Mortar protection

New silicone resin-based hydrophobic powder for the dry mix market

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Hydrophobic additives are frequently used to minimise visual defects and physical damage caused by water penetration in the porous nature of cement-based materials. Test results are presented on new silicone hydrophobic powders which produced a very substantial reduction in water absorption. Efflorescence was therefore much reduced, and retention of colour in a pigmented mix after weathering was greatly improved.

The porous structure of construction materials based on Ordinary Portland Cement results in a high sensitivity to capillary water absorption. Control of water absorption is therefore the key to reduce various kinds of water-induced damage such as efflorescence, staining, spalling due to freeze-thaw cycles, chemical attack and corrosion of reinforcing steel.

A number of solutions have been used in the past to decrease water absorption, such as post-treatment with water repellents or the use of so-called 'hydrophobic admixtures' within the cement matrix itself to provide integral water repellency. Siloxanes and alkoxysilanes have now become a well-known class of materials used both as post-treatment water repellents [1, 2], admixtures in non-load-bearing concrete [3] or as post-treatment or admixture in fibre reinforced cement boards [4].

The nature of siloxanes and alkoxy silanes

Silicone is a generic term describing polymers based on a siloxane backbone (i.e., based on the repeating unit Si-O-Si). Polydimethylsiloxanes or PDMS (see *Figure 1*) are the siloxanes most commonly used worldwide, both in terms of volume and application areas. They are available as low or high viscosity fluids. Terminated by a silanol group (as in *Figure 1*), they are reactive. Their low surface tension, good resistance to UV radiation (relative to organic polymers) and high gas permeability are of great benefit in the field of hydrophobic treatment.

Silanes are molecules based on one silicon atom which bears four substituents. Alkyl trialkoxy silanes (see *Figure 1*) are used in hydrophobic additives, either for post-treatment or admixture as they have good reactivity towards inorganic, silanol-rich surfaces. The aliphatic chain (i.e. isobutyl or octyl chain) confers the hydrophobic character to the treated substrate. Upon hydrolysis and condensation, silanes create a resinous network which bonds covalently to the surface of treated materials, providing water resistance with outstanding durability.

Silicone resins are obtained by a sequence of controlled hydrolysis and condensation reactions of individual or mixtures of silanes (see *Figure 1*). Silicone resins with alkoxy groups and hydrophobic alkyl groups can be designed so as to diffuse within the cement matrix and react with the surface of pores. The reaction leads to their chemical anchorage to the treated materials.

Formulating effective hydrophobic additives

It is often the case that the basic chemicals used as water repellents need to be further formulated to enable their effective use. This additional formulation step will be termed the delivery system. For example, water repellents can be used as such, as solvent-based solutions, as emulsions or again as powders.

The delivery system needs to be adapted to the application method, which can range from the use of emulsions for post-treatment water repellents or hydrophobic admixtures into mortar/concrete slurry or silicone hydrophobic powder in dry mixes.

Dry mixes cover the range of high performance mortars designed for specific applications such as masonry mortar, tile adhesive, grouts, render and skim coats. Amongst these applications, some require protection against water penetration (notably tile grouts and render) thanks to the use of an 'integral water repellent', delivered as a powdered additive. Historically, oleochemicals and metal soaps were used for this purpose [5]. As water insoluble particles, they act as

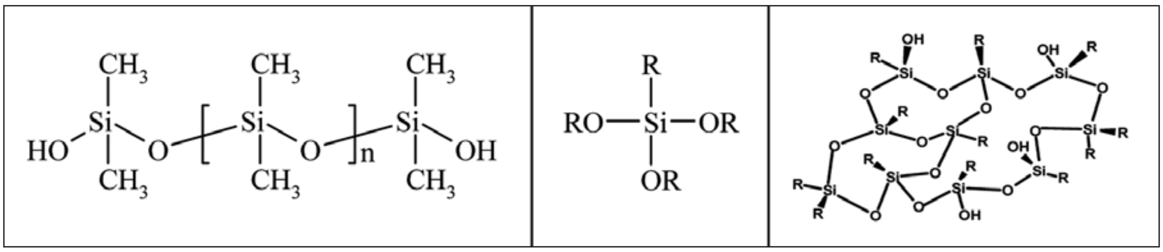

Figure 1: Structure of polydimethylsiloxane, alkyl trialkoxysilane and schematic representation of a silicone resin, where R can be ethoxy, methoxy, methyl, phenyl or octyl groups

'pore blockers' which will decrease the gas permeability of the cement matrix. Often, they are not evenly distributed within the matrix, leading to poorer control of efflorescence. Some difficulty in handling or processing them, the difficulty in wetting dry mixes modified with them or their lower durability in the cement matrix (poorer weathering) have driven the development of new powdered hydrophobic additives based on silicone chemistry.

Extending the benefits of silicone chemistry

In the last 5-10 years, silanes and siloxanes have been formulated and transformed from low viscosity liquids to powdered additives in order to be used in dry mix formulations as an 'integral water repellent' [6]. The first silicone hydrophobic powders offered on the market were based on simple polydimethylsiloxane, but there was scope for further improvement (see *Figure 2*).

Silicone hydrophobic powders based on silane or a mix of silane and siloxane appeared to significantly improve the hydrophobic performance both initially [7] and after ageing [8]. Accelerated ageing studies clearly demonstrated the benefit of silicone hydrophobic powder based partially or entirely on alkyl alkoxy silane. These hydrophobic powders are now commonly used in dry mix formulations.

Research into new hydrophobic active materials identified some specific liquid silicone resins which provide further improved hydrophobic performances. These are now being used to develop new improved hydrophobic powders for the dry mix market.

This paper focuses on silicone-based hydrophobic additives formulated as powders. In this document, the phrase 'hydrophobic performance' describes the extent to which a powdered hydrophobe used as an admixture in a cementitious matrix can significantly decrease the tendency of the set matrix to absorb water by capillary action.

Some benefits obtained by the addition of silicone hydrophobic powders will be illustrated below.

Performance tests on hydrophobic silicone resins

Mortars were prepared according to EN 196-1 and tested to assess their rate of setting (by the Vicat needle method), consistency (by penetration method), air content and mechanical properties. Results will not be described here, but it can be said that the addition of the new res-

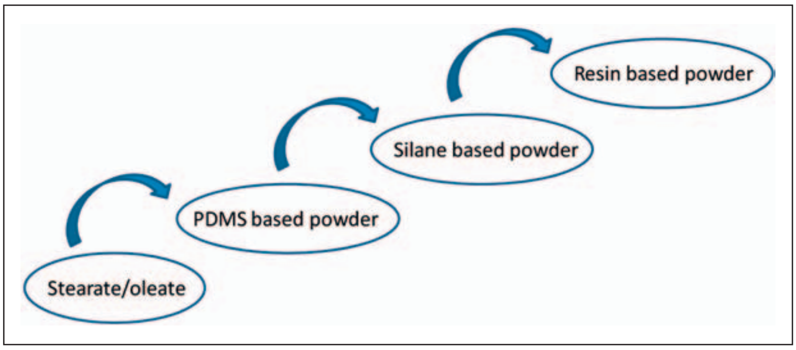

Figure 2: Evolution of technology used to make powdered hydrophobic additives

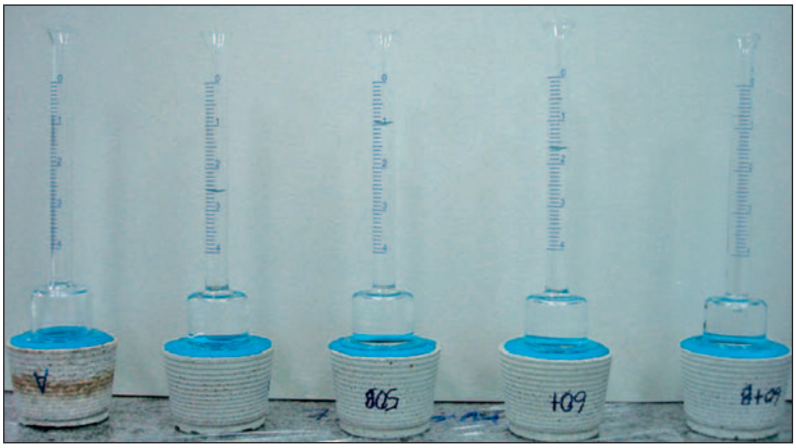

Figure 3: Measure of the capillary water absorption of reference and modified mortar blocks by using "Rilem" tubes affixed to the block surface

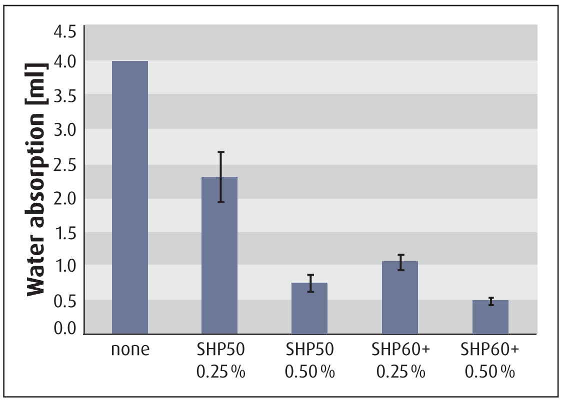

Figure 4: Capillary water absorption after 24 hours of contact with water of mortar blocks tested according to the "Rilem" tube method

Results at a glance

››› Materials based on ordinary Portland cement are to some degree porous, leading to capillary water absorption and consequent damage ranging from efflorescence to spalling and corrosion of reinforcing steel.

››› Hydrophobic additives formulated to combat this were originally based on oleochemicals and metal soap, but powdered silanes and silicone resins offer better performance, gas permeability and weathering resistance.

››› Test results are presented on two new hydrophobic silicone resins, formulated into powder additives for use in dry mix formulations. Both additives substantially reduced water absorption compared to an untreated cement mix.

››› Both primary and secondary efflorescence were greatly reduced. Colour retention was studied by incorporating ultramarine blue into mortar blocks which were weathered naturally. Only the hydrophobic silicone additives were able to effectively prevent fading of the pigment.

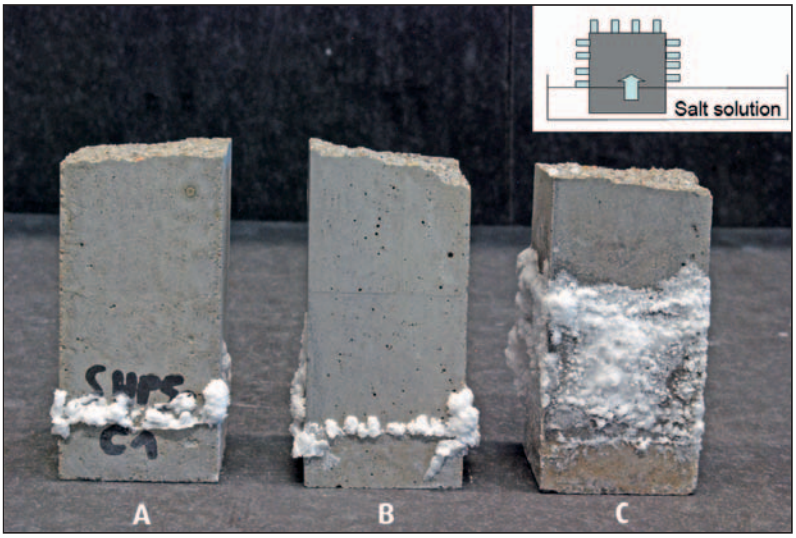

Figure 5: Illustration of salt transport through EN 196-1 mortar with no additive (C) or with 0.25 % "SHP 50" (A) or 0.25 % "SHP 60+" (B) on dry mix weight (cement + sand); inset: schematic representation of the experimental setup

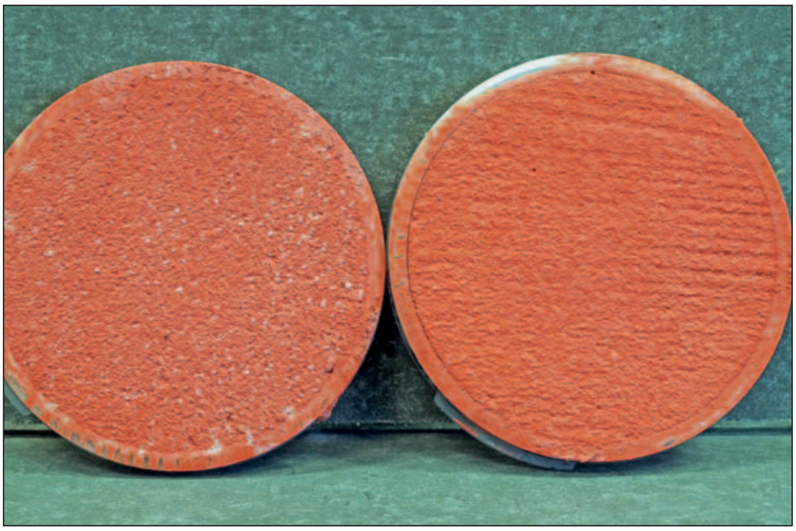

Figure 6: Surface of pigmented reference mortar (left) or modified with 0.25 % "SHP 60+" on dry mix weight (cement + sand) (right) after setting in a cold environment

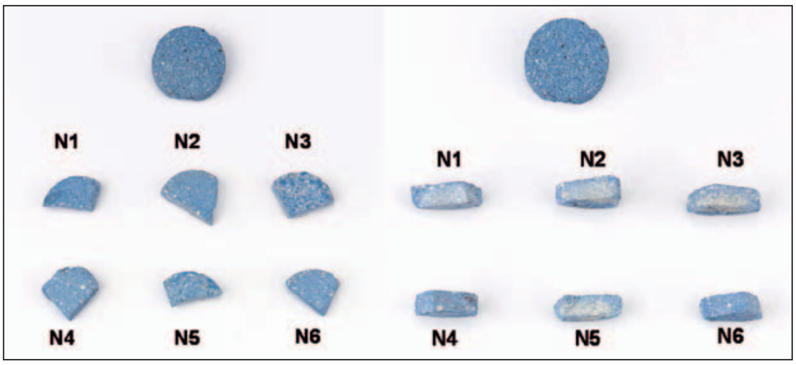

Figure 7: Appearance (top and cross-section views) of mortar blocks modified with different additives after two years natural ageing in Barcelona; see Table 1 for identification key; trends are identical when CEM III cement is used (White spots are due to the aggregates)

in-based hydrophobic powder has only a limited impact on these measurements.

A set of mortar blocks was prepared with a sand/cement ratio of 3/1 and a water/cement ratio of 0.5. All samples were cured for 28 days and dried overnight at 70 °C before testing. Mortars were prepared with either no additive (as a reference), with a silane/PDMS based powder ("SHP 50") and with a new silicone resin-based powder ("SHP 60+") at 0.25 % and 0.50 % of the overall dry mix weight.

Capillary water absorption of mortar blocks was assessed by fixing a "Rilem" tube on the surface of the blocks (this is a graduated tube with a wider lower end in contact with the mortar material). The absorption of water is read on the graduated scale and is reported as a function of time.

Figure 4 shows the plot of the water absorption measured after 24 hours for the different blocks (reference and modified with either of the two additives). *Figures 3* and *4* clearly illustrate the improved hydrophobic performance of the silicone resin-based hydrophobic powder.

Efflorescence and its control

One of the purposes of an integral water repellent is to ensure that the visual appearance of cement-based surfaces is retained for a longer time. Efflorescence is one potentially deleterious process which can detrimentally alter the visual appearance of cement-based render due to the formation of a white haze on the surface.

Efflorescence is due to the movement of water containing dissolved salts through the interconnected pore system from the bulk of the mortar to the external surface. When the water evaporates, the soluble salts will crystallise and leave a white haze on the surface.

Primary efflorescence is due to migration of calcium hydroxide produced during the initial phase of cement hydration to the surface. Upon reaction with atmospheric carbon dioxide, it produces water-insoluble calcium carbonate, which is not easily washed or brushed off. This mainly happens in cold and humid months of the year.

Secondary efflorescence is due to the transport of salts in the already set and cured cement matrix.

Mortar blocks were prepared according to the EN 196-1 norm (450 g of CEM II 32.5N cement mixed with 1350 g of normalised DIN sand with 225 g of water and silicone hydrophobic powder) and cured for 28 days before testing. Reference and modified mortar blocks were placed vertically in a saturated sodium chloride solution so that 1 cm of the blocks was immersed. After a couple of days, salt transport through the reference mortar blocks is evidenced by the precipitation of salts at the surface. Blocks modified with silicone hydrophobic powders show minimal evidence of efflorescence (see *Figure 5*).

Primary efflorescence was evidenced by carrying out initial cure of pigmented mortar in a cold atmosphere. *Figure 6* shows the surfaces of reference and modified mortar after setting. The reference mortar shows white spots of efflorescence at the surface, while the surface of the mortar modified with silicone resin-based hydrophobic powder is defect-free.

Efflorescence (both primary and secondary) can thus be minimised by reducing the capillary water absorption and transfer of water through the cement matrix. This set of results illustrates that the addition of the silicone resin-based hydrophobic powder leads to significant reduction of primary and secondary efflorescence.

Colour retention of ultramarine blue is enhanced

Coloured decorative renders are obtained by the addition of pigments to the dry mix formulation. During water absorption and drying cycles, some pigments can be washed out from the cement matrix, leading to fading of the colour. This is especially detrimental to aesthetics, whether for concrete paving or façade renders.
Ultramarine blue pigment was used to characterise the benefits of an integral water repellent on colour retention. A chemical reaction between conventional ultramarine pigments and cement during setting leads to colour fading. Nubiola's "Nubicem B-101" is a chemically modified type of ultramarine, compatible with cement-based materials.
In order to improve colour retention, it is important to avoid prolonged contact with water (e.g. with a high water-cement ratio, long curing times with high humidity or regular contact with water when set). A study of the long-term stability of this pigment in combination with different hydrophobic agents was carried out.
Different blocks were prepared by using CEM I or CEM III cement, by adding a water retention additive ("Bermocoll ML11" methyl ethyl hydroxyethyl cellulose at 0.15 %) and 0.5 % integral water repellent (stearate or the silicone hydrophobic powder Dow Corning "SHP 50") Details are summarised in *Table 1*.
The different mortar formulations were naturally exposed in Barcelona (Spain) for two years. Pictures of the blocks after ageing are shown in *Figure 7*. These clearly show that some depletion of the ultramarine pigment does occur in the cross-section of most mortar blocks. This colour fading of the interior of the specimen may finally lead to depletion of pigment at the surface and to surface colour fading.
Blocks modified either with cellulose ether, stearate or a mix of both show hardly any improvement in the cross-section colour fading. On the contrary, the blocks modified with "SHP 50" hydrophobic powder show no cross-section colour fading, demonstrating the benefit of silicone hydrophobic powder on colour retention of coloured render or concrete blocks, and this through the complete section of the blocks.
This set of results demonstrates the benefit of using the new "Nubicem B" series pigments in combination with silicone-based integral water repellents such as "SHP 50" and "SHP 60+".

Table 1: Cement formulations used in colour fading tests

Sample	Sample	Additives
Aggregates (quartz and calcareous filler), 80 parts "Nubicem B-101" pigment (4 % on cement content)		
CEM III cement (20 parts)	CEM I cement (20 parts)	
I1	N1	No additives
I2	N2	+ cellulose
I3	N3	+ stearate
I4	N4	+ "Dow Corning SHP 50"
I5	N5	+ stearate + cellulose
I6	N6	+ "Dow Corning SHP 50" + cellulose

Effective protection for construction materials

This set of results clearly demonstrates the benefit of silicone hydrophobic powder for the protection of cement based construction materials against the deleterious impact of water ingress. Protection against efflorescence and colour fading is demonstrated.
The new silicone-resin based hydrophobic powder shows improved hydrophobic performance leading to better protection of the construction material against water ingress.

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