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Disfiguring Biocolonization Patterns after the Application of Water Repellents

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Abstract

As a result of a multi-year conservation/restoration program for the gardens of the National Palace of Queluz in Portugal, the opportunity to evaluate the long-term performance of conservation interventions on the marble statues that decorate these Baroque gardens was presented.

The observations have shown that although water repellents may reduce the rate of biocolonization on the statues and vases they strongly influence re-colonization patterns. In general, unsightly streaking develops which can be attributed to the formation of preferential water paths. The latter will favour biological colonization and eventually, be literally etched into the stone.

It would appear that the application of higher amounts of a water repellent, and in solution rather than in an aqueous emulsion, enhances the appearance of streaking on these marble elements. Further research is needed to elucidate these observations. A practical solution to the problem presented by these decorative elements was found by regular application of a biocide, since this can be applied locally by maintenance personnel, while water repellents require a professional application.

Keywords: water repellents, biocolonization, soiling, streaking, marble statues, oligomeric siloxanes

Entstellende Bewuchsmuster nach einer Hydrophobierung

Zusammenfassung

In den Gärten des Nationalpalastes von Queluz, Portugal, wurde ein Jahre dauerndes Programm des Konservierens und Restaurierens durchgeführt. Dadurch ergab sich die Möglichkeit, das Langzeitverhalten von konservierenden Maßnahmen an den Marmorstatuen, die den Barockgarten zieren, auszuwerten.

Die Beobachtungen zeigten, dass Hydrophobieren zwar die Geschwindigkeit des Biobewuchses auf den Statuen und Vasen reduzierte, dass jedoch das Muster des erneuten Bewuchses dadurch beeinflusst wurde. Im Allgemeinen konnte man feststellen, dass sich unansehnliche Streifen ausbildeten. Diese Erscheinung konnte auf bevorzugte Läufe des herabrinnenden Wassers zurück geführt werden. Dies führt zu bevorzugtem Biobewuchs entlang der Wasserläufe und schließlich wird an diesen Stellen der Stein ausgewaschen.

Es scheint so, als ob die Verwendung von größeren Mengen eines Hydrophobierungsmittels, das in Lösung vorliegt und nicht in Form einer wässrigen Emulsion, das Auftreten von Streifen auf den Marmorskulpturen beschleunigt. Weitere Untersuchungen sind nötig, um diese Beobachtungen zu untermauern. Eine praktisch durchführbare Lösung für das an diesen zierenden Elementen aufgetretene Problem wurde gefunden, es wurden regelmäßig Biozide angewendet. Biozide können durch das für den Unterhalt des Gartens beschäftigte Personal aufgetragen werden, während Hydrophobierungsmittel durch Spezialisten angewendet werden müssen.

Stichwörter: *Hydrophobierungsmittel, Biobewuchs, Verschmutzung, Streifenbildung, Marmorstatuen, Oligomere Siloxane.*

1 Introduction

The function of water repellents is to prevent the ingress of liquid water into stone or masonry surfaces. Therefore, surfaces treated with a water repellent will have a lower time-of-wetness than untreated ones. In principle, this will decrease the deposition of air pollutants, dust, and the development of biological colonization. In summary, general soiling will be reduced. Based on the above premise, water repellents have been applied to many buildings and monuments, in the hope of improving their protection and decreasing their need for maintenance. This paper addresses only the issue of biological re-colonization after treatment with a water repellent.

Although in general it is considered that algae are not damaging to inorganic construction materials this is not the case for calcareous substrates since the acid and chelating agents liberated by microorganisms can etch them significantly [1-3]. Thus, surface roughness will increase after colonization has been established. In turn, increased roughness will favour further colonization, or faster re-colonization after a cleaning, because dirt will be trapped and moisture retained preferentially. Nonetheless, it is to be taken into account that cleaning may increase or even decrease surface roughness depending on the applied methodology and the skill of the operators. For some cleaning methodologies, biological re-colonization may be accelerated [4].

In principle, the application of a water repellent will reduce the incidence of biocolonization by preventing liquid water from entering the pore system of the material. Although in most cases this is the case, there are instances in which unexpected effects have resulted with regards to biological re-colonization. The study discusses the rather disfiguring condition that resulted some years after the application of water repellents to marble statues that decorate the gardens of the National Palace of Queluz, Portugal.

2 General Background

The National Palace of Queluz, located some 12 km west of Lisbon, was used by the Royal Family as a summer residence between the 17th and 18th century. Several construction campaigns modified the original simple country estate and its present configuration dates from the 18th century. The Palace has some 15 hectares of grounds, mostly a park, but with formal French style gardens close to the building presently housing a museum. The gardens are decorated with stone statues, busts, vases, balustrades and fountains. There are also some sculptures cast in lead, glazed ceramic vases and a creek that has been bound in a canal lined with azulejo tiles.

As a result of a multi-year restoration project undertaken by World Monuments Fund-Portugal (WMF-P) and the Instituto Português do Património Arquitectónico e Arqueológico (IPPAR), presently substituted by the Instituto dos Museus e da Conservação (IMC), the gardens and all its decorative elements are currently undergoing diverse conservation and restoration interventions. For the case of the stone sculptures, the aim and the methodology being used for their conservation has been described in detail elsewhere [5].

Among the first actions undertaken in this project was the creation of a data base of all the stone elements in the garden and to collect as much information about any previous interventions they might have undergone [6]. No records of interventions prior to 1977 exist, which does not necessarily mean that no actions were carried out previously. After 1977, conservation interventions were implemented based on the perceived need. That is, the most soiled statues, or those which had suffered some damage, i.e., from a branch falling on them, were subjected to a conservation or restoration intervention (see Figure 1). As is a regrettable customary practice, not all interventions have been documented with a written report. And when there is a written report, it generally does not provide sufficient detail to allow understanding how the actual intervention was carried out. Unfortunately, this is yet one of the most unsatisfactory issues in conservation [7].

The search through the records showed that the water repellent favoured was a solvent based oligomeric siloxane with an active ingredient concentration of 8 % that was usually applied by brushing. However, after 1999, only aqueous emulsion formulations were used. These were based, according to provided information, on the dispersion of essentially the same oligomeric siloxane in water at the same concentration of the active ingredient.

3 The Problem

During the documentation phase of the stone statuary subproject, it was observed that some sculptures, which were known to have received a water repellent treatment, showed a particular kind of

Figure 1: Appearance of a *putti* group before the intervention in 1996/7. Note the dark soiling resulting from biocolonization. This same group is shown in Figure 3 some years after cleaning.

Figure 2: The streaking pattern is particularly noticeable under the arm of the Triton. The pattern results from uneven biocolonization. The marble statues are in a fountain that had been cleaned and treated with a water repellent four years before the photograph was taken (Photo 2003).

streaking resulting from the biocolonization pattern developed. This is shown in Figure 2, taken some four years after the application of the water repellent. The appearance of this unsightly streaking was attributed to the water repellents used since statues that had not been treated with a water repellent showed a more uniform biocolonization.

Thus began a thorough examination of those statues that did present this evident streaking and those that did not show it. It was found that apart from the statues in the above mentioned fountain, restored and cleaned in 1998/9, four other figure pairs, cleaned in 1996/7, also showed this occurrence. All of these sculptures had been treated by the same conservation firm, applying the mentioned solvent based water repellent by brushing.

Interestingly, the four figure pairs belonged to a group of six pairs, which decorate a balustrade that limits the formal Malta garden by the palace. The record compilation showed that a different conservation firm had treated the other two pairs using the same water repellent at about the same time (1997). Curiously, these two pairs showed the streaking effect to a far lower degree, as shown in Figure 3. However, the more exposed areas, such as the top of the heads, were far darker from heavier biocolonization.

4 Discussion

To try to elucidate the differences observed between the two groups of statues, the conservators responsible for these interventions were contacted to find out what water repellent had been used and how it had been applied, given the importance of the application method to the performance of the product [8]. As mentioned, both had used the same water repellent, a solvent based oligomeric siloxane (8 % concentration), and both had applied it by brushing. The conservator that had treated the four statue groups in 1996/7 indicated that he had applied at least two coats wet-on-wet. The second conservator had applied only two coats, wet-on-wet.

Figure 3: Note the difference in streaking from the *putti* pair on the left treated in 1996/7 and that on the right, treated by a different conservation firm in 1997. Photographs taken in January 2003. The group on the left shows more distinct streaking than that on the right, although this one has more generalized colonization on the more exposed areas.

The two *putti* groups (Figure 3) are located close to each other and with similar environmental exposure. They were cleaned at practically the same time and the same water repellent was applied by brushing. Nevertheless, a different re-colonization pattern developed, suggesting, by the fact that the second group had heavier colonization on the most exposed areas as occurs normally on untreated objects, that these had received a lower amount of water repellent. This would suggest that the streaking pattern is enhanced when more water repellent is applied.

It is to be mentioned that no control of the concentration of the active ingredient in the water repellent used was carried out. However, the fact that the patterns were repeated on different statues at different times as a function of the conservation firm applying them, suggests that the concentration of the oligomeric siloxane in the commercial water repellent was relatively constant for different batches purchased at different times, and that the application technique could be reproduced within one team.

Since biocolonization will develop preferentially on surfaces that are damp, it is important to consider how water flows over the object in question during rain events, or as a result of moisture condensation upon dew point crossings, especially when considering objects with complex geometry such as statues [9]. For these objects, preferential water paths will develop and therefore algae growth will be favoured along them. The growth will increase roughness along these paths and in turn, will enhance colonization and eventual re-colonization after cleaning.

The surfaces of the statues showing the streaking were examined in detail. It was found that the colonized paths were clearly rougher than the cleaner surfaces beside them. Roughness was estimated by touch by three different people under blindfold conditions since this method has proved to be accurate enough for practical purposes [10].

Given the above considerations, it is important to consider the role that water repellents play under these circumstances. When a water repellent is applied to a surface of uneven roughness it is evident that the distribution of the product over this surface will also be uneven. Rougher areas, such as those created by localized biocolonization on preferential water paths, will absorb more product than the smoother areas around them. Nonetheless, because of the higher roughness, any water drops that form there may spread faster promoting the formation of a water film [11] as well as being preferential tar-

Figure 4: Three bi-face busts to which an aqueous emulsion of an oligomeric siloxane was applied after cleaning in 1999, four years before the photograph was taken (Photos 2003). Note the difference in biocolonization depending on the location of the busts. From left to right, increasing shade.

gets for biocolonization as discussed above. Thus, in spite of the fact that more product penetrated into the crevices of the surface, colonization is still likely to develop there first. This hypothesis could explain how the unsightly streaking is enhanced even after the application of a water repellent.

5 Water Based Formulations

Comparison of the above mentioned statues with others treated with an aqueous emulsion showed that streaking was not as marked for the latter, although because of their location in a shady area, re-colonization was far more advanced, as shown in Figure 4. The three busts shown belong to a set of four that adorn a balustrade around a fountain located under trees, which shade them to a greater or lesser degree most of the year. The fainter streaking obtained with the water emulsions appears to reflect their slightly lower performance compared to solvent based products [12-13].

In 1995, the bi-faced busts shown in Figure 4 had suffered a previous cleaning but no water repellent had been applied. Since objects in shadier areas are colonized far more rapidly than those in full sunlight, the resulting soiling from biocolonization was heavy enough to warrant, four years later, in 1999, another cleaning when the aqueous water repellent emulsion (of the same oligomeric siloxane at 8 % concentration) was applied. Their appearance after another four years, in 2003, show that only one of them could be considered as requiring another intervention, confirming the effectiveness of water repellents in reducing biocolonization rate. A point to be noted is that objects located in full shade tend to be colonized more evenly, as can be seen in the pictures shown above.

A further example to illustrate the fact that the application of water repellents promotes streaking can be found in the marble vases that decorate the garden. These objects, being of regular shape, do not develop preferential water paths, although biocolonization may favour one side over another depending on their orientation (see Fig. 5 a). However, after cleaning and application of the aqueous emulsion of the water repellent, faint streaking was observed to develop on them as well, as shown in Figure 5 b. This streaking is particularly noticeable when moisture condensation occurs, early in the mornings, confirming that water repellents tend to favour the development of preferential water paths.

Preferential water paths can be explained by the fact that water repellents in general will inhibit the spreading of rain or dew drops. The drops will retain their spherical shape and, as surface absorption is strongly reduced, they can only evaporate or run down the surface. As during high humidity periods, such as is frequent in these gardens, evaporation is limited, the drop will run down the surface inducing the formation of “running” strips and the eventual preferential water paths. The accumulation of dust and spores will be favoured along these paths leading to the formation of a localized biofilm. Thus, the more efficient the water repellent is, the more concentrated will the biocolonization be in the preferential water paths.

Figure 5: ***(a)****:* A marble vase on the same balustrade of the *putti* from Fig.3 that did not receive a water repellent treatment. Note the even biological colonization that is mainly favoured by the orientation of the object.
(b)*:* A marble vase located on the balustrade of a sunny terrace, cleaned and treated with the aqueous water repellent emulsion in 1999, shows the resulting tell-tale streaking nine years later (Photo 2008).

It is to be noted that the busts shown in Figure 4 and the vase of Figure 5 b were treated by a third firm, using the same aqueous emulsion of the water repellent applied by brushing. The difference in the degree of biocolonization between these objects emphasizes the importance of shade in the rate at which the object will be colonized.

6 Conclusions

The long-term project being developed for the stone statues in the gardens of the National Palace of Queluz has allowed to evaluate the performance of water repellents based on oligomeric siloxanes, both in solution as well as in aqueous emulsion.

The evaluation of treatment performance in real life situations is difficult, especially when dealing with biological factors since as yet they are not easily characterized or understood. Biological re-colonization depends on many factors, such as location, substrate nature, object geometry, and previous treatments that may have affected their surface roughness. The present study aims to draw some conclusions from the comparison of marble objects located in relative close proximity and for which some information was available regarding the treatments applied to them in the past ten years. From these, the conclusions summarized below could be drawn.

The applied water repellents have been effective in retarding biocolonization. However, their application has resulted in more or less unsightly streaking that can be attributed to the induced preferential water paths and their subsequent biocolonization. This pattern may be enhanced by the complex geometry of the statues. That the streaking is apparently more noticeable if more water repellent is applied, or if it is applied in solution rather than in an aqueous emulsion, requires further study to confirm and elucidate this observation.

A practical solution to this particular problem at the Gardens of the National Palace of Queluz has been found in the development of a regular maintenance program based on the application of a biocide. The reason for this choice lies in the fact that microorganisms rarely colonize a surface uniformly and while a biocide can be applied locally to the more susceptible areas, this cannot be done with a water repellent. Furthermore, these products require a careful and even application over the entire surface to avoid differences in appearance when it rains and for a uniform protective action. While in buildings with defined physical surface breaks, localized applications can be made to the more susceptible areas, this is not possible when dealing with statues given their complex geometry. Finally, it is to be remembered that while biocides can be applied by unskilled labour with a minimum of training the application of a water repellent requires proficiency.

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