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TEOS and Silicon Based Water Repellents: Influence of Application Order and Timing

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Abstract

A study was carried out to evaluate the efficiency of three different types of silicon based water repellents with regards to the application schedule and order when both consolidation and water repellent treatments are used. A water based gel, an aqueous emulsion and a solvent based water repellent were applied to Maastrichter limestone treated with ethyl silicate (tetraethoxysilane or TEOS) after one day, three days, one week and two weeks. Other samples were treated first with the same water repellents, subsequently, at the same time intervals, with the consolidant. The uptake of each product was calculated. The effectiveness of the water repellent treatment was tested by measuring the water absorption with the Karsten (Rilem) pipe, before and after artificial ageing. The change in colour induced by the application of these products was monitored throughout the ageing cycle.
Water absorption measurements showed that a poor performance is only obtained when the aqueous emulsion was applied one day after the ethyl silicate. Applying ethyl silicate after the water repellent treatment did not interfere with the water repellency of the products. The resulting consumption was lower than that registered for untreated samples but hardly influenced by the time schedule. Important changes in the colour of the treated surfaces were detected.

Keywords: water repellent, ethyl silicate, scheduling, artificial ageing, colour change

1 Introduction

Restoration of external masonry generally consists of many different phases, beginning from the repair of its materials and the cleaning of its surfaces, to the application of a consolidant, often followed by treatment with a water repellent product.

Among the many different strengthening products that have been used over the past century, the consolidant that best seems to be standing the test of time in terms of effectiveness, durability and lack of side effects on damaged historical masonry, is ethyl silicate (tetraethoxysilane or TEOS). For water repellent treatments, silicon based products in the form of silanes and oligomeric siloxanes are now used world wide. Consolidants and water repellents are usually tested separately [2-9] while in practice they are often combined. Application of these products are not standard operations: the real necessity for their suitability must be thoroughly verified before any treatment is carried out. But given the need for the application of both products, it is the norm that the consolidant be applied first, then the water repellent product [1]. The time lapse that is necessary between the application of these products depends on their nature, i.e. if the hydrophobic product is water based or if it is diluted in an organic solvent. When water repellent products are used after an ethyl silicate based consolidant, manufacturers suggest to wait two weeks before applying the solvent based product, and four to eight weeks for water emulsions. Such long intervals are necessary in order to allow the ethyl silicate to polymerise, lose its hydrophobic effect on the treated surface and also to avoid any possible chemical interference from the consolidant [1]. Such application schedules are generally difficult in practice and hence it is critical to define the minimum time lapse required between both applications so as to obtain an efficient combination treatment. Another issue is whether it would be possible to apply a water repellent product *before* the consolidant yet retain the good performance of the water repellent treatment. This is particular critical when water based water repellent products are used which are not compatible with the consolidant as solvent based ones are.

The following study aimed to evaluate the efficiency of three different types of silicon based water repellent products with varying application schedules and order with respect to the consolidant. A water based gel, an aqueous emulsion and a solvent based water repellent product were applied to limestone treated with ethyl silicate after one day, three days, one week and two weeks. Other samples were treated first with the same water repellent products, then at the same intervals with the consolidant. The uptake of each product was calculated. The effectiveness of the water repellent treatment was tested by measuring the water absorption with the Karsten pipe before and after artificial ageing. The change in colour induced by the application of these products was monitored throughout the ageing cycle, since colour change induced by treatments on historical masonry should generally be avoided.

2 Experimental part

2.1 Products

The consolidant used for this experience was FTB–SH 75, a commercial 75 % formulation of ethyl silicate having a mass return of 39,6 %.

The water repellents used were:

Product **A**: Rewah Stonegel, a gel containing silanes and oligomeric siloxanes with methyl and octyl as hydrophobic groups and ethoxy as reactive group (mass return: 18,2 %)

Product **B**: Rewah Aquasil RS 8, a water based emulsion containing oligomeric siloxanes with methyl and octyl as hydrophobic groups and ethoxy as reactive group (mass return: 7,2 %)

Product **C**: Rhodia, Rhodorsil 240, oligomeric methyl siloxane diluted to 10% with white spirit (mass return: 7,2 %)

All products have been examined by Fourier Transformation Infra-Red (FT-IR)-spectroscopy (Nicolet, KBr method, solid transmission). The mass return is determined by adding 0.5 g of product in an aluminium cup followed by conditioning at 20 °C till constant weight. The relative humidity (R.H.) is kept constant at 55 %. The values presented are the average of three measurements.

2.2 Substrate

Samples of Maastrichter stone cut to the size of 15x5x2 cm^3 were used for this experiment. Maastrichter is a pale yellow biogenic limestone quarried between Belgium and The Netherlands. It has been used as a building stone in Romanesque and Gothic monuments mainly in the province of Limburg. The stone used has a lime content between 90 and 96 %, a bulk density of 1.370 $kg \cdot m^{-3}$ and an average total porosity measured by mercury intrusion porosimetry of 47,5 % mainly consisting of pores with a diameter between 10 and 35 µm. The samples were conditioned at 20 °C and at 55 % RH before treatment.

2.3 Treatment

2.3.1 Part I

For the first part of this study, the Maastrichter stone samples were initially treated twice with the consolidant on one face (15x5 cm^2), on two successive days. These applications were done by capillary absorption during ten seconds. The three water repellent products were then applied on the consolidated face after one day (a), three days (b), one week (c) and two weeks (d) in a single application. The gel (A) was applied by brush while the emulsion (B) by low pressure spray. The solvent based water repellent C was applied by capillary absorption during five seconds. Previous studies had confirmed that 5 seconds of capillary absorption are representative for in practice applications. The evaluation of the water repellent treatment and the artificial ageing commenced at least one month after the last application of the consolidant which corresponds to at least two weeks after the application of the water repellent product.

2.3.2 Part II

For the second part of the study, the samples were first treated with the water repellents on one face (15x5 cm^2). Product A was applied by brush and products B and C by five seconds of capillary absorption. Two applications of the consolidant were then carried out on the same side by spray, at the same time intervals (a, b, c, d) as in part I (2.3.1), on two successive days. The evaluation of the water repellent treatment and the artificial ageing commenced at least one month after the last application of the consolidant.

2.3.3 Artificial ageing

All of the treated samples were artificially aged for a total of eight weeks. Every two weeks the ageing was interrupted and the samples dried overnight (60°C) before testing. The ageing program is run in accordance to SAE J 1960 [9], which in practice has shown to be the equivalent of 20 to 30 years of natural ageing for water repellents [10].

2.4 Evaluation of the treatment

2.4.1 Water absorption

To evaluate the effectiveness of the water repellent treatments, water absorption measurements were carried out with the Karsten (Rilem) pipe [11]. The graduated pipe was applied to the sample and filled with water. The water absorption for each sample was measured as the difference between the quantity of water (ml) absorbed after five and fifteen minutes ($\Delta_{15\text{-}5}$) [10]. Water absorption measurements were carried out four weeks after the consolidation treatment, as well as after every two weeks of artificial ageing.

2.4.2 Colour change

Colour variations were monitored with a BYK Gardner color-guide 45/0 colourimeter. Overall changes in the colour of the surface (treated minus untreated sample) are expressed as $\Delta E=[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{0.5}$, where L*, a*, and b* are the luminosity and colour parameters of the CIE lab system [12]. Colourimetry values were measured at least four weeks after the consolidation treatment, as well as after every two weeks of artificial ageing.

3 Results and discussion

3.1 Part I

3.1.1 Consumption

Since product A is a gel, a fixed amount of product can be applied to the surface by brush: the quantity of product that remains there is not much influenced by the absorption properties of the treated sample. On the other hand, the consumption of the liquid products B and C depends directly on the absorption capacity of the substrate. As was shown in previous studies, solvent based products like C, reduce their uptake up to 45% with respect to untreated surfaces, when they are applied at least one day after the TEOS [10].

As for the aqueous emulsion B, a previous consolidation lowers remarkably the consumption, compared to the untreated samples (3.750 $g{\cdot}m^{-2}$), especially when it is applied within three days (Figure 1). This is likely due to the incompatibility of the water based emulsion and the ethyl silicate that still contains non-reacted ethoxy groups and therefore is still hydrophobic.

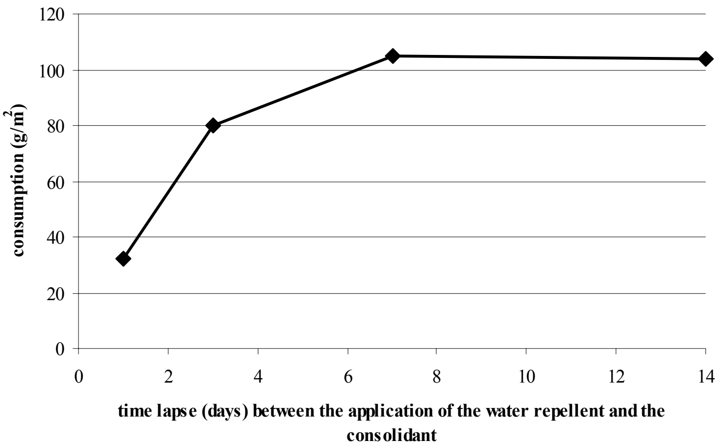

Figure 1: Consumption of the aqueous emulsified water repellent product B applied by spray at different time intervals on samples treated with TEOS. The average consumption of the water repellent on samples not treated with a consolidant is 3.750 $g{\cdot}m^{-2}$.

3.1.2 Water absorption

The results from water absorption measurements have shown a lower performance of the water based emulsion B after ageing, but only when it was applied one day after the consolidation treatment. When the application was scheduled at least three days after the consolidant, the treatment seemed to guarantee better water repellence, even if the consumption had been far lower than that registered on untreated samples.

Product C as well as A resisted well to the eight weeks of artificial ageing, regardless of the time lapse between the application of the consolidant and the water repellent.

3.1.3 Colour change

Samples treated exclusively with a water repellent showed, for all three water repellents, an increase in ΔE value (from 10-20 to 35-40) as they were aged artificially, as shown for product A in Figure 2. A similar result was observed for the samples that had been previously treated with the consolidant. ΔE values up to 40 were registered, confirming that a visible difference in colour had occurred. Figure 3 shows ΔE values for samples treated with water repellent B by spray after the consolidation at 1 day, 3 days, 1 week, and 2 weeks intervals, as the artificial ageing progressed. No correlation between any specific schedule and colour change could be observed.

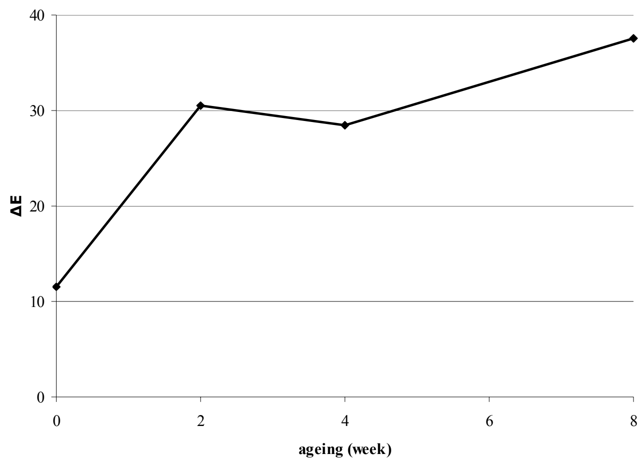

Figure 2: Colour variation (ΔE) of samples treated with water repellent product A (gel) as a function of weeks or artificial ageing.

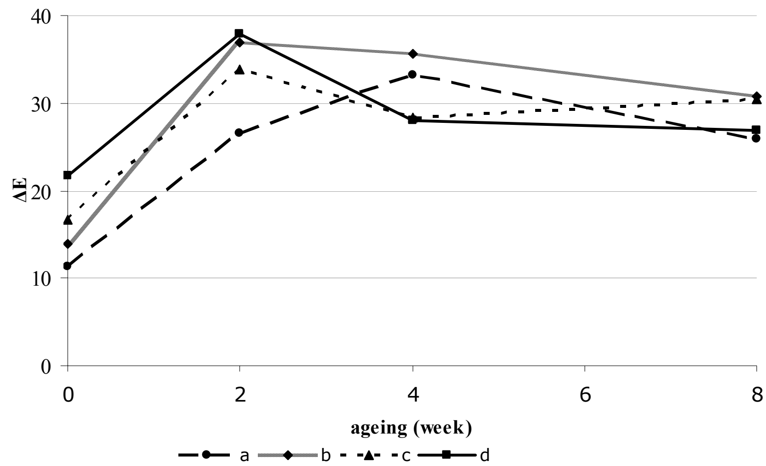

Figure 3: Colour variation (ΔE) of samples treated with TEOS, then with the aqueous emulsified water repellent product B by spray at different time intervals (one day (a), three days (b), one week (c) or two weeks (d)) as a function of weeks or artificial ageing.

3.2 Part II

3.2.1 Product consumption

On samples treated first with the water repellents, no significant differences in the uptake of the consolidant were noted as the time interval varied (Figure 4) as might have been expected, especially for those samples treated beforehand with the water based emulsion B. However, the total consolidant consumption is lower than that registered on untreated samples treated by capillary absorption during 10 seconds (9.200 g·m^{-2}).

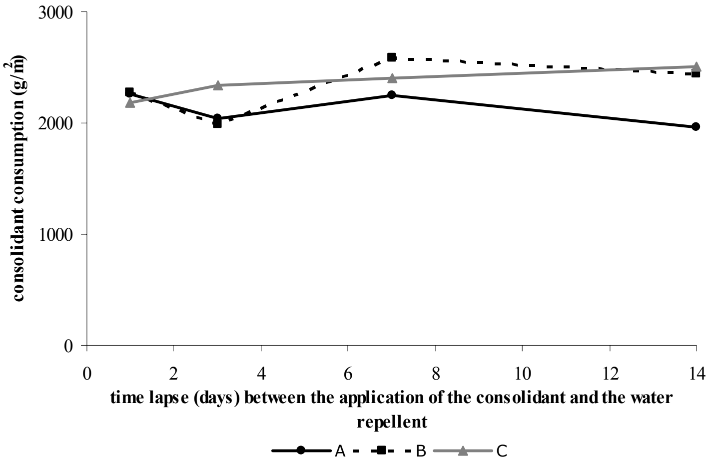

Figure 4: Total consumption of two applications of consolidant on samples treated with water repellent products A, B and C at different time intervals.

3.2.2 Water absorption

All the samples treated first with water repellent products, then at different intervals with two applications of the consolidant, showed no water absorption, even after artificial ageing.

3.2.3 Colour change

All samples showed ΔE values ranging from 25 to 40. This significant variation in colour remained more of less constant for the water repellent product A (Figure 5) and B as the samples were aged. But the majority of the samples treated with water repellent product C showed instead a decrease in colour change after two weeks of ageing, then settled at ΔE values between 25 and 30 (Figure 6). No correlation between any specific schedule and colour change could be observed.

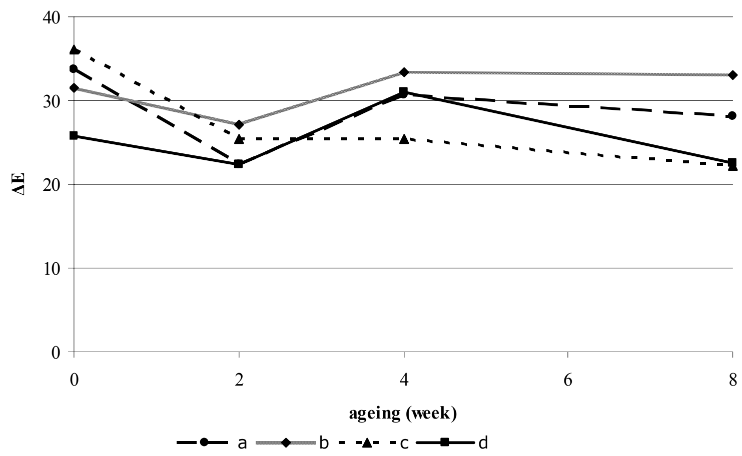

Figure 5: Colour variations of samples treated at first with water repellent product A (gel) followed by two applications with TEOS at different time intervals (one day (a), three days (b), one week (c) or two weeks (d)).

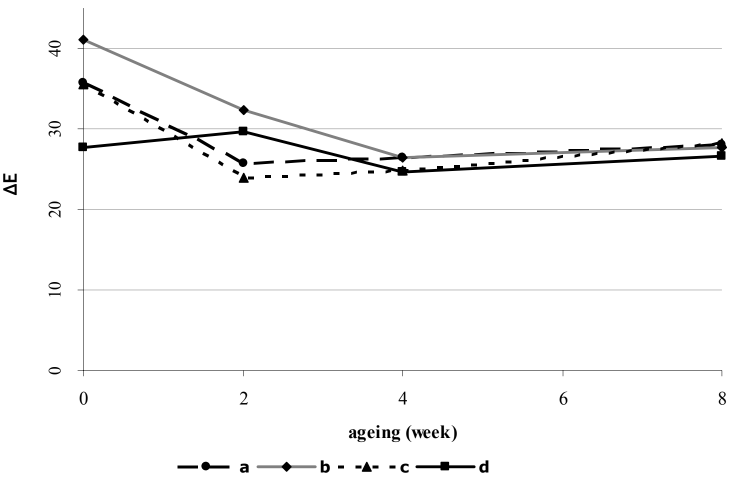

Figure 6: Colour variations of samples treated at first with water repellent product C (solvent based) followed by two applications with TEOS at different time intervals (one day (a), three days (b), one week (c) or two weeks (d)).

4 Conclusions

By varying the application schedule and the application order between TEOS and different silicon based water repellent products some interesting results were obtained. When the aqueous emulsified water repellent product was applied after the consolidant, a minimum of three days was necessary between applications for the water repellent treatment to be effective. The other types of water repellents (gel and solvent based) were effective even when applied one day after the consolidant, although their consumption was lower than on the untreated samples. According to these results, it may therefore not be necessary to wait four weeks before applying water based emulsions on surfaces consolidated with ethyl silicate, but it is necessary to point out that such a short time lapse will result in a reduced uptake of water repellent product.

When the water repellent products were applied before the consolidant, all three products performed well. These results indicate that it is possible to invert the traditional order of application of water repellent product and consolidant. The total quantity of consolidant absorbed is reduced to about 25 % but hardly influenced by the time schedule.

All three water repellent products induced strong alterations in the colour of the samples. This is a key issue when treating historical masonry. Special attention must be paid to avoid visible changes in the appearance of the original stones or bricks and thus reduce the aesthetic value of the building itself.

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