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Water Repellents and Other "Protective" Treatments: A Critical Review

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Abstract

The key function of a water repellent is to prevent penetration of liquid water - through capillary action - into masonry by changing the surface properties of the material to which it is applied. This surface modification reduces soiling and decay from environmental influences and biocolonization. Although in principle achieving this objective appears to be a straightforward task, in practice it proves to be far from simple. The paper focuses on the use of silicon-based water repellents, since these are the most frequently used products.The influence that various factors have on the performance of water repellent treatments are discussed. These factors include the formulation of the product, e.g., as a solution, water-emulsion, or cream (paste); the nature of the active alkyl group in the agent; the composition and porosity of the substrate; the depth of penetration of the treatment; and the type of weathering to which the treated object is subjected. Understanding the interaction of these variables will help elucidate the reason for performance failure or durability of a treatment. Within the framework of traditional sacrificial coatings, recently developed "protective" layers produced by biogeneration are discussed. The parameters influencing their behaviour, such as diminished porosity, small reduction of water-vapor permeability, and adhesion to the substrate, are analyzed to better understand their performance.Finally, emphasis is placed on the fact that treatments do not replace regular maintenance and may require different types of maintenance at different intervals.

1 Introduction

The recognition that moisture in buildings contributes to deterioration has prompted the search for mitigation methods since the earliest dates. Throughout history, a range of protective materials has been applied to exposed surfaces to prevent the ingress of water, including oils, waxes or paints [1]; sacrificial layers [2]; and renders [3]. With all the improvements that modern technology has brought into the field, current protective treatments can still be divided into these types. Progress has been achieved mainly in the development and production of water repellent agents, a significant improvement on traditional oil and wax finishes. New methods and approaches have recently been developed in the area of sacrificial coatings that have still to prove their effectiveness and long-term durability. The subject of renders, including their historic value and conservation, is a vast topic that deserves a separate discussion and will not be addressed here.

The first and probably the most popular water repellent agents belong to the family of alkyl silicon products, i.e., alkyl siliconates, alkyl silanes, siloxanes, polysiloxanes and silicone resins. All of these products originate from the ethyl silicate first developed by the French chemist Ebelman around 1845. By 1872 the first silicone fluids were synthesized by the German chemist Ladenburg, who had worked with the French Friedel and the American Crafts in Paris prior to the Franco-Prussian War. By 1912, Stock reported identifying the hydride of silicon or silane, and Kipping in England had shown that the Grignard reaction was a most effective means of attaching organic groups to silicon. Commercial development of organosilicon products started in the U.S. through the formation of the Dow Corning Corporation in 1943, and three years later General Electric Company started its production of silicones [4]. Water repellents for the protection of building materials were commercialized in the U.S. and Europe by the mid-twentieth century. Water-dispersions of these materials made their appearance on the market around 1990 because of increased environmental concerns regarding solvents used in the earlier formulations.

Other water-repellents are based on metal-organic compounds, such as aluminum stearates; purely organic resins, such as acrylates; and fluorine-containing polymers, such as perfluoropolyethers or polyfluorourethanes. Although the latter promise to be a good alternative to the standard siloxane based formulations [5, 6, 7], the discussion will be limited to the silicon-based systems, since these are the most frequently used water repellents to date.

2 Function and Performance of Water Repellents

2.1 Introduction

The key function of a water repellent is to prevent penetration of liquid water - through capillary action - into masonry by changing the surface properties of the material to which it is applied, as summarily stated by van der Klugt and Koek [8]. This surface modification also serves to reduce soiling and decay from environmental influences and biocolonization [9].

Although in principle achieving water-repellency appears to be a straightforward task, in practice it proves to be far from simple. There are several reasons for the difficulties encountered. First, the variations in the nature of the water repellent itself. Even when dealing with only the “simple” system, i.e., silane, siloxane, or silicone resin, its appropriate characterization - which ranges from varying chemical composition of the active ingredient and its concentration in the solvent to the presence and nature of the catalyst - and that of the substrate, are critical since their interaction will affect the performance of the product [10-13]. Unfortunately, most papers describing results from tests and actual field applications seldom adequately identify the products used.

A lack of understanding of the chemistry of silicon-bearing water repellent products, particularly in the early years, led to their misapplication and to some catastrophic failures. For instance, a 40-story sandstone building in Boston turned black upon treatment because of the oxidation of iron minerals present in the stone [14]. These unfortunate experiences may well be the reason why water repellents are not as frequently applied in the U.S. as in Europe, although with the recent advent of the water emulsion formulations the situation is changing rapidly.

A good overview of the requirements for water repellent treatments, testing procedures for their evaluation, and recommendations on their application is presented by Snethlage and Wendler [15].

2.2 Influence of the formulation

Because of environmental concerns about solvent-based water repellents, water-based emulsions were introduced in the late 1980s. In general, studies have found that emulsions provide protection similar to solvent-based formulations [16, 17] although they show lower penetration depths [18]. While some studies found that they introduced less active agents into the subtrate when it was damp [17, 19] - the amount of moisture inversely influencing penetration depth [20] - another study showed that performance, as measured by water uptake, improved when they were applied to some damp materials, such as brick, concrete and low porosity calcareous stones [21]. It has also been suggested that the presence of salts within porous materials may de-stabilize the emulsion of water-borne products [22]. Although water-based formulations provide good protection for granites and low porosity limestones, they show lower performance than solvent-based formulations when subjected to freeze-thaw cycling [23].

Even for solvent-based formulations, different results are observed depending on the degree of polymerization. For example, although a commercial siloxane product may lose initial hydrophobicity faster than a silane formulation, it provides better long-term protection for granites and limestones [23, 24].

Silicon-based formulations, including recently developed creams, i.e., pastes [26, 27], do not affect the water vapour permeability of the substrate, as tested on cement mortars [28]. These creams were specifically developed to obtain good penetration depth in low porosity concrete, but whether their use can be extended to other materials such as stone or brick is yet to be proven.

2.3 Influence of the alkyl group

The hydrophobicity imparted by silicon-based compounds depends on the alkyl, "R" group(s) attached to the silane, siloxane or silicone resin. It has been repeatedly suggested that both increased length and branching of the R group improves performance, in particular alkali-resistance of these water repellents [29-33]. Nevertheless, most commercial products are formulated with methyl groups, at best replacing some of the methyl groups with propyl, butyl or octyl groups, since "in practice, it is sufficient to substitute some of the methyl with other alkyl groups" to achieve better alkali resistance [33]. Analysis carried out on commercial products confirmed the presence of n-propyl, isobutyl, n-octyl, and even phenyl groups replacing some methyl groups [34]. Why a phenyl group would be used to replace the methyl group is puzzling, since it has also been reported to have low alkali resistance [32]. In recent years, silane formulations containing only higher alkyl groups, such as isobutyl, have been commercially available, but no systematic study of the composition of these products has as yet been undertaken.

Studies carried out with commercial alkyl silanes containing only methyl, or either iso-butyl or n-octyl groups, showed that the porosity of the stone was critical in determining the performance of the water repellent, based on the amount of moisture remaining in test samples of dense and porous sandstones, limestones, and tuffs after total water immersion and drying. Only octyl-containing silanes, or synthetically produced pentyl and hexyl silanes, provided relative water-repellency for denser stones [35]. These studies were complemented by applying treatments to synthetic materials having mono-modal pore size distribution. Results showed that the treatment shifted pore diameter maxima towards smaller pores and that the shift was greater for bodies with smaller pore diameter maxima. Hence, in stones with smaller pores, a larger alkyl group is required to counteract the stronger "forces" of finer capillaries that tend to retain moisture. This range of pore diameters, 3.5 to 17 µm, was also pointed out as having more influence on the water repellent performance than the total porosity of the substrate [11]. However, this range will depend on the nature of the substrate because of its interaction with the water repellent [21].

Other studies showed that replacement of some methyl groups by longer alkyl groups was not as significant for performance as the substrate (brick and various limestones) when evaluated after artificial weathering [34]. Field tests in which methyl silicones and methyl-octyl silicones were applied to different stones and weathered in either an urban or an industrial environment also confirmed this observation [36]. They also showed that poorer performance was obtained for the methyl-octyl silicones when applied on a clay-containing sandstone (average pore diameter 7.4 µm) than on a quartzitic sandstone (average pore diameter 4.4.µm). Furthermore, through the application of DRIFT (*Diffuse Reflectance Fourier Transform Infra Red Spectroscopy*) it was shown that the hydrophobicity could be attributed only to the methyl group [36].

Application of TOF-SIMS (*Time of Flight-Secondary Ion Mass Spectrometry*) to the surface analysis of in situ weathered stones treated with a propyl-octyl silane and methyl-octyl siloxane found that the presence of octyl groups induced higher molecular weight condensation products, while the propyl group showed the presence of silsesquioxanes, cage-like molecular structures that form on the surface layer of fully condensed alkyl ethoxy silicates [37].

Only few studies have been carried out on concrete to validate the claim that longer and branched R groups show better alkali-resistance [21].

2.4 Influence of the substrate

The discussion has focused mainly on natural stones, with only some references to concrete, which deserves to be addressed by itself.

When using silanes for impregnation, either as monomers or dimers, it should be taken into account that the polymerization reaction competes with the evaporation rate of the liquid agent [11]. Hence, environmental conditions for application are critical but, so far, cannot be defined a priori. Studies have shown that water-based emulsions of siloxanes are more susceptible to the moisture content within the substrate than solvent-based formulations [17, 19], although other studies highlight that this is dependent on the substrate [21]. In part, this is due to the fact that the substrate plays an active role in the polymerization reaction [11, 34]. Since most materials and natural stone in particular are variable both in composition and texture, it follows that the performance of the treatment may vary significantly. Results from studies show that in general water repellent treatments perform well when applied to bricks, but show a rather erratic behaviour when applied to limestones [11, 12, 34]. Even on sandstones, the presence of clays may interfere with the treatment [38]. Moreover, it appears that the hydrophobization improved if the silicon-based water repellent was applied in mixture with or after a silicate ester consolidation, suggesting that the consolidant served as an “anchor”, i.e., a uniform substrate, for the water repellent [35, 38, 39]. However, the combination formulation of the silicate ester - hydrolyzed or with a catalyst - showed significant differences, as reported in the results for 8-year field exposure tests [36].

2.5 Influence of the application technique

Another reason for variation in water repellent performance can be found in the application method. Even under laboratory conditions it was found that only capillary absorption, as compared to brushing or spraying, gave reproducible results [40, 41]. Since the application method strongly influences penetration depth, and this in turn directly affects the performance and durability of the treatment [30, 31], it is evident that developing a good application method is of paramount importance for the success of treatment [42]. The difficulty in achieving this is testified by the years of research spent in improving spray systems [43-45]. Good penetration has been achieved even on dense concrete (w/c = 0.40) when application procedures, i.e., number of sprayings and/or subsequent sprayings, were adjusted to the condition of the substrate, such as the amount of moisture present [46].

An improvement for dense materials such as concrete is the use of a “thickened” water repellent which is sprayed or brushed on as a cream [26, 27]. This allows for longer contact times between the agent and the surface resulting in increased capillary absorption. Another approach has been the development of a “box technology” that floods the concrete surface with the selected water repellent for a minimum time pre-determined experimentally for the particular concrete [47]. The system has produced penetration depths of at least 6-mm in dense concretes (w/c = 0.35) and over 1-cm for other mixes.

On the other hand, hydrophobization of highly porous stones presents other problems, since larger pores may not be easily rendered water-repellent [48], and improved application techniques for in situ treatment of large masonry structures made of stones such as the *Carparo* calcareous tuff, are yet to be developed [49].

2.6 Durability of the Hydrophobization

The durability of water repellent treatments based on silicon-containing products has been estimated in the best cases to last some 15 years [39], while in general a drop of hydrophobicity is already observed after 5 years [50, 51]. However, recent evaluation of water repellent treatments on brick masonry has shown that some were still performing well after 36 years [52]. While the success of the latter might be attributed in part to the influence of the substrate, the former has been attributed to careful application by trained personnel that resulted in good penetration depth [11]. Studies appear to indicate that silicon-based compounds are not susceptible to UV radiation [23, 50] and that loss of water-repellency can be attributed to “soiling” of the treated surface through deposition of hydrophilic particles [50]. This suggestion is based on the result of long-term exposure testing in which samples receiving direct rain impact maintained better surface water-repellency than those in sheltered positions where dust accumulated [53]. The loss of surface hydrophobicity occurred in the outermost 1-mm layer - observed after only one year of outdoor exposure [24] - while the area right behind it is still hydrophobic [50]. Thus, once the exterior surface is wet, it remains damp for longer periods of time than if the material had not been treated at all. However, if the amount of water repellent is high so that a thicker “network” is formed [50], this effect is not as evident as confirmed by other studies [24]. It was also observed that limestone surfaces, because of their nature, may be more prone to both the above “soiling” phenomena and subsequent biological growth [50].

Results for 8-year urban and industrial environmental field tests of different stones treated with a propyl-octyl silane and methyl-octyl siloxane showed that the silane retained its hydrophobicity far better than the siloxane. This latter agent was particularly affected by the industrial environment [37].

While durability estimates reported above were obtained from evaluation of in situ treatments, it is difficult to extrapolate results to other types of stones and/or environments. Therefore, most performance assessment data for water repellents is obtained by artificial weathering tests. Except for a few standardized tests, such as the sodium sulfate crystallization test, which in general does not serve to mimic real-life conditions, tests vary greatly in design. Consequently, results may appear contradictory, such as those that show the substrate influencing and alternatively not influencing the performance of the water repellent [34, 35] or moisture in the substrate negatively and alternatively positively influencing the performance of water-based emulsions [17, 19].

The development of artificial ageing processes to mimic real weathering is challenging [54]. So far, the VENUS (*Versuche zur Entwicklung naturnaher Umweltsimulationskonzepte*) simulation chamber has proved fairly successful in obtaining results that follow trends observed in actual weathering [55, 56]. However, only general information is provided as to cycling conditions, making it difficult to compare results between laboratories. Furthermore, the issue of salt crystallization in marine environments is not considered. To evaluate the latter, saline spray chambers have been used fairly successfully [23]. Other studies have combined artificial ageing with inoculation of pure bacteria cultures to assess the durability of water repellent treatments [57].

Apart from the accelerated weathering issue, test design to measure a given effect is critical, as pointed out in a study evaluating hygric and hydric dilation [57], when determining the penetration depth achieved with a treatment [18], or even when trying to evaluate results from field tests [37].

But regardless of how well a treatment performs, its durability will be a function of subsequent maintenance, such as regular cleaning.

2.7 Influence of a second treatment

The situation is even more complex when a second treatment is required, such as application of an antigraffiti coating. Whether the water repellent or the antigraffiti coating is to be applied first, depends on the type of substrate; the type of antigraffiti coating, i.e. permanent or temporary (sacrificial); and whether the water repellent is applied in solution or as a water emulsion [58].

In the case of biocides, the order in which the products are applied is critical for their performance. If the biocide is applied after the water repellent treatment - in the study an alkyl silane and a methyl siloxane in conjunction with an ethyl silicate - the performance of the water repellent is not affected. However, if the biocide is applied first, the effectiveness of the water repellent depended on the nature of both agents and could not be predicted a priori [59].

2.8 Negative effects of water repellent treatments

Unfortunately, water repellents may also induce some negative behaviour in treated material as discussed by Sasse and Snethlage [60]. Among these are increased hygric dilation of the substrate upon treatment and uneven decrease of effectiveness. In this last case, some areas lose water repellency faster than others, allowing water penetration, increasing frost susceptibility, and eventually scaling of the remaining water repellent. They may also interfere with future repointing of the masonry or other surface treatments [15].

Similarly, cracks in a hydrophobized surface may allow water to penetrate into the substrate and collect behind the water-repellent area. However, no consensus exists as to the critical width of cracks that may induce this problem. Some field tests performed on hydrophobized walls into which 1-mm thick cracks were introduced in the mortar joints showed that their presence did not affect the moisture behaviour of the unit [61], while laboratory studies suggest that 0.3-mm should be the maximum width [62].

Another negative factor is an increase in flexural strength in the first 3-cm of a treated specimen upon weathering. This effect depends on the stone, the treatment and whether the weathering is natural or artificial [55, 63]. As pointed out by Wendler [50], future retreatments could further increase surface stiffness as compared to the rest of the material, an effect that is to be avoided as much as possible [60].

Although water repellent treatments do not decrease significantly the water vapour permeability of substrates [28], they may reduce the drying rate of damp walls [64]. It is, however, fundamental to understand the sources of wetting of the wall, since in the case of a rain-wetted wall, the water repellent treatment allowed its drying which otherwise could not occur [62].

3 Function and Performance of Protective Coatings

Interest in the development of sacrificial layers has increased in recent years after a period in which “fashion” in the name of material authenticity stripped bare stone surfaces [2, 65, 66]. Paint systems should be considered within this category, and the requirements for these systems have already been discussed thoroughly [15, 60]. The general recommendation is that sacrificial layers such as oil-paints should not be damp-proof. However, it is pointed out that if the surface film is maintained, avoiding the formation of cracks and fissures which would allow the penetration of water, the systems are indeed protective. It could be added, because, although self-evident, this point is generally forgotten, that the design of the building and its maintenance with regards to water penetration prevention is just as critical for the performance of a damp-proof surface film [67]. In summary, if the building is dry and carefully maintained, a film-forming paint layer is a good protection for surface water penetration.

In confirmation of the above considerations, it was found during the evaluation of washes (*Schlämmen),* e.g. lime washes, that the best performance resulted from those that were capable of bridging substrate fissures, had good coverage, and did not crack upon ageing [68].

Newly developed products for use as sacrificial layers are purely mineral [69] or of biologic origin [70]. In either case, protection against water penetration relies on reducing surface porosity. A similar effect can be achieved by a light surface polishing during cleaning [59, 71]. The sacrificial layer will also decrease water vapour permeability, even if minimally. This may not be as problematic as it sounds, as clearly demonstrated in studies evaluating clear coatings, *Lasuren*, for their salt crystallization performance [72]. The study showed that their presence advanced the deterioration front to just below the coating, while untreated specimens deteriorated deeper in the substrate. However, a point that still needs to be addressed is the influence of the adhesion strength, i.e., bonding, of the coating to the substrate. If this is higher than the cohesion of the substrate, it will induce surface loss by detaching part of the surface when failure occurs.

Sacrificial layers of biologic origin are generally of calcitic nature and are therefore susceptible to dissolution. Their effectiveness is yet to be evaluated, since the preliminary results of 3-year field testing do not show a clear pattern [70]. Since the main function of these sacrificial layers, as the name implies, is to be forfeited to weathering instead of the original material, this implies regular re-application. So far, the question as to whether these newly developed sacrificial layers perform better than the traditional washes has yet to be addressed.

4 Conclusions

The success of a treatment does not depend on the treatment alone, where by "treatment" only the product and its application is understood. It also needs to take the substrate into account as well as the structure of which the substrate is part. In a word, the approach must be "holistic". Unfortunately, even professionals in the field tend to take a "short-cut" approach rather than follow the prescribed protocol for documentation, testing and evaluation before applying water repellents or sacrificial coatings to a building [73].

It is also clear that protective treatments, be they water repellent or sacrificial layers, require regular maintenance. What technology has achieved is to change the required maintenance. For example, a wash may need a yearly touch-up in very exposed areas, while a hydrophobized surface needs to be kept clean in the non-exposed surfaces. Furthermore, retreatment with water repellents, if properly applied, can be spaced at longer intervals than washes. Whether this is more sustainable has yet to be proven, but the methods for its evaluation have already been proposed [74].

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