A-1-3 Evaluation of an oil and water repellent on masonry substrates

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ABSTRACT: Decorative masonry substrates of various colours and surface finishes such as natural stone, coloured concrete blocks and pavers, and decorative concrete are often used in modern building construction. However, stains such as those from plant leaves, animal droppings, food, and other staining materials are easily absorbed by these decorative substrates due to the permeable structure of masonry substrates. Removing stains from the surface of these building materials is difficult. Costs of cleaning and maintenance are high. Treating these substrates with an oil and water repellent such as a fluorinated polymer sealer is a common method to impart stain resistant properties to the substrate surface. However, such a fluorinated polymer sealer provides inefficient and limited protection to the substrate in that the sealer only provides a thin film over the surface and does not penetrate into the substrate due to the large molecular size of the polymer. The combination of a silane/siloxane and a fluorinated polymer would be an ideal penetrating sealer to treat such masonry substrates to effect water and stain resistance. Such a combined sealer not only provides oil and water repellent effects to the surface but also achieves penetration depth resulting in highly efficient protection against water and stains for the treated surface. An innovative sealer made from a silane/siloxane and a fluorinated acrylic has been developed in this research and this paper provides a performance comparison between the fluorinated polymer sealer and the combined sealer of the silane/siloxane and the fluorinated polymer on various natural and man-made masonry substrates.

KEY-WORDS: Oil and water repellent, stain resistant sealer, penetrating sealer, masonry substrates, silane/siloxane, fluorinated polymer.

INTRODUCTION

Modern building construction often requires decorative masonry materials of various colours and surface finishes. These decorative masonry materials include natural stone substrates, coloured concrete blocks and pavers, and decorative concrete which are often used for paving, floors, garden features and feature walls. However, these decorative building materials are easily stained by plant leaves, animal droppings, food, and other stains due to the permeable structure of masonry substrates. Removing stains from the surface of these building materials is difficult. Costs of cleaning and maintenance are high.

Treating the above decorative masonry substrates with an oil and water repellent such as a fluorinated polymer is a common method to impart to the substrate stain resistance [1-4]. However, fluorinated polymer sealer provides inefficient and limited protection against water and stains for substrates. This is because the fluorinated polymer generally forms a thin film over the substrate surface with no or limited penetration depth into substrate capillaries due to the large molecular size of the polymer. Such a thin protective film is not efficient against water and stain penetration for the treated substrate. This thin film is also inadequate against physical wear and tear over time.

Silane/siloxane materials have been effective water repellents for treating masonry substrate [5]. Silane/siloxanes can deeply penetrate into masonry capillaries lining the capillary walls where the silane/siloane crosslinks with the substrate via chemical bonding forming a permanent hydrophobic impregnation zone within the surface. This hydrophobic zone within the substrate surface provides sufficient protection against water penetration. It is assumed that adding a silane/siloxane into a fluorinated polymer would make an ideal penetrating sealer to provide sufficient protection against water and stains for the substrate. Such a combined sealer not only imparts oil and water repellent effects but also provides durable protection for the treated substrate due to deep penetration depth attributed to the silane/siloxane in the combined sealer.

An innovative sealer made from a silane/siloxane and a fluorinated acrylic polymer has been developed in this research. This paper provides performance comparisons between the sealer of a fluorinated polymer and the combined sealer of the fluorinated acrylic polymer and a silane/siloxane on various natural and man-made masonry substrates used in this research. The performance comparison tests in this paper includes penetration depth, water repellent effect via capillary water absorption, oil and water repellent via staining tests, and the wear and tear durability test. The test results confirmed that the combined sealer of the fluorinated acrylic and the silane/siloxane exhibited superior performance compared to those of the substrates treated with the fluorinated acrylic polymer sealer.

EXPERIMENTAL

Penetrating sealers

Two oil and water repellent sealers were prepared and tested for this research. They were:

- Fluorinated acrylic polymer supplied by DuPont. The fluorinated polymer sealer was prepared from a fluorinated acrylic polymer diluted in organic solvents recommended by the manufacturer.

- Combined sealer of the fluorinated polymer (same as above) and silane/siloxane supplied by Dow Corning. The combined sealer was prepared by mixing the silane/siloxane with the above fluorinated acrylic sealer.

Masonry substrates

Masonry substrates vary significantly in chemical composition and physical properties. We selected the most commonly available natural stone and man-made substrates for this research. They included sandstone as a permeable natural stone substrate, granite as a dense natural stone substrate and wet-cast concrete paver as a man-made medium density substrate. All these substrates were cut to approximately 10cm x 10cm with a thickness of approximately 2cm. The substrate samples were clean and dry before testing.

Application of sealers

Sealer was applied to the vertical surface of the substrates via a hand-sprayer. This is to allow natural absorption of sealer by substrate and, at the same time, allow excess sealer to run off the substrate surface avoiding hydrostatic pressure which may interfere with the natural absorption of sealer by the substrate. Application was repeated 4 times wet-in-wet to ensure an adequate amount of sealer was absorbed by the substrate. The method of wet-in-wet application is the method of re-application of the sealer immediately when the previously applied sealer was absorbed by the surface while the surface remains wet. The wet-in-wet method was to ensure enough sealer was absorbed by the surface.

This method was commonly recommended by manufacturers of many commercial penetrating sealers. The exact application rate was difficult to define but the above impregnation method was to ensure that the substrate was fully saturated by the sealer via natural capillary absorption of the substrate. Comparison and control samples were applied at the same time under the same conditions in order to obtain comparison test results for the purpose of this research. Repeated sample of each test was also conducted in order to obtained accurate test results. After application, the treated substrates were left to cure and dry at room conditions for 7 days before any performance test was conducted.

Performance tests and test methods

Penetration Depth

Penetration depth is an important parameter for evaluating a penetrating sealer. High penetration depth not only improves the efficiency of water or stain resistant effects, but also ensures the durability of the treatment. In this research, the penetration depth was measured by breaking the treated substrate and wetting the freshly broken surface with an ink solution. The un-wetted dry zone abutting the treated surface was measured with a ruler as the penetration depth.

Water Repellent Effect via Capillary Water Absorption

The purpose of applying water repellent or oil and water repellent to masonry substrates is to impart water or stain resistant effect for the substrate. Water repellent or stain resistant effects of a treated substrate may be evaluated by the contact angle method. The contact angle of a water droplet or oil droplet on the treated surface directly relates to the surface tension of the treated surface. The surface tension theoretically determines the water repellent effect of the treated surface. However, the contact angle method only reveals a static hydrophobic effect of the treated surface but not the efficacy of the water resistant treatment in practice.

Measuring capillary water absorption is the most effective and practical way to evaluate the efficiency of a water repellent treatment. Masonry substrates have porous and permeable structures with hydrophilic capillaries which attract water or stains therefore being permeable to water or stains. After treatment with a penetrating sealer, the sealer penetrates into the capillaries lining the capillary walls where the sealer lowers the surface tension of capillaries converting hydrophilic capillaries into hydrophobic or oleophobic capillary surfaces forming an impregnated zone within the treated surface. This hydrophobic or oleophobic impregnation zone acts as a protective barrier against water or stain penetration. Therefore determining capillary water absorption directly reveals the efficiency of a water repellent treatment.

The capillary water absorption was measured according to DIN 52617 with some modifications. Substrates were laid with the treated faces down on a saturated sponge submersed in a water bath. The water level was maintained at the top surface of sponge in the water bath. This is to ensure the treated surface is in close contact with water but not submersed in water avoiding water penetration under hydrostatic pressure but allowing measurement of the capillary water absorption. Weight increase due to water absorption of the substrate was measured over time and the result was calculated as a weight percentage increase which was presented in a water absorption chart. For avoiding test errors and for comparison purpose, the same type of substrates treated with both sealers and control were always tested at the same time under the same test conditions.

Oil and Water Repellent or Stain Resistant Effect

Apart from measuring contact angle, there is no standard method to measure oil and water repellent or the stain resistant effect of an oil and water repellent sealer. As discussed above, contact angle method does not reveal the true efficacy of a penetrating sealer in practice. Therefore, we developed a practical method to evaluate the stain resistant effect of an oil and water repellent sealer in this research. In this method, the substrate surface was stained with various staining materials and then visually checked for staining.

Stains used in this research included:
- Food dye. Queen Blue food dye diluted at 1:20 in water.
- Red wine. Australia Shiraz red wine with 13.5% alcohol.
- Olive oil. Extra virgin olive oil having a yellowish colour for easy viewing.

The staining test was conducted by placing 0.5ml of the above staining materials as droplets onto the horizontal substrate surface. After 10 minutes, the stain droplets were removed from the surface by a pipette. The surface was then wiped with a dry cloth followed by washing with a nylon brush under running tap water aided by a dishwashing detergent. The substrate was left to dry and then visually checked for staining. Instead of ranking the surface staining with a Fig., staining results were presented in photographs side by side for direct comparison between the two sealers or compared to controls for the purpose of this research.

Wear and Tear Durability

The stain resistant effect of an oil and water repellent is attributed to a thin film formed from the fluorinated polymer over the treated surface. Such a thin film may withstand static deterioration such as UV degradation or weathering but may not survive physical wear and tear. Therefore, a wear and tear durability test was conducted in this research. In the wear and tear durability test, the substrate was first subjected to 500 cycles of brushing with a nylon brush under running tap water aided by a dishwashing detergent. The substrate was then subjected to the staining test followed by the capillary water absorption test to evaluate the wear and tear durability of the sealers used in this research.

RESULTS AND DISCUSSION

Penetration depth

As discussed, the penetration depth is the key parameter relating to the efficiency of an oil and water repellent. Fig. 1 displays penetration depths of substrates treated with the two sealers used in this research. The left substrate in each photo was treated with the combined sealer of the fluorinated acrylic and the silane/siloxane. The right substrate in each photo was treated with the fluorinated acrylic sealer. The quantitative penetration depths were plotted in Fig. 2.

Fig. 1. Penetration depth test: sandstone (left), wet-cast concrete (middle) and granite (right).

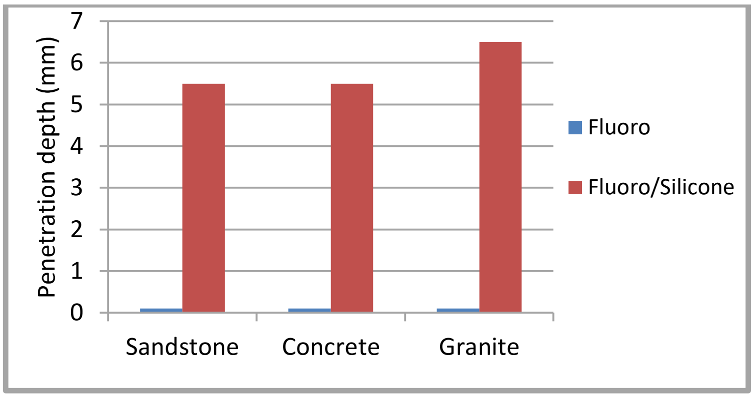

Fig.2. Quantitative penetration depths (mm) of substrates treated with the fluorinated acrylic sealer (Fluoro) and the combined sealer of the fluorinated acrylic and the silane/siloxane (Fluoro/Silicone).

Results shown in Fig.1 and 2 indicated that the combined sealer of the fluorinated acrylic and the silane/siloxane achieved significant deep penetration depths for all substrates. In contrast, the fluorinated acrylic sealer presented poor penetrating depth results. The test results proved that the fluorinated polymer had very limited ability to penetrate into the masonry capillaries due to the large molecular size of the fluorinated polymer. In addition, the negatively charged masonry capillaries would impart electrostatic attraction and hydrogen bonding to the polymer backbone to interfere with the mobility of the polymer molecule to adversely affect the penetration of the fluorinated polymer into the substrates.

This test proved that adding a silane/siloxane into a fluorinated acrylic polymer significantly improves the penetration depth of the fluorinated polymer sealer.

Water repellent effect via capillary water absorption test

Capillary water absorptions of the substrates treated with the two sealers used in this research were measured according to the capillary water absorption test method. The test was continued for 28 days in order to evaluate a long term water resistant effect against water penetration for substrates. The capillary water absorptions of the substrates treated with both sealers of this research together with controls are presented in Fig. 3, 4 and 5.

Results in Fig. 3, 4 and 5 revealed that all substrates treated with the combined sealer of the fluorinated acrylic and the silane/siloxane show constant and significantly lower water absorptions over the 28 day test period, compared to those of substrates treated with the fluorinated acrylic sealer and the controls. The substrates treated with the fluorinated acrylic sealer exhibited insufficient water absorption results particularly at the near end of the test period. It achieved low water absorptions within initial 24 hours of the test period, but gradually lost the water resistant effect to exhibit high water absorptions at the end of the test period. This indicated that the thin film of the fluorinated polymer over the treated surface is not sufficient enough against long term water penetration. It is understood that, due to the porous surface finish, the thin film over the substrate surface would have many imperfections or weak points which would allow some water penetration which would increase over the extended period. In contrast, the combined sealer of this research provided a deep penetration depth forming a thick hydrophobic zone as an effective barrier against water penetration over an extended period.

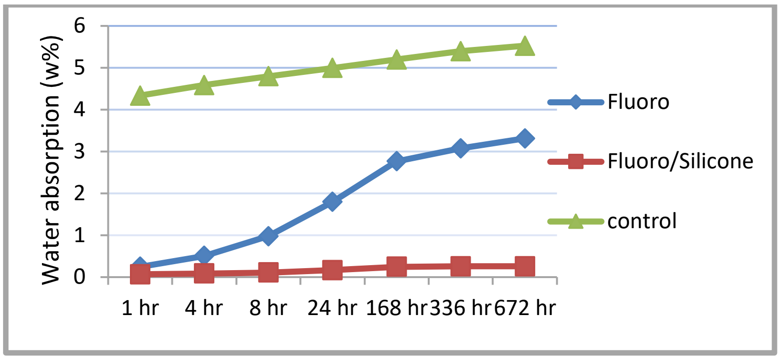

Fig.3. Capillary water absorption of sandstone treated with the fluorinated acrylic sealer (Fluoro), the combined sealer of the fluorinated acrylic and the silane/siloxane (Fluoro/Silicone), and the control.

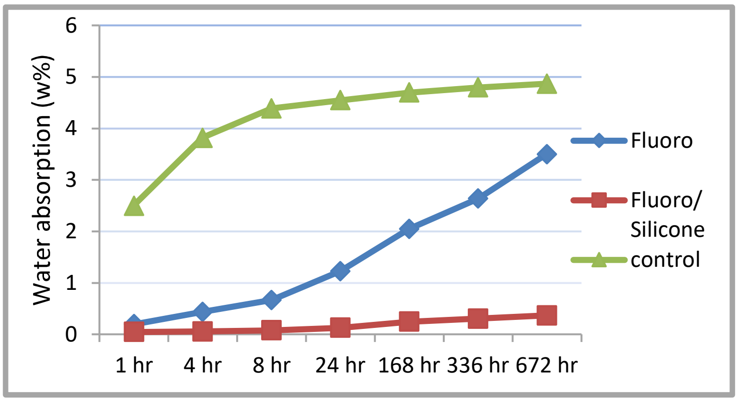

Fig.4. Capillary water absorption of wet-cast concrete treated with the fluorinated acrylic sealer (Fluoro), the combined sealer of the fluorinated acrylic and the silane/siloxane (Fluoro/Silicone), and the control.

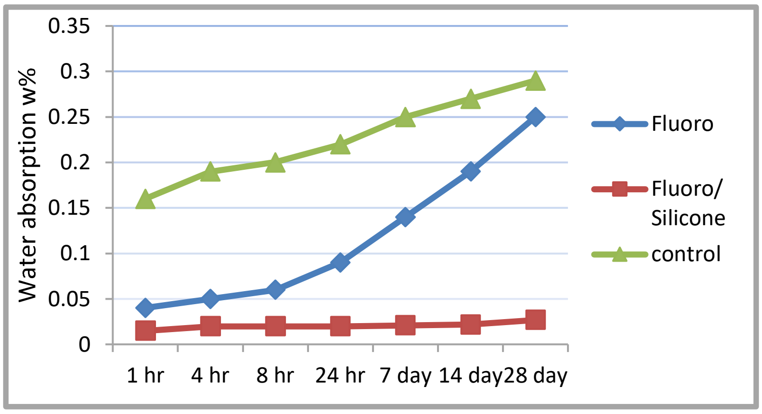

Fig.5. Capillary water absorption of granite treated with the fluorinated acrylic sealer (Fluoro), the combined sealer of the fluorinated acrylic and the silane/siloxane (Fluoro/Silicone), and the control

The water absorption results in this research proved that the combined sealer of the fluorinated acrylic and the silane/siloxane provided significantly better protection against water penetration than that of the single fluorinated polymer sealer for the treated substrates.

Oil and water repellent or stain resistant effect

Oil and water repellent effects of the substrates treated with the fluorinated acrylic sealer and the combined sealer of the fluorinated acrylic and the silane/siloxane were conducted according to the test method specified in the Experimental section above. The results are presented in Fig. 6, 7 and 8. Photos on the left display the beading effects of staining materials on the treated surface. Photos on the right display the state of the surfaces after staining materials were removed and surfaces were cleaned and dried. Control substrates were also listed in the photos. All tests were conducted at the same time under the same test conditions for comparison purposes of this research.

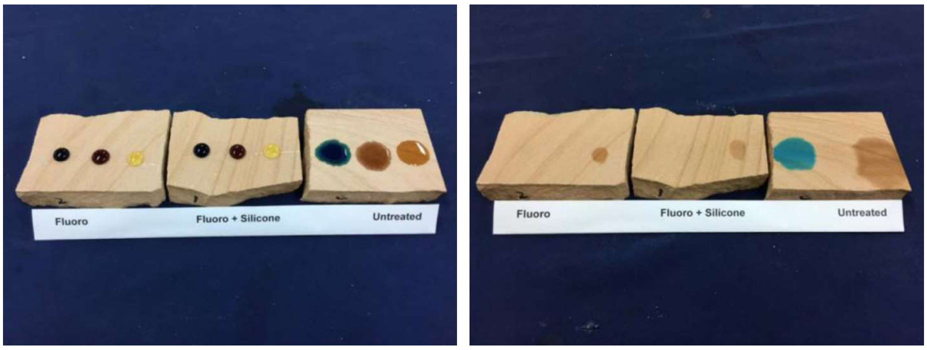

Fig.6. Sandstone: beading effects of staining materials (left photo), and staining status after surface being cleaned and dried (right photo).

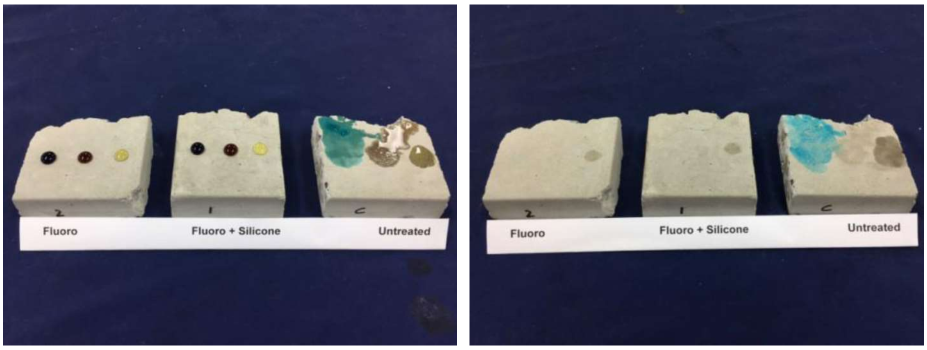

Fig.7. Concrete: beading effects of staining materials (left photo), and staining status after surface being cleaned and dried (right photo).

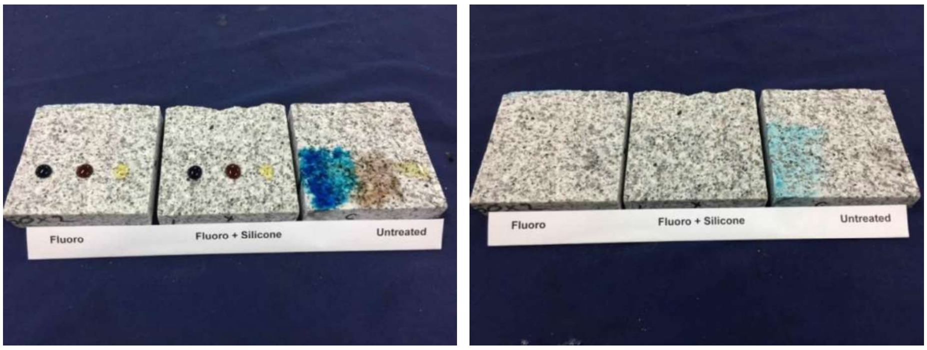

Fig.8. Granite: beading effects of staining materials (left photo), and staining status after surface being cleaned and dried (right photo).

The staining test results indicate that substrates treated with both sealers of this research exhibited good stain resistant effects to all treated substrates compared to those of controls. Both sealers provided excellent resistant to food dye and red wine stains with slightly less resistance to oil staining. However, it was noticed that the substrates treated with the combined sealer of the fluorinated acrylic and the silane/siloxane exhibited slightly better (not significant) stain resistant results. This result may imply that adding a silane/siloxane to a fluorinated acrylic sealer could enhance the oil and water repellent effect of the fluorinated polymer sealer. This effect was further confirmed from the following test.

Wear and tear durability

The same substrates after the above staining tests were subjected to a wear and tear durability test according to the test method specified in the Experimental section above. The results are shown in Fig. 9, 10 and 11. Photos on the left display beading effects of staining materials on the treated surface. Photos on the right display the state of the surfaces after staining materials were removed and surfaces were cleaned and dried. There was no control included in this test.

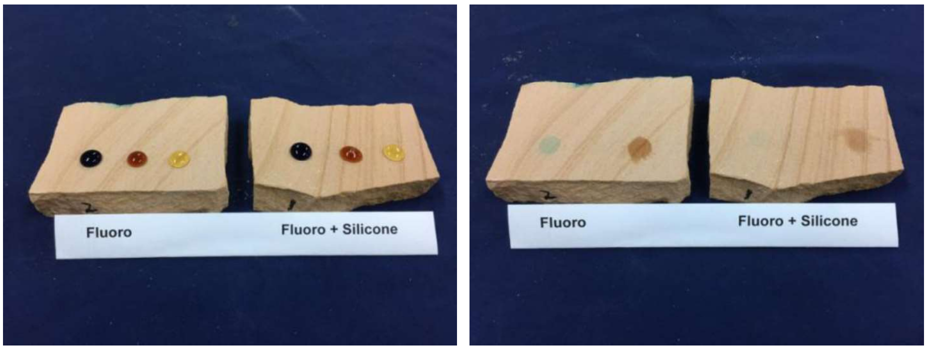

Fig.9. Sandstone after wear and tear durability test: beading effects of staining materials (left photo), and staining status after surface being cleaned and dried (right photo).

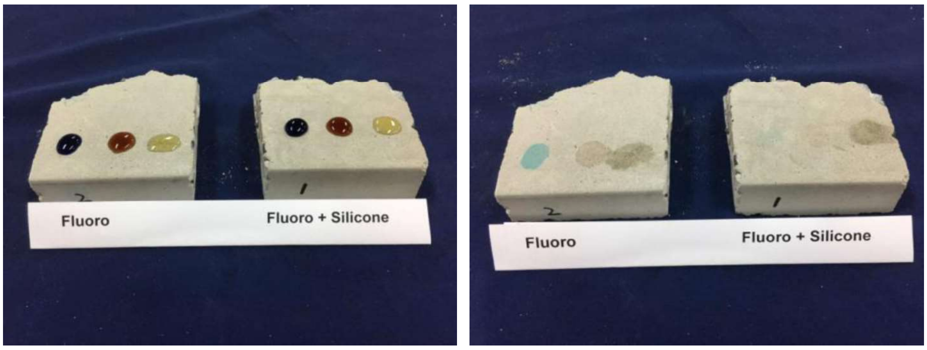

Fig.10. Concrete after wear and tear durability test: beading effects of staining materials (left photo), and staining status after surface being cleaned and dried (right photo).

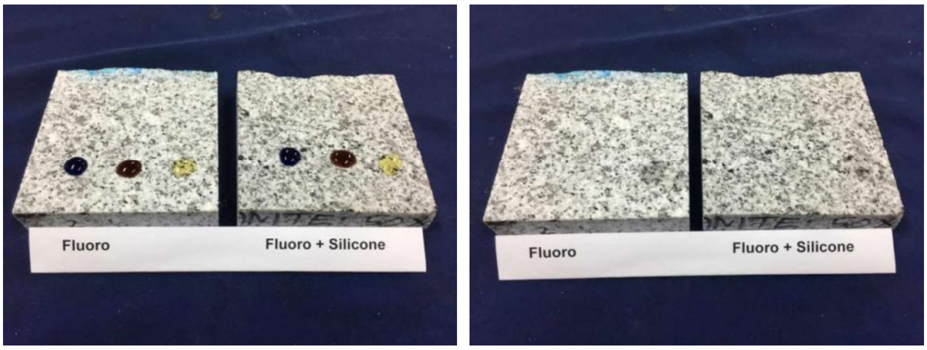

Fig.11. Granite after wear and tear durability test: beading effects of staining materials (left photo), and staining status after surface being cleaned and dried (right photo).

The above results indicate that, after the wear and tear durability test, weaker stain resistant effects of both sealers were observed compared to that from the first staining test. However, unlike the first staining test results, the substrate treated with the combined sealer of the fluorinated acrylic and the silane/siloxane has shown a substantially better stain resistant effect than that of the substrate treated with the fluorinated acrylic sealer after the wear and tear durability test.

Like any coating, the thin film formed by the fluorinated polymer relies on physical adhesion to stay on the substrate surface. This thin film would have limited resistance to physical wear and tear causing deterioration in stain resistance. In the combined sealer, however, the silane/siloxane may help to "lock in" the fluorinated polymer, by the silane/siloxane crosslinking with the substrate via chemical bonding, resulting in better adhesion between the fluorinated polymer and substrate. This "lock in" effect is a hypothesis by this research, which requires further study in order to provide theoretical support. The better adhesion is believed to improve the wear and tear damage of the thin film of the fluorinated polymer resulting in better resistance to water and stains after the wear and tear. This is known that a silane/siloxane does not exhibit oil and water repellent effect but this "lock in" effect enhances the oil and water repellent effect of the fluorinated polymer by possibly improving the adhesion between the polymer and the surface.

The capillary water absorptions of the treated substrates after the wear and tear test further confirmed that the combined sealer of fluorinated acrylic and silane/siloxane showed superior durability results compared to that of the fluorinated acrylic sealer (see Fig. 12, 13 and 14)

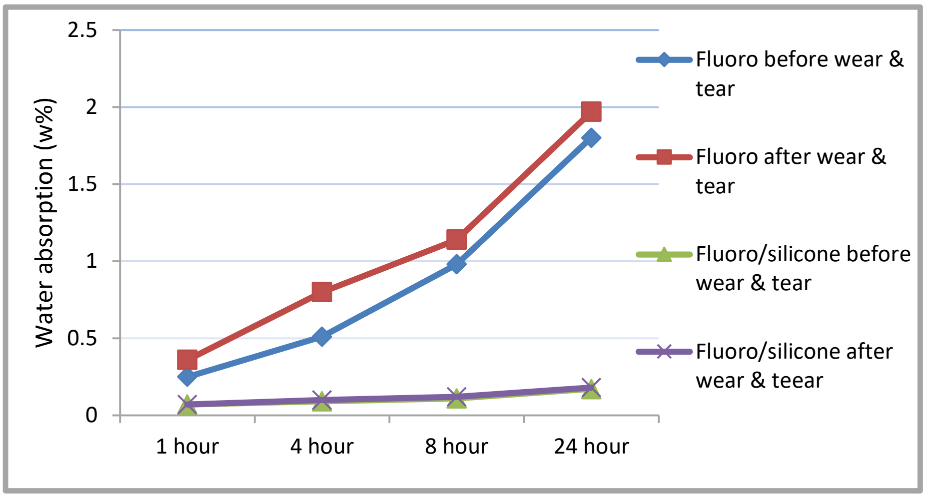

Fig.12. Capillary water absorptions of the treated sandstone before and after wear and tear durability test

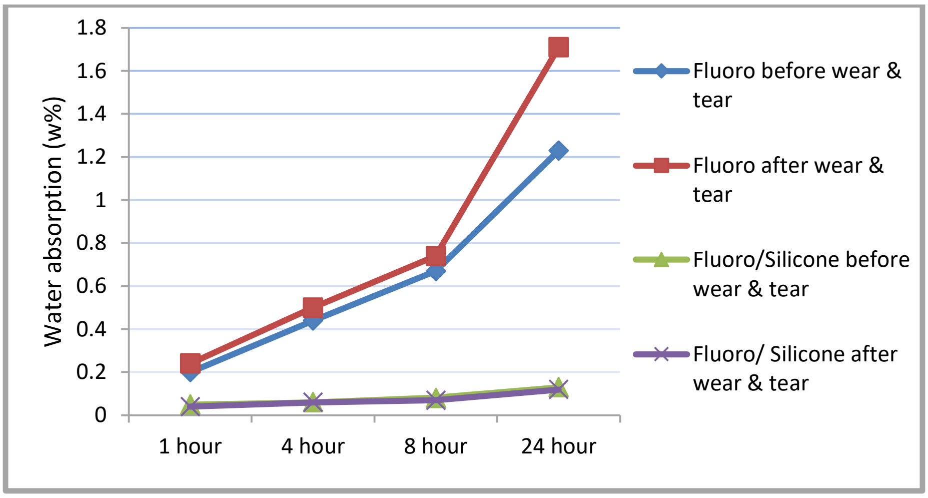

Fig.13. Capillary water absorptions of the treated concrete before and after wear and tear durability test

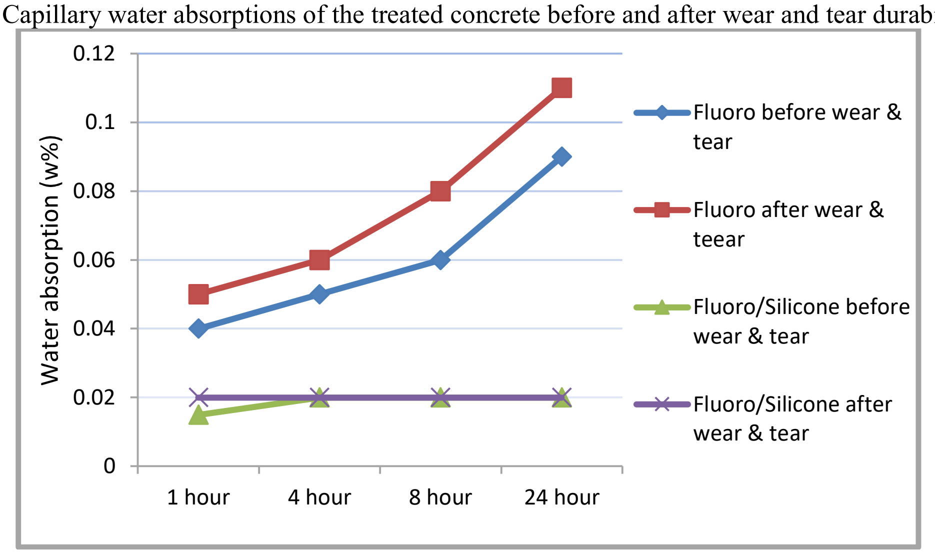

Fig.14. Capillary water absorptions of the treated granite before and after wear and tear durability test

The above capillary water absorption results reveal that the water resistant effect of the fluorinated acrylic is adversely affected by the wear and tear durability test. This was caused by deterioration of the thin film of the fluorinated polymer due to physical wear and tear. In contrast, the capillary water absorptions of substrates treated with the combined sealer of the fluorinated acrylic and the silane/siloxane were intact from the wear and tear durability test. The deep water repellent zone attributed to the silane/siloxane would provide adequate resistance to the surface wear and tear to provide sufficient protection against water penetration for the treated surface.

CONCLUSIONS

Most oil and water repellent sealers for treating masonry substrates are based on fluorinated polymer or similar fluorinated materials. The fluorinated material is a good static oil and water repellent agent but may not be an efficient penetrating sealer for effecting masonry stain resistance. The test results in this research reveal that the fluorinated acrylic polymer sealer provided good initial or static oil and water repellent effect to the treated substrates but, due to lack of penetration depth, failed to provide sufficient protection against water and stain penetration over the extended test period. The oil and water repellent effects of the fluorinated polymer relied on the thin film over the treated surface which appears to be inefficient for water and stain resistance and inadequate against physical wear and tear for an extended test period.

However, the results in this paper confirmed that adding a silane/siloxane into a fluorinated acrylic polymer significantly improved the efficiency of the fluorinated polymer sealer. The combined sealer of the fluorinated acrylic and silane/siloxane achieves a deep penetration depth into the treated substrate providing significantly better protection against water and stains. Further, the results in this paper reveal that adding a silane/siloxane into a fluorinated polymer enhanced the oil and water repellent effect and improved the wear and tear durability of the fluorinated acrylic sealer. This effect may be attributed to the effect of silane/siloxane crosslinking within the substrate via permanent chemical bonding, which improves the adhesion of the fluorinated polymer to the substrates.

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