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Novel stabilizers improving the rheology profile of **SILICATE PAINTS**

what is precious to you?

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Novel stabilizers improving the rheology profile of silicate paints

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AUTHOR

Mr. Jesus Pitarch Lopez

Scientist at Clariant in the department “Group Technology & Innovation” (GTI), responsible for chemical research in the competence center “Interface & Formulation Technology”.

Born in 1976, Jesus Pitarch Lopez studied chemistry at the University of Valencia/Spain. After his PhD at the University of Erlangen/Germany and a postdoctoral research at the Max-Planck-Institut for colloids and interfaces in Potsdam/Germany, Jesus Pitarch Lopez joined Clariant in 2005 where he has been working over ten years on several innovation projects.

CLARIANT INNOVATION CENTER

Industrial Park Höchst

Building G860

August-Laubenheimer-Strasse 1

65926 Frankfurt

Tel: +49 69 305 18292

E-mail: Jesus.PitarchLopez@clariant.com

CO-AUTHORS

Mr. Jörg Rüger

Global Application Manager for Paints & Coatings

Business Unit Industrial & Consumer Specialties

Mr. Rainer Kupfer

Head of Competence Center Industrial Applications

Business Unit Industrial & Consumer Specialties

Jesus Pitarch, Group Chemical Research, Clariant, Frankfurt am Main

BACKGROUND AND SCOPE

The inherent alkalinity of mineral paints (pH-value between 11.0 – 11.4) inhibits the growth of microorganisms, thus protects the paint both against bacteria in the can and against molds and algae after application on the substrate. As biocides can cause allergenic reactions, mineral paints – being biocide-free systems - have very good potential to meet the needs of consumers which are more and more concerned regarding the use of goods and materials in their daily life which may have a negative impact on their health.

Key ingredient in the aqueous paint formulation to achieve a biocide-free conservation is water soluble potassium silicate, also known as potassium waterglass. The properties of waterglass as binder, able to bond chemically to the mineral substrate, are well-described and potassium silicate is broadly used in the formulation of dispersion silicate paints according to DIN 18363 (with a maximum concentration of 5 wt. % of organic ingredients such as polymeric binders) and organosilicate paints (which may contain a higher concentration of organic load). However, one of the major drawbacks concerning the use of waterglass is that the texture of the paint changes dramatically during storage, evolving from a low viscosity dispersion to a highly-viscous paste, leading to difficulties in handling and application.

Special additives, called stabilizers, are typically employed in order to moderate the changes in viscosity and texture of the paints. Surprisingly, very little has been reported about the rheology of silicate paints and, especially, about the evolution of their rheological properties during storage and the impact of stabilizers on that evolution.

The intention of this work has been to get insights into the rheological properties of dispersion silicate paints, which are directly related to their microstructural characteristics and thus will help to better understand the nature of the colloidal assembly in the paints.

- For this scope, firstly, several paints available from German DIY-stores were thoroughly characterized and typical patterns (rheological fingerprint) identified.
- In a second step, the rheological properties were evaluated during storage for several lab samples which only differed in the class of stabilizers used.

Following this approach, new solutions for improved stabilization of silicate paints were identified.

Jesus Pitarch, Group Chemical Research, Clariant, Frankfurt am Main

METHODS

The paint samples were characterized in a Haake Mars III rheometer. A 60 mm cone and plate with a cone angle of 1° or 35 mm parallel plates were used depending on the test requirements. Since sample history may significantly influence the results of the measurements, an accurate protocol was followed for sample taking, loading and pre-shearing in order to make sure that all samples had experienced the similar process immediately before the measurements started. In table 1 all the types of measurements are listed which were done in this study, as well as the parameters used to describe the rheological behavior of the samples and their link to performance properties of the paints.

Dynamic oscillatory measurements conducted applying a strain ramp at constant frequency of 1.592 Hz were used to investigate the viscoelastic properties of the paints and the plateau value of the elastic modulus G′ was selected as one key descriptor of the paints.

The yield stress τ_0 defined as the stress at which the sample begins to flow, was determined by measuring a stress ramp and plotting in a double logarithmic scale the change in deformation caused by increasing the applied shear stress. Both the elastic module and the yield stress give an indication of the strength of the colloidal assembly in the paint. As both attributes are describing material properties under low stress conditions, they can be linked to the leveling and sagging behavior of the paints and thus to the quality of the final film.

In addition, the change of viscosity of the samples under shear was evaluated by using shear up-and-down ramps. The viscosity at different shear rates may help to understand the behavior of the paint during high shear processes such as rolling or brushing, or moderate shear steps like stirring and brush loading. Moreover, the area between the up and down curves is an indication of the thixotropy of the paints, which refers to a restructuration of the colloidal assembly in the paint over time when a constant shear is applied and is shown in form of lower viscosity values in the down rather than in the up-shear ramp. The thixotropy can be seen as the energy needed to achieve the restructuration of the colloidal assembly.

The kinetics of viscosity recovery after a process of high shear was also investigated as this is another important parameter in the evaluation of the paint performance. For this purpose, the paint sample was sheared at low rate followed by a period of constant high shear, after which the shear rate was immediately decreased to the initial low value. The initial slope of viscosity versus time after the jump from high shear to low shear was selected as key descriptor to evaluate the response of the samples.

METHOD	KEY DESCRIPTOR	LINKED TO
Strain amplitude oscillatory test	Plateau value of elastic modulus	• Strength of colloidal assembly • Appearance of the paint
Stress ramp	Yield stress	• Strength of colloidal assembly • Appearance of the paint • Leveling / sagging
Shear rate ramp	Viscosity	• Brushing / rolling • Stirring / shaking
	Thixotropy	• Time-dependent flow behavior • Effort of homogenization
Shear recovery	Speed of viscosity recovery	• Leveling / sagging • Splatters

Table 1: Rheological methods used in this work, the key descriptor obtained from the measurement and its link to the performance properties of the paint

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RHEOLOGICAL CHARACTERIZATION OF COMMERCIAL SILICATE PAINTS

Three silicate paints from a DIY-store with similar declared ingredients (potassium waterglass, polymer dispersion, titanium dioxide, calcium carbonate, silicates, water and additives) were characterized.

All three paints had a similar appearance when the cans were opened, showing strong syneresis and a highly thick, pasty appearance. Remarkably, the rheological properties of all the samples were very similar, which allowed to easily define a "rheological fingerprint" for this type of paints which is listed in table 2.

KEY DESCRIPTOR
Plateau value of elastic modulus >1000 Pa
Yield stress >100 Pa
Viscosity >2000 mPas @ 60s-1
Thixotropy >15000 Pa/s
Speed of viscosity recovery > 60 Pa

Table 2: Typical rheological profile of silicate paints based on the characterization of 3 commercial paint samples. Measurements were carried at 23°C

Interestingly, it was found that under the experimental conditions used to determine the yield stress, the samples showed systematically wall slip effects, noticed by the presence of two inflexion points in the double logarithmic plot of deformation versus shear stress (figure 1). Wall slip phenomena have been reported for colloidal suspensions and explained in terms of the formation of a thin layer of fluid existing next to the test geometry which shows in certain range of low shear stress lower viscosity than the bulk sample. Therefore an apparent yield stress is detected, which is lower than the real yield stress of the bulk. In principle, the clear detection of wall slip can be seen as a characteristic of the silicate paints arising from specific colloidal interactions induced by waterglass.

Yield Stress

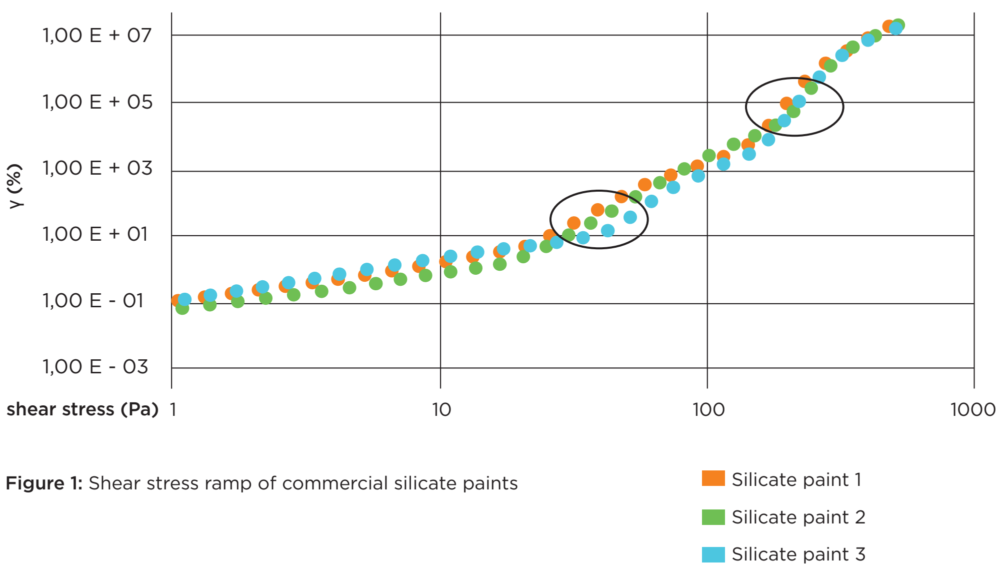

Figure 1: Shear stress ramp of commercial silicate paints

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For comparison, a commercial dispersion paint was also characterized under the same conditions and no wall slip could be detected. In general, the yield stress in the silicate paints was found to be one order of magnitude higher than for typical dispersion paints (figure 2).

Yield Stress

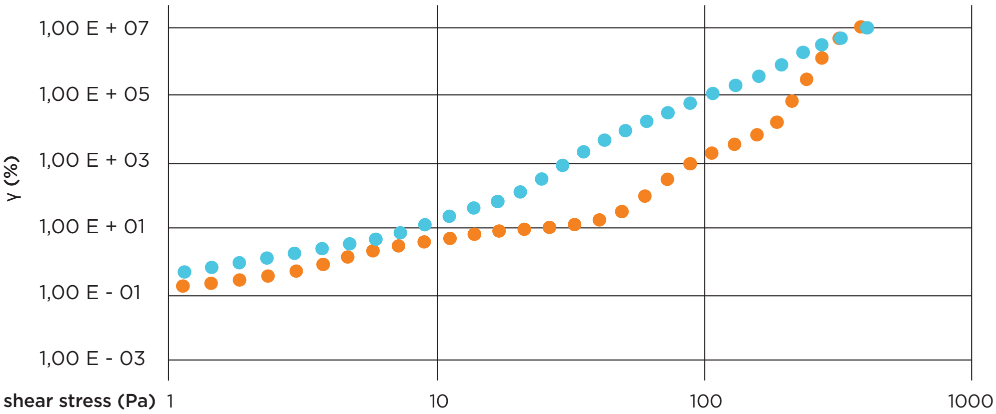

Figure 2: Yield stress differences between commercial latex paint (~10 Pa) and silicate paint (~100 Pa)

Characteristic response pattern was also identified during the shear recovery measurements (figure 3). Besides the very fast kinetics of recovery, the viscosity measured immediately after the transition from high (60 s-1) to low shear (0.1 s-1) was found to be higher than the viscosity during the first low shear step, and it decreased after 30 – 60 seconds to reach a plateau value. This behavior suggests that due to the fast recovery, the system is entrapped in a microstructure of high viscosity which relaxes under low shear in a more favorable colloidal arrangement. In contrast, a typical dispersion paint shows a slower recovery and the viscosity increases progressively until the plateau value is reached.

Viscosity recovery

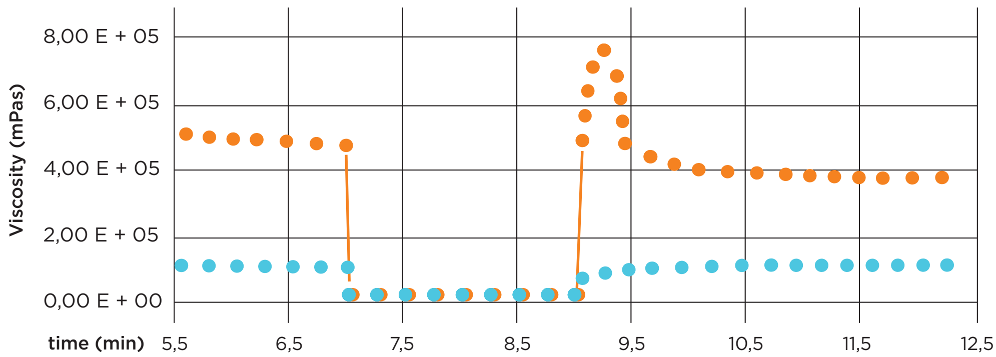

Figure 3: Shear recovery curves for commercial silicate and latex paint.

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As expected from the pasty appearance of the silicate paints, high elastic moduli were measured, pointing to a strong colloidal network (figure 4). Strongly shear thinning behavior was detected from the shear rate ramp measurements (figure 5). The samples showed high viscosity at low shear rates, as expected for the strong elastic network, and due to the significant thixotropy, high effort is needed to stir and homogenize the paint. However, under the high shear rates which dominate during the application process, the viscosity becomes rather low and the paint gets fluid.

Elastic Modulus

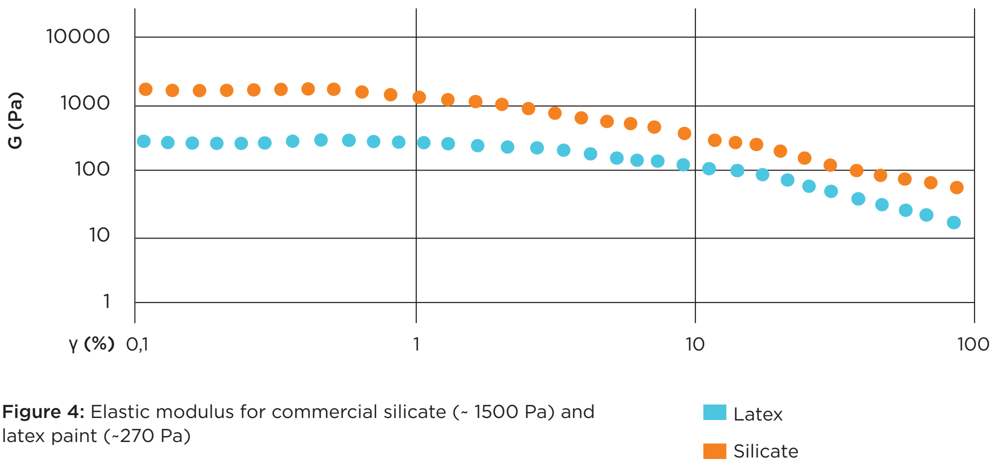

Figure 4: Elastic modulus for commercial silicate (~ 1500 Pa) and latex paint (~270 Pa)

Viscosity & Thixotropy

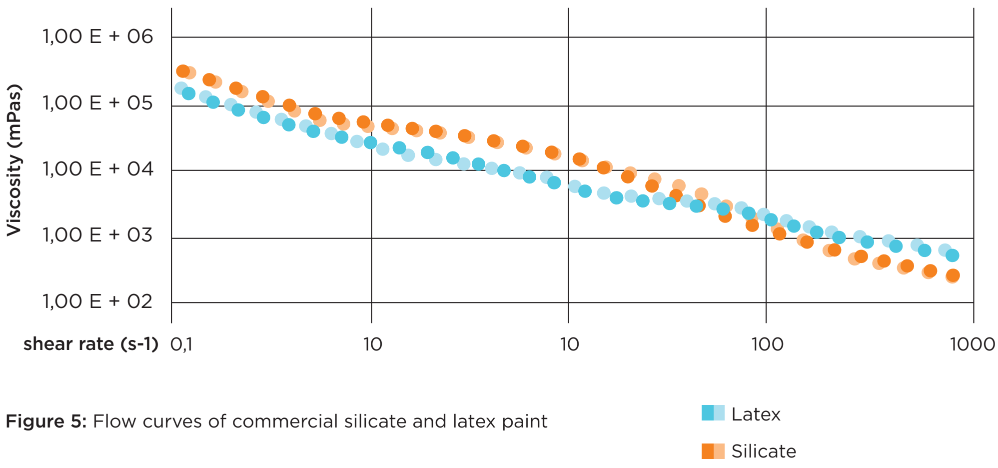

Figure 5: Flow curves of commercial silicate and latex paint

To summarize, dispersion silicate paints show a strong shear rate and time dependent flow behavior with very fast recovery kinetics.

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NOVEL STABILIZERS

Two new alternatives for better stabilization of silicate paints are presented:

- A stand-alone stabilizer based on diquat technology
- A stabilizer combination comprising
  - VOC- & SVOC-free amine derivative with >75% renewable content
  - Diquat technology

Performance tests were conducted in a dispersion silicate paint guide formulation at a total stabilizer active concentration of 0.37%, as listed in table 3. As benchmark, current stabilizing technology based on a combination of amine derivatives and other actives was used. To show the effect of the stabilizers, the key rheological attributes of the paints were measured after sample preparation and 28 days storage at room temperature and at 50°C. Quantitative comparison in the evolution of thixotropy, viscosity, elastic modulus and speed of viscosity recovery are provided in the figures 6 to 9.

TEST FORMULATION **According to DIN 18363 (organic matter < 5%)**	
Water	29.93%
Dispersing Agent	0.20%
Stabilizers	0.37%
Thickener	0.40%
Defoamer	0.15%
TiO_2	10.00%
Talc	5.00%
$CaCO_3$ (type d50% 1 μm)	10.00%
$CaCO_3$ (type d50% 2 μm)	16.00%
$CaCO_3$ (type d50% 5 μm)	3.70%
Emulsion polymer 50% solids	8.00%
Silicone additive	0.25%
Potassium waterglass solution	16.00%

Table 3: Guideline recipe used to test the performance of stabilizers

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Thixotropy

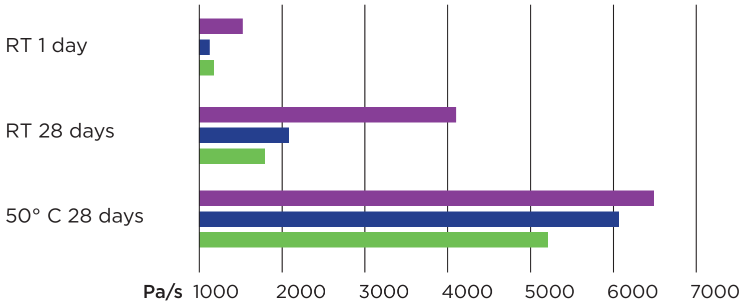

Figure 6:
Changes of thixotropy during storage

Elastic modulus

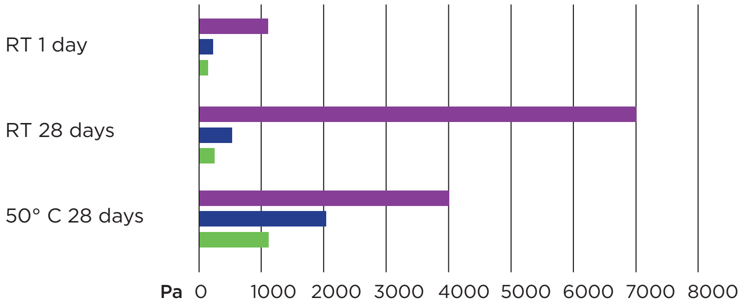

Figure 7:
Changes in the elastic modulus during storage

Viscosity @ 60 s-1

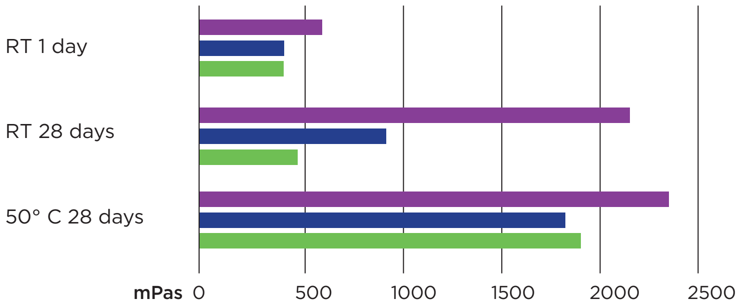

Figure 8:
Changes in viscosity during storage

Viscosity recovery

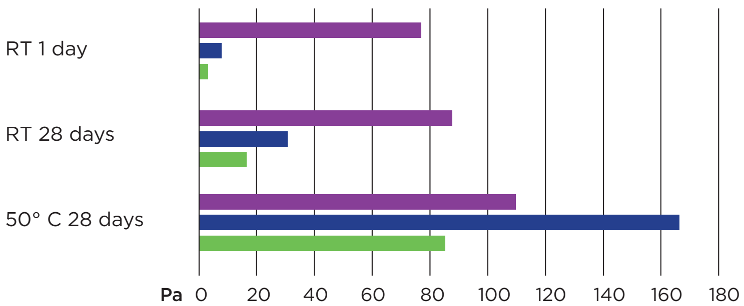

Figure 9:
Changes in speed of viscosity recovery during storage

Benchmark
New combination
New stand-alone

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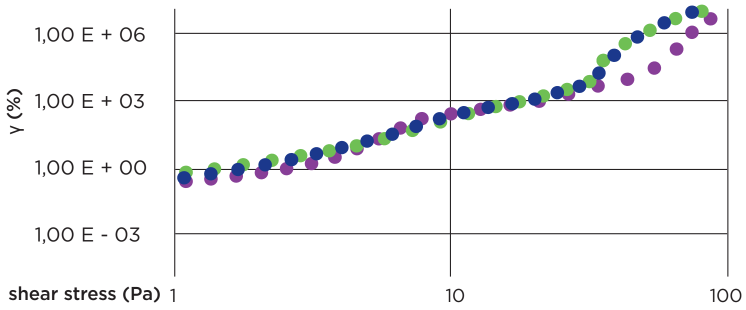
In general, for all the rheological attributes investigated lower values are found after sample preparation for the new stabilizers compared to the benchmark. Interestingly, only slight variations occur after four weeks of storage at room temperature, indicating a clear ability of the new stabilizers to slow down the change in the rheological properties of the paint. Due to strong wall slip effects, only a qualitative evaluation of the yield stress was possible, but the trend was confirmed and the changes in the shear ramp curve during storage were more dramatic for the benchmark sample than for the samples with the new stabilizers (figure 10). Moreover, the new stabilizers give the paints a more plastic consistency, reflected in the significantly lower plateau values for the elastic module even after four weeks of warm storage.

Shear ramp - 1 day at room temperature



Shear ramp - 28 days at room temperature

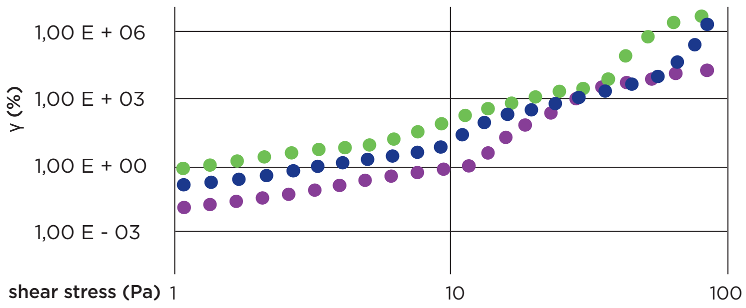


Figure 10:
Shear ramp for the three lab samples after one day and 28 days of storage at room temperature

- Benchmark
- New combination
- New stand-alone

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SUMMARY

The rheological properties of commercial dispersion silicate paints have been investigated. High elastic moduli and yield stresses revealed the existence of a strong colloidal network. This network is sensitive to changes in the shear rate, as indicated by the strong shear-thinning behavior observed during the ramp measurements. Time-dependent reassembly of the network occurs under constant shear, as evidenced by the thixotropic behavior of the paints. In addition, viscosity recovery experiments revealed a very fast regeneration of the colloidal network once shear is stopped.

The methodology employed to characterize the commercial paints was applied to evaluate the performance of new stabilizers in a guide paint recipe in comparison to current stabilizer technology. Two new options for stabilization of dispersion silicate paints have been identified:

- **A stand-alone stabilizer based on diquat technology**
- **A stabilizer combination comprising**
  - **VOC- & SVOC-free amine derivative with >75% renewable content**
  - **Diquat technology**

The new stabilizers slow down the change of the rheological properties of the paint during storage in comparison to the benchmark. They ease handling and application of the paint and, in addition, give the paints a more plastic consistency.