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Neuburg Siliceous Earth as a siliceous alternative to calcium carbonate in MS parquet adhesives

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1 Introduction

MS Polymers are part of reactive one-component systems. The polymers were developed in Japan in the mid-70s, and initially were used predominantly in elastic sealants. Since several years, MS polymers find also application in formulations for parquet adhesives, where they offer the following benefits:

- very low emissions
- absence of isocyanates, solvents, silicone and PVC
- environmental friendliness and no odor
- rapid curing at ambient temperature without formation of blisters
- pH around neutral
- outstanding low-temperature elasticity
- inherently good adhesion on various substrates
- good paintability

The objective of the present study is to introduce Neuburg Siliceous Earth in appropriate formulations as a partial or complete replacement for the conventional fillers. In so doing, the usual methods of preparation and application were maintained, and the batches were subjected to pertinent tests.

Note:

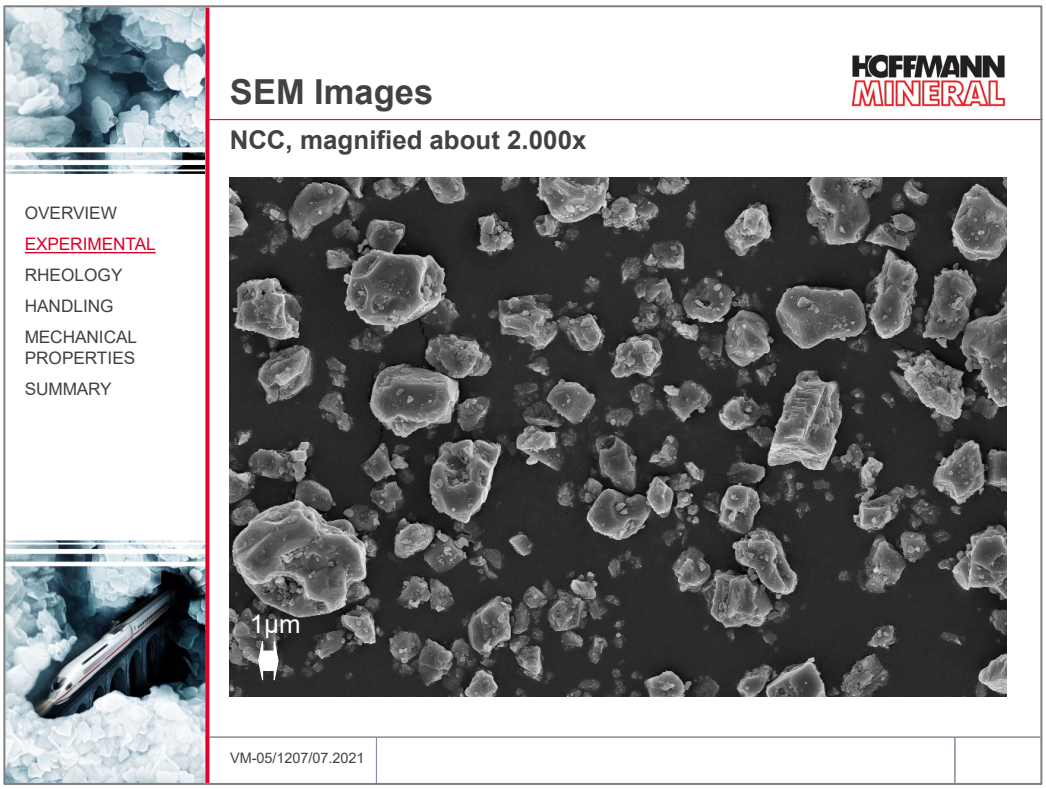
This study is intended to show the basic effects of the various Neuburg Siliceous Earth grades, although the formulation and raw materials used are in some cases no longer state of the art or are subject to other restrictions.

2 Experimental

2.1 Filler morphology and characteristic properties

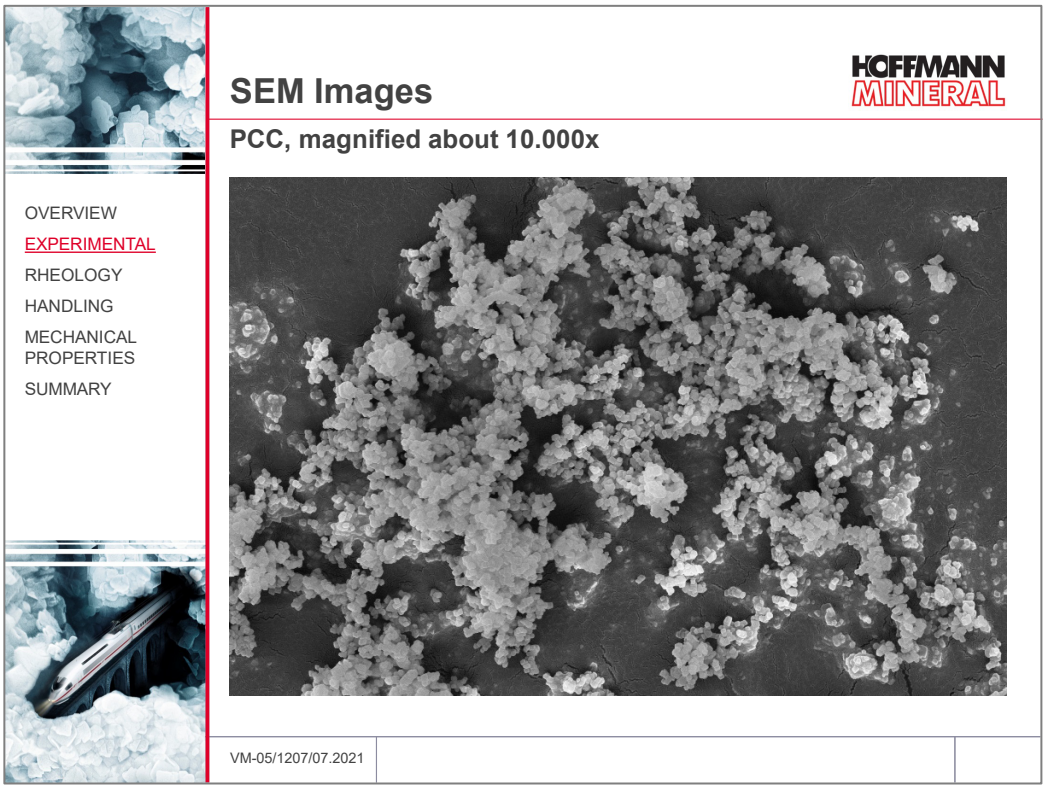
Natural calcium carbonate (NCC)

The natural calcium carbonate used was a modification of limestone surface treated with stearate, presenting a compact shape, low oil number and low specific surface area.



Precipitated calcium carbonate (PCC)

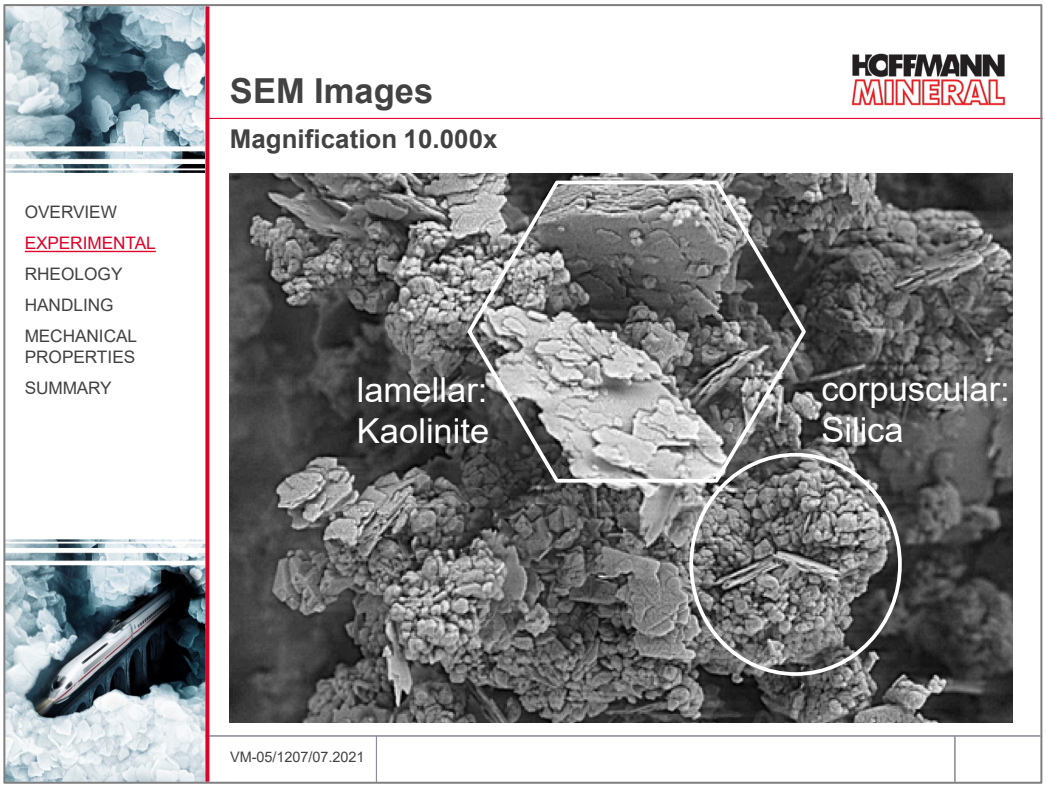
The stearate treated precipitated calcium carbonate was an ultrafine grade with a high specific surface area.

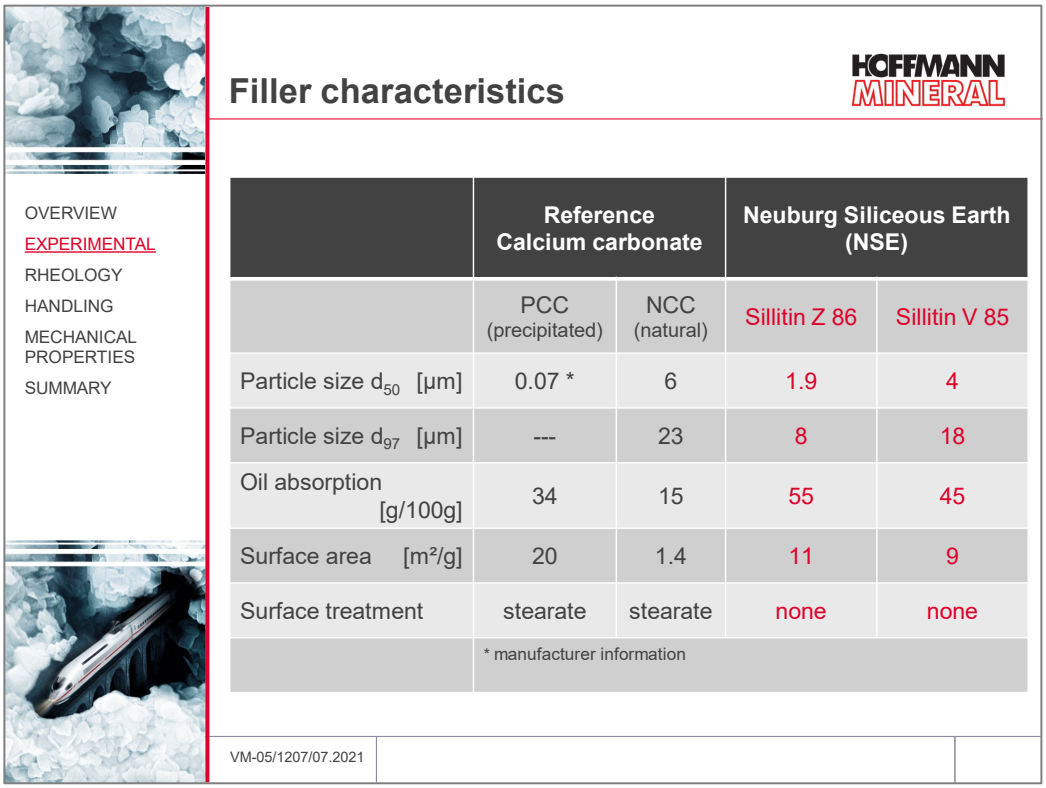


Neuburg Siliceous Earth

The Neuburg Siliceous Earth, extracted in the surrounding of Neuburg (Danube), is a natural combination of corpuscular Neuburg silica and lamellar kaolinite: a loose mixture impossible to separate by physical methods. As a result of natural formation, the silica portion exhibits a round grain shape and consists of aggregated, crypto-crystalline primary particles of about 200 nm diameter. Such a structure is responsible for a relatively high specific surface area and oil absorption, which result, besides rheological activity, also in favorable mechanical properties.

The morphology of the Neuburg Siliceous Earth is illustrated in the following picture:





	Reference Calcium carbonate		Neuburg Siliceous Earth (NSE)	
	PCC (precipitated)	NCC (natural)	Sillitin Z 86	Sillitin V 85
Particle size d_{50} [µm]	0.07 *	6	1.9	4
Particle size d_{97} [µm]	---	23	8	18
Oil absorption [g/100g]	34	15	55	45
Surface area [m²/g]	20	1.4	11	9
Surface treatment	stearate	stearate	none	none
	* manufacturer information			

2.2 Formulation

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MS Formulation

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Parquet adhesive	PCC / NCC	NSE / NCC	Neuburg Siliceous Earth (NSE)		
MS Polymer (high modulus)	100	100	100	100	100
Plasticizer (PP-glycol)	50	50	50	50	50
Titanium dioxide	10	10	10	10	10
Rheological additive (RA) Crayvallac SLX (micronized amide wax)	3	3	3	0	3 (5 / 7.5 / 10)
Light stabilizer / UV-Absorber	2	2	2	2	2
PCC	100	---	---	---	---
NCC	150	150	---	---	---
NSE	---	100	250	250	200
Drying agent	2	2	2	2	2
Adhesion promoter (AS) (3-amino propyl triethoxy silane)	3.5	3.5	3.5	7	7
Catalyst	1	1	1	1	1
Total (parts by weight)	**421.5**	**421.5**	**421.5**	**422**	**372**

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Starting from the base formulation with precipitated (PCC) and natural calcium carbonate (NCC),

a) only the precipitated calcium carbonate,

b) both calcium carbonates

were replaced by an equal weight of Neuburg Siliceous Earth (NSE). Additionally, one formulation was prepared without rheological additive.

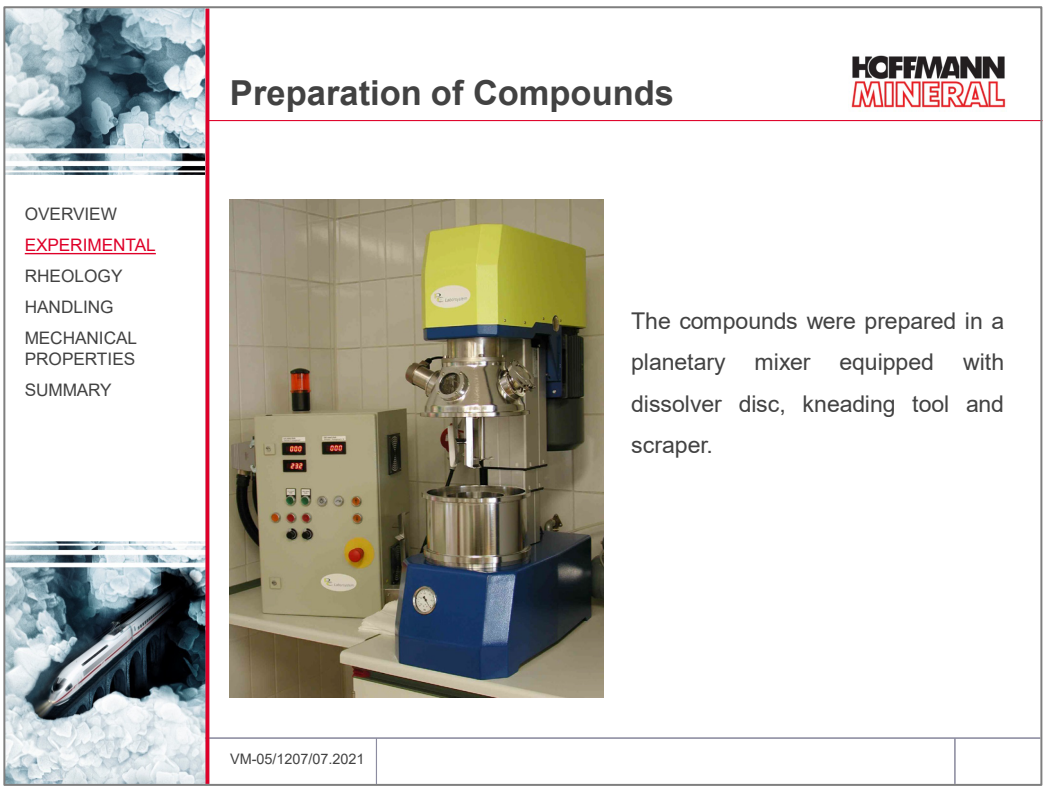
A further test series was made up with reduced filler content.

In the batches with Neuburg Siliceous Earth, the aminosilane based adhesion promoter will partly be adsorbed at the siliceous filler surface and, therefore, immobilized, resulting in a reduced contribution towards improved adhesion.
For this reason, the amount of bonding agent was increased here from 3.5 to 7 pbw [1].

The other ingredients were kept constant in all formulations.

[1] *The original base recipe contained as adhesion promoter 3 pbw DAMO (diaminosilane with primary and secondary amino groups). Increasing the amount of this product in the NSE batches would have necessitated a labelling of the formulations as Xi = irritating (DAMO has to be labelled at concentrations >1 %).*
Alternatively, A 1100 (a primary aminosilane which does not require an obligation for labelling even at higher concentrations) was used, and the amount in the calcium carbonate batches slightly increased to 3.5 parts, in order to keep the properties at the level of the original base formulation.
A further way to avoid the labelling obligation due to the increase of bonding agent is the use of the surface treated NSE grade Aktisil AM along with an unchanged DAMO concentration. The results with such an approach were comparable with the Sillitin Z 86 batches with 7 pbw A 1100.

2.3 Preparation of batches



The fillers were pre-dried along with the titanium dioxide [2].

Binder, plasticizer, rheological additive and light stabilizer were added first.

Fillers and titanium dioxide were then added and dispersed for 45 min under vacuum. During this time, the temperature of the batch was kept for 30 min between 60 and 90 °C in order to sufficiently activate the rheological additive.

After cooling down to 50 °C, at intervals of 5 min the drying agent, the bonding agent and the catalyst were added and stirred in.

After short deaeration, the batches were filled into cartridges.

[2] *Tests were also carried out without pre-drying the fillers and otherwise unchanged processing conditions. Neither the NSE nor the calcium carbonate batches showed any differences with respect to storage stability vs. the formulations with pre-dried fillers. Obviously, the vinylsilane drying agent in the formulation is sufficiently active to bind the moisture present in the fillers. It was only with a reduced concentration of drying agent that the batches began to harden in the cartridges.*

3 Results

3.1 Rheology

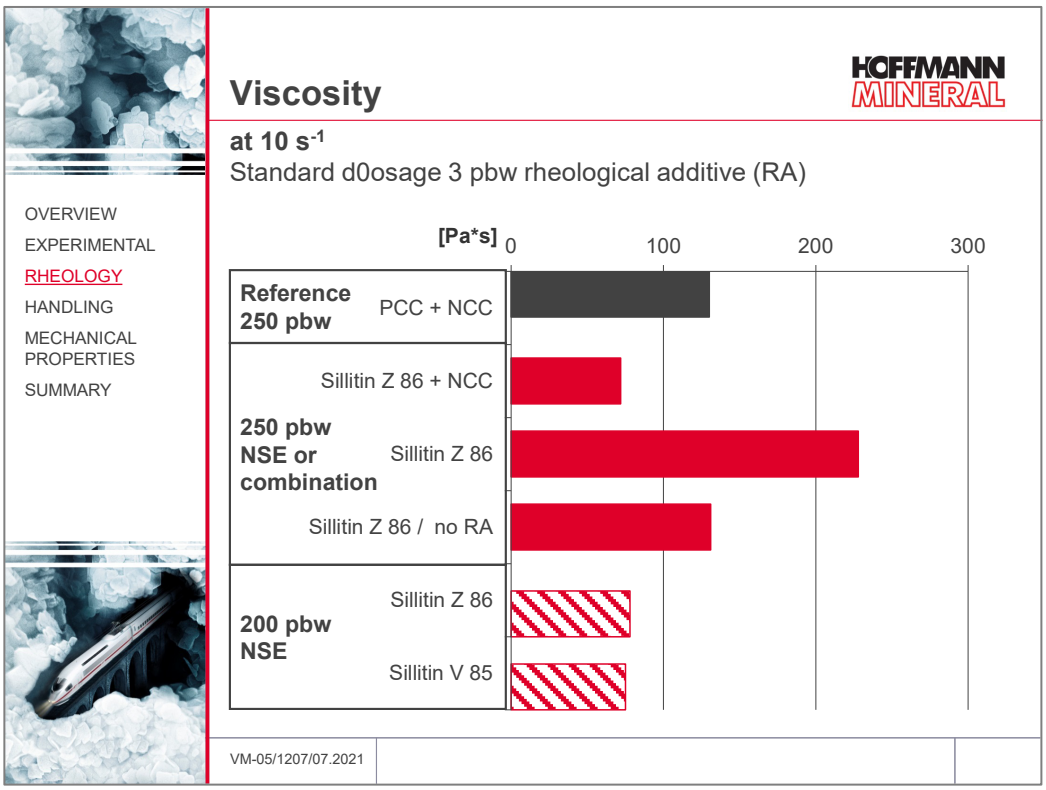
The rheological tests were carried out with a plate/plate instrument (diameter 25 mm, gap 1 mm). For each determination, the system was filled anew. The tests were run under rotation.

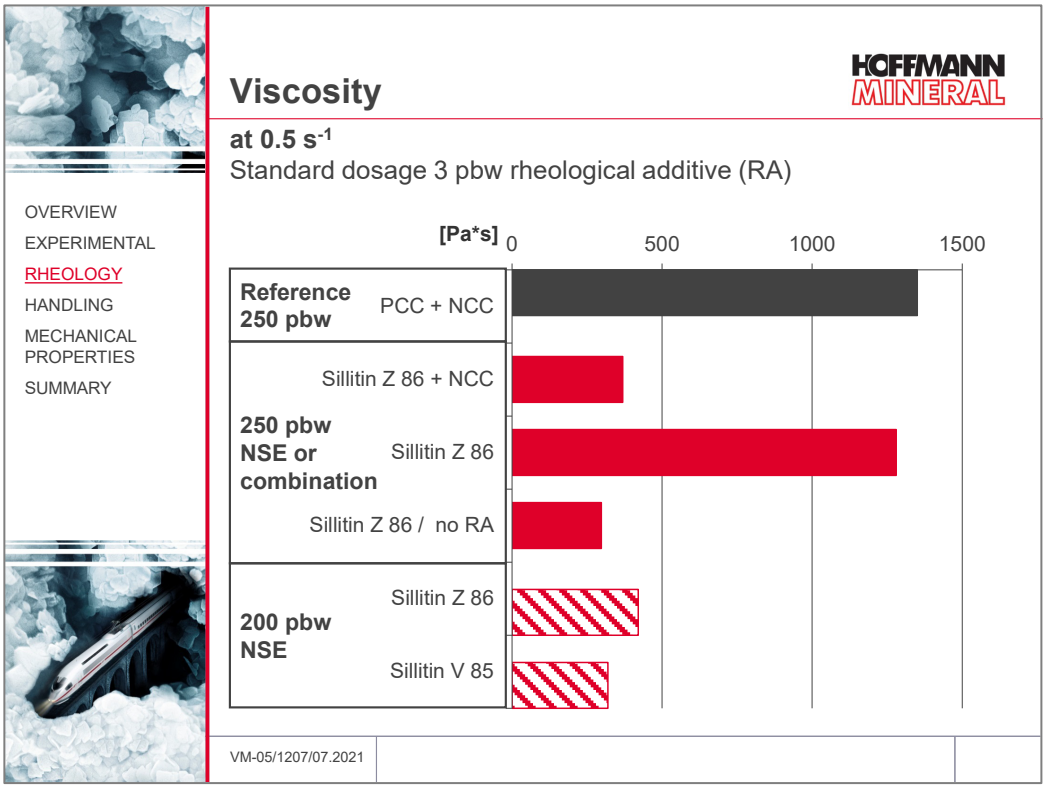
Viscosity

The viscosity results were interpolated for the shear rate levels indicated, from a shear rate controlled flow diagram (logarithmic increase from 0.1 to 100 s^{-1}). In particular, comparisons were made between the viscosities of the batches at 0.5 and 10 s^{-1}.

When replacing precipitated calcium carbonate with Neuburg Siliceous Earth at equal weight, the viscosity comes out markedly lower, but if in addition the natural calcium carbonate is exchanged, the viscosity increases strongly at higher shear rates. This is true for the formulations with 3 pbw of the rheological additive. Leaving out the rheological additive brings down the viscosity to the original level.

A reduced filler loading also leads to a markedly lower viscosity.

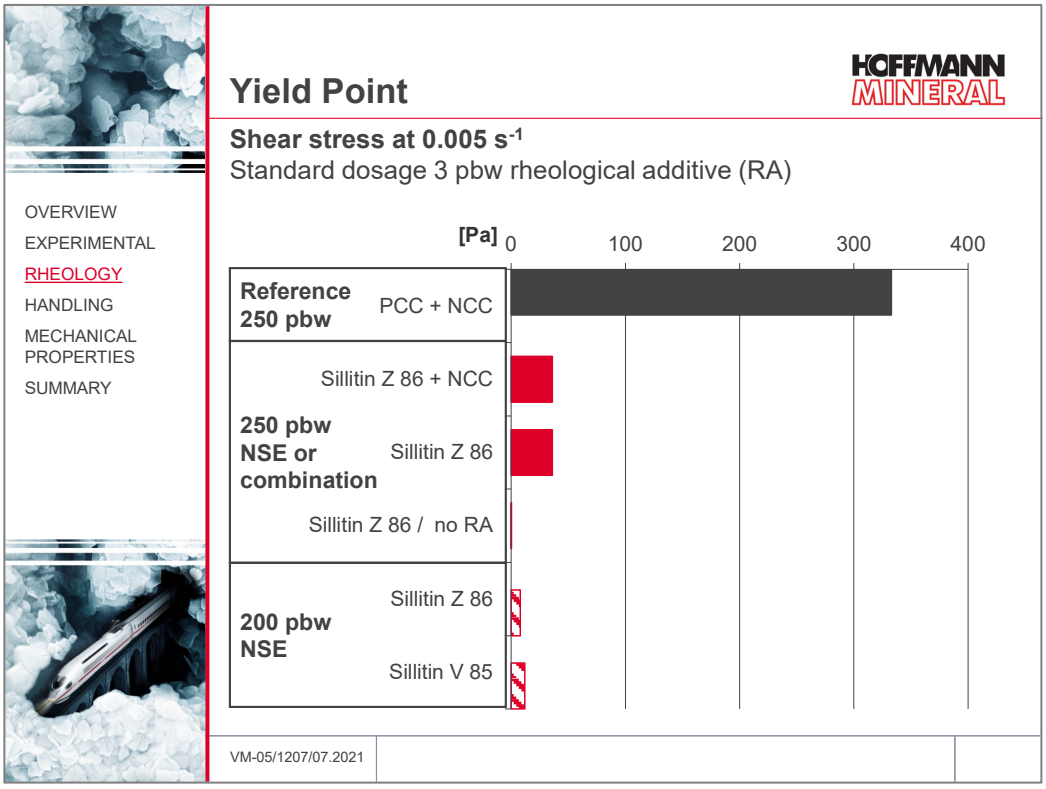




Yield point

The yield point was determined by linearly increasing the shear stress from 2.5 to 1000 Pa with a rate of 2.5 Pa/s. The result was expressed as the shear stress at a shear rate of 0.005 s^{-1}.

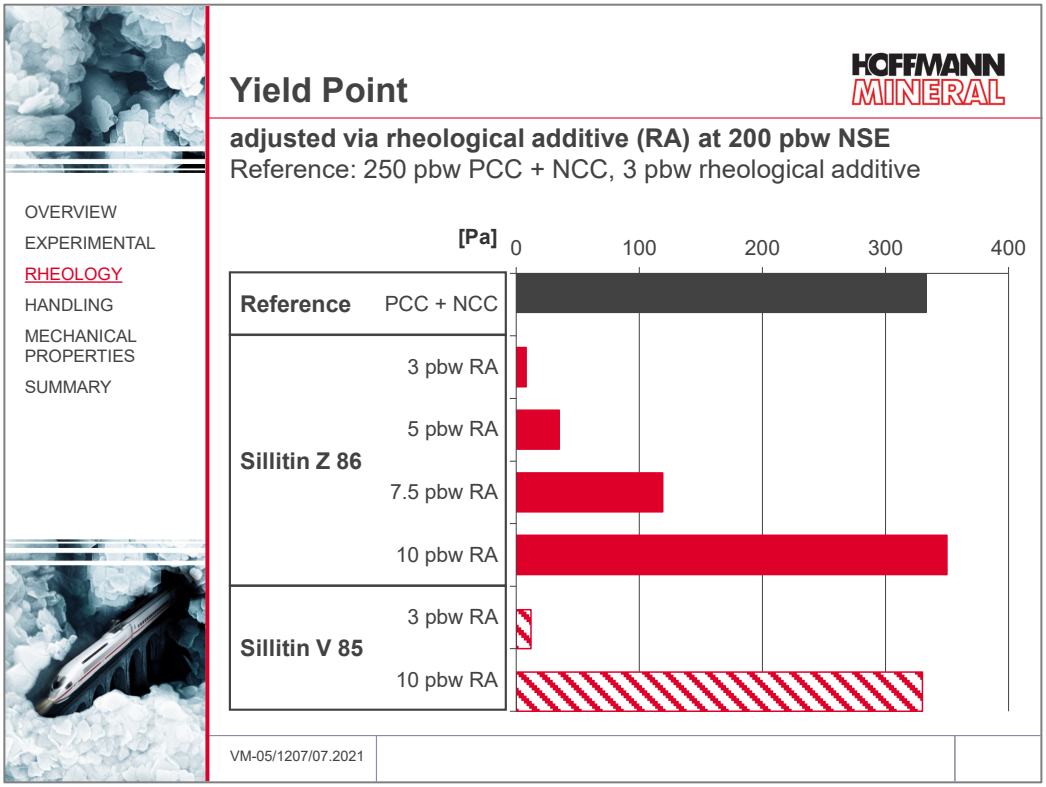
Working with Neuburg Siliceous Earth distinctly reduces the yield point of the batches in spite of the normal addition of the rheological additive.



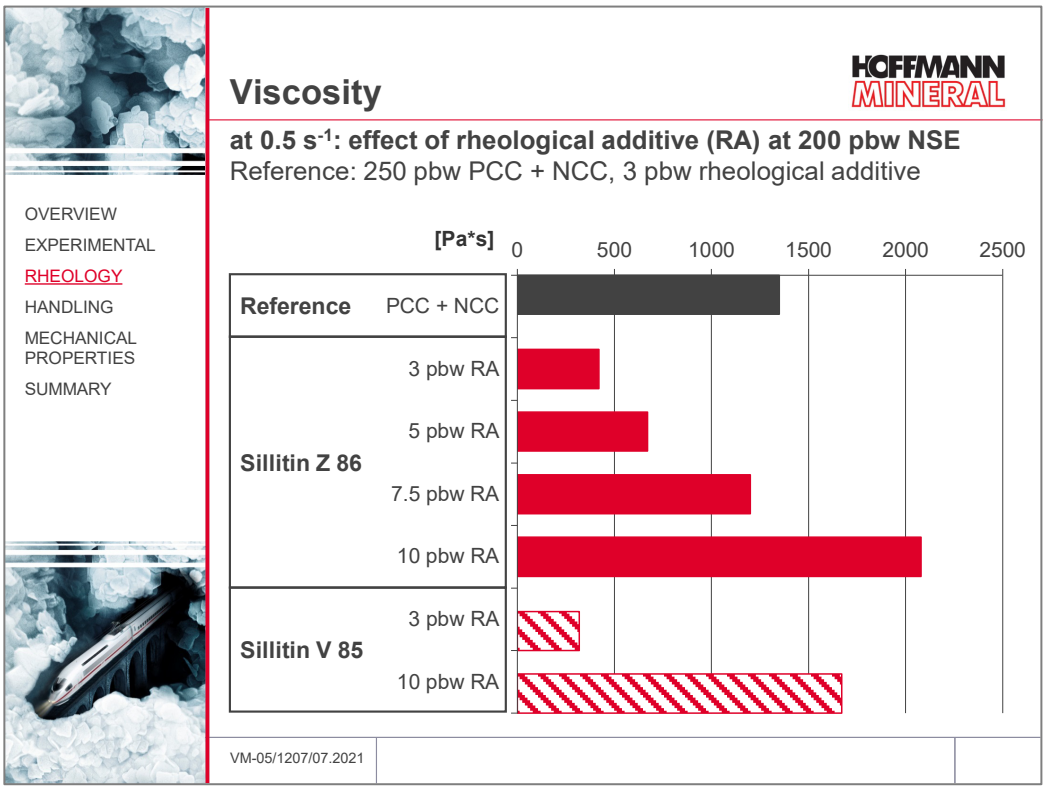
In a further test series, the concentration of the rheological additive was varied in order to affect the yield point. In view of the mentioned viscosity increase when replacing the calcium carbonate at equal weight, tests were only run with a reduced filler loading of 200 pbw.

From the range of Neuburg Siliceous Earth products, in addition to Sillitin Z 86 also Sillitin V 85 with a lower oil number was considered.

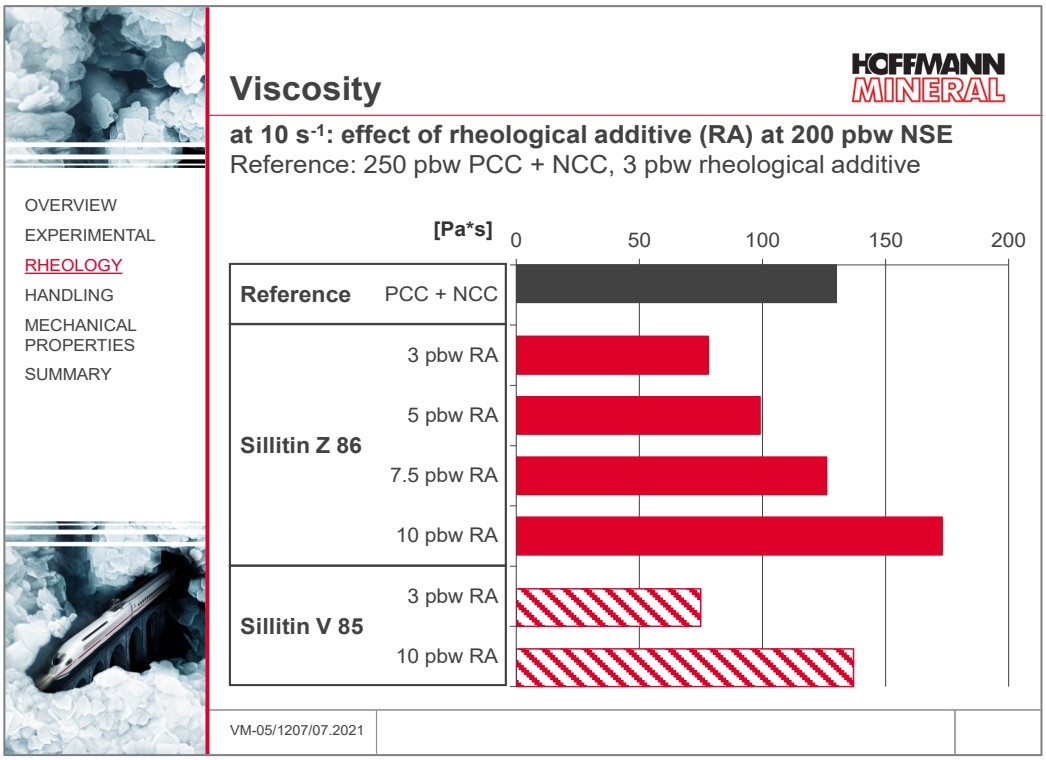
In order to arrive at a yield similar to the reference formulation, working with Neuburg Siliceous Earth requires a concentration of the rheological additive between 7.5 and 10 pbw.



Along with the yield point, with higher additions of the rheological additive also the viscosity shows an increase, and this more so with Sillitin Z 86 with Sillitin V 85.



At comparable yield point, the viscosity at 10 s^{-1} with Sillitin V 85 is at level with the reference formulation.

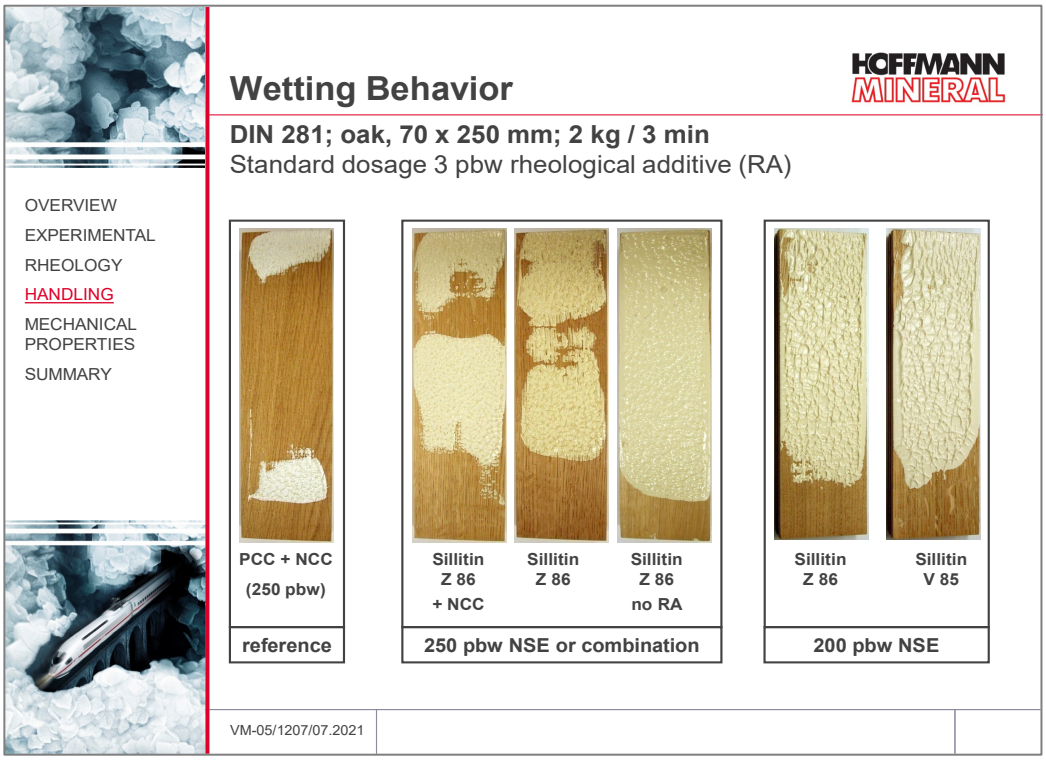


3.2 Handling

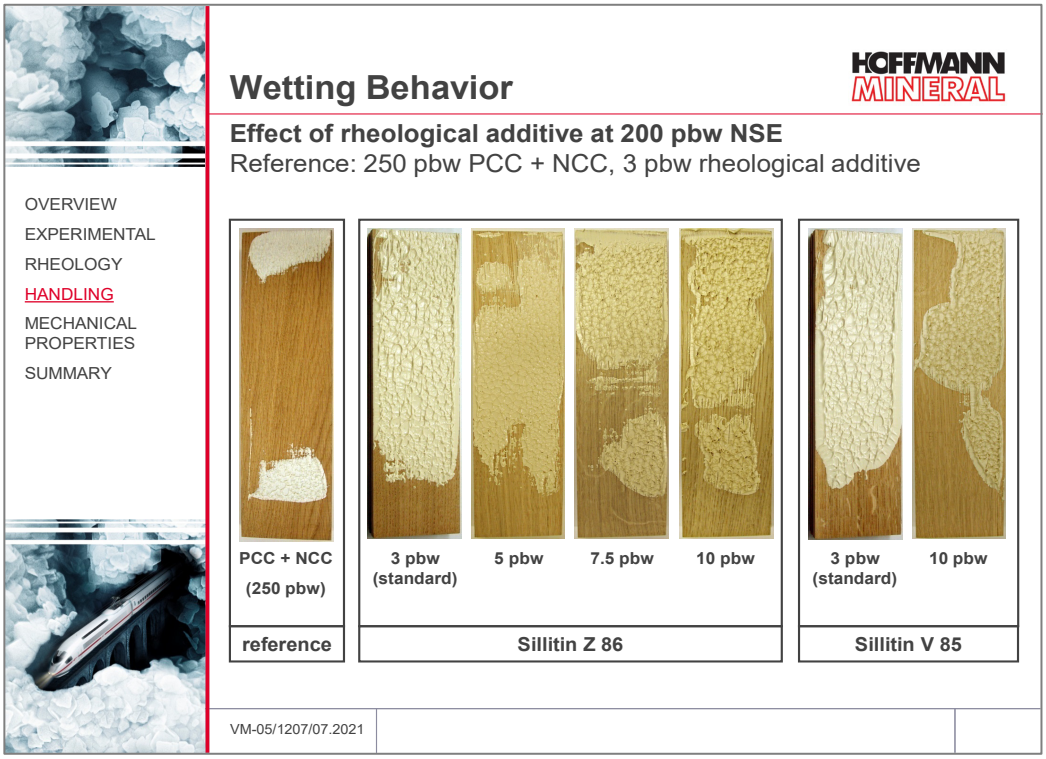
Wetting properties (DIN 281)

A chipboard plate was coated at 1 mm layer thickness with the formulation, and after 1 minute a plane oak wood parquet board (70 x 250 mm) was placed on top in a way that one longitudinal and one transversal side finished flush with the chipboard. The parquet wood was immediately loaded with a 2 kg weight. After 3 minutes the parquet board was lifted on the jutting-out side via a quarter-circle movement without lateral shifting.

In accordance with the lower yield point, the batches with Neubug Siliceous Earth give evidence of a markedly better wetting capacity than the reference with calcium carbonates.



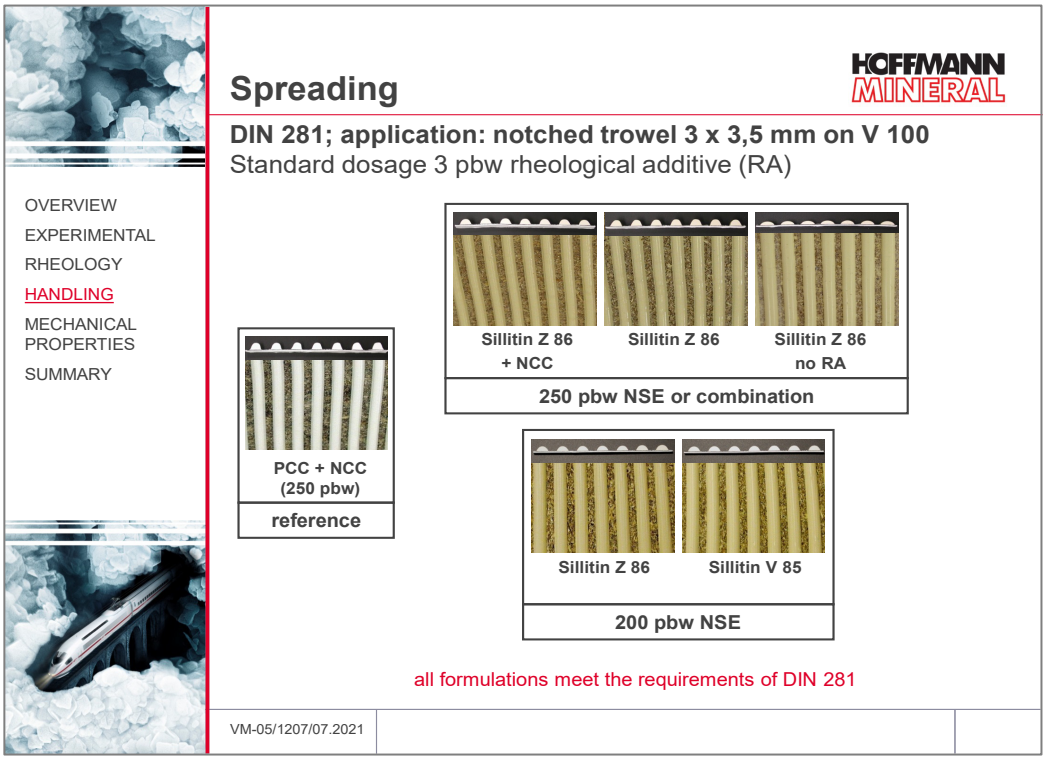
Even with the highest addition of the rheological additive (and the same yield point as the reference formulation), the batches with Neuburg Siliceous Earth give rise to markedly superior wetting. [3]



Spreading properties (DIN 281)

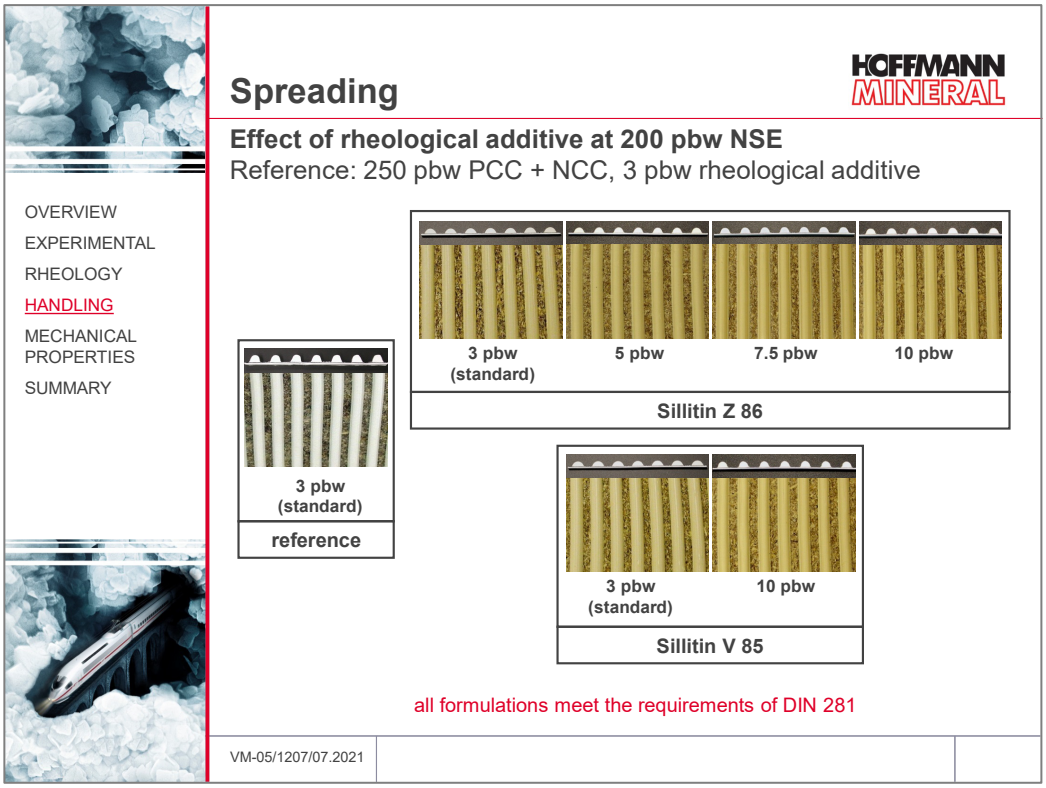
The adhesive was spread with a notched trowel (teeth 3 mm deep and 3.5 mm large) onto a chipboard plate. The structure with its grooves must be maintained after the application.

In spite of their lower yield point and the superior wetting properties, the formulations with Neuburg Siliceous Earth, even in combination with the regular dosing of the rheological additive of 3 pbw, fulfill the requirements of the standard.



[3] *The color differences of the batches in the figure are caused by differing lighting conditions when taking the photographs. They do not necessarily represent the actual color of the formulation.*

The requirements of the standard are also met with the lower filler content. The height of the adhesive grooves indicates the relation with the yield point and thus with the amount of rheological additive.



3.3 Mechanical properties

Varying the amount of rheological additive does hardly at all influence the mechanical and adhesion properties. Therefore, in the following only the results with the standard loading of rheological additive will be presented.

Preparation of test samples

For tensile and hardness tests, sheets with a thickness of about 2 mm were prepared. After curing the sample sheets for 14 days at standard conditions (23 °C and 50 % relative humidity), dumbbell samples S2 according to DIN 53504 were died out and tested.

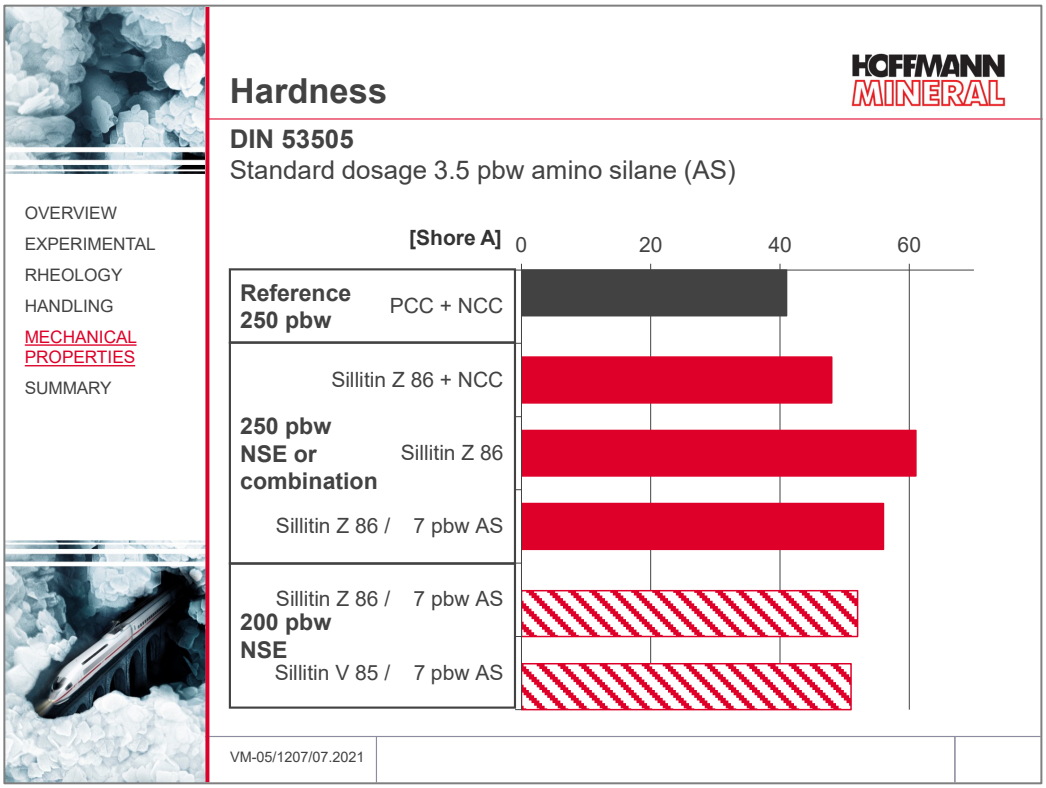
For the tensile shear tests, samples were prepared according to DIN 281: the adhesive was spread onto an oak mosaic parquet lamella (138 x 23 x 8 mm) and spread with a notched trowel (teeth 3 mm deep and 3.5 mm large) vertically to the longitudinal side over the area to be bonded. A second parquet lamella was laid on top in a way to generate a bonded area of 6 cm² (23 x 26 mm). The bonded area was then loaded for 1 min with a weight of 2 kg.

After a curing time of 4 weeks at standard climate the tensile shear test was carried out with a speed of 20 mm/min.

Hardness (DIN 53505)

Hardness was determined on three S2 dumbbells piled up above each other.

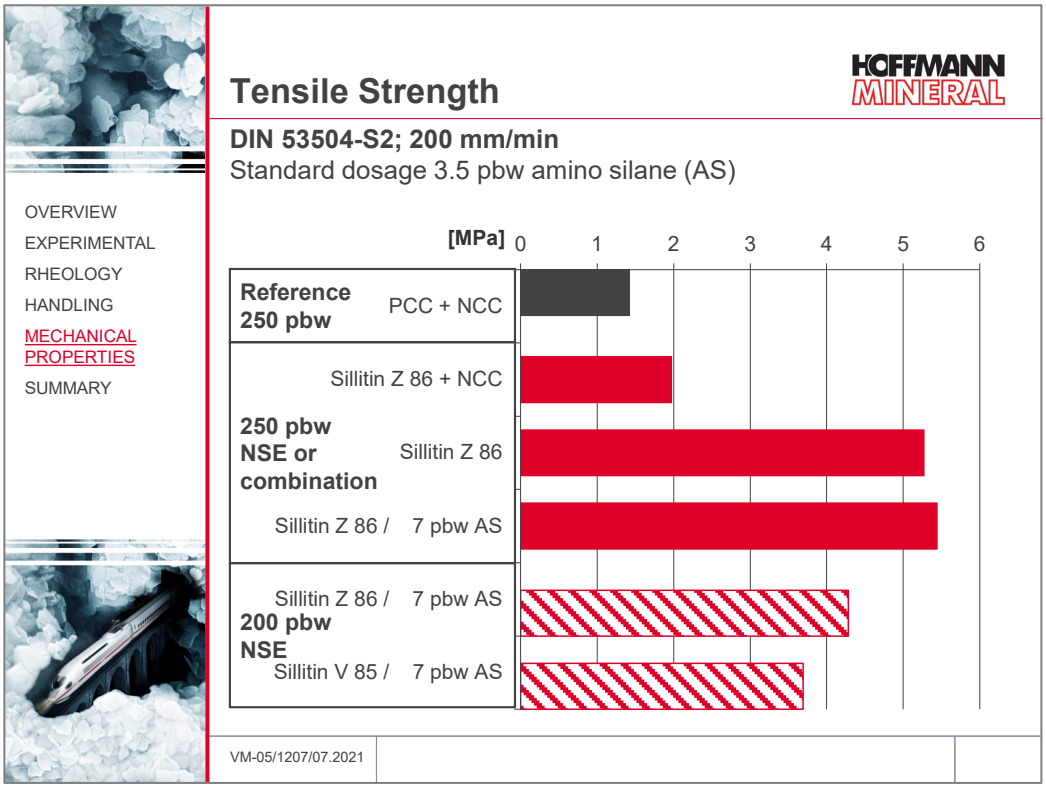
Neuburg Siliceous Earth, even at reduced filler content, leads to a higher Shore A hardness than the calcium carbonates used.



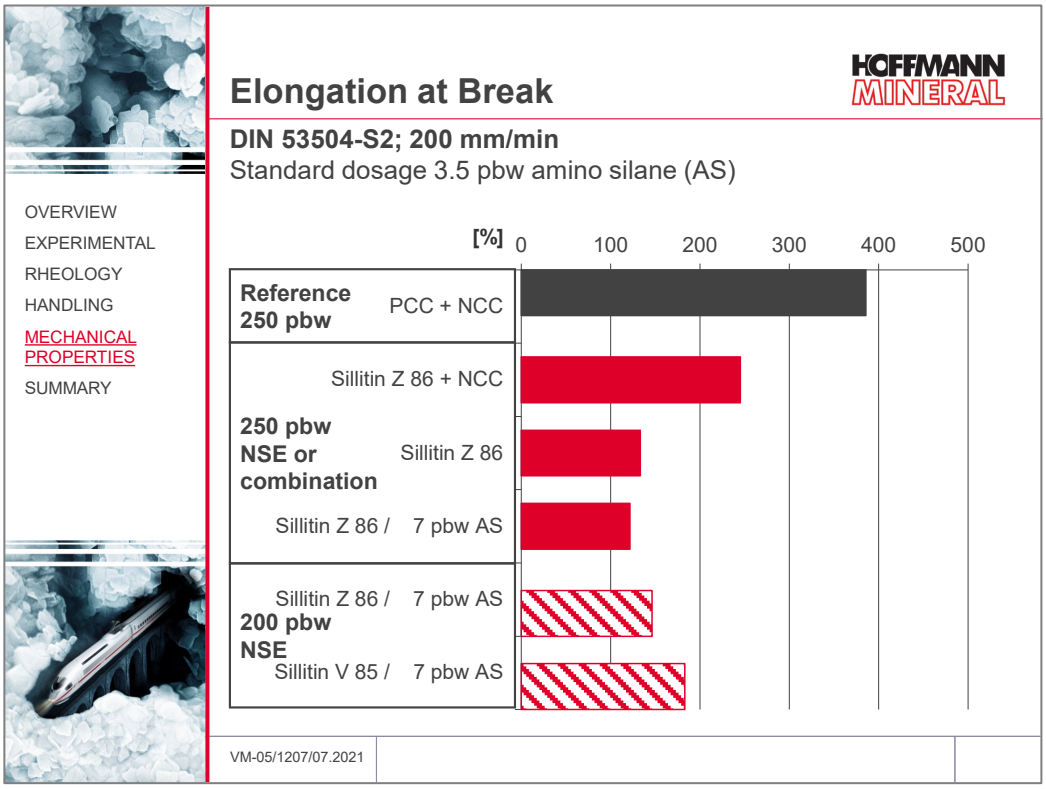
Tensile test (DIN 53504)

Tensile strength and elongation at break were determined on S2 dumbbells at a test speed of 200 mm/min.

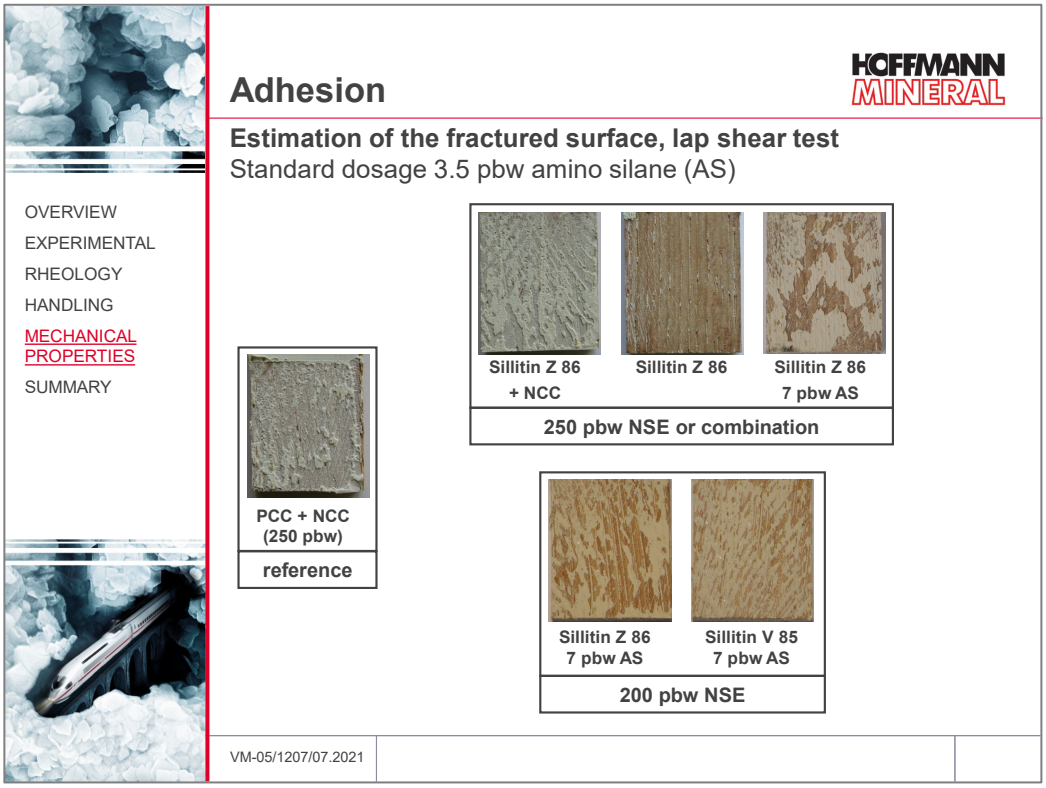
With Neuburg Siliceous Earth, even at reduced filler loading a substantial increase of tensile strength can be obtained.



On the other hand, the high elongation at break of the calcium carbonate could not be attained with Neuburg Siliceous Earth. Between the two grades tested; Sillitin V 85 tends to give higher values.



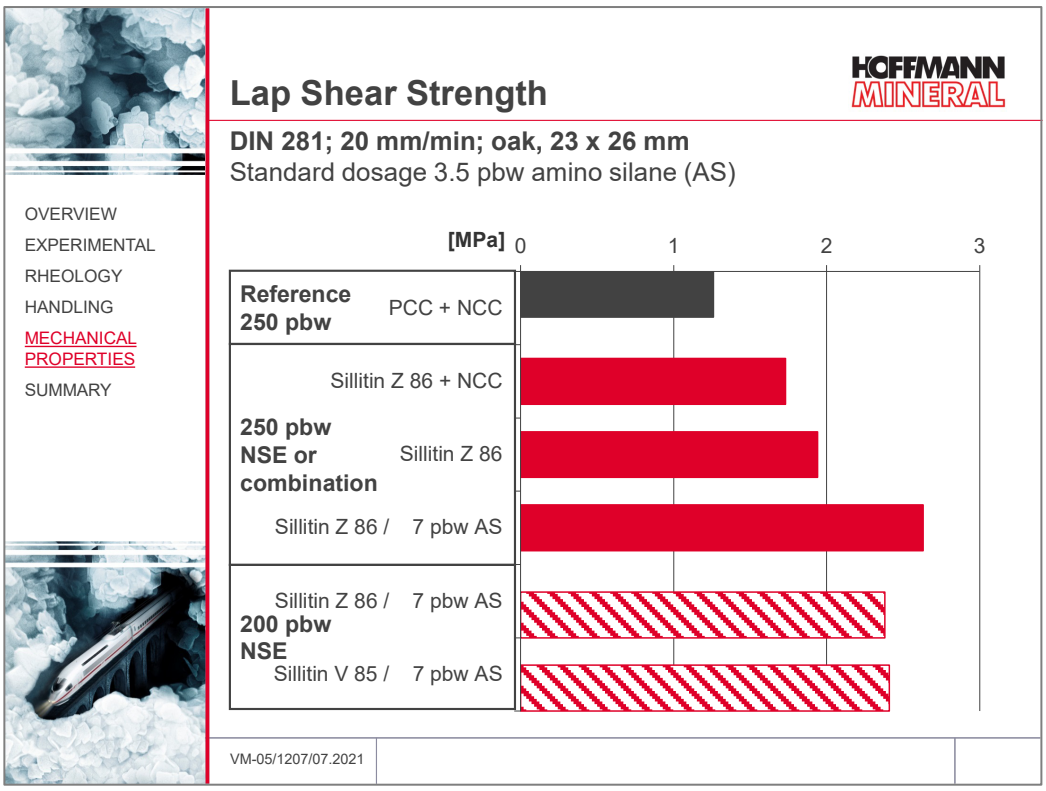
Lap shear test (DIN 281)



Although the fracture surfaces of the formulations with Neuburg Siliceous Earth, contrary to the reference formulation, do not give evidence of 100 % cohesive failure, these fillers all the same lead to a marked increase of the tensile shear strength.

Increasing the bonding agent concentration to 7 pbw causes a further significant increase of the tensile shear strength. Also images of the fracture surface give evidence of markedly improved adhesion.

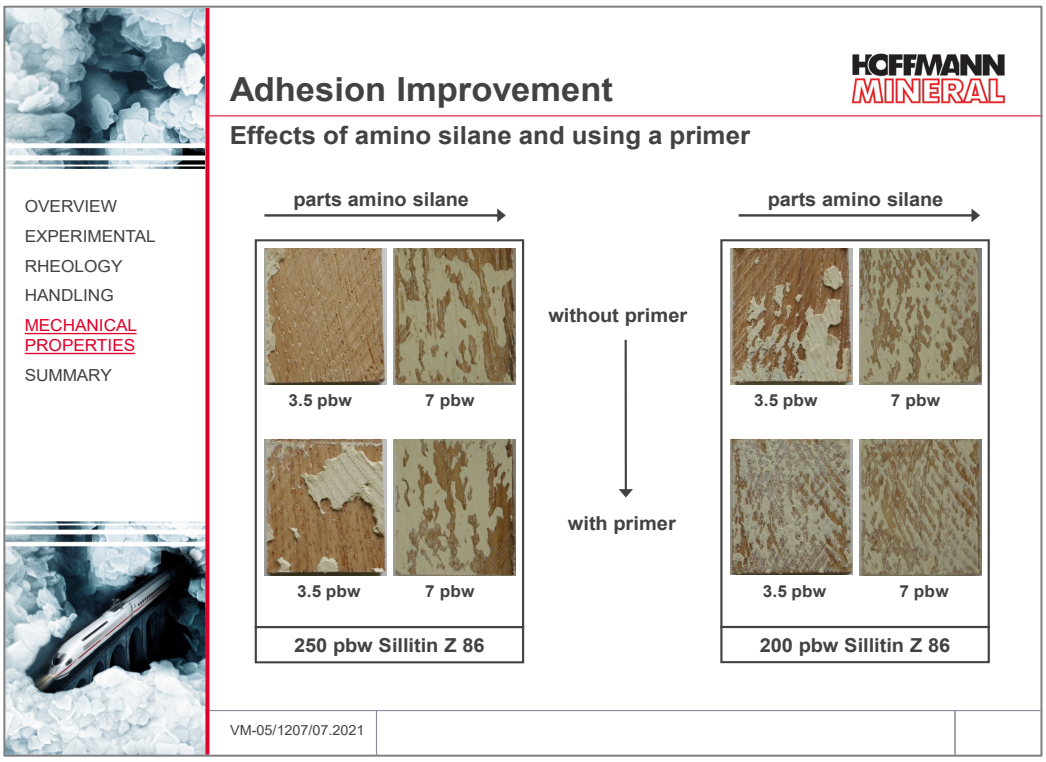
Reducing the filler loading to 200 pbw only generates a relatively minor reduction of the tensile shear strength.



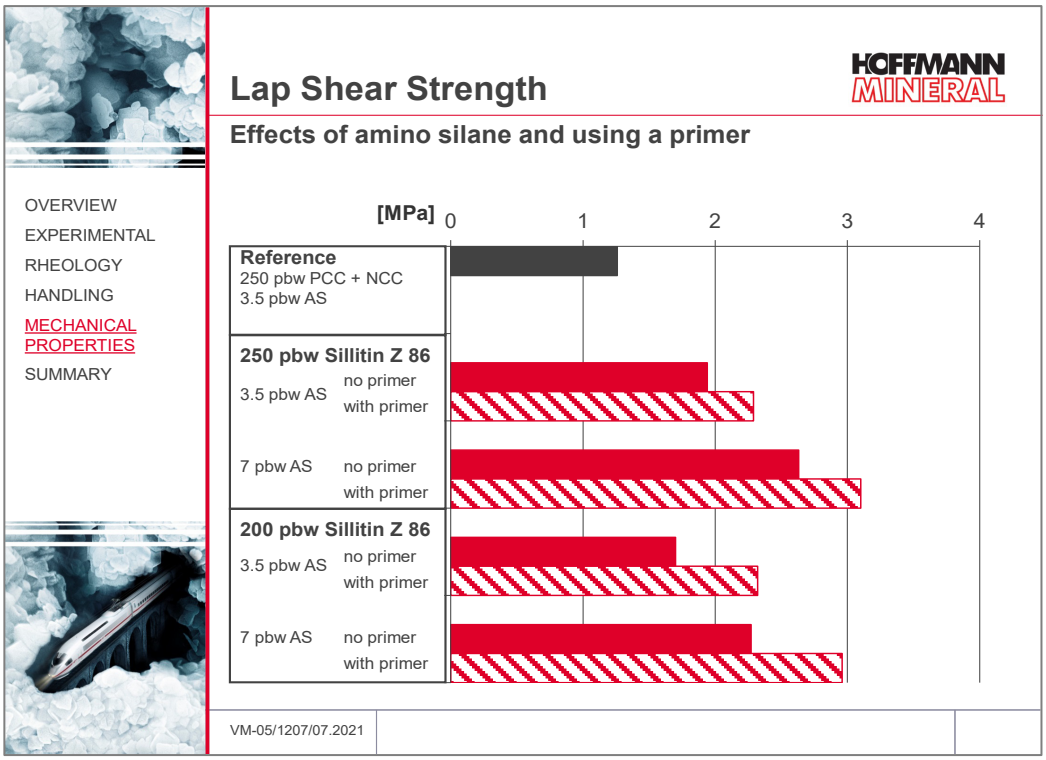
Lap shear test (DIN 281)

As the tensile shear strength had come out markedly below the tensile strength as determined in the tensile test, it was tried to improve the adhesion by working with a primer on polyacrylate/methoxysilane base. The basic interest here was to find out the highest level of tensile shear strength that could be obtained with Neuburg Siliceous Earth at optimum adhesion.

The figure shows for both filler loadings the effect of the increased aminosilane bonding agent addition onto the adhesion properties as well as of working with a primer.



The very best results for the tensile shear strength were obtained with an increased dosing of the adhesion promoter in conjunction with the use of a primer. [4]



[4] *Primers generally find application in certain areas of wood-to-wood bonding (e.g., in boat manufacture for adhesion within the yacht decks).*

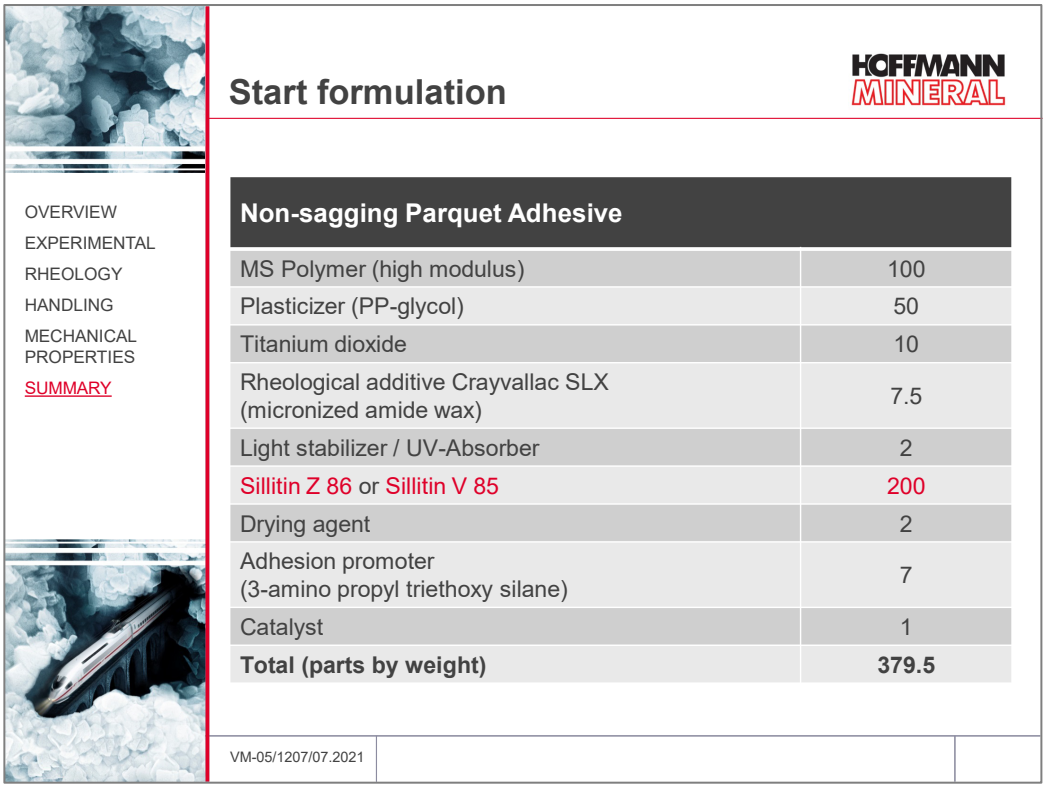
4 Summary

Compared to the tested calcium carbonates, the use of Neuburg Siliceous Earth gives the following benefits:

- bright color formulations when working with Sillitin Z 89 or Sillitin V 88
- unchanged storage stability (6 months at ambient temperature)
- viscosity in between precipitated and natural calcium carbonate
- no yield point, free adjustable with rheological additive
- higher hardness
- **higher tensile strength**
- **significantly higher lap shear strength, potentially still to be increased**

5 Recommendation and suggested starting formulation

- Sillitin V 85 (especially for low viscosity formulations) or Sillitin Z 86, recommended loading 200 pbw
- adjustment of the yield point by a rheological additive, preferably 5 to 10 pbw for non-sagging formulations
- 3.5 to 7 pbw aminosilane adhesion promoter for good adhesion
- use of a primer to further improve adhesion with the result of even higher lap shear strength



Start formulation

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Non-sagging Parquet Adhesive	
MS Polymer (high modulus)	100
Plasticizer (PP-glycol)	50
Titanium dioxide	10
Rheological additive Crayvallac SLX (micronized amide wax)	7.5
Light stabilizer / UV-Absorber	2
Sillitin Z 86 or Sillitin V 85	200
Drying agent	2
Adhesion promoter (3-amino propyl triethoxy silane)	7
Catalyst	1
Total (parts by weight)	**379.5**

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