Efficient Hydrophobation of Concrete with Novel Silicone Products

W. Keller  
Wacker-Chemie GmbH München, Munich, Germany  
R. Hager  
Wacker-Chemie GmbH München, Werk Burghausen, Burghausen, Germany  

Abstract

The presented class of products is an important addition to the existing variety of silicone based formulations for use in building protection. Compared to most silicone masonry water repellents marketed so far – which are usually applied as liquid formulations – this new protection system has a higher viscosity.

The novel product line shows significant innovative features:

- **easy application** with airless spraying equipment or other means
- „**over-head “ application possible (no dropping of product)
- **better working efficiency** by achieving a high impregnation depth with a **one-step**-application because of possible higher film thickness
- **optimum distribution of the product** on the construction material by **achieving** a constant film thickness — and thus constant quality of the impregnation
- **optimum control overpenetration depth** (product absorption) by adjusting the film thickness (> 5 mm penetration at up to 300 g/m²)
- **no loss of active material** due to evaporation or low viscosity on vertical sites, thus providing minimization of environmental pollution
- much **higher content of active silicones** compared to regular emulsions
- **high penetration depth** better than pure silane compositions by longer **contact** time

Because of the combination of above mentioned product specifications this novel product is highly recommandable for water repellent treatment of construction materials, especially concrete. It was possible to verify the lab data by field trials on selected concrete structures.

These results as well as the hydrophobing effects and application methods of the above mentioned product line — as well as a general introduction into silicone masonry water repellents — will be dealt with in the presentation.

Keywords:
Concrete Protection, Creme, Hydrophobation, Silanes, Silicones, Siloxanes, Masonry Water Repellents
1. Introduction

One of the main physical properties of silicones is their pronounced water repellent effect on treated substrates. So shortly after industrial production had started some decades ago, silicones were used as impregnating agents, e.g. for textiles or building materials.

Today a variety of customized silicone products is used to protect buildings and building materials against moisture and subsequent physical, chemical, and biological deterioration. During the years, the change in building materials used, tougher performance requirements, and greatly enhanced environmental awareness were some of the driving forces for continuous innovation in the field of silicone masonry water repellents.

One of the changes in product formulation which is still going on is the tendency to use water based rather than solvent based products. One further step will be a change of physical state. Up to now, ready-to-use silicone based masonry water repellents have always been liquid, now a new generation of pasty and solid products is being developed.

The use of pasty agents is especially interesting for protection of concrete structures, where a very dense material of relatively low water absorption is to be treated and a sufficient contact time is often not reached by using liquid products.

2. The importance of surface treatment in concrete protection

Reinforced concrete for many years had the image of a non-corroding, maintenance-free building material that was said to have a lifetime of some centuries. With such a common belief it was out of question why surface protection should be sensible – it was not. The disillusionment came in the 70s, when corrosion of many of the reinforced concrete structures became a public issue.

Damage of reinforced concrete is mainly caused by diffusion of carbondioxide into the concrete and subsequent carbonation of the containing lime, as well as absorption of pollutants like chloride ions. A crucial role in deterioration plays the penetration of water into the concrete by which the speed of corrosion is multiplied. The following points have to be considered:

- Preventive protection of non-corroded concrete
- Establishment of a lasting corrosion protection
- Protection of new concrete replacing old, deteriorated concrete
- Increase of chemical and mechanical resistance of the concrete mixture

A simple classification of surface protection systems, which is technically sensible as well, is the classification by thickness of the protecting layer:

- hydrophobing impregnation, which has no measurable “thickness”
  - water repellent + (if needed) oil repellent and/or strengthening
- so called “sealings” (about 50 \( \mu m \) thick), which can not fill pores totally
  - strengthening effect and partly clogging of pores
- filmforming coatings (some 100 \( \mu m \) thick)
  - clogging of pores, \( \text{CO}_2 \)-diffusion hindered, reduction of water uptake
3. Molecular basis of silicone masonry water repellents

Most of today’s silicone masonry water repellents are based on polymeric silicone resins as the basic chemical structure. Since the monomeric silane building blocks to these resins are trifunctional alkyltrialkoxysilanes $\text{RSi(OR')}_3$, the resulting resin can be considered as an organomodified quartz ($\text{RSiO}_{3/2}$ instead of $\text{SiO}_{4/2}$). Thereby the water repelling effect is caused by the hydrophobicity of the alkyl group R.

Because quartz — or more general silicate — is the binder of most natural and artificial stones and masonry, the resemblance between silicone resins and quartz is the reason why silicone resins are so suitable to be used on building substrates, particularly in terms of durability and service life.

Silicone masonry water repellents, in contrast to filmforming organic polymers, do not seal the surface pores of masonry. They only modify the pores of the substrate in such a way that liquid water absorption is suppressed, while the pores remain open and water vapour permeability is not affected. Chemically spoken, covalent Si-O-Si bonds are formed between the SiOH groups of the substrate pores and the SiOR of the silicone, thus rendering the pores water repellent but leaving them water vapour permeable.

In the beginning of silicone masonry water repellents, solutions of polymeric methylsilicone resins in aromatic solvents were used. Since fully cured resins of high molecular weight are not soluble any more, lower molecular weight precursors have been used for that purpose.

On many low porous substrates like concrete, the penetration depth of silicone resin solutions or their precursors is not sufficient to meet current performance requirements. On these substrates the silicone resins have to be replaced by agents with even lower molecular weight, which are monomeric alkyltrialkoxysilanes or oligomeric alkylalkoxysiloxanes $\text{R}_n\text{Si}_y(\text{OR'})_z$.

After application to the masonry structure, all the mentioned agents will react with water or humidity to the cured silicone resins, which are anchored to the substrate by stable covalent Si-O-Si bonds while alcohol is liberated as by-product.

Modern silicone masonry water repellents are preferably mixtures of alkylalkoxysilanes and oligomeric siloxanes. The alkoxy groups OR’ are either methoxy or ethoxy groups. The organic groups R are methyl or longer chain hydrocarbon substituents like octyl groups. Long chain substituents impart alkaline stability to the hydrophobing agents, since thermodynamical and kinetical effects prohibit decomposition of the cured resins by alkaline chemicals or substrates.

Until the mid 80s, silicone masonry water repellents were mainly used as solutions in organic solvents. There were only two exceptions: undiluted 100% products and water based siliconates — both for special applications.

Since solvents only act as a transport medium, after having fulfilled this function, they are simply emitted into the atmosphere. For this reason and due to increased public awareness in terms of ecology and health, there is only one implication for masonry water repellents as well as for paints:

Replace organic solvents by water wherever possible!
4. Aqueous silicone masonry water repellents

Besides the silicionate approach mentioned above which is by now well known for almost 40 years, basically there are two ways of dissolving and dispersing organosilicone substances in water:

- Producing silicone emulsions
- Introducing hydrophilic functional groups into polysiloxanes to get selfemulsifying systems

These two modern approaches to water based masonry water repellents will now be dealt with in more detail.

4.1 Emulsion approach

Silicone emulsions for masonry protection have been used successfully in mainly three application:

- Silicone resin emulsions as binders in silicone resin emulsion paint
- Emulsions of special linear polysiloxanes as additives in masonry paints
- Emulsions of low molecular alkylalkoxysilanes and -siloxanes as penetrating water repellents and primers

4.1.1 Silicone resin emulsion paint

Silicone resin emulsion paint is regarded as the most modern of currently available facade coating systems [1]. Coatings with silicone resin emulsion paint are water vapour permeable like mineral paints but at the same time are also water repellent like filmforming dispersion paints. These unique properties result from the main binder component, an emulsion of a solid silicone resin. Since solid products can hardly be emulsified, the silicone resin either has to be dissolved in organic solvents or the emulsifying process has to be done with a liquid precursor of the – finally solid – resin. Of course, the solvent-free approach is more desirable due to ecological factors.

4.1.2 Silicone additives

Silicone additives are added to coating materials, mineral paints, dispersion paints, plasters, etc. in small quantities in order to change the coating’s properties permanently – especially to improve water resistance while obtaining high water vapour permeability. Modern additives are solvent-free emulsions of functional reactive polysiloxanes. The following chemical structure is an example of such a high-performance siloxane:

\[
H_2N(CH_2)_3NH(CH_2)_3Si(OCH_3)_2O[Si(CH_3)_2O]_6Si(OCH_3)_2(CH_2)_3NH(CH_2)_2NH_2
\]

In many cases only 1% of the additive is required to reduce the water uptake by more than 90%, e.g. from 5 kg/m² down to 0.5 kg/m² (after 24h).
4.1.3 Masonry water repellents

For a long time it was thought impossible to create stable water based masonry water repellents. One of the main demands for masonry water repellents is that they have to be well penetrating into the stone. If other parameters are kept constant, the penetration of a liquid into a building material is better when the viscosity is lower. In contrast to homogenous solvent based products where the viscosity of the whole solution is relevant, in emulsions only the viscosity of the oil phase – i.e. the silicone – is important [2]. Of course, to get good penetration results, low molecular weight alkylalkoxysilanes and -siloxanes have to be chosen. The problem, however, is that these agents hydrolyze and polymerize in water, thereby forming larger and larger molecules up to solid silicone resins. Consequently their penetration behaviour turns worse and worse with time.

In the mid 80s it was found that the hydrolysation speed of alkoxysilanes can be slowed down if silanes $\text{RSi(OR')}_3$ with longer chain organic substituents R (e.g. octyl or isooctyl) are used. The same effect results of the use of ethoxy instead of methoxy substituents as groups OR' [3]. Emulsions made of the mentioned silanes are storage stable for several months. Their main disadvantage is that the formation of the final water repellent polysiloxane in the masonry structure takes a rather long time. This problem could be solved by formulating an emulsion containing not only silane but also oligomeric and polymeric siloxanes [4].

Similar to solvent based products, such emulsions are:

- Storage stable over more than one year (before and after dilution)
- Well penetrating into mineral substrates
- Stable against alkalinity
- Suitable for all mineral substrates, concrete as well as natural stone

4.2 Selfemulsifying microemulsion approach

The storage stability problems with water sensitive alkylalkoxysilanes and -siloxanes when brought into contact with water via emulsifying were the reason for another development. Some years ago, Wacker-Chemie GmbH introduced a technology of water based silicone masonry water repellents – the so-called Silicone Microemulsion Concentrates – abbreviated and registered as WACKER SMK® technology [5].

Silicone Microemulsion Concentrates in terms of WACKER SMK® are low viscous, clear, anhydrous, and solvent-free liquids based on alkylalkoxysilanes and -siloxanes which – simply upon being poured into water – spontaneously form extremely fine particle (1 O-80 nm) silicone microemulsions.

It is well known that microemulsions of so small particle size require 10 times more emulsifier than common emulsions with particle sizes of 500-1000 nm. In addition, a co-emulsifier is necessary to achieve microemulsions.

Following this thought, conventional emulsifiers are unsuitable for use in masonry water repellent microemulsions because emulsifiers in the high amounts necessary prevent the development of the desired water repellency.
The concept behind silicone microemulsions of WACKER SMK® is therefore that emulsifier and coemulsifier are at the same time active ingredients and lose their emulsifying activity after being used.

WACKER SMK®s are diluted to form microemulsions by simply being poured into water. This should be done directly before application to the substrate since contact with water causes the reactive components to begin reacting within the microemulsion droplets. After activation, the silicone microemulsions gradually lose their effectiveness, e.g. their ability to penetrate into dense building materials.

Main advantages of the WACKER SMK® technology are:
- Solvent free products of 100% active ingredients
- Storage stability of the concentrates over years
- Easy to use
- Concentrated form (lower storage, transport, packing costs, and duty)
- Environmentally friendly (diluted with water)

Table 1 shows a comparison of performance between a solvent based allround impregnant (WACKER 290), a WACKER SMK® type product (WACKER SMK® 13 11), and a silane/siloxane emulsion (WACKER BS 1001) as described in the preceding chapter. All products were used in a concentration of 10% actives on three substrates: lime sandstone, brick, and concrete.

It can be concluded that there are some differences in performance between the three product types, but all penetrate well into the substrate and reduce the capillary water absorption sufficiently.

Table 1: Performance of solvent diluted (WACKER 290), emulsion (WACKER BS 1001) and microemulsion based (WACKER SMK® 13 11) masonry water repellent.

<table>
<thead>
<tr>
<th>Product</th>
<th>Substrate</th>
<th>Impregnant uptake [g/m²]</th>
<th>Penetration depth [mm]</th>
<th>Water uptake 24 h [g/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Lime sandstone</td>
<td>0</td>
<td>0</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Brick</td>
<td>0</td>
<td>0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>Concrete</td>
<td>0</td>
<td>0</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>Lime sandstone</td>
<td>550</td>
<td>6.8</td>
<td>0.16</td>
</tr>
<tr>
<td>WACKER 290</td>
<td>Brick</td>
<td>2185</td>
<td>&gt; 35</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Concrete</td>
<td>210</td>
<td>2.4</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Lime sandstone</td>
<td>540</td>
<td>5.1</td>
<td>0.18</td>
</tr>
<tr>
<td>WACKER SMK 13 11</td>
<td>Brick</td>
<td>1654</td>
<td>&gt; 35</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Concrete</td>
<td>150</td>
<td>1.2</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Lime sandstone</td>
<td>530</td>
<td>4.6</td>
<td>0.19</td>
</tr>
<tr>
<td>WACKER BS 1001</td>
<td>Brick</td>
<td>1020</td>
<td>&gt; 35</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Concrete</td>
<td>167</td>
<td>2.3</td>
<td>0.22</td>
</tr>
</tbody>
</table>

5. Novel pasty silicone masonry water repellents

Silicone based water repellents in the past have always been liquids. The disadvantage of liquids is that excess material is running down at vertical surfaces and subsequently penetrating into the ground, thereby polluting the environment.
Another point is safety reasons, e.g. if the water repellent agent has to be applied by flooding „over head”, the applicator can hardly avoid to be contaminated with chemical substances (solvents plus actives).

Most interesting in these terms is the impregnation of reinforced concrete, particularly road constructions and bridges. In the past undiluted alkylalkoxy silanes $\text{RSi(OR')}_3$ were often used for this purpose. Since high performance concrete is a rather dense substrate, only highly concentrated (up to undiluted) and low viscous products penetrate sufficiently. Once chosen, even these products have to be applied at least two times in order to achieve a penetration depth of some millimeters and a coverage rate of at least 100 g/m$^2$. In addition, monomeric undiluted silanes are the most volatile of all silicone products and so lots of active material is lost by evaporation into the atmosphere [6].

Therefore the challenge was to develop a product line with the following characteristics:

- Excellent penetration even into high grade concrete
- Only one application step to obtain a sufficient coverage rate
- No volatility problems
- Good beading effect
- Water based and solvent free

These requirements could be met by changing the physical state of the silicone masonry water repellents from liquid to pasty.

The first attempt to realize this was to combine silanes or siloxanes with thickening agents as bentonite or montmorillonite [7]. A main disadvantage of such products is that the thickener remains on the surface, thereby affecting the appearance and having to be removed later. Another drawback is the fact that the volatility problems with such a product are even worse than with the pure silanes because the agent is applied in a thick layer and the volatile components have plenty of time to evaporate instead of penetrating into the concrete.

Very recently pasty products have been developed which are not subject to these disadvantages. Their formulation principle is totally different from those mentioned above. Their pasty consistency is not achieved by using a thickening agent, it is achieved by a special emulsification process which is stopped at the stage of a high viscous phase and renders a storage stable product. As silicone active ingredients preferably mixtures of alkylalkoxy silanes and -siloxanes are used. By variation of the silane: siloxane ratio „tailor-made“ impregnants for different substrates can be formulated. The actives content normally ranges above 80% while the rest of the product is water.

These products are preferably applied via spraying with a modified airless equipment. This way, very easily layers up to 0.5 mm thickness can be achieved without losing any material on vertical substrates. Within a few hours the silicone penetrates completely leaving no visible remainings on the surface.

For demonstrating the performance of the new pasty products, a formulation was chosen which contained 80% actives and a silane/siloxane ratio of 9:1 (WACKER BS 69001). Concrete cubes (grade B35, 10 cm edge length) were covered horizontally with a 0.4 respectively 0.8 mm layer of WACKER BS 69001.
For comparison, well established liquid products were tested which were applied on to the concrete cubes by 5 minutes immersion (coverage rate approx. 100 g/m²). All treated cubes were stored at ambient conditions for 2 weeks, immersed in water for 7 days, and then the water uptake was determined.

From the experiment’s results it could be concluded that the pasty product penetrates tremendously well (at 0.8 mm layer 3 times better than the 100% silane) and at the same time is the only product in the test series which reduces the water uptake over 7 days by more than 90%. The penetration of the diluted products – especially the silane emulsions – is extremely poor compared to the performance of WACKER BS 69001. As a consequence the water uptake reduction of these products is significantly lower.

Although water beading is sometimes considered as an „eye catch effect“ (which might be true to some extent), a lack of beading effect is usually correlated with a lack of water repellency. For that reason water beading is important, even on concrete structures. In the formulation of the pasty product this fact was taken into account by chasing a silane/siloxane mixture as active ingredient and not a pure silane. Therefore, in contrast to pure silanes which evaporate from the surface near area, WACKER BS 69001 provides good water beading as soon as the emulsifier residues on the top of the surface are washed out.

6. Summary and prospect

Although it may sound a bit strange, several ways have been developed in order to formulate water sensitive water repellents into water. Meanwhile silicone emulsions and microemulsions are available for almost all applications where some years ago exclusively solvent diluted products were used.

Sometimes not only organic solvents but also active ingredients have to be considered as a problem in terms of ecology and health. An example are the undiluted, volatile alkylalkoxysilanes which are currently used for concrete protection. Due to their volatility, not negligible amounts of these chemicals are emitted to the atmosphere during application.

In order to offer an alternative, pasty products were developed that penetrate into concrete orders of magnitude better than silanes. As water based formulations, these solid-free pastes – or cremes, as they are sometimes called – are much more acceptable regarding environment nd health.

This latest development is a good example that even the physical state of well established products is not invariable. The future of silicone based water repellents will be full of suspense – won’t it?

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7. E.F. Karlson, Swedish patent 9400952-9 (filed 22.3.1994)