Neuburg Siliceous Earth in silicate emulsion paints

Author: Bodo Essen
Hubert Oggermüller

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HOFFMANN MINERAL GmbH • Muenchener Strasse 75 • D-86633 Neuburg (Donau) • Phone +49 (0) 8431 53-0
www.hoffmann-mineral.com • e-mail: info@hoffmann-mineral.com

Contents

1 Introduction

Silicate emulsion paints are a coating class from the field of high-quality architectural paints. Depending on requirements, they perform decorative or functional tasks indoors or outdoors. On the binder side, the properties of the "water glass" (aqueous potassium silicate solution) known from silicate paints are advantageously combined with those of an organic polymer dispersion.

As a purely inorganic component, the water glass serves the purpose of forming a chemically solid, inseparable bond with the mineral substrate by means of a chemical silicification process. The result is an extremely resistant coating, which is highly open to diffusion due to its fine porous structure. The very high pH-value of the water glass solution has an antimicrobial effect and enables environmentally friendly, completely biocide-free formulations.

By adding a smaller amount of organic polymer dispersion, contained pigments and fillers can be better fixed in the coating matrix. Adhesion problems to non-purely mineral substrates, e.g. synthetic resin plasters, are reduced and resistance to soiling, abrasion and chalking is improved. The water-repellent effect is reinforced and is supported for exterior applications by the addition of hydrophobing additives.

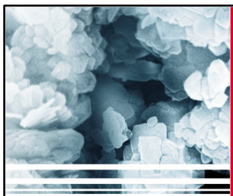
The main technical advantage of silicate emulsion paints is their one-component processability. Compared to the classic 2K silicate paints, they allow ready-to-use, universal and easier application even in the DIY sector.
However, the option for storage, on the other hand, makes very high demands: To prevent reactions of the water glass solution with formulation components already in the container, sufficient stabilization of the entire composition is necessary. This is intended to ensure the constancy of the rheological profile in order both to guarantee consistently good processability and to prevent premature viscosity increase and limited storage stability.
The fillers and pigments used must also meet these requirements. Due to soluble, multivalent cations or direct reaction with the water glass, they often lead to premature viscosity increase and thickening, which stands in the way of storage and shelf life in line with market requirements. Rheological stabilization despite latently high reactivity therefore also depends to a decisive extent on the targeted selection of the fillers used.

This technical report goes into this subject in greater depth and, using Neuburg Siliceous Earth as an example, shows ways to improve performance in a silicate emulsion facade paint. In addition, the filler effects on the coloristic properties after paint application are briefly sketched in order to highlight the possible applications in the decorative area.

2 Experimental

2.1 Base Formulation

A silicate emulsion paint from the company Wöllner, pigmented with 10 % white titanium dioxide, was chosen as the base formulation for the façade coating as shown in *Fig. 1.*
On the binder side, the aqueous formulation contains a styrene/acrylic acid ester dispersion as an organic component in addition to a commercial, stabilized potassium silicate solution. Other primarily stabilizing additives and an additional hydrophobing agent round off the formulation's suitability for outdoor use. At 33 parts by weight, the filler represents the largest proportion of the formulation and was varied for the tests.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

Base Formulation

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		Parts by weight [pbw]
Water deionized		27.6
Betolin V 30	Thickener	0.2
Sapetin D 20	Dispersant	0.2
Betolin Quart 44	Stabilizer for silicate solution	0.3
Byk 032	Defoamer	0.2
Silres BS 1306	Water repellent	1.0
Betolin A 11	Viscosity stabilizer	0.5
Crenox R-KB-5	Titanium dioxide	10.0
Fillers varied	Silicates (Base), Carbonates, Neuburg Siliceous Earth and combinations	33.0
Mowilith DM 765	Styrene / acrylic acid ester dispersion (50 % w/w)	8.0
Betolin P 35	Potassium silicate solution (29 % w/w)	18.0
Total		99.0
Solids content w/w [%]		54.1

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Fig. 1

2.2 Filler Characteristics

Fig. 2 gives an overview of the fillers tested and their most important key figures. With approximately comparable densities, the differences in oil absorption are mainly due to the widely varying particle sizes. Siliplast 910, as a coarse filler, shows the highest particle size. The other competitive fillers are noticeably finer. While the first three fillers have a silicate structure, Omyacarb 5 GU is a purely carbonate grade. The Neuburg Siliceous Earth is represented by Sillitin V 88 and the very fine grade Sillitin Z 89 with a particle size comparable to Chinafill KF 82.

Filler Characteristics

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INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY

	Particle size d_{50} [µm]	Oil absorption [g/100g]	Density [g/cm³]
Siliplast 910 Mixture of feldspar, kaolin and quartz	14	23	2.6
Chinafill KF 82 Kaolin	2	50	2.6
Talkum N Talc	5	35	2.7
Omyacarb 5 GU GCC	5	16	2.7
Sillitin V 88 Neuburg Siliceous Earth	4	45	2.6
Sillitin Z 89 Neuburg Siliceous Earth (NSE)	2	55	2.6

VM-0/0520/05.2020

Fig. 2

Neuburg Siliceous Earth is a naturally occurring combination of corpuscular Neuburg Silica and lamellar kaolinite; a loose mixture impossible to be separated by physical methods (*Fig.3*). The silica portion exhibits a round grain shape due to natural formation and consists of aggregated primary particles of about 200 nm in size. This unique structure results in a relatively high specific surface area and the comparatively high oil absorption value.

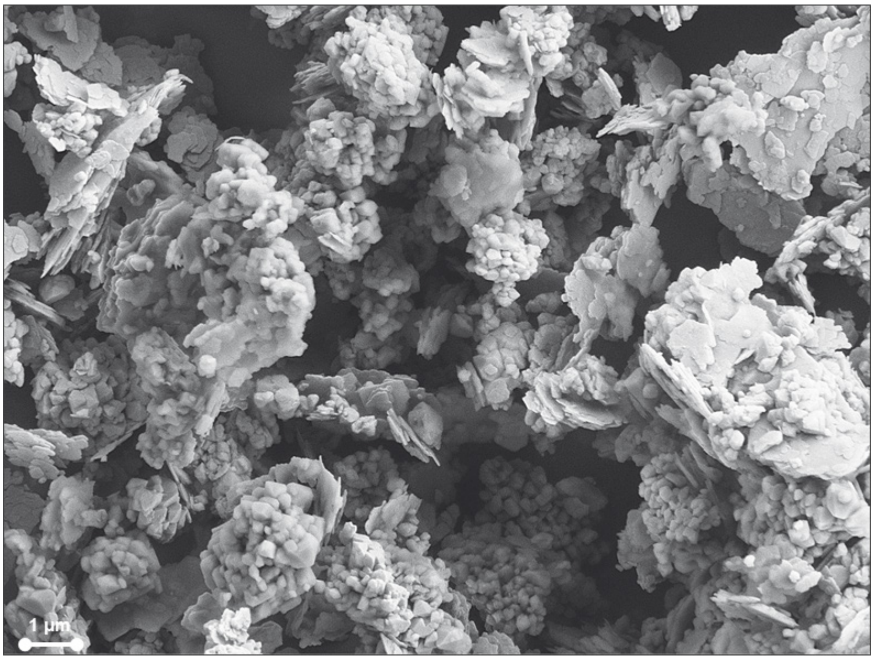
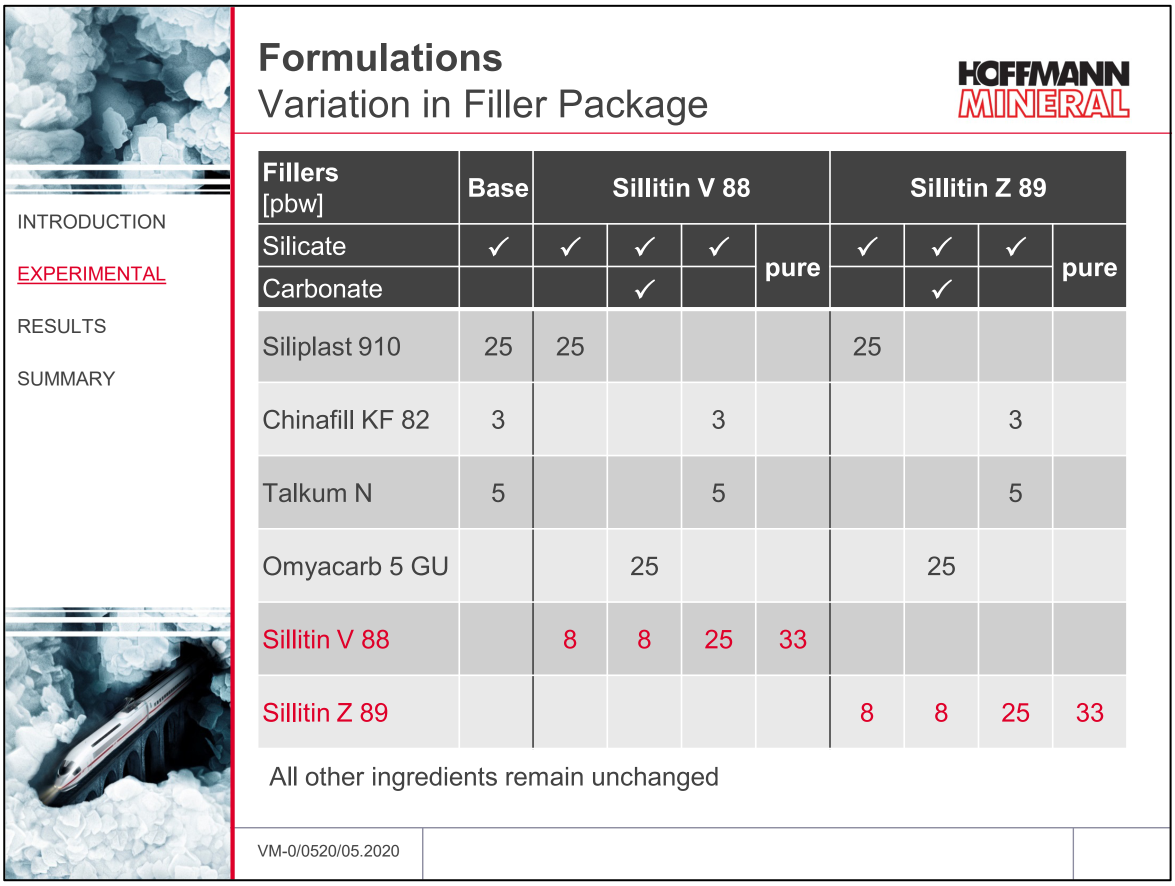


Fig. 3

2.3 Filler Variations

The fillers are varied with equal weight starting from the purely silicate-based combination as shown in *Fig. 4.* Initially, the coarse Siliplast main filler remains in the formulation and only the two accompanying fillers are replaced by the respective Neuburg Siliceous Earth grade. To investigate the influence of a carbonate filler, the main filler is replaced by the Omyacarb in the next step. As variants with higher Neuburg Siliceous Earth dosage, the follow-up combination with Chinafill and talc or pure NSE dosage with replacement of all fillers of the base formulation is used.

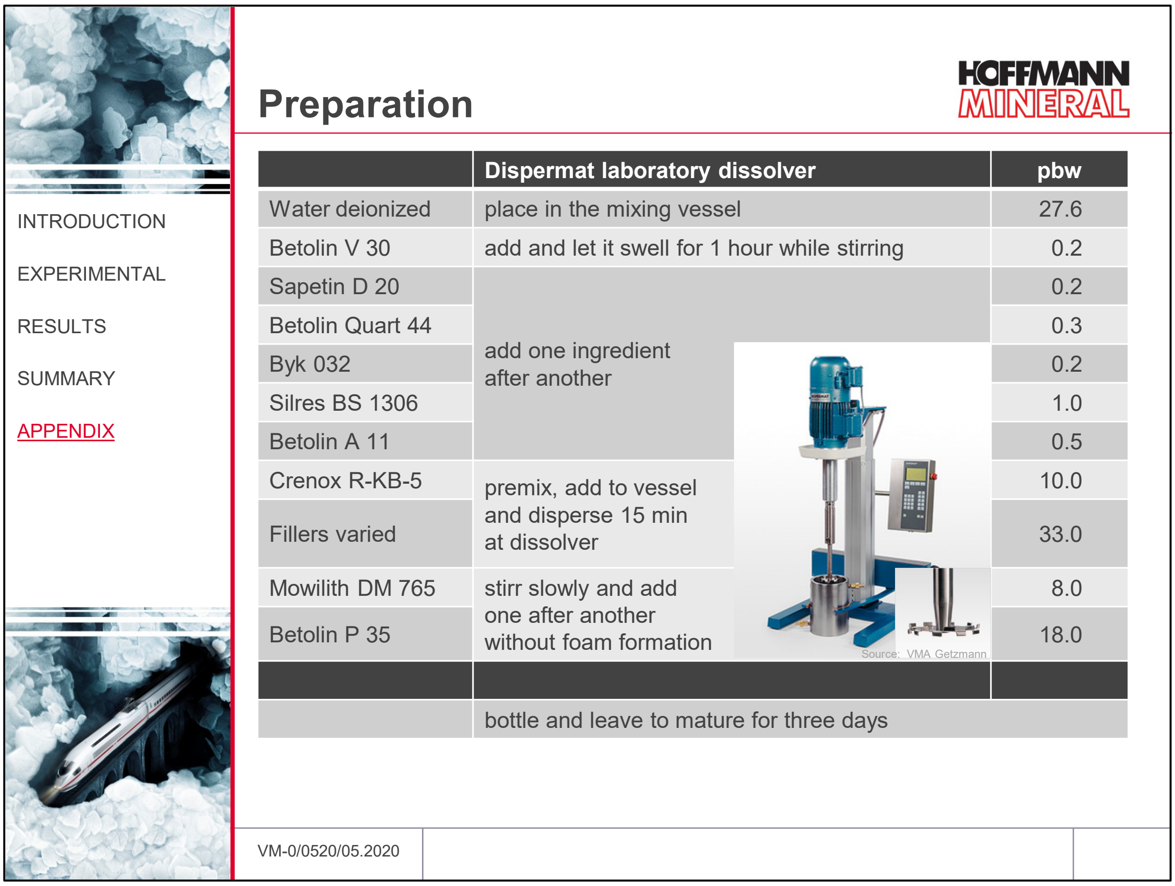


Fillers [pbw]	Base	Sillitin V 88				Sillitin Z 89			
Silicate	✓	✓	✓	✓	pure	✓	✓	✓	pure
Carbonate			✓				✓		
Siliplast 910	25	25				25			
Chinafill KF 82	3			3				3	
Talkum N	5			5				5	
Omyacarb 5 GU			25				25		
Sillitin V 88		8	8	25	33				
Sillitin Z 89						8	8	25	33

Fig. 4

2.4 Preparation of Batches, Application and Testing

The preparation was carried out with a Dispermat laboratory dissolver from VMA Getzmann with toothed disc in the manner shown in *Fig. 5.*



	Dispermat laboratory dissolver	pbw
Water deionized	place in the mixing vessel	27.6
Betolin V 30	add and let it swell for 1 hour while stirring	0.2
Sapetin D 20	add one ingredient after another	0.2
Betolin Quart 44		0.3
Byk 032		0.2
Silres BS 1306		1.0
Betolin A 11		0.5
Crenox R-KB-5	premix, add to vessel and disperse 15 min at dissolver	10.0
Fillers varied		33.0
Mowilith DM 765	stirr slowly and add one after another without foam formation	8.0
Betolin P 35		18.0
	bottle and leave to mature for three days	

Fig. 5

At the end of the maturing period, the formulation batches were divided up. One part was used to determine the storage stability with regard to the evaluation of the sedimentation behavior and possible segregation or gelation processes in the container. The other half was subjected periodically to rheological tests on a rheometer MC1 from Paar Physica with Z3 cylinder system.

To evaluate the coloristic properties, a fully hiding coat was applied to fiber cement boards and the data were collected with a Luci 100 colorimeter.

3 Results

3.1 Storage Stability

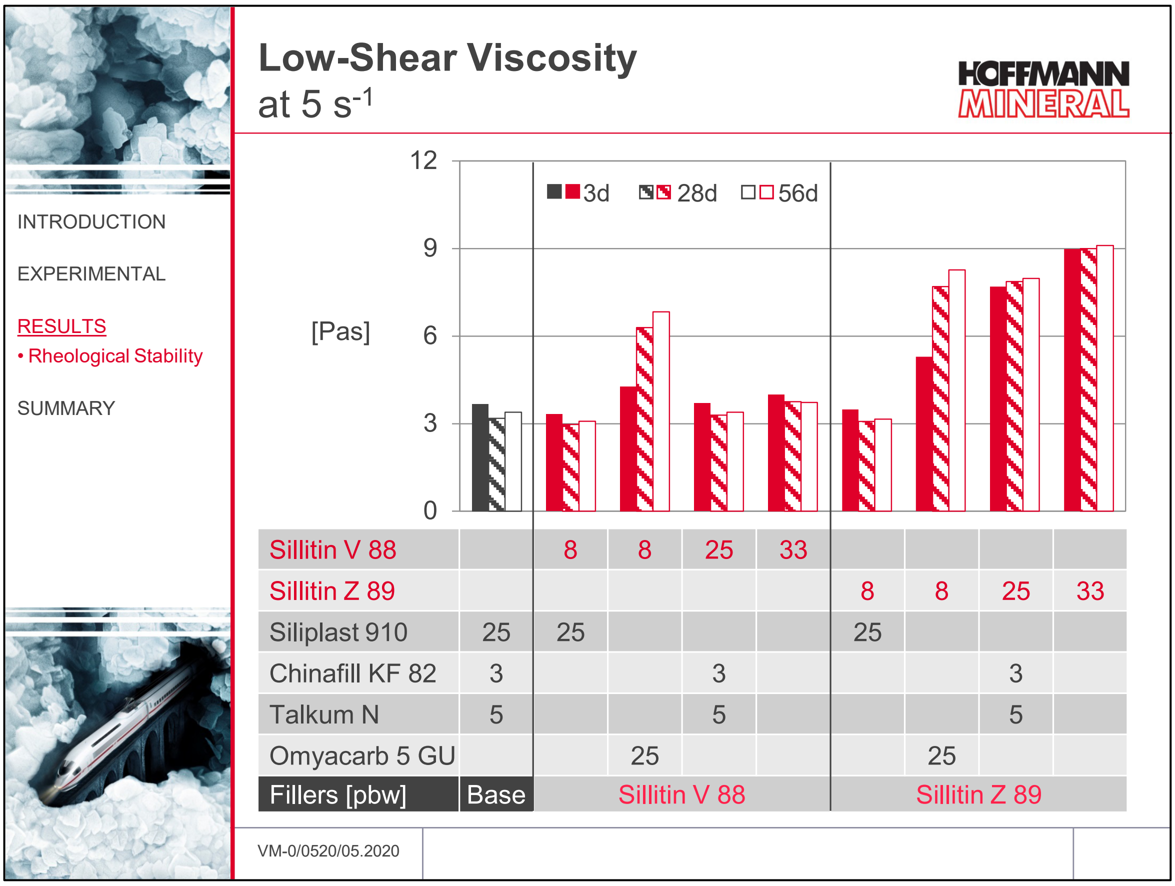
All formulation variants showed excellent storage stability at room temperature of 23°C. No signs of sedimentation, syneresis or gelation were found in the formulations.

3.2 Rheological Stability

3.2.1 Low Shear Viscosity

The evaluation of viscosity in the low shear range allows a more precise assessment of the filler contribution to the shelf life of the formulations.

Fig. 6 shows the development of the viscosity values over a storage period of approximately 2 months. The data are taken from the underlying viscosity curves, which were measured with controlled shear rate.



Sillitin V 88		8	8	25	33				
Sillitin Z 89						8	8	25	33
Siliplast 910	25	25				25			
Chinafill KF 82	3			3				3	
Talkum N	5			5				5	
Omyacarb 5 GU			25				25		
Fillers [pbw]	Base	Sillitin V 88				Sillitin Z 89			

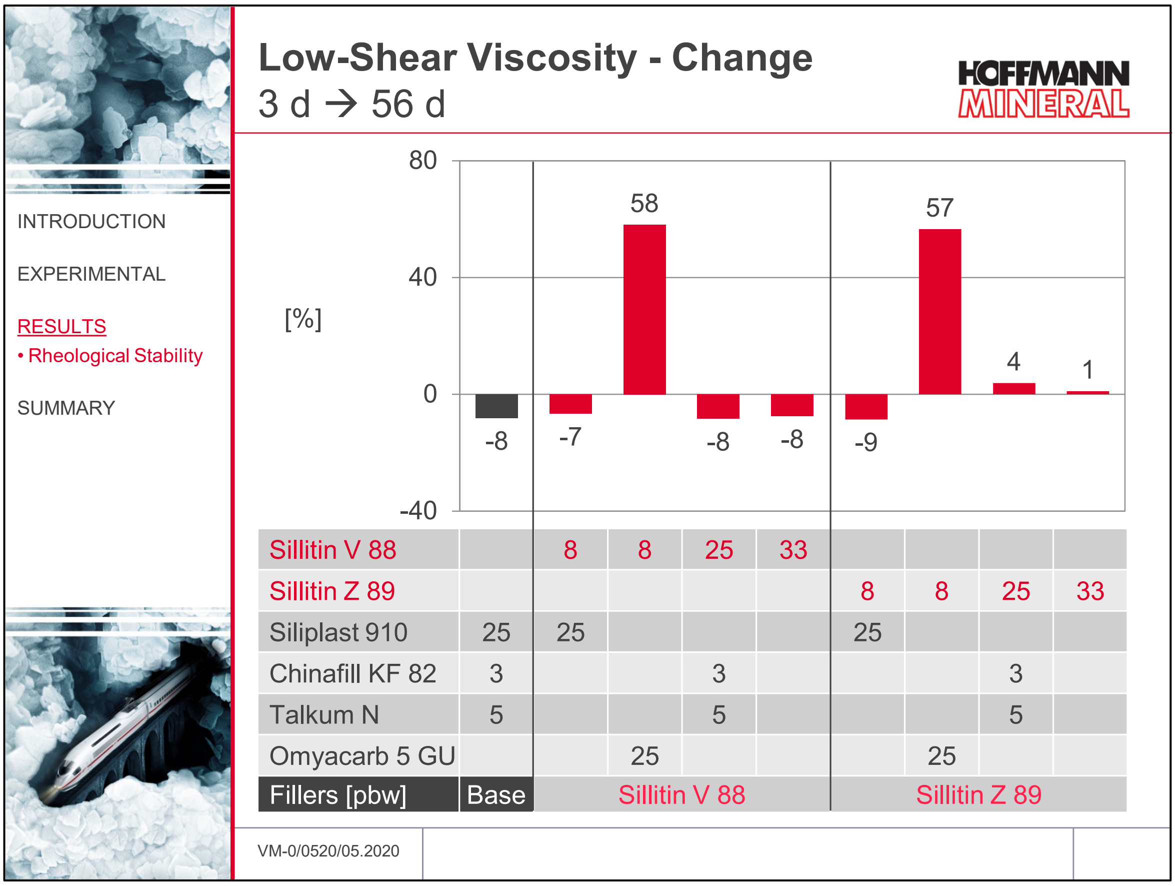
Fig. 6

The use of Sillitin V 88 basically shows no effect on the low shear viscosity. The properties of the base formulation can be readjusted independently of the dosage.

With Sillitin Z 89, on the other hand, the level is controllable depending on the dosage and accompanying filler, and when used alone, achieves almost a tripling of the basic formulation. Sillitin Z 89 is therefore not only suitable for rheology control in the present silicate emulsion paint, but as a very fine-particle filler also for low-viscosity systems susceptible to sedimentation.

The strong increase in viscosity when using the carbonate Omyacarb filler is striking. All other variants maintain a stable level over time or even drop slightly at the beginning. In order to objectively evaluate the degree of increase/decrease, the values can be considered as a relative change from the initial level (see *Fig. 7*, next page).

The strongly destabilizing effect of a carbonate main filler in direct comparison to the Siliplast cannot be compensated by combining it with a small amount of NSE filler. Further tests in a pure carbonate variant confirmed an even higher thickening effect if a comparable quantity of finely divided calcium carbonate is used instead of 8 parts by weight of NSE.



Fillers [pbw]	Base	Sillitin V 88				Sillitin Z 89			
Sillitin V 88		8	8	25	33				
Sillitin Z 89						8	8	25	33
Siliplast 910	25	25				25			
Chinafill KF 82	3			3				3	
Talkum N	5			5				5	
Omyacarb 5 GU			25				25		

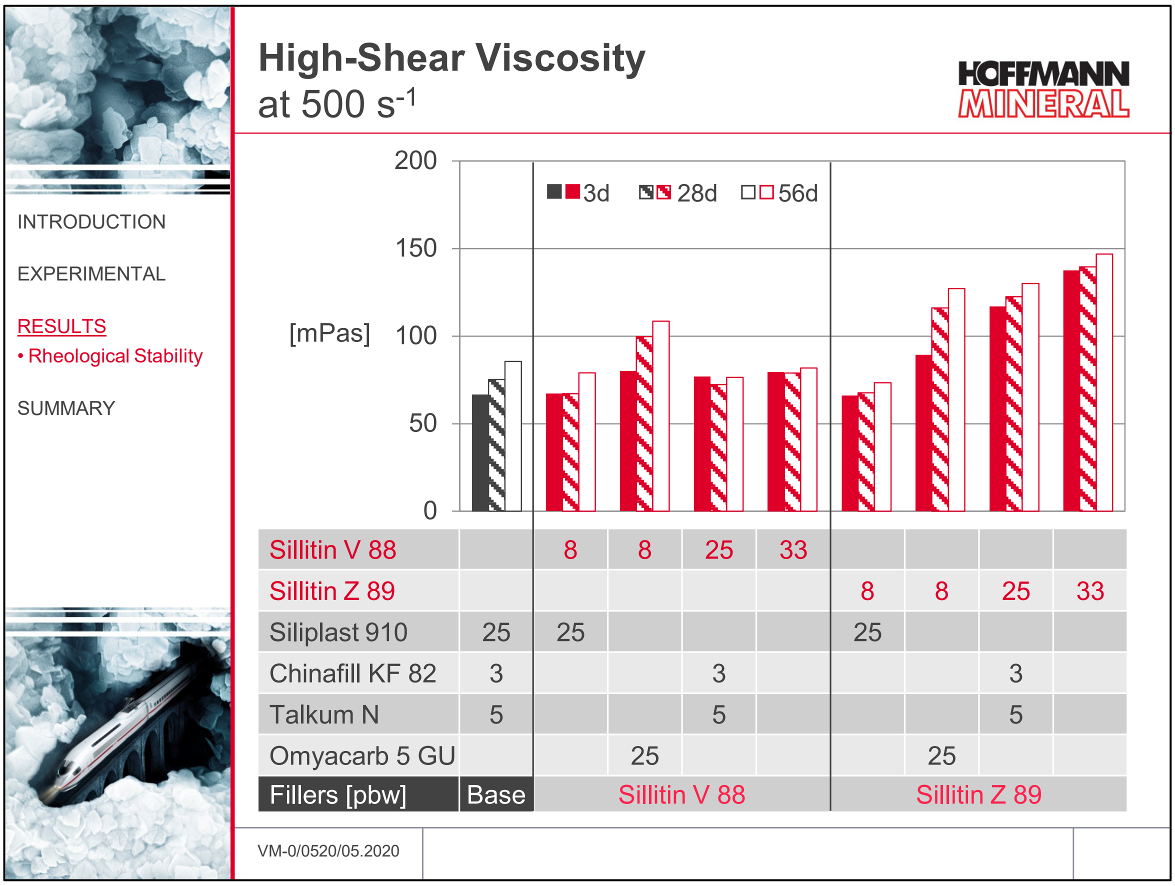
Fig. 7

If, on the other hand, the Siliplast from the base formulation is combined with a little dosage of Neuburg Siliceous Earth or replaced by Sillitin V 88 and Sillitin Z 89 as new main fillers, the viscosity increase is strongly inhibited comparable to the base formulation. With additional replacement of the accompanying fillers, Sillitin V 88 can be used in pure form without further loss of stability. With Sillitin Z 89 even the best results are achieved. Together with the high viscosity level, this filler provides the performance basis for very storage-stable formulations.

3.2.2 High Shear Viscosity

For stored silicate emulsion paints, high shear viscosity is mainly a characteristic of the conditions under which the paint is processed later. The rheological behavior in this area should be as stable as possible in order to achieve a comparable profile with regard to applicability, penetration into the substrate and layer thickness formation, even with time-delayed application. These requirements exist in principle for use as a protective facade paint and are particularly important for achieving a uniform visual appearance in dark, highly pigmented coatings.

The viscosities measured in *Fig. 8* are significantly lower than the values for low shear viscosity. The reason for this is the highly shear-thinning, pseudoplastic behavior of the formulations.



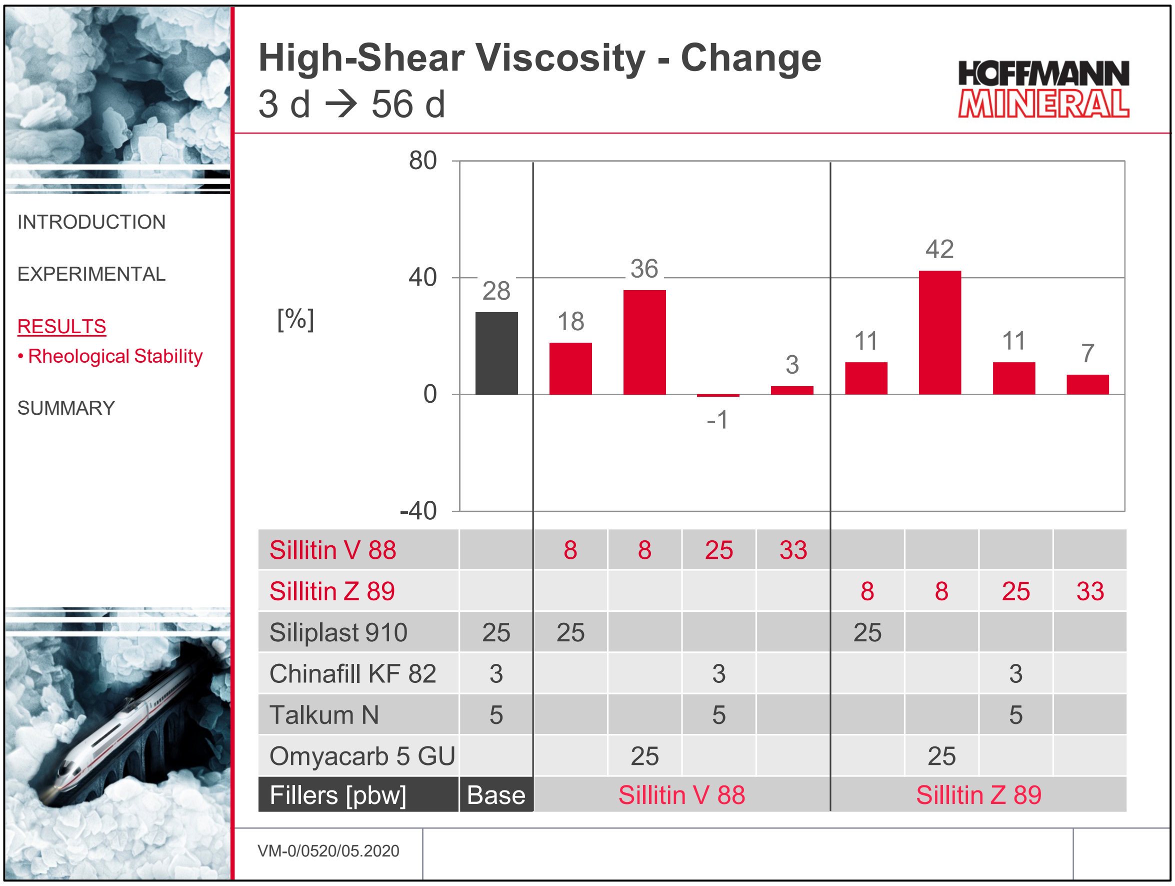
Fillers [pbw]	Base	Sillitin V 88				Sillitin Z 89			
Sillitin V 88		8	8	25	33				
Sillitin Z 89						8	8	25	33
Siliplast 910	25	25				25			
Chinafill KF 82	3			3				3	
Talkum N	5			5				5	
Omyacarb 5 GU			25				25		

Fig. 8

The figure reflects the results as for low shear, although the absolute differences are somewhat smaller. Low viscosity at the level of the base formulation is obtained for Sillitin V 88, and rising values with increasing dosage for Sillitin Z 89.

In the high shear range, the tendency of viscosity increase under storage is slightly increased and no longer limited only to the use of the carbonate filler. Especially with the purely silicate fillers of the base formulation, a moderate thickening effect can be observed, as shown on the following page.

The viscosity increase of the base formulation increases by almost 30% within the test period, but can be reduced by replacing the accompanying fillers Chinafill / talc by Sillitin V 88 or Sillitin Z 89 (*Fig. 9*). The stabilizing effect is further improved by a higher Neuburg Siliceous Earth dosage; the increase in viscosity is strongly inhibited and with Sillitin V 88 even completely prevented.
The advantageous filler effects are also confirmed in the formulations with the sole use of Neuburg Siliceous Earth. A high dosage of Sillitin Z 89 and preferably Sillitin V 88 thus has a particularly favorable effect in all areas of high shear stress, where high rheological stability is required to ensure uniform, consistent processing properties.



Fillers [pbw]	Base	Sillitin V 88				Sillitin Z 89			
Sillitin V 88		8	8	25	33				
Sillitin Z 89						8	8	25	33
Siliplast 910	25	25				25			
Chinafill KF 82	3			3				3	
Talkum N	5			5				5	
Omyacarb 5 GU			25				25		

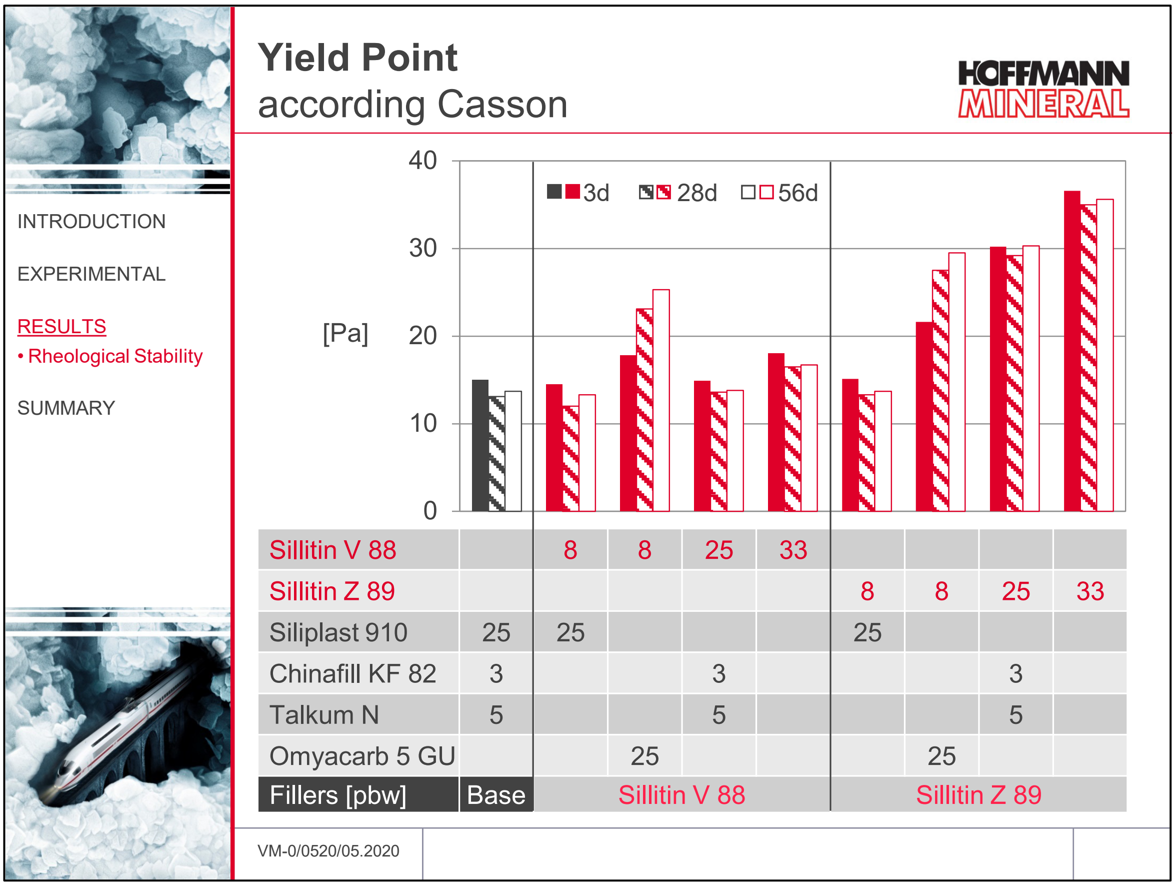
Fig. 9

3.2.3 Yield Point

The yield point is an important parameter in the evaluation of rheological properties. Not only can it have a stabilizing effect on storage stability, but it also influences spreadability and sag resistance after application.

The filler effects already discussed in terms of viscosity behavior also become apparent in the evaluation according to *Fig. 10.* The use of Sillitin V 88 pure offers a somewhat higher yield point; the other variants with this filler remain at the lower level of the base formulation.

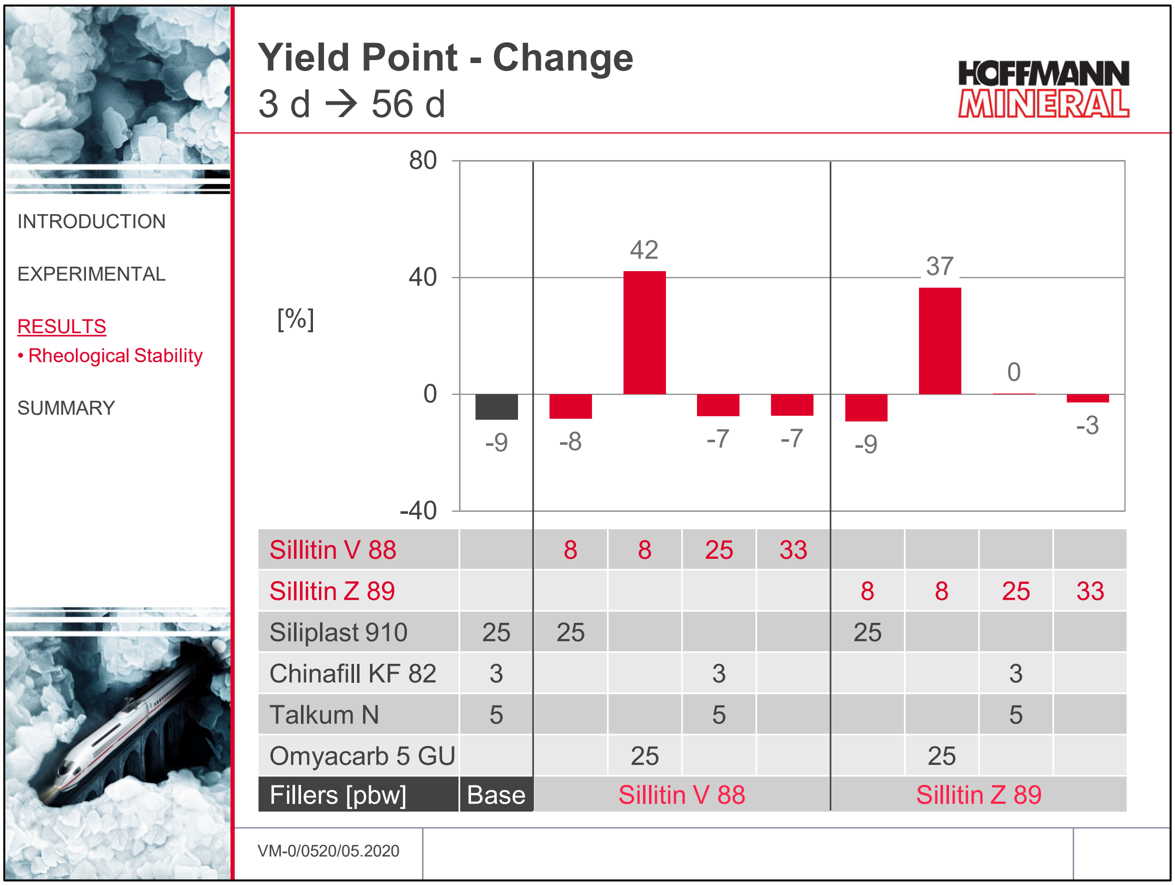
Due to its low yield point, Sillitin V 88 supports easy and effortless application by brush or roller. Sillitin Z 89 is more suitable for the application of thicker layers in one-step. The immediate build-up of yield point after application also reduces paint runners and optimizes edge coverage.



Fillers [pbw]	Base	Sillitin V 88				Sillitin Z 89			
Sillitin V 88		8	8	25	33				
Sillitin Z 89						8	8	25	33
Siliplast 910	25	25				25			
Chinafill KF 82	3			3				3	
Talkum N	5			5				5	
Omyacarb 5 GU			25				25		

Fig. 10

While according to *Fig. 11* the two variants with Omyacarb show a clear increase in the yield point over the storage time, the values in the other NSE formulations hardly change. On the contrary, compared to the base formulation, Sillitin Z 89 even causes a visibly better constancy and stabilization of the yield point profile when the grade is used as main filler or pure.



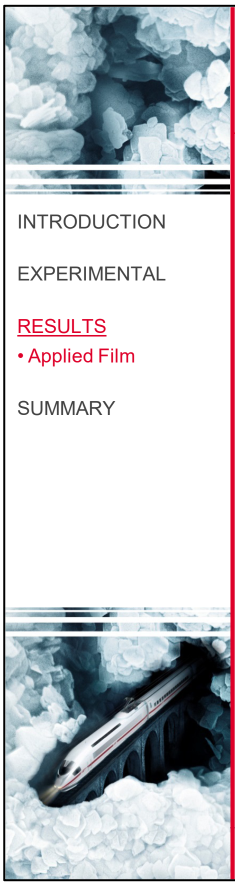
Fillers [pbw]	Base	Sillitin V 88				Sillitin Z 89			
Sillitin V 88		8	8	25	33				
Sillitin Z 89						8	8	25	33
Siliplast 910	25	25				25			
Chinafill KF 82	3			3				3	
Talkum N	5			5				5	
Omyacarb 5 GU			25				25		

Fig. 11

3.3 Color of Applied Film

In addition to the positive effects on rheological stability and shelf life, the optical properties of Neuburg Siliceous Earth that result after application and film drying are particularly noteworthy.

Starting from the base formulation, the color location is practically not shifted by the use of Sillitin V 88, with Sillitin Z 89 only slightly (*Fig. 12*). Carbonate as main filler in combination with Neuburg Siliceous Earth leads to the highest brightness, but as already shown, at the expense of acceptable storage stability. In order to meet both requirements, the Neuburg Siliceous Earth should be the main part of the filler package, or be used alone. Compared to the base formulation, the brightness is thus noticeably improved and with Sillitin Z 89 almost reaches the very high level of the carbonate variant.



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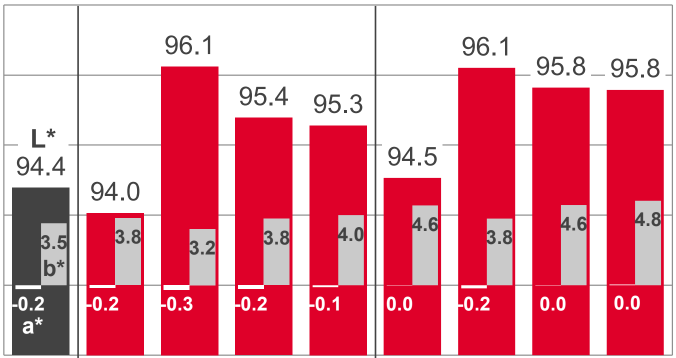
INTRODUCTION

EXPERIMENTAL

RESULTS
• Applied Film

SUMMARY



Sillitin V 88		8	8	25	33				
Sillitin Z 89						8	8	25	33
Siliplast 910	25	25				25			
Chinafill KF 82	3			3				3	
Talkum N	5			5				5	
Omyacarb 5 GU			25				25		
Fillers [pbw]	Base	Sillitin V 88				Sillitin Z 89			

VM-0/0520/05.2020

Fig. 12

Together with high fineness of particle size, Sillitin Z 89 is therefore also recommended for formulations with high hiding power or partial replacement of cost-intensive white pigments. If this aspect is particularly important, comparable calcined grades of Neuburg Siliceous Earth can be used for very bright and color-neutral formulations.

4 Summary

Sillitin V 88 and Sillitin Z 89 show very good storage stability without sedimentation in the present silicate emulsion paint. Depending on the requirements, comparable or increased viscosity or yield point can be adjusted. The rheological stability compared to the use of silicate and especially carbonate fillers is significantly improved and creates the necessary basis for durable silicate emulsion paints with a constant processing profile.

The optimized and adaptable rheological properties combine advantageously

- additional durability plus for the storage in container
- thickening protection compared to the use of carbonate fillers
- best paint stabilization with NSE pure application
- prerequisite for consistently good processing properties

The extensive preservation of color neutrality with increased brightness additionally offers

- improved hiding power
- savings potential in white pigment consumption

The following products are recommended for use in silicate emulsion paints:

Sillitin V 88

- Low viscosity and yield point, even at higher dosage
- Particularly viscosity stabilizing in the high shear range for easy and consistently good processability during application
- Coarser grade, slightly more color-neutral than Sillitin Z 89

Sillitin Z 89

- Viscosity level and yield point adjustable via dosing
- Especially viscosity stabilizing in the low shear range for good sedimentation protection during storage or high sag resistance and edge coverage after application
- Finer grade with higher brightness
- Improved hiding power and suitable for TiO_2 replacement

For very color-critical applications, additionally also Silfit Z 91 as a representative of the calcined Neuburg Siliceous Earth, which is not discussed in this report.

NSE fillers should preferably be used in combination with silicate fillers or pure. The Neuburg Siliceous Earth grades can also be combined with each other, so that many properties can be specifically adapted to the requirements.