THE CONSOLIDATION OF NATURAL STONE WITH A STONE STRENGTHENER ON THE BASIS OF POLY-SILICIC-ACID-ETHYLESTER

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SUMMARY

Only a prehydrolyzed silicic acid ethyl ester can be applied safely and gives better results in consolidation. The MOTEMA®-Stone Strengthers are ready-to-use products designed for the restoration of natural stone, stucco and frescos which are damaged by weathering influences. In addition other building materials such as bricks or terracotta can be consolidated. During application, the material’s capillary system absorbs the product and will transport it within deeper zones. The Poly-Silicic-Acid-Ethyl-Ester reacts with the water absorbed at the capillary walls and silicic acid gel is formed. In the past years, this technology was been used on many objects in Europe, including the works in the Forum Romanum in Rome, the reconstruction of the Greek Theatre, part of the temple of Apollo Licio in Metaponto in the south of Italy, the southportal of the cathedral in Worms and this year on buildings in Petra.

In 1978 we did not pay attention to the safety-relevant data of the monomer tetra ethyl silicat (silicic acid ethyl ester), because we did not intend to use a monomer ester as a stone strengthener. On the market "solvent free" stone strengtheners are offered as very environmentally beneficial. This means a solvent free, catalized silicic acid ethyl ester. We have examined the possibility of the combination of the polyester within the monomer ester as a solvent, in order to be able to offer also a "solvent free" stone strengthener.

To do this, we had to consider safety-related data. We determined that the MAC of tetra ethyl silicate is only 20 ppm, but that it has no odour before 85 ppm. This means that one can inhale a toxic amount before noticing any odour.

ZUSAMMENFASSUNG


1 INTRODUCTION

The reason for weathering of natural stone and in particular of sand stone is the loss of the grain-grain-linkage. The reduction of adhesion can penetrate deeply on the inside of the stone. The purpose of strengthening is to restore the bond between separate grains. Today organic silicic acid esters are almost exclusively used. Through hydrolysis, alcohol is decomposed and absorbed as the binder SiO₂-gel. This gel should reach all weathered areas, penetrating uniformly and deeply into the material.

2 SELECTION OF PRODUCTS

Earlier products such as baryta water, fluates and water-glass did more harm than good to the natural stone and are of no importance today. Also the reconstructive saturation with reaction resin solutions according to DIN 16945 must be judged very sceptically. The application of polymer solution, e.g. polymethylmethacrylate, is especially suitable for selected natural stones. However, those products, also in combination with hydrophobizing agents, will not be examined here. [1]
Silicic acid ester are esters of ortho silicic acid with the following structural formula:

\[
\begin{align*}
\text{O} \cdot \text{R} \\
\text{R} \cdot \text{O} \cdot \text{Si} \cdot \text{O} \cdot \text{R} \\
\text{O} \cdot \text{R}
\end{align*}
\]

Both esters react in the same way:

\[
\text{Si(OH)}_4 + 4 \text{H}_2\text{O} \rightarrow \text{SiO}_2 \cdot \text{aq} + 4 \text{ROH}
\]

R-OH = methanol: CH₃OH, or = ethanol: C₂H₅OH

The monomer methyl ester is considerably more reactive than ethyl ester. Because it is highly toxic - causing serious necrosis of cornea, with danger of blindness - this methyl ester cannot be purchased on the free market and consequently cannot be applied. This leaves only ethyl ester.

This silicic acid ethyl ester (SAE) has a molecular weight of 208 and a boiling point of 163°C and hydrolyzes slowly in water, which leads to the problem of evaporation. Much of the applied compound would evaporate before it could penetrate deeply into the weathered stone. For this reason this monomer ester is catalyzed generally using dibutyltinlaurat. The hydrolysis of the ester then proceeds more quickly. This reaction is strongly influenced by temperature, moisture on and in the object and atmospheric humidity. Under disadvantageous conditions, there is a danger of glazing on the surface.

The tensile strength cracks with catalized customary silicic acid ethyl ester products depending on depth of penetration - as described by Ettl/Schuh [2] - are explainable by the different reactions due to temperature and humidity within the stone.

3 ALTERNATIVES

The monomer silicic acid esters were already on the market for more than 10 years in 1978, when our customers asked for a slowly hydrolysing stone strengthener. Chemistry prescribes an increase in
pressure and temperature as a means of accelerating chemical reactions. Both are out of question for stone consolidation.

A polymerization at room temperature proceeds substantially quicker, if the first phase takes place in advance in a separate reaction before remixing prepolymerisat with the monomers. This reaction is accomplished in the workshop by increased temperature. We examined whether the Trommsdorf-effect is also applicable by silicic acid ethyl ester after pre-hydrolysis. Corresponding references were found in the bibliography. [3]

In test series, the most favourable relation between viscosity and reactivity were determined. We found an oligomer consisting of an average of 4 molecular components to be especially suitable. The structural formula can be presumed as follows:

\[
\begin{align*}
H_5C_2O & \quad OC_2H_5 \quad OC_2H_5 \\
C_2H_5-O-Si-O-Si-O-C_2H_5 \\
H_5C_2O & \quad O \quad OC_2H_5 \\
H_5C_2O & \quad Si-OC_2H_5 \\
OC_2H_5 & \\
\end{align*}
\]

This oligomer has an average molecular weight of appr. 650 and a SiO₂-content of 40 to 50 % w/w. The viscosity rises from 1 mPa·s of the monomer ethyl ester to 5 mPa·s, which is still acceptable. The increased viscosity can be reduced by adding a solvent. This is necessary anyway, because a stone strengthener with an SiO₂-content of 40 to 50 % w/w should not be applied.

How can the secretion "in situ", i.e. in the depth of the stone, be controlled?

On every crystal surface in a stone and particularly on quartz there exists a stratum of water molecules. This so-called Helmholtz-Stratum has a strength of ca. 3 molecule layers.

Helmholtz-Stratum with anions, cations and water-dipoles [EAGLAND]

There is a zone inside the stone which contains water and which is required for the hydrolysis of the poly silicic acid ester. The enrichment of water can be additionally supported by using a hygroscopic solvent, such as ethanol. Ethanol has a boiling point of 78 °C, can be combined with silicic acid (ethyl) ester products as well as with water in every proportion and is physiologically harmless.
The most important data of the ready-to-use PSAE-product in ethanol:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form</td>
<td>Liquid</td>
</tr>
<tr>
<td>Colour</td>
<td>Colourless</td>
</tr>
<tr>
<td>Odour</td>
<td>Alcoholic, aromatic</td>
</tr>
<tr>
<td>Active content</td>
<td>28% SiO₂</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.94/20°C</td>
</tr>
<tr>
<td>Viscosity</td>
<td>2 mPa·s/23°C (Brookfield)</td>
</tr>
<tr>
<td>Flash point</td>
<td>12°C</td>
</tr>
<tr>
<td>Hazard classification</td>
<td>3 (flammable liquids)</td>
</tr>
</tbody>
</table>

The slower hydrolysis in comparison with the catalized silicic acid ester was accepted intentionally, because it has a decisive advantage: during the hydrolysis of ester a relatively large amount of ethanol has to escape from the system. The consequence is a strong shrinkage and high tensile strength which are caused in the gel. During the hydrolysis of a silicic acid ester, silanole are developed as an intermediate stage.

\[
\begin{align*}
  \text{Si-OR} + \text{H-O-H} & \iff \text{Si-OH} + \text{ROH} \\
  \text{Si-OH} + \text{RO-Si} & \iff \text{Si-O-Si} + \text{ROH} \\
  \text{Si-OH} + \text{HO-Si} & \iff \text{Si-O-Si} + \text{ROH} \\
  \text{R-Si(OH)₄} + 2 \text{H₂O} & \longrightarrow \text{SiO₂} + 4 \text{ROH}
\end{align*}
\]

(1) (2) (3) (4)

This becomes apparent through a passing hydrophobical stage on the consolidated stone. If the gel exists as a silanole for a longer time and if during this stage a large amount of ethanol can be separately evaporated, the shrinkage of the gel is substantially diminished after the complete hydrolysis and dehydration. Tension is reduced and the consolidations are more uniform. This is shown in the following diagram. The non-pre-condensed, high catalized product shows a rough increase of the consolidation towards the surface. The pre-condensed product on the other hand has a well-balanced consolidation profile with a smooth inward course.
Foto 1: Pure silicic acid gel with parts of not finilized hydrolysis.

Foto 2: MOTEMA®-PKSE-Steinfestiger 28 on Sander-Sandstone.
4 SAFETY RELEVANT DATA

In 1978 we did not pay attention to the safety-relevant data of the monomer tetra ethyl silicat (silicic acid tetra ethyl ester), because we did not intend to use a monomer ester as a stone strengthener.

On the market "solvent free" stone strengtheners are offered as very environmentally beneficial. This means a solvent free, catalized silicic acid tetra ethyl ester. We have examined the possibility of the combination of a polyester within the monomer ester as a solvent, in order to be able to offer also a solvent free stone strengthener. To do this, we had to consider safety-related data. We determined that the MAC of tetra ethyl silicate is only 20 ppm, but that it has no odour before 85 ppm. This means that one can inhale a toxic amount before noticing any odour. [6] The following table compares the most important safety-relevant data of silicic acid ethyl- (SAE) and poly silicid acid ethyl esters (PSAE).

<table>
<thead>
<tr>
<th></th>
<th>SAE</th>
<th>PSAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol.-weight:</td>
<td>208</td>
<td>≈ 650</td>
</tr>
<tr>
<td>Boiling point:</td>
<td>163 °C</td>
<td>&gt; 200 °C</td>
</tr>
<tr>
<td>CAS-Nr.</td>
<td>78-10-4</td>
<td>68412-37-3</td>
</tr>
<tr>
<td>EG-Nr.</td>
<td>014-005-00-0</td>
<td>none</td>
</tr>
<tr>
<td>Danger symbol:</td>
<td>Xn, =hazardous</td>
<td>no particular dangers</td>
</tr>
<tr>
<td>Possible dangers:</td>
<td>flammable, hazardous by</td>
<td>known</td>
</tr>
<tr>
<td>Exposition limit:</td>
<td>20 ppm = 170 mg/m³</td>
<td>none</td>
</tr>
<tr>
<td>(MAC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smellability:</td>
<td>85 ppm</td>
<td>350 ppm (Ethanol)</td>
</tr>
<tr>
<td>Steam pressure:</td>
<td>&lt; 2 hPa</td>
<td>2.4 hPa</td>
</tr>
<tr>
<td>Minimum level for odour:</td>
<td>85 ppm</td>
<td>350 ppm (ethanol)</td>
</tr>
<tr>
<td>Toxic reactions:</td>
<td></td>
<td>not irritating</td>
</tr>
<tr>
<td>- skin</td>
<td>moderately irritating</td>
<td>slightly irritating</td>
</tr>
<tr>
<td>- eyes</td>
<td>not sensitized</td>
<td>none</td>
</tr>
<tr>
<td>- inhalation</td>
<td>irritating</td>
<td></td>
</tr>
<tr>
<td></td>
<td>noxious</td>
<td></td>
</tr>
</tbody>
</table>
5 CONCLUSION

In our opinion, only a stone strengthener based on a poly silicic acid ester can satisfy the requirements of natural stone and working hygiene.

REFERENCES


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