

An Unsatisfactory Case of Water Repellents Applied to Control Biocolonization

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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

1 Introduction

The function of water repellents is to prevent the ingress of liquid water into the stone or masonry surface on which they are applied. 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 a word, general soiling will be reduced.

On the basis of 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. Although in most cases the application of water repellents has performed as expected, there are instances in which unexpected effects have been obtained.

The study presents the results observed some years after the application of water repellents to stone 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. 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 that now houses 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 [1].

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 [2]. 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 usual, not all

interventions have been documented with a written report. And when there is a written report, it generally does not provide sufficient detail so as to be able to understand how the actual intervention was carried out. Unfortunately, this is yet one of the most unsatisfactory issues in conservation [3].



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.

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 streaking resulting from uneven biocolonization, as shown in Figure 2. This was clearly evident some four years after the intervention at the time the statues were photographed.

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 had been treated by the same conservation firm, using the same water repellent.



Figure 2: Particularly noticeable is the streaking under the arm of the Triton resulting from uneven biocolonization. The marble statues are in a fountain that had been cleaned and treated with a water repellent four years previous to the photograph date.

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 the other two pairs had been treated by a different conservation firm, 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 were far darker from heavier biocolonization.

The search through the records also showed that apparently only aqueous emulsion formulations were used after 1999. These were based on the dispersion of the same oligomeric siloxane formulation in a water emulsion at the same concentration of the active ingredient.

4 Discussion

To try to elucidate the differences observed 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 [4]. 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 only applied 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. Note the difference in biocolonization distribution, streaked on the left and less streaked though more intense in some areas on the group right.

As mentioned above, the two putti groups (Figure 3) are located close to each other, have similar environmental exposure, 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.

Comparison with the statues treated with an aqueous emulsion showed that these barely had any streaking 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 two trees which shade them to a greater or lesser degree most of the year. These had been treated by the second firm, thus confirming the pattern observed with the putti.

Although there was no control of the concentration of the active ingredient in the water repellent used, 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.

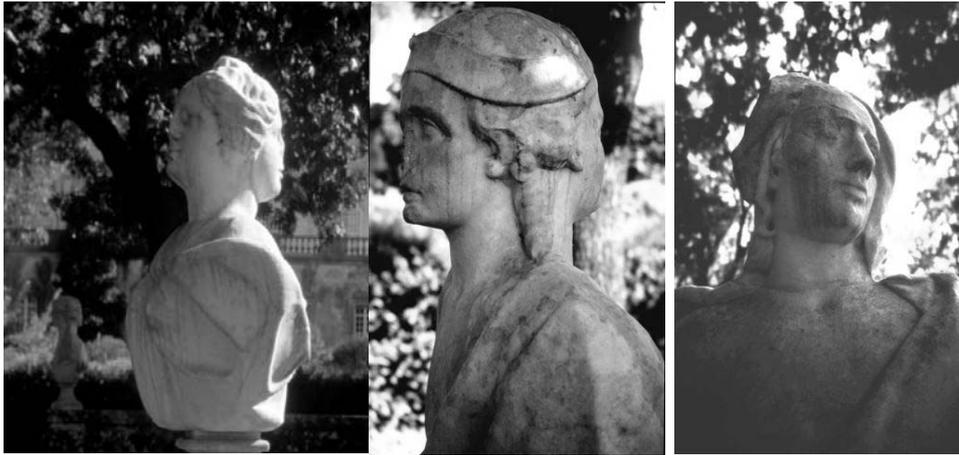


Figure 4: Three bi-face busts to which an aqueous emulsion of an oligomeric siloxane was applied after cleaning in 1999. Photos taken in 2003. Note the difference in biocolonization depending on the location of the busts. From left to right, increasing shade.

4.1 Water repellents and re-colonization

An important point in considering re-colonization is the location of the object. Objects in shadier areas are colonized faster than those in full sunlight. Furthermore, those located in full shade tend to be colonized more evenly, as can be seen in the pictures shown above.

Although in general it is considered that algae are not damaging to construction materials this is not the case for calcareous substrates which are etched significantly by the acid and chelating agents liberated by micro-organisms [5-7]. Thus, surface roughness will increase significantly after an object has been colonized. Depending on the cleaning method used, surface roughness may increase further or even decrease, and biocolonization may even be accelerated [8]. Increased roughness will favour faster re-colonization because dirt will be trapped and moisture retained preferentially.

Another point to consider is water flow over an object during rain events, even prior to the application of a water repellent, especially when considering objects with complex geometry such as statues [9]. It is inevitable that preferential water paths will develop along these intricate surfaces. Preferential water paths imply that these will remain damper for longer times and, therefore, algae growth will be favoured along them. Their growth will increase roughness along these paths which, in turn, will enhance their colonization and eventual re-colonization after treatment.

Examination of the surfaces which showed these paths proved them to be 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 targets 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.

But although previously etched water paths may heighten the streaking after the application of a water repellent, this is not a necessary condition, i.e, it may happen on smooth surfaces to which a water repellent is applied. For example, marble vases that decorate the garden do not develop preferential water paths, although biocolonization may favour one side over another depending on their location. However, after cleaning and the application of a water repellent—the water emulsion, specifically—faint streaking was observed to develop on them as well, confirming that water repellents tend to favour the development of preferential water paths. This can be explained by the fact that water repellents will inhibit the spreading of rain or dew drops. The drops will retain their spherical shape and, as surface absorption is strongly reduced, it can only evaporate or run down the surface. As during high humidity periods 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.

The data obtained so far suggest that the application of a water-repellent reduces the overall rate of biocolonization. For example, the two putti groups shown in Figure 3 are located in similar exposures and both were cleaned at practically the same time and the same water repellent was applied. However, the one from the second group apparently had less water repellent applied to it and consequently the streaking effect was minimal yet the group showed localized heavier biocolonization supporting the hypothesis that less water repellent was applied to it.

The bi-faced busts shown in Figure 4, four years after the 1999 intervention, had suffered a previous cleaning in 1995. However, at the time, no water repellent was applied. The resulting soiling from biocolonization, please refer to Figure 1 for comparison, was heavy enough to warrant the 1999 cleaning where the aqueous emulsion was applied. Their appearance four years later show that only one of them could be considered as requiring another intervention.

To emphasize the importance of shade in the rate of biocolonization, Figure 5 shows one statue of another set located on a balustrade of a terrace at the Palace with no shade whatsoever. These were similarly treated as the bi-faced busts with an aqueous emulsion of the water repellent applied in 1999. Eight years after the treatment, only minor biocolonization is visible.

5 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 oligomeric siloxanes based water repellents, both in solution as well as in aqueous emulsion.



Figure 5: Statues on the terrace balustrade treated with an aqueous emulsion of an oligomeric siloxane after cleaning in 1999. On the left, one of these statues shows development of bio-colonization on the more exposed head. Photos 2007.

To be taken into account is that evaluation of treatment performance in real life situations is difficult, especially when dealing with biological factors that, because of their complexity, are not as yet characterized or understood. Biological re-colonization depends on many factors, such as location, substrate nature, object geometry, and previous treatments which 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 of 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, more or less unsightly streaking also resulted from the application. Streaking is the consequence of biological colonization developing along preferential water paths resulting from the application of water repellents and 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 studies to confirm and elucidate this observation.

A practical solution to this problem 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. 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 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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References

- [1] A.E. Charola, M. Vale Anjos, J. Delgado Rodrigues, A. Barreiro, Developing a maintenance plan for the stone sculptures and decorative elements in the gardens of the National Palace of Queluz, Portugal *Restoration of Buildings and Monuments* 13(6) (2007) 377-388.
- [2] M. Vale Anjos. Relatório da estatuarria de pedra do Palácio Nacional de Queluz. Report to WMF-P, Lisbon (2004)
- [3] J.M. Teutonico, A.E. Charola, E. De Witte, G. Grassegger, R.J. Koestler, M. Laurenzi Tabasso, H.R. Sasse, R. Snethlage, Group Report "How can we ensure the responsible and effective use of treatments (Cleaning, consolidation, protection)" In: *Saving our Architectural Heritage. The Conservation of Historic Stone Structures*, N.S.Baer and R. Snethlage, Editors, John Wiley & Sons, Chichester (1996) 293-313.
- [4] A. Gerdes, F.H. Wittmann, Quality Control of Surface Treatments with Water Repellent Agents *Proceedings of the 1st International Symposium on Surface Treatment of Building Materials with Water Repellent Agents*, A.J.M.Siemes, L.G.W.Verhoef, F.H.Wittmann, Editors, Delft University of Technology, Delft (1995) 15-1 – 15-7.
- [5] R.J. Koestler, A.E.Charola, M. Wypyski, J.J. Lee, Microbiologically Induced Deterioration of Dolomitic and Calcitic Stone as Viewed by SEM. *Proceedings, 5th International Congress on Deterioration and Conservation of Stone*, G. Felix, Editor. Presses Polytechniques Romande, Lausanne (1985) 617-626.
- [6] C. Ascaso, J. Wierzchos, J. Delgado Rodrigues, L. Aires-Barros, F.M.A. Henriques, A.E.Charola. Endolithic Microorganisms in the Biodeterioration of the Tower of Belem. *International Journal for Restoration of Buildings and Monuments* 4 [6] (1998) 627-640.
- [7] C. Ascaso, J. Wierzchos, V. Souza-Egypsi, A. de los Rios, J. Delgado Rodrigues In situ Evaluation of the Biodeteriorating Action of Microorganisms and the Effect of Biocides on Carbonate Rock of the Jeronimos Monastery (Lisbon). *International Biodeterioration and Biodegradation* 49 (2002) 1-12.
- [8] M.E. Young. Algal and Lichen Growth after Chemical Stone Cleaning. *Journal of Architectural Conservation* 3 (1998) 48-58

- [9] L.G.W. Verhoef, Water—A Paradox, the Prerequisite of life but the Cause of Decay. Proceedings of Hydrophobe III. 3rd International Conference on Surface Technology with Water Repellent Agents. K.Littmann and A.E.Charola, Editors. Aedificatio Publishers, Freiburg (2001) 21-36.
- [10] C.A. Grissom, A.E. Charola, M.J. Wachowiak. Measuring Surface Roughness of Stone: Back to Basics. Studies in Conservation 45 [2] (2000) 73-84.
- [11] J. Carmeliet. Water Transport—Liquid and Vapour—in Porous Materials: Understanding Physical Mechanisms and Effects from Hydrophobic Treatments. Proceedings of Hydrophobe III. 3rd International Conference on Surface Technology with Water Repellent Agents. K.Littmann and A.E.Charola, Editors. Aedificatio Publishers, Freiburg (2001) 171-178

