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Evolution of Silicone Based Water Repellents for Modern Building Protection

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Abstract

Damp masonry is a threat to architectural structures while also posing a hygienic problem to living conditions in the building's interior. Hydrophobic agents have been the preferred method for protecting masonry facades and building surfaces against moisture entry and weathering. Early water repellent systems had to be externally applied on finished constructed parts and outside structures. Such systems were mainly solvent based using silicone resins as the active ingredient. Later on, environmentally friendly aqueous formulations using oligomeric siloxanes and alkylsilanes as the active components enjoyed broad acceptance and provided architectural structures with excellent water repellency and long durability. While external hydrophobisation still accounts for the major share in the before mentioned applications, integral hydrophobisation has received increasing attention. In the latter case, building protection is already taken into consideration during the actual construction phase. Powdered additives composed of silane/siloxane blends based on an inorganic carrier can be easily applied to dry-mix mortar systems and provide outstanding water repellence once these are set. In this paper an overview is given on the various hydrophobisation systems which are currently available to provide sustainable protection of buildings and architectural structures. Furthermore, an insight into the chemistry which is involved with such additives is also provided.

Keywords: water repellent, hydrophobisation, silanes, siloxanes, water emulsions, solvent based

1 Introduction

Water and humidity penetration into facades, buildings and architectural constructions consisting of mortar, concrete, natural stones or bricks is one of the major reasons for their deterioration, both at the material and structural level.

For many years, the application of water repellent agents based on silicone technology has been the preferred method for protecting masonry facades and building surfaces against moisture entry and weathering thereby increasing their service life. The first protection formulations successfully marketed were based on liquid hydrophobisation systems that were to be applied externally on finished constructed parts or facades. Over the past decade, the importance of building protection has been increasing steadily. Nowadays, it is often taken into consideration already during the construction phase. This trend is further supported by general technological advancements such as the development of the dry-mix technology.

2 Damages caused by water

The majority of building materials are porous. Water may penetrate these pores. When water freezes in winter the ice that forms can induce cracks in the material. In nature this freeze-thaw process turns hard rock into sand in the course of time. In the presence of water, salts contained in the masonry as well as mineral binders are subject to transport and chemical reactions. It is important to mention that damage to buildings is not only caused by the natural weathering but also by high air pollutant concentrations. High emission concentrations of SO_2 and NO_x especially in industrial areas, have dramatically increased the damage to mineral substrates. Physical, chemical or biological damage to buildings is always to a major extend due to the presence of water. The simple rule applies: hydrophobisation means building protection.

Salt blooming, i.e., efflorescence (Fig. 1) is the most apparent moisture induced damage. Minerals and salts dissolved in water can penetrate the building material and get to its surface as the water evaporates and the salts recrystallise. Soluble salts in the masonry are also hydrophilic centres which may cause damp zones by their tendency to absorb moisture. Recrystallization cycles, by the developed recrystallisation pressure, will induce damages to the surface of the masonry and may also lead to structural cracks in the masonry. As a consequence, water may penetrate the building substrate more easily, thereby increasing the damp zones and generating an ideal medium for micro-organisms like algae or fungi infestation. Moss and fungal attack are not only unpleasant but also unhealthy. In addition moisture also reduces heat insulation causing higher energy costs.

A Salt blooming

B Growth of moss

C Reduced heat insulation

Figure 1: Damages caused by water penetration

In summary, water is one of the main causes for the damages to building materials. In order to counteract them, precautions have to be taken. Among these, the use of hydrophobic products based on silicone technology has shown the best performance. Otherwise, expensive restoration works will be necessary.

3 Mechanism of the water absorption

Water absorption and penetration into the substrate take place through defective joints, cracks, leaking seals and construction errors. Design faults in window surrounds, guttering, and down pipes can be also provide water entry points. Walls may also absorb large quantities of water during rainfall. Hygroscopic salts reduce the speed of the drying process. Osmosis within the wall will contribute to distribute the moisture making it difficult to identify the damp source and find a solution for it. Water vapour generally condenses below the dew point. However, water vapour inside the masonry capillaries still can condense above the dew point. In lower wall areas, rising damp and infiltration of ground water can also occur [1]. Figure 2 gives an overview of the different water uptake mechanisms.

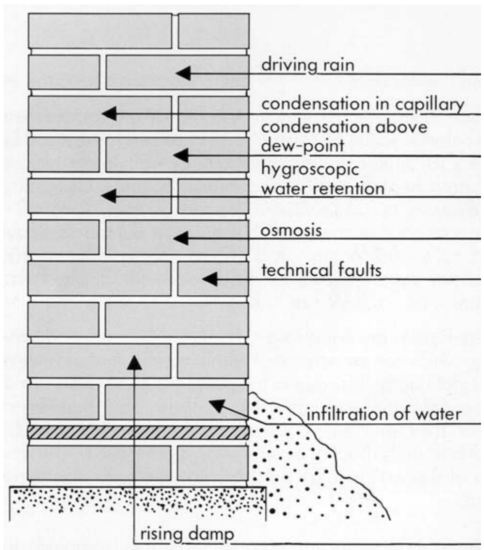


Figure 2: Overview of the different water uptake mechanisms

4 Requirements for water repellents

The main function of water repellents is to prevent liquid water from penetration into the building materials. To achieve long term performance water repellents need to penetrate beyond the surface layer into the interior substrate of the porous material. By forming distinct chemical bonds with the substrate, subsequent washing out can be avoided. UV-stability and good resistance against weathering and high alkalinity are basic requirements for the good performance of a water repellent treatment. The optical appearance of the substrate, such as colour and hue, should not be affected. The formation of visible, sticky films is also not acceptable. Transmission of water vapour needs to be guaranteed to achieve good respiration properties of the building. In summary, water repellent treatments should:

- Reduce liquid water absorption;
- Prevent water absorption during driving rain with heavy winds;
- Achieve a high penetration depth;
- Prevent the formation of efflorescence;
- Protect against de-icing salts;
- Reduce soiling and biofilm formation; and,
- Not influence the appearance of the substrate.

5 Silicone technology

5.1 Industrial applications

Silicones have been used in industrial and consumer applications since the 1950's [2]. In our everyday life we are confronted with silicone containing products, as for example the hair shampoos that contain silicones as conditioners, or in our clothing when silicones are used in pre-treatment applications of the textiles to provide a soft wear feeling. The field of applications of silicone based products is manifold and covers applications in almost every industry including automotive, electronics and construction industry. The range goes from silanes as coupling and bonding agents, e.g., on glass fibres, to silicones as surface active ingredients having defoaming, wetting or lubrication applications, to elastic materials like silicone rubbers as sealing materials for joints in sanitary installations.

5.2 Structures and properties

Among all different kind of hydrophobic products developed for the building industry, silicone resins, silanes, oligomeric and polymeric siloxanes have proved to perform best in protecting masonry façades from water penetration and environmental influences. The starting point for all of these materials is pure silicon which can be obtained from the reduction of silicone dioxide. Silanes are produced in the so-called Müller-Rochow synthesis where alkylchlorides are reacted with silicon in the presence of copper catalysts to alkylchlorosilanes. These can be separated by distillation. By further reaction with alcohols, alkylalkoxysilanes, silanes with different organic modifications, can be derived. Subsequent hydrolysis and condensation reactions lead to oligomeric and polymeric silicone chains depending on the amount of water used in the process (Fig.3).

Equilibration reactions of low molecular weight cyclic siloxane units and chain stoppers can also be used to obtain high molecular weight siloxanes and silicone oils with defined molecular weights. Silicones contain organic groups, predominantly methyl groups, which are bound to the silicon atom. The latter are linked through Si-O-Si bonds which allow a high flexibility of the molecule so as to conform to a given environment. Silicone resins are higher molecular weight products of two and or three dimensional units derived from condensation reactions of silanes [3].

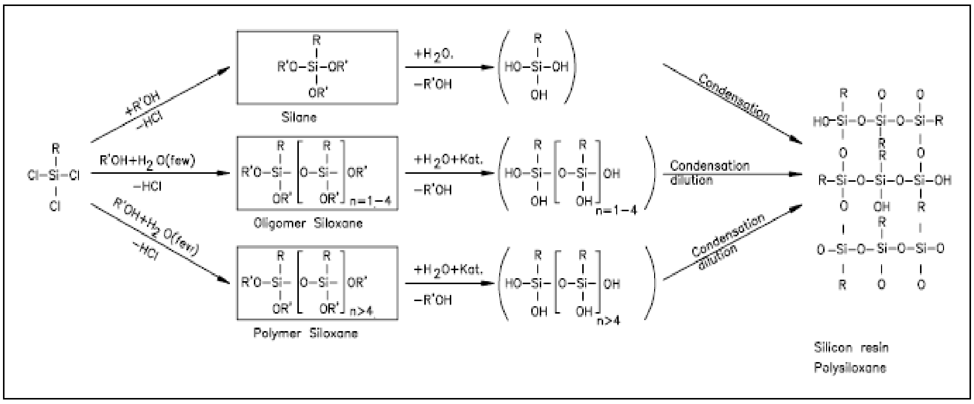


Figure 3: Chemical reaction steps involved in the production of silicone products

5.2.1. Silanes

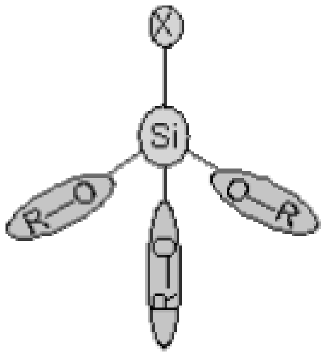


Figure 4: General structure of silane with X = alkyl group e.g. n-butyl - ; n-octyl; and, R = methyl or ethyl-group

Silanes are monomeric molecules which contain only one silicon atom and hence they are of low molecular weight, (Fig.4). In the construction industry, alkyltrialkoxysilanes such as *iso*butyltriethoxysilane, n-octyltriethoxysilane and *iso*-octyltriethoxysilanes are well adapted for hydrophobisation purposes. Longer alkyl chain-length provides steric protection to the Si-O bond which make these products unique in rendering concrete water repellent. Due to their lower reactivity silanes can achieve excellent impregnation depths even in alkaline substrates. After application to the substrate they undergo condensation reactions and crosslink under elimination of alcohol. On neutral surfaces this reaction often needs the presence of a catalyst system, e.g., organo-tin catalysts.

5.2.2. Siloxanes

Siloxanes and silicone oils are oligomeric or polymeric molecules based on Si-O-Si chains. Because of their low intermolecular forces these oils are liquid even at high molecular weight and over a wide temperature range. Technically interesting is also the fact that silicone oils are good insulators. The surface tension of silicone oils depends on molecular weight, increasing from 15.7 mN/m for hexamethyldisiloxane to about 22 mN/m for medium and high molecular weight oligomers and polymers. This is much lower than those for organic oils, i.e., with carbon chains, which are usually in the range of 30-35 mN/m. Also to be mentioned is their high thermo stability.

In organo-modified siloxanes some of the methyl groups at the silicon atoms are substituted by other organic groups (Fig.5).

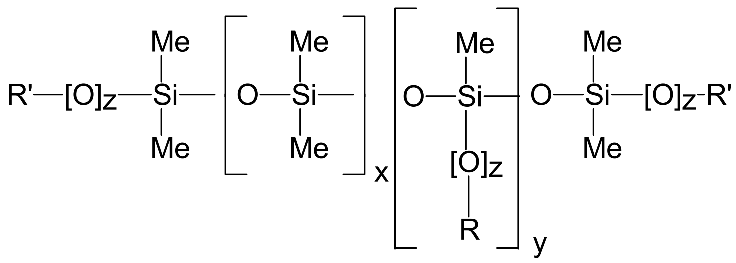


Figure 5: Generic structure of organo-modified siloxanes. R and/or R' in the structure represent various organic substituents, e.g., aliphatic and/or aromatic groups attached to a linear, comb-like, or branched siloxane backbone. In general, the organically substituted silicones have relatively short siloxane lengths (x+y = 10-200). If Z = 0 the organic group is directly linked to the silicon via Si-C bonds.

In construction applications organo-modified siloxanes are mainly used for hydrophobisation of neutral and natural substrates. They also are applicable for treatment of aged concrete with a lowered pH value due to carbonation. The main applications for these products are façade treatment and protection against rising damp. Due to their higher reactivity compared to that of monomeric silanes, siloxanes do not need a catalyst for curing. On high alkaline substrates the curing process of siloxane is so fast that it does not allow the molecule to penetrate very deep into the substrate.

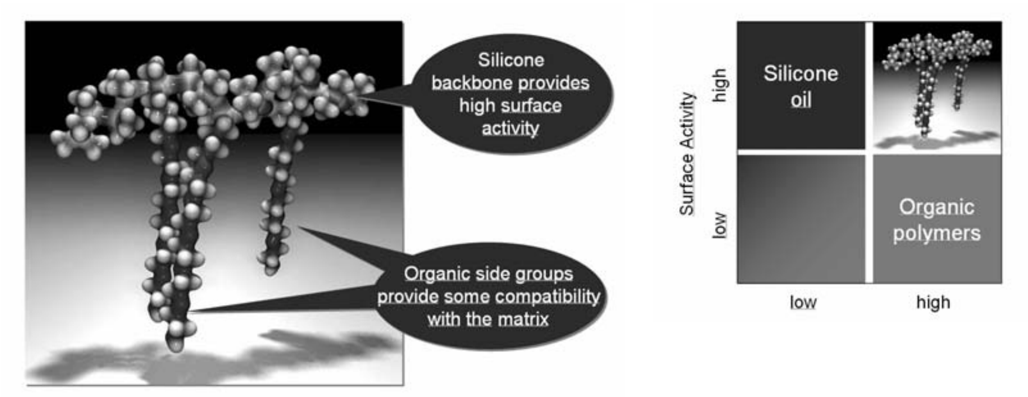
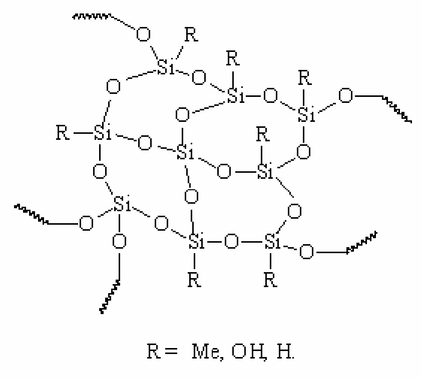


Figure 6: Organo modified siloxanes combining good surface activities of silicones and good compatibility with organic compounds.

5.2.3 Silicone resins



Silicone resins (Fig. 7) are highly branched polysiloxanes of higher molecular weight. They provide excellent beading properties but also have some disadvantages as low alkaline stability, and poor solubility properties. These products must be diluted to 5-10% solids in solvents to achieve a good impregnation depth. Emulsified products hardly can perform as well because of insufficient penetration into the substrate.

Figure 7: Structure of a silicone resin.

6 Chronological formulation development

Over the last decades silicone based water repellent systems have gone through a constant process of change driven by legislative and commercial aspects (Fig.8). The first representatives appeared in the 1960s when high molecular weight silicone resins dissolved in organic solvents, mainly alcohols, containing approx. 60 -70 % of active material were developed for this application. Learning from the drawbacks of these products, low molecular weight oligomeric siloxanes were developed in the 1970's. For the protection of concrete, alkoxysilanes gave the best results and they were commercially available for this application since approximately 1980. Later on, combination products of silanes and low molecular weight siloxanes were marketed as more generally applicable products. For the preparation of ready-to-use products these systems had to be diluted with white spirits or alcohols. Depending on the system and the substrate type, the active matter of the formulated products ranged from 5 to 100 %. For environmental reasons the market asked for "green products" with a lower content of volatile organic compounds (VOC), ideally without any solvents. As a consequence, water based emulsion products were developed. Top performing products, like an emulsion based on organo modified siloxanes/silanes, were curable without additional catalyst. Paste-like water repellents completed the product range for external treatment since early 2000 providing alternative treatment methods. During the last years new developments have focused on products for dry-mix mortar systems. Today a broad range of powder based silanes and modified siloxanes in which the water repellents are applied on an inorganic carrier are available.

Year	Chemistry	Technology
~1966	Silicone Resins	Liquid, solvent based
~1972	Oligomeric Siloxanes	Liquid, solvent based
~1980	Alkoxysilanes	Liquid, solvent based
~1985	Alkoxsilanes/olig. Siloxanes	Liquid, solvent based
1988	Alkoxysilanes	Liquid, water based
1994	Alkoxysilanes / organo modified siloxanes	Liquid, water based
2000	Alkoxysilanes / organo modified siloxanes	Pasty, water based
2002	Alkoxysilanes	Powder
2005	Alkoxysilanes / organo modified siloxanes	Powder

Figure 8: Chronological course of the development of water repellents for construction

7 Mode of action

What the discussed silicone compounds have in common is that in their structure they all carry hydrophobic alkyl chains and hydrophilic SiOR groups (with R = methyl, or ethyl). The hydrophobicity mainly depends on the length of the alkyl group. Longer alkyl chains give also good resistance against alkalinity as they set up a steric shield for the Si-O-Si bonds which are prone to hydrolysis.

When applied to the substrate, the alkoxy groups of these products react with water or humidity to form a non-stable silanol intermediate which will spontaneously polycondensate to form a hydrophobic film (Fig. 9). At the time, the reactive OH-groups from the silanols can form irreversible bonds with the mineral substrate. These can be regarded as an anchorage system between the hydrophobic film and the building substrate. Hence, by treatment with silicone compounds the building material becomes hydrophobised as a result of a chemical modification and newly formed bonds. The performance and durability of the water repellent treatment depends on the penetration depth of the silicone material and the active content of the applied product.

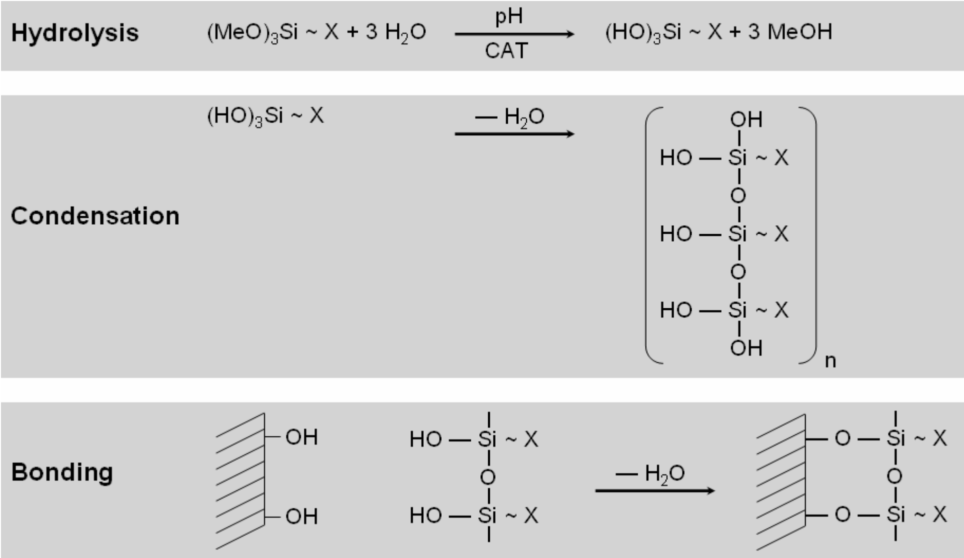


Figure 9: Mode of action of silicone compounds on substrates.

The different penetration depths attained by one and the same product on substrates of different alkalinity show that there is a reaction with the mineral substrate (Fig. 10). In the chemical reaction of the alkoxy groups of the silanes/siloxanes with the hydroxyl groups of the mineral substrates, the alkalinity has a catalytic effect [4].

Due to the large differences in surface tension of water and silicones (72 $mN \cdot m^{-1}$ and 22 $mN \cdot m^{-1}$, respectively) water cannot penetrate the impregnated areas. It is important that the application of silicone based products does not block the substrate pores and that the formed water repellent film remain permeable for water vapour. In contrast to a coating layer, the breathing activity of the construction material remains entirely unaffected. Organosilicone compounds are characterised by their excellent ability to penetrate very deeply into the substrate. Furthermore, they do not form any damaging substances and the surface does not become sticky over time.

A pH 13, concrete B pH 7, red brick C pH 9, sand lime brick

Figure 10: Impregnation depth attained depending on alkalinity.

8 Hydrophobising agents in dry mortar formulations

Today advanced dry mortar products are widely used in the construction industry. Dry-mix technology can be described as a highly controlled process of pre-blending and batching of all the necessary ingredients. It provides numerous advantages which are crucial for modern and efficient construction work. Different types of mortar can be produced with well-defined properties to achieve reproducible performance of high quality. Only the water has to be added on site. A high level of consistency and reliability is achieved and the overall construction process becomes more productive and cost-efficient.

For superior hydrophobicity and durability high performance water repellents based on silanes/oligomeric siloxanes, sometimes in combination with organic components, were developed. Since the active ingredient of these compounds is often a liquid, it is converted into a powder by "attaching" it to an inorganic carrier such as silica, carbonates or talc to make it compatible with and easily integrated to the dry-mix systems.

Silane/siloxane based powdery water repellents provide superior performance compared to metal salts of fatty acids and are easy to handle and dose. They provide an outstanding water repellency and an excellent beading effect along with true long term performance resulting in sustainable protection of buildings and architectural constructions. The areas of applications include their use in dry-mix for masonry mortars, high cement mortars, renders, plasters, tile grouts and joint fillers [5].

9 Examples for substrate treatment

Natural stones, red bricks, sand lime brick

Oligomeric siloxanes, solvent based

Alkoxysilanes / organo modified siloxanes, water based

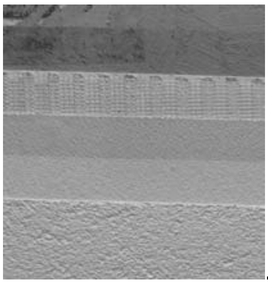
Dense concrete in rough environment

Alkoxysilanes 100% actives

Paste made of alkoxysilanes with >70% actives

Concrete facades

Alkoxysilanes/organo modified siloxanes / silanes. Solvent and water based with 10 to 20% actives

.

Dry-mix mortars for renders, tile grouts etc.

Silicone powder

0.1 to 0.5 % silicone powder refer to dry mortar provides excellent protection

10 Outlook

For decades hydrophobisation products based on silicone technology for application in the construction industry have been subjected to constant changes. The key drivers for innovations in product performance and costs have been safety aspects, environmental obligations and product convenience. In the future, protection and preservation of architectural buildings and monuments will be of even higher importance for many reasons. Among these, changes of global climate conditions and stricter legislation requirements are to be mentioned. Today, building protection is already considered during the construction phase. Therefore, immediate developments in the water repellents industry will be dominated by dry-mix applications.

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