difference can be observed between the formulations.

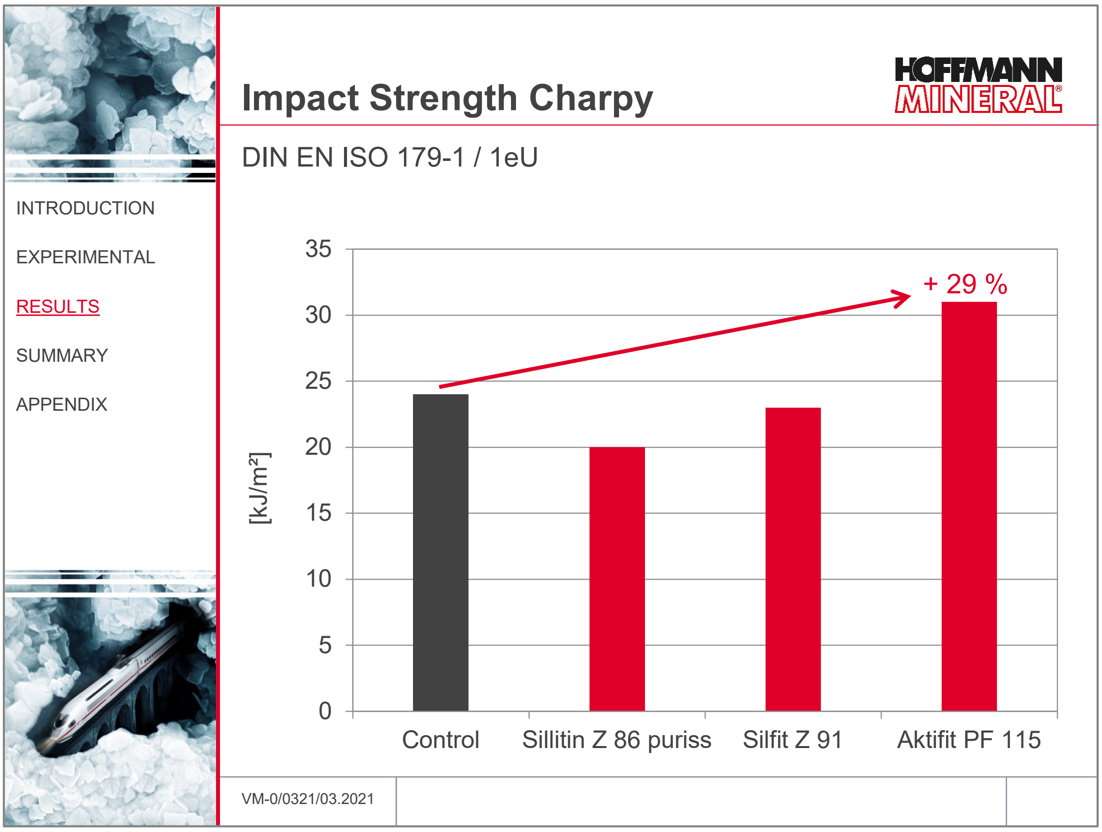


With Neuburg Siliceous Earth, a marked increase in tensile strain at break is obtained, especially with the two calcined grades. Silfit Z 91 and Aktifit PF 115 achieve an approx.

80 % increase in tensile strain at break and thus indicate a higher formability and flexibility of the coating.

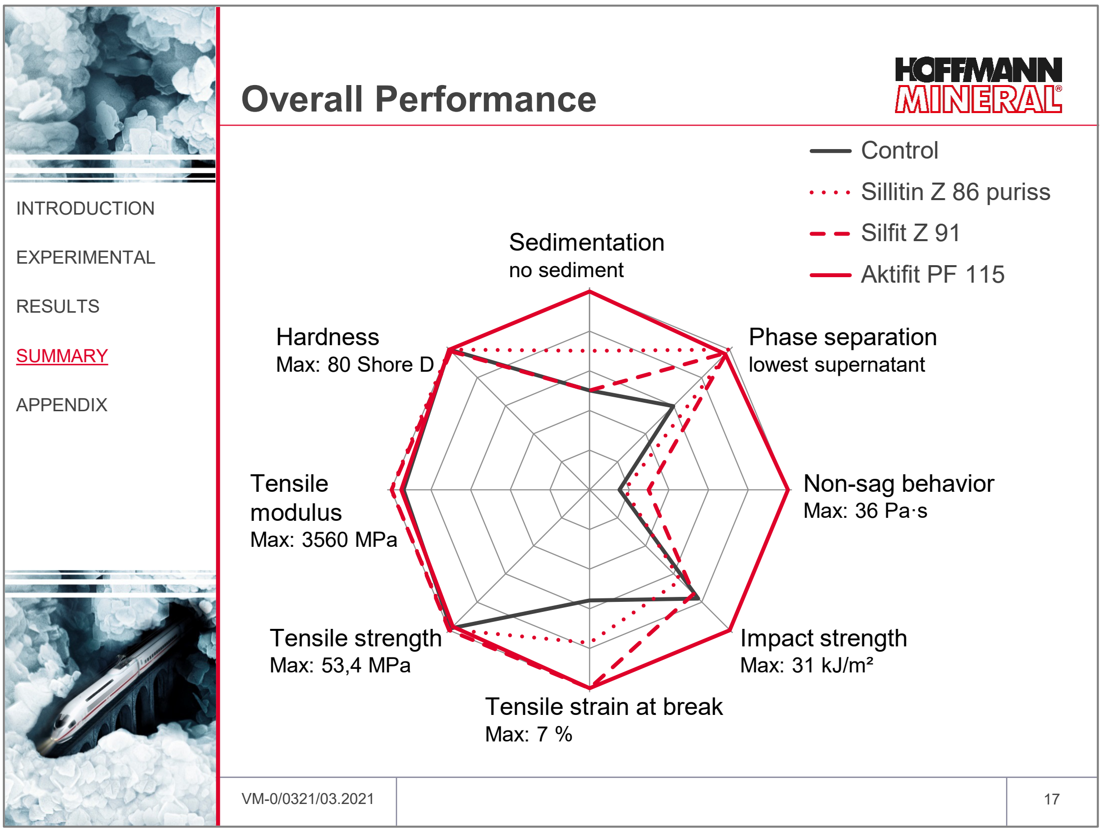
3.2.4 Impact strength

The test was performed according to DIN EN ISO 179-1 on unnotched specimens with a 4J pendulum.



While the formulations with the non-surface treated Neuburg Siliceous Earth grades Sillitin Z 86 puriss and Silfit Z 91 are on a somewhat lower or comparable level as the control formulation, the impact strength with Aktifit PF 115 increases markedly by approx. 30 %.

4 Summary



Neuburg Siliceous Earth is very well suited as a functional, mineral filler for heavy-duty 2K PU coatings.

The selected products can be easily incorporated and dispersed as mineral fillers.

Already the cost-effective Sillitin Z 86 puriss offers advantages in terms of storage stability and tensile strain at break compared to the filler combination of the mica-chlorite-quartz intergrowth (leucophyllite) and the surface-treated quartz flour used in the control formulation.

Silfit Z 91 and Aktifit PF 115, the two calcined Neuburg Siliceous Earth grades, give a further increase in tensile strain at break.

Aktifit PF 115 is also characterized, besides the improved impact strength, by the rheological activity. This allows the application of higher film thicknesses without sagging tendency and, as a positive side effect, prevents the formation of sediment during storage of the A-component.

In addition, the corrosion protection effect of the coating with Neuburg Siliceous Earth products should be improved, which would be expected for the hydrophobic Aktifit PF 115 in particular.

Product recommendations:

Sillitin Z 86 puriss	+ cost-effective standard product + improved storage stability (significantly less supernatant / slightly reduced sediment) + improved tensile strain at break
Silfit Z 91	+ color neutral + improved storage stability (significantly less supernatant) + significantly improved tensile strain at break
Aktifit PF 115	+ color neutral + high rheological activity (non-sag behavior) + strongly improved storage stability (significantly less supernatant and no sedimentation) + significantly improved tensile strain at break + higher impact strength

5 Appendix

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Table of Results

HOFFMANN MINERAL

		Control	Neuburg Siliceous Earth		
			Sillitin Z 86 puriss	Silfit Z 91	Aktifit PF 115
Viscosity Component A @ 0.1 s^{-1}	Pa·s	5.4	6.4	10.7	35.9
@ 1000 s^{-1}	Pa·s	3.8	5.1	5.8	5.4
Sedimentation 3 months @ 40°C Supernatant	%	44	6	8	9
Hard sediment	%	5	3	5	---
Hardness, 15 s	Shore D	81	81	80	81
Tensile modulus	MPa	3340	3560	3560	3380
Tensile strength	MPa	52.7	53.2	53.4	52.0
Tensile strain at break	%	3.9	5.4	7.0	7.0
Impact strength Charpy	kJ/m²	24	20	23	31

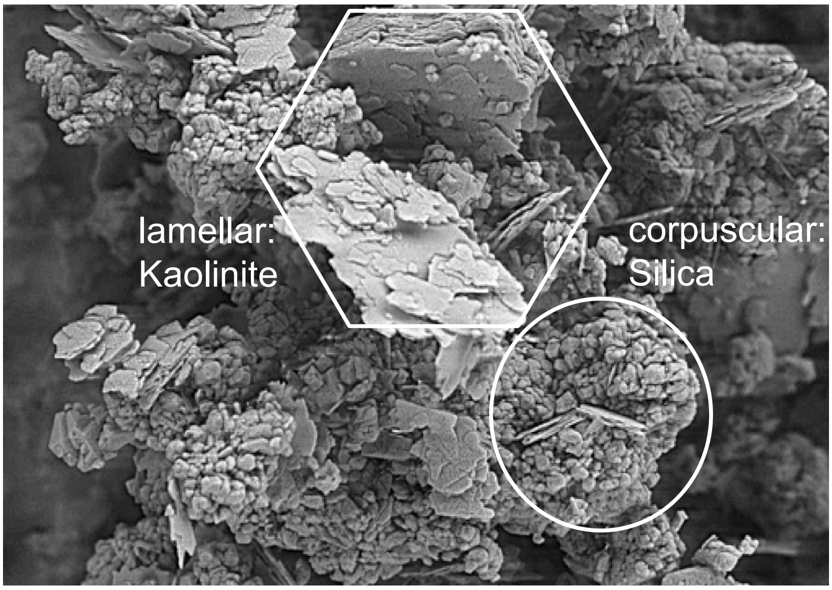
VM-0/0321/03.2021

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
APPENDIX

Morphology of Neuburg Siliceous Earth

HOFFMANN MINERAL

Magnification 10.000x



VM-0/0321/03.2021

INTRODUCTION

EXPERIMENTAL

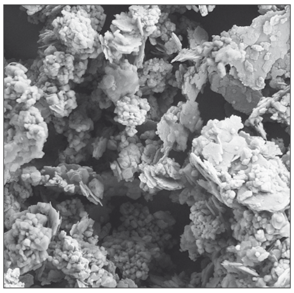
RESULTS

SUMMARY

APPENDIX

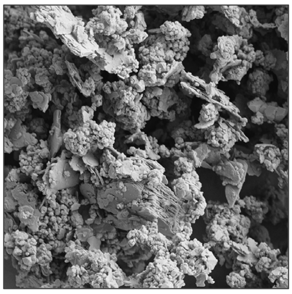
Calcined Neuburg Siliceous Earth

A downstream thermal process lead to the calcined products SILFIT and AKTIFIT, based on SILLITIN Z 86.



Neuburg Siliceous Earth

Calcination Process →



Calcined Neuburg Siliceous Earth

Additional application benefits, as well as the removing of crystal water included in the kaolinite. The silica part remains inert.

VM-0/0321/03.2021

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.