CHEMICALLY RESISTANT ENAMEL

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Chemically Resistant Enamel

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1. Introduction

Especially at low firing temperatures, it is difficult to achieve a good resistance against acids. When the firing temperature is approximately 700°C, the possibilities are limited. The development presented in the following lecture provides a simple method to improve the resistance of low melting enamel. I would like to give an overview of various quartz modifications. The significant improvement of the chemical resistance of the enamels is confirmed by boiling tests. The application of the new batch compositions is demonstrated using a series of examples.

2. Improvement of the Chemical Resistance

To reach the optimum possible chemical resistance, enamels with appropriate composition are selected. Two possibilities to improve the chemical resistance and their related disadvantages are given in **Figure 1.**

1. **An increase of the resistant frit portion has the following disadvantages**

   1. Higher viscosity
   2. Bad wetting
   3. The enamel does not burn out thoroughly
   4. Higher price with equal viscosity

2. **An increase of the quantity of resistant mill batch additives has the following disadvantages**

   1. Matt surfaces
   2. Altered colour
   3. Poor adhesion

Fig. 1

The chemical resistance of enamels is determined mainly by the content of quartz.

Enamels with an SiO_2 content higher than 60% will become accordingly viscous and are difficult to process. The firing temperatures are above 850 °C and closed, flawless direct-on enamelling is hardly possible.

To achieve better processability, these enamels may have a higher alkali content. Lithium, in particular, enhances the chemical resistance and permits a lower firing temperature. As a side effect, however, the enamels become much more expensive.

To regulate the firing behaviour and the chemical resistance, it is a common practice to influence the properties by means of batch additives. The most frequently used additive is quartz in various grain sizes. Zirconium silicate and various other silicate compounds are also used.

These additives do not only make the enamels harder, they also change the brilliance and the colour.

With direct-on enamels, the additives also cause impairment of the adhesion.

3. Modifications of Quartz

The normal fireproof batch additive is quartz in the various grain sizes. Quartz is used to improve the chemical resistance and to control the firing behaviour.

If the enamels are fired at low temperatures, for example, 700°C, there is only a limited choice of enamel frits with high chemical resistance. By addition of quartz, the enamels will become too hard quite easily.

In individual cases, solid colloidal silicon dioxide is added to the enamels. With majolica enamel, in particular, solid colloidal silicon dioxide is used to improve the chemical resistance. These fine quartz types also feature a certain suspension and set-up behaviour and change the rheologic properties. The maximum amount of additive is 4%. Higher quantities cause surface flaws and make the enamel surface matt. The specific weight of these silicon dioxides is very low. The high volume of these powders also causes problems during mill filling.

In order to avoid the disadvantages mentioned above, the use of liquid colloidal silicon dioxide in enamels was investigated.

For comparison, tests using the 3 quartz modifications – fine quartz, solid colloidal silicon dioxide and liquid colloidal silicon dioxide - were made.

The mean grain size, the specific surface area (BET – Brunauer, Edward Teller) and the density are given in the table in **Figure 2**.

	Quartz W 500	Solid colloidal silicon dioxide	Liquid colloidal silicon dioxide
Mean grain size nm	13 000	16	8
Specific surface area m^2/g	1,36	110	330
Density g/cm^3	2,63	0,05	1,21

Fig. 2

As shown in the table, liquid colloidal silicon dioxide has the smallest mean grain size. Compared to the finest quartz quality, the mean grain size of liquid colloidal silicon dioxide is by 1000 times lower.

The specific surface area is by 200 times larger compared to the one of fine quartz.

The density of the 3 quartz modifications varies widely.

Due to the large specific surface, in particular, a very high reactivity must be expected.

As shown in **Figure 3**, the diverging density has a considerable effect on the volume of the substances.

With an equal SiO_2 quantity, the volume of the solid nanoscale SiO_2 is very big. The inclusion of such a volume into the enamel batch will result in a change of the rheologic properties. The addition of quartz and liquid colloidal silicon dioxide does not cause any problems.

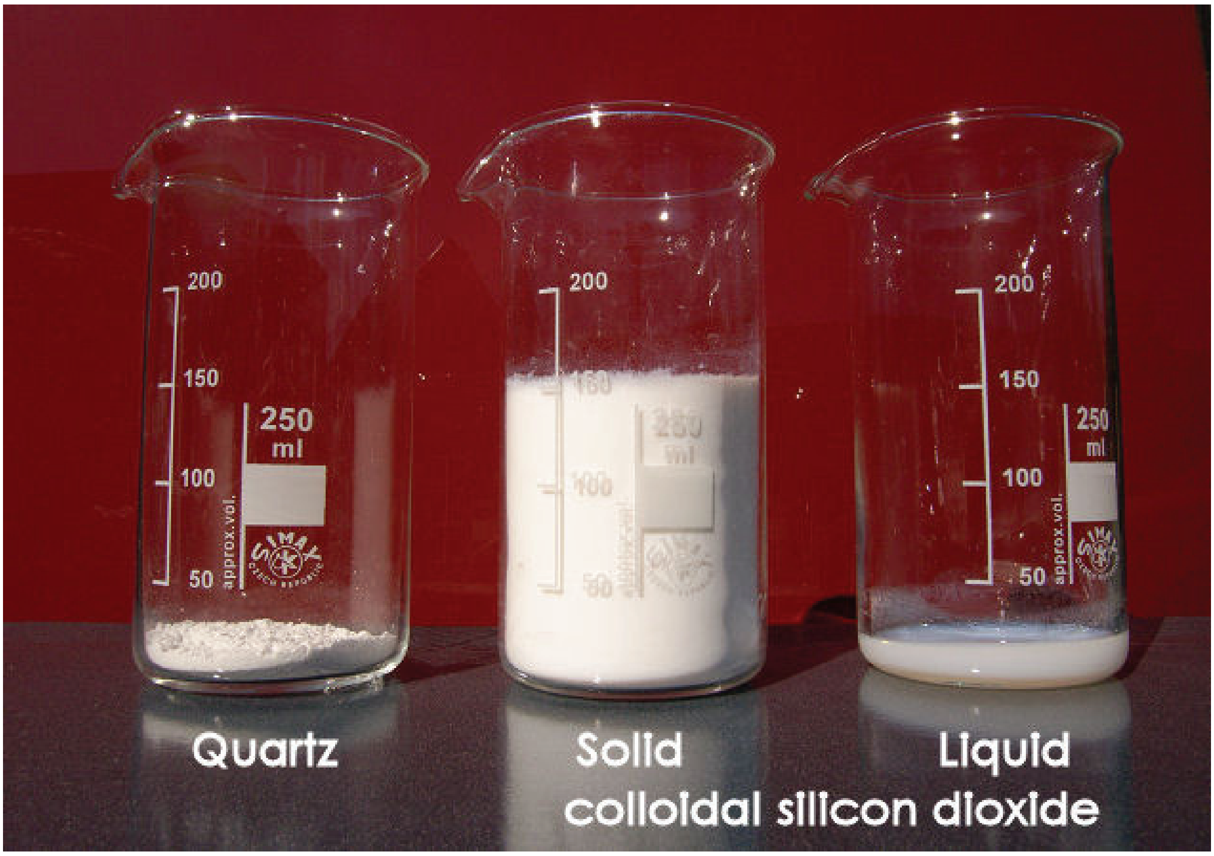

Fig. 3

4. Enamel Batches with Liquid Colloidal Silicon Dioxide

Due to these properties of liquid colloidal silicon dioxide, the product can be used for enamel batches very easily. The advantages of liquid nanoscale silicon dioxide in the enamel batch are listed in **Figure 4.**

Liquid nanoscale silicon dioxide offers the following advantages:

- The portion can be calculated as a batch raw material
- High chemical resistance at low firing temperature
- Smooth surfaces
- Hard biscuit
- The surface remains wet during a longer time
- Easy improvement of the resistance against acids

Fig. 4

Due to the high reactivity of the liquid nanoscale silicon dioxide, the quartz content of the enamel from the enamel recipe can be applied to the mill batch. The quartz from the raw material recipe can be used as a mill batch.

The quartz content and the water from the liquid colloidal silicon dioxide can be calculated and included into the batch.

Consequently, it is possible to use softer enamels and to fire them at lower temperatures. The chemical resistance corresponds to the one of considerably harder enamels.

Due to the low quantity of batch additives, very beautiful surfaces with high brilliance and smoothness are produced.

Portions of liquid colloidal silicon dioxide in the mill batches make the biscuit hard and touchproof. It is also possible to use the product in the ground enamel for the 2c/1f coating. This offers the advantage that the surfaces remain wet during a longer time.

The advantages become particularly obvious when considering the chemical resistance. In normal enamel batches, the mill quartz can be replaced by liquid nanoscale silicon dioxide. This is a simple method to improve the quality significantly.

5. Comparison of Chemical Resistances

Equal portions of 20 parts of quartz of various modifications were milled into a soft frit combination. For the investigations, fine quartz, nanoscale solid quartz and nanoscale liquid quartz were milled into a soft enamel with equal portions of SiO_2. The test plates were burned in at 700 °C during 6 minutes and tested in compliance with EN 14483-2-10. Testing according to EN 14483-2-10 is done using 6% citric acid boiling over 2.5 h.

Figure 5 very clearly reveals a significant improvement of the acid resistance due to the use of liquid colloidal silicon dioxide.

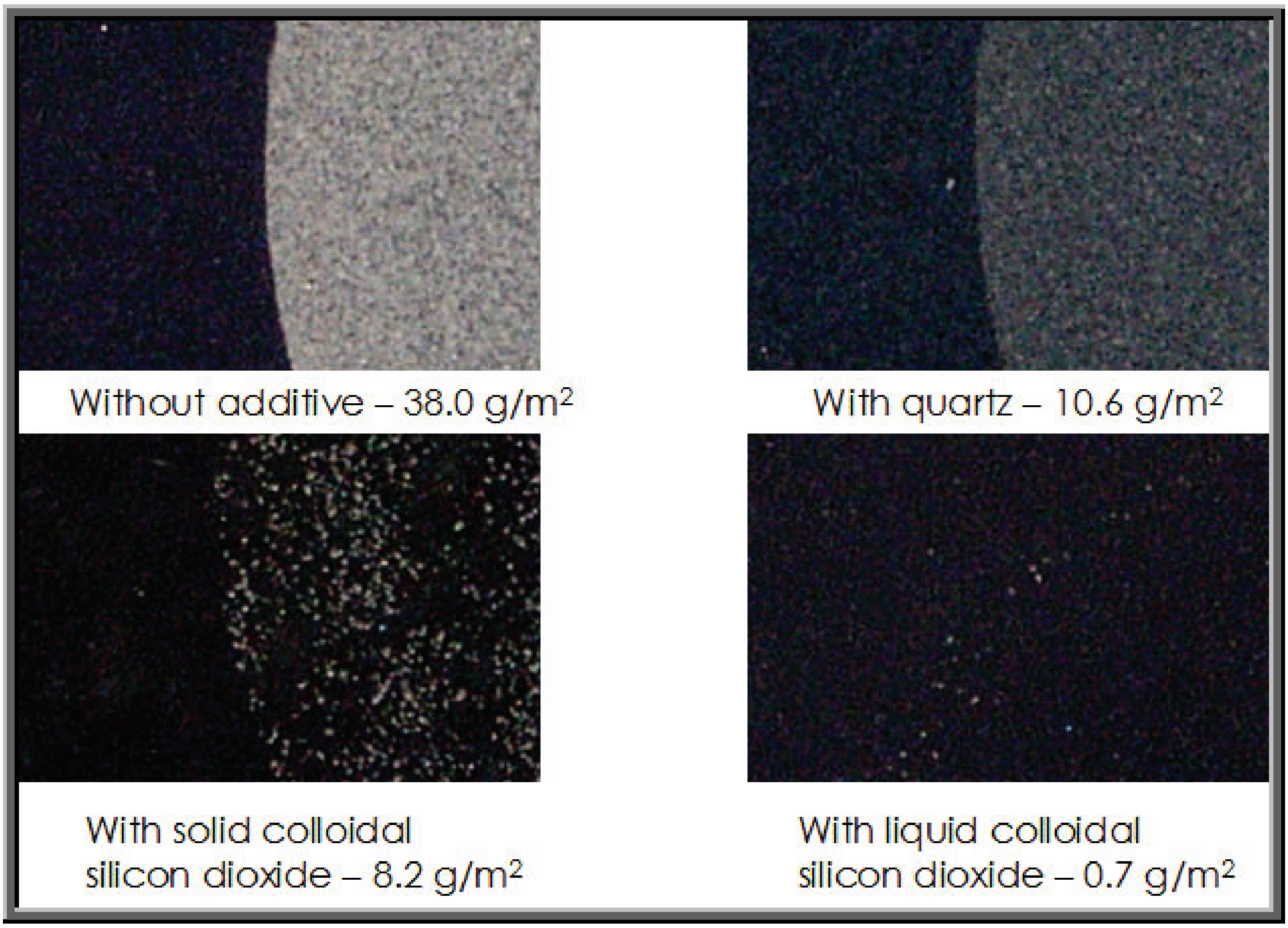

Fig. 5

The enamel degradation is 38.0 g/m^2 without any additive at all, 10.6 g/m^2 with fine quartz, 8.2 g/m^2 with solid nanoscale quartz and 0.7 g/m^2 with liquid nanoscale quartz.

On the picture with liquid colloidal silicon dioxide, the homogeneous enamel structure is demonstrated very beautifully. On the picture relating to the solid colloidal silicon dioxide test, the surface is less homogeneous and reveals areas in which the citric acid has caused noticeable corrosion. Due to the large volume of solid nanoscale silicon dioxide, it is not possible to accomplish a homogeneous surface.

The liquid, nanoscale SiO_2 integrates itself into the enamel structure very homogeneously and improves the acid resistance considerably.

Figure 6 additionally confirms the improvement of the chemical resistance using the boiling test according to EN 14483-2-13. The boiling test according to EN 14483-2-13 is carried out using water over 48 h.

	Liquid phase g/m²*day	Vapour phase g/m²*day
Enamel without additive	4,8	26,0
Enamel with quartz	1,6	20,8
Enamel with solid colloidal silicon dioxide	1,7	18,8
Enamel with liquid colloidal silicon dioxide	0,2	21,9

Fig. 6

After adding liquid colloidal silicon acid, the water resistance increases clearly. The picture shows very clearly that the liquid nanoscale silicon dioxide is included homogeneously into the enamel batch. The behaviour of fine quartz and solid nanoscale silicon dioxide relating to water resistance is equivalent. There are no differences in the degradation during the vapour phase due to the different quartz modifications.

6. Summary

The table in **Figure 7** gives a summary of the advantages of liquid nanoscale silicon dioxide.

- Easy improvement of chemical resistance
- Ideal for enamels with low firing temperature
- Quartz from the enamel recipe can be added using nanoscale SiO_2
- The mill water is added using the nanoscale SiO_2
- After application, the surface remains wet during a longer time
- Homogeneous enamel structure after firing

Fig. 7

An improvement of the chemical resistance is achieved easily.

The usual quartz content of the mill batches can be replaced by liquid colloidal silicon dioxide simply by calculating the solid components. This does not influence the rheologic properties. A considerable improvement of the acid resistance, in particular, is obtained. The brilliance of the enamel is increased as well.

Very good suitability for enamels with low firing temperature.

At low firing temperature, fireproof batch additives tend to dissolve poorly in the enamel matrix. The melting temperature of the fireproof substances is far higher than the firing temperature of the enamels. For this reason, the enamel dissolution capacity is very low at low firing temperatures. Due to a particle size of 8 nm, however, liquid nanoscale silicon dioxide dissolves excellently in the enamel, also if the firing temperature and firing time are low.

Quartz from the enamel recipe can be added using liquid nanoscale silicon dioxide.

Hard chemically resistant enamels can be softened by reducing the quartz content in the enamel recipe. The reduced quartz content is added from the mill batch subsequently. Due to the nanoscale silicon dioxide particles, an enamel structure equivalent to the hard enamel type made from the melt is produced.

The mill water is added using the liquid nanoscale silicon dioxide.

As the mill batches all contain different quantities of water, the water from the liquid colloidal silicon dioxide can be taken into account as mill water when calculating. The rheologic properties are not changed due to the additive.

After application, the surface remains wet during a longer time.
Due to this property, the ground coat of enamel can be processed with liquid colloidal silicon dioxide using the 2coat/1fire method. The processing quality is improved considerably.

Homogeneous enamel structure after firing

Despite the short firing time and the low firing temperature, the nanoscale structure of the liquid silicone dioxide is integrated perfectly into the enamel matrix.

In summary, it can be said that liquid nanoscale silicon dioxide opens a large variety of possibilities for easy enhancement of the enamel properties.