Studies on Polymeric Conservation Treatments of Ceramic Tiles with Paraloid B-72 and Two Alkoxysilanes

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ABSTRACT: The aim of this study was to evaluate the effect of different polymeric protections applied on ceramic tiles on their mechanical and water absorption properties. Three conservation products were used: the acrylic polymer Paraloid B-72 and two alkoxysilane-based formulations (tetraethoxysilane (TEOS) and IN2210, a polidimetilsiloxane-based formulation). The coatings were applied onto handmade tiles manufactured according to a 18th century procedure. Different application procedures (immersion, brushing, and spraying) were tested. The protection effectiveness was assessed through capillary water absorption and four point bending tests. The mineralogical characterization of tiles was undertaken by XRD. The best protective properties of the tiles were achieved by immersion treatments with Paraloid B-72 based on the protocols followed by the museums restoration departments. Nevertheless, the results of the present work show that the second immersion in Paraloid B-72 solution, commonly made, can be eliminated, as it does not provide any significant increase in the hydrophobic or mechanical properties of the tiles. As a result, there are obvious economical benefits, as the coating process became less time-consuming and more environmental friendly, as the amount of organic compounds is reduced. On the other hand, the use of small volumes of Paraloid B-72 solution applied by brush, or IN2210 sprayed can provide good results, if the only purpose of the treatment is the increase of the hydrophobic properties. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2833–2839, 2010

Key words: coatings; monument protection; Polysiloxanes; Paraloid B-72; mechanical properties

INTRODUCTION

Tiles are used either in the interior or in the exterior of buildings, as wall coverings. In particular, tiles that cover the façades of the buildings are exposed not only to thermo hygrometric cycles but also to atmospheric pollutants, which may cause or even accelerate the materials degradation. Besides their protective importance tiles also have aesthetic functions and are an important part of the cultural heritage of several countries as in Portugal, where they have been used without interruption since the 15th century. During the last decades, cultural heritage issues merited increasing attention of the scientific community, but there are many works focused on stone and mortar protection[1–10] the literature on ceramic tiles conservation is scarce.[11–13]

The growth of the protecting activity of buildings contributed to the appearance of a wide variety of products used in restoration treatments. Different types of synthetic coatings have been used for the protection of historical monuments.[5] The most common coatings are based on acrylics,[1,5–7,9] alkoxysilanes,[3–5,9] fluorinated polymers,[4–6] and hybrid organic and inorganic products.[5] A good coating should provide impermeability to liquid water, permeability to water vapour, oil repellence, absence of colour, chemical inertness, and environmental stability. Inorganic materials such as silicates of sodium, potassium, or lithium have also been successfully applied in the protection of monuments.[5]

As aforementioned, polymers based on acrylics copolymers are widely used in the protection of monuments. They are commercially designated by Paraloid, Primal, Acrilem, and Elvacite.[1,14] Paraloid B-72 is, by far, the most used acrylic polymer, although there are several types of Paraloid formulations available, such as, Paraloid B-66 and Paraloid B-67.[5,9] Acrylic based polymers are polymerized *in situ* to form protective films.[5]

In the last 20 years, the alkoxysilanes (silanes), such as methyltrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS), have been extensively used in monuments protection.[5,15] After the application of the polymer on the stone surface, the alkoxysilanes are hydrolyzed by water to produce alkoxysilanols, which polymerize in a condensation reaction to give

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a silicone polymer. The water necessary for this reaction may come from the atmosphere or from the stone itself or may be added for that purpose.[15] In the latter case, a solvent may be needed to make the mixture miscible. A catalyst may also be added.[5,15] The condensation and often the hydrolysis reactions take place after the polymer has been absorbed by the stone.[15] This procedure is known as *in situ* sol-gel process.[5]

Among the commercially available TEOS based products, the most used is Wacker OH that consists of partially hydrolyzed and prepolymerised tetraethoxysilane and tin dibutyldilaurate catalyst in ethanol.[16]

The consolidation of stones with alkoxysilane has some disadvantages as the variation in composition and structure of stones may modify consolidant–stone interaction.[17] Also, the drying of the gel is accompanied with shrinkage, which may lead to cracks inside the stone.[18] The addition of titania, alumina or silica particles to Wacker based consolidant showed a significant reduction on the silicate shrinkage and an increase in mechanical properties.[16]

Although it was not yet performed on monuments protection, the application of TEOS based silica aerogels obtained by a two-stage sol–gel process[19–21] could lead to a decrease in the volume shrinkage giving rise to a better coating.

Several works describe the applications of mixtures of Paraloid B-72 dissolved in an alkoxysilane such as MTMOS, as the acrylics polymers provide adhesive properties to the mixture that the alkoxysilane by itself is not able to provide.[15] A mixture of an acrylic polymer (Paraloid B-72) with silicone (Dri-Film 104) known as *Bologna Cocktail* was also employed on stone monuments.[10]

The changes in the surface chemistry properties obtained with fluorinated polymers as protective coatings leads to the increase of surface hydrophobicity.[5,15,22] However, fluorinated polyurethanes and polytetrafluoroethene (PTFE) have a poor ability to adhere to the stone. In fact, an evaluation of the behaviour of Paraloid B-72 as protective product on stones in comparison with a fluoroelastomer coating revealed that the acrylic based polymer had a better performance.[6] Subsequent developments report the synthesis of compounds containing functional groups that provide a better adherence to the stone surface.[5,15]

Recently, nanocomposites or dispersion of nanoparticles have been introduced in the protection field.[23,24] For example, a nano-scale dispersion of an organoclay was introduced in Fluormet CP, a blend of fluoroelastomers and acrylic polymers with successful results in the consolidation and protection of stone.[25]

As previously mentioned, the literature on the protection and conservation of tiles is rare.[11–13] Protective materials used on tiles were Paraloid B-72,[11,12] Wacker OH,[11,13] mixtures of both,[13] and a polyurethane based coating.[11] The treatments with Paraloid B-72 and polyurethane were found to be effective in blocking the porosity, while Wacker OH was deposited on the pores walls without causing an effective blocking of the porosity.

As referred, there are several conservation products commercially available, but the selection of the most appropriate protection product is a delicate task, as many factors are involved, such as the properties of the substrate. The products can be diluted with solvents, usually organic solvents, to reduce their viscosities that give rise to a deep penetration.[3,4] Due to the increase of environmental awareness, studies concerning the decrease of the amount of organic solvents used in coating process became important, as well as the development of water-based emulsions protecting products.[1]

In this work, the efficacy of tile protection by synthetic coatings was studied. The substrates used were handmade tiles, which are manufactured in a factory, according to 18th century procedure. The purpose of using these tiles is to try to reproduce the behaviour of old tiles, which are rare and more difficult to obtain. Three protective products, selected from two of the most widely employed consolidant families were used, namely, two alkoxysilane-based formulations (tetraethoxysilane and a polidimetilsiloxane-based formulation) and an acrylic-based resin (Paraloid B-72). The silane based formulations were applied to the tiles as received to promote *in situ* hydrolysis and condensation reactions, following the procedure described for stones.[5,15] Water absorption and bending strength tests were conducted in both treated and untreated samples to evaluate the effect of the protection treatments on the tiles properties.

EXPERIMENTAL

Samples preparation

Tiles received from the factory "*Fábrica Sant' Anna*" (Lisbon, Portugal) were cut into pieces of approximately 140 mm × 30 mm × 8 mm (length × width × height).

The protective products tested in this work were: Paraloid B-72, poly(ethyl methacrylate-co-methyl acrylate); TEOS, tetraethoxysilane (Fluka, 98%); and IN2210, a polidimetilsiloxane based product commercialized by Sista (Henkel). TEOS and IN2210 were applied as received, without any further dilution, whereas Paraloid B-72 was further diluted.

The products were applied by different methods: brushing, spraying or immersion. Before any treatment, tiles were dried overnight at 105°C in an oven with forced ventilation, after which they were weighted. For spraying and brushing treatments the amount of impregnation product was measured with a graduated cylinder and applied on the tiles surface with a brush or with a sprayer. The amount of polymer used was different in each case, but typically had the values of 1.0, 3.5, and 7.0 cm^3. Immersion treatments were made with Paraloid B-72 solution following the actual protocol used in museums, namely in 'Museu Nacional do Azulejo' (Lisbon, Portugal). The samples were first immersed in acetone, until no bubbles release was observed (typically 30 min.), and then immersed twice in the Paraloid B-72 solution for 3 h. Before the second immersion treatment with Paraloid B-72 was applied, the previously treated sample was left to dry at room temperature until a constant weight is achieved. To disclose the importance of this multi-steps methodology, a sample submitted to only one immersion in Paraloid B-72 solution was also prepared. The samples were placed in a way that only the ceramic body was in contact with the polymer solution. In any case, to check the amount of product absorbed the final weight of the samples was determined.

Samples were denoted by the name of the impregnation product. In the case of Paraloid treated tiles, the concentration of the polymer in solution was also indicated. The application procedure is also referred in the sample designation where capital letters are used: S for spraying, B for brushing, and I for immersion. The amount of polymer used in an impregnation treatment will also be written, after the capital letter. If a sample suffered two treatments, for instance with 7.0 cm^3 of polymer solution in each one, it will be denoted by 7 + 7. It must be noted that, in spaying and brush methods the maximum amount of solution used was 7 cm^3, which corresponds to the volume of the open porosity of the specimens.

X-ray powder diffraction

The mineralogical composition of the ceramic body of the tiles was determined by powder X-ray diffraction (XRD). To perform the analysis, after removing the glaze the ceramic body was crushed to powder in an agate mortar. XRD patterns were recorded on a Philips PW 1730 diffractometer using CuKα (λ = 1.5406 Å) graphite-monochromatised radiation. Patterns were obtained by step scanning from 15 to 50° 2θ, with a step size of 0.05° 2θ, a time per step of 0.5 s and 40 kV and 30 mA in the X-ray tube.

Water absorption

Capillarity water absorption tests were conducted at room temperature following to the UNI 10,921/2001 specifications.[26] Specimens were previously dried overnight at 105°C. After cooling to room temperature and weighing, the samples were placed over a 1 cm filter paper pile that was immersed in distilled water up to half of its height. Periodically the samples were removed, dried with a lint free cloth, and weighed in a Metler AE 240 analytical balance. The total absorption capacity was determined by the amount of water retained after 24 h.

Bending strength

Four point bending tests were made to evaluate the flexural strength of treated and untreated tiles (inner span of 40 mm and outer span of 80 mm). The tests were conducted in a universal testing machine (Model 4302, Instron Corporation, Canton). The cross-head speed was 0.5 mm/min and a load cell of 10 kN was used. Three samples were tested for each conservation treatment. Tests were performed with 24 untreated samples, which were analyzed using the Weibull statistics.[27,28]

RESULTS AND DISCUSSION

Mineralogical composition

Figure 1 displays the X-ray diffraction pattern of the ceramic body. The crystal phases were identified by means of the diffraction data collected by International Center for Diffraction Data (ICDD).[29] The result shows that besides quartz (SiO_2, ICDD: 33–1161) and calcite ($CaCO_3$, ICDD: 5–586), presented in the raw material, neoformed mineral phases, formed at the expenses of original existing ones are also found. Gehlenite ($SiO_2 \cdot Al_2O_3 \cdot 2CaO$, ICDD: 35–755), resulting from the reaction of clay minerals and calcite, and diopside ($CaMgSiO_6$, ICDD: 11–654) and wollastonite ($CaSiO_3$, ICDD: 42–547), silicates were formed at the expense of dolomite and calcite, respectively. Traces of mulite ($3Al_2O_3 \cdot 2SiO_2$, ICDD: 15–776) are also present as expected, as the firing

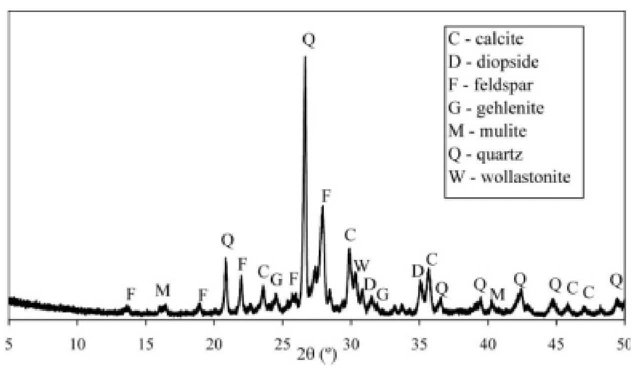

Figure 1 X-ray diffraction pattern of the ceramic body.

temperature attained in the furnace is around 1020°C.

The set of peaks that appear at 2θ between 27° and 29° are identified in Figure 1 as feldspars. These minerals could exist in the raw material but can also be formed by the reaction of calcite and kaolinite during the calcinations.[30] Nevertheless, some contribution of other phases must be considered, namely diopside and wollastonite. The latter must be responsible by the small peaks at 27.6° and 28.5° 2θ, and the former contributes to the intense peak centered at 28° 2θ.

It is worth to note that the X-ray diffraction pattern resembles the patterns obtained for old ceramic tiles.[12] In fact, the presence of quartz, calcite, gehlenite, diopside, and mulite was detected in ceramic tiles of the 17th, 18th, and 19th–20th centuries although the relative amount of each crystalline phase is different.[12] This seems to point out that the technological procedure was close to one of the 18th century, but the raw material used seems to be richer in quartz. So, with some precaution one can consider that the results obtained with these contemporary tiles can be extrapolated to old tiles for which the consolidation treatments are of fundamental importance.

Amount of polymer absorbed

The amounts of polymer retained (*rp*) and the results of capillary water absorption essays are shown in Table I. On the samples treated with Paraloid B-72, the immersion in solution provides the greatest amounts of polymer absorbed in accordance with the results reported for stone consolidation.[2] On the other hand, a second treatment, either by immersion or by spray, doubles the amount of Paraloid absorbed. This could mean that spraying is a suitable procedure, nevertheless, confronting the rp values of samples Paraloid-10-S-7 and Paraloid-10-B-7, the loss of polymer is evident. In the case of TEOS there is no such difference. This is most likely because during spraying there is a considerable volatilization of the Paraloid solution, where the solvent is acetone. In fact, experimentally we observed that spraying last quantities of solution was always very difficult as it became more viscous (even using a 10% solution). Experimental work using 15 and 25% Paraloid solutions was found to be especially difficult. In particular, spraying with a common laboratory sprayer was almost impossible. The application of the samples, Paraloid-10-B-7 and Paraloid-15-B-7, by brush was also not an easy task since a considerable amount of polymer is retained in the brush.

Whatever the methodology used with TEOS and IN2210 the amount of polymer absorbed was always smaller than what is found for Paraloid treated tiles.

Water absorption tests

The capillary water absorption essays enable the evaluation of the absorption coefficient, *A*. This coefficient is determined from the slope of the initial part of the graphic representation of the weight difference between dried and wet samples per unit area of the ceramic body in contact with water, against the square root of the immersion time. The maximum water content, *CI*, is defined as the water

TABLE I
Amounts of Polymer Retained and Results of Water Absorption (The Error Associated to Data Is Less than 1%) and Mechanical Tests

Sample	*rp*[a] ($mg\ cm^{-2}$)	*CI* (%)	*A* ($g\ cm^{-2}\ s^{-1/2}$)	*op* (%)	σ_f (MPa)
Untreated	–	16.5	1.7×10^{-2}	27.7	16.94 ± 2.22
Paraloid-10-I –a	0.78 ± 0.25	0.4	3.0×10^{-5}	0.8	23.57 ± 4.56
Paraloid-10-I-b	1.44 ± 0.38	0.4	3.0×10^{-5}	0.7	25.62 ± 3.98
Paraloid-10-S-7	0.27 ± 0.01	15.7	8.0×10^{-4}	26.6	15.98 ± 4.06
Paraloid-10-S-7+7	0.45 ± 0.15	8.9	2.0×10^{-4}	14.5	18.01 ± 1.09
Paraloid-10-B-7	0.50 ± 0.04	0.2	5.0×10^{-5}	0.4	15.72 ± 4.15
Paraloid-10-B-3.5	0.27 ± 0.03	2.0	5.0×10^{-5}	3.4	19.62 ± 2.24
Paraloid-15-B-7	0.35 ± 0.03	0.2	1.0×10^{-5}	0.4	17.88 ± 1.14
TEOS-S-7	0.05 ± 0.01	17.0	4.2×10^{-3}	28.7	17.67 ± 3.30
TEOS-S-7+7	0.15 ± 0.12	14.5	2.0×10^{-4}	24.8	15.93 ± 2.04
TEOS-B-7	0.04 ± 0.01	16.1	1.0×10^{-4}	27.6	17.37 ± 2.91
TEOS-B-7+7	0.07 ± 0.01	14.4	6.0×10^{-4}	22.6	18.24 ± 3.93
IN2210-S-7	0.07 ± 0.01	0.6	5.0×10^{-5}	1.1	19.93 ± 2.76
IN2210-S-1	0.02 ± 0.01	1.4	3.0×10^{-4}	2.4	15.34 ± 2.35

S, spraying; B, brushing; I, immersion (a - means only one immersion and b - means two immersions); 7, 3.5 and 1cm^3 are the amounts of product used; 7+7 – means two treatments with 7 cm^3 of product each.

[a] *rp*: amount of polymer retained per unit surface.

saturation amount relative to the weight of the dried sample, and estimated from the amount of water retained after 24 h. The open porosity, *op*, is calculated according to the equation:

$$op = \frac{(w_{\text{sat}} - w_{\text{dried}})/d_{\text{water}}}{V_{\text{sample}}} \quad (1)$$

where w_{sat} and w_{dried} are the weights of the water saturated and dried sample, respectively, d_{water} is the water density, at the working temperature, and V_{sample} the volume of the sample.

The values of all the evaluated parameters are displayed in Table I. Starting the analysis with the tiles treated with Paraloid by immersion, that is, the procedure commonly used in museums restoration departments, it is interesting to note that although the second immersion lead to an increase of the amount of polymer retained there is no significant changes in what concerns the water absorption properties. On the other hand, for the samples where the polymer was applied by brushing, in particular samples Paraloid-10-B-7 and Paraloid-15-B-7, the values of *CI* and *A* are of the same order of magnitude of those obtained with the tiles treated by immersion. The inefficiency of spraying is evident since only the sample treated with a two steps protocol shows some improvement in its hydrophobic character expressed in the decrease of *CI* and *A*.

Tiles treated with the two alkoxysilane-based formulations show distinct behavior. In fact, although a decrease of the water capacity absorption coefficient is observed for both formulations, with IN2210 it was possible to obtain values of the same order of magnitude of those presented by the more efficient Paraloid treatments, and a significant decrease of *CI*. For TEOS treated samples a less pronounced increase of hydrophobic characteristics upon impregnation was observed. Nevertheless, a decrease of two orders of magnitude on the water capacity coefficient is noticed, in almost all the samples; and for the samples where a second application of TEOS was made, either by brush or spraying, the maximum water content is around 12% lower than that of the untreated sample. These results show that although the methodology used lead to the impregnation of a relatively small amount of polymer, *in situ* hydrolysis and condensation reactions occurred to some extent.

Mechanical properties

The efficiency of the coatings' protection on tiles mechanical properties was evaluated by bending tests that were carried out on both untreated and treated samples. An example of a four bending test of a ceramic tile is shown in Figure 2.

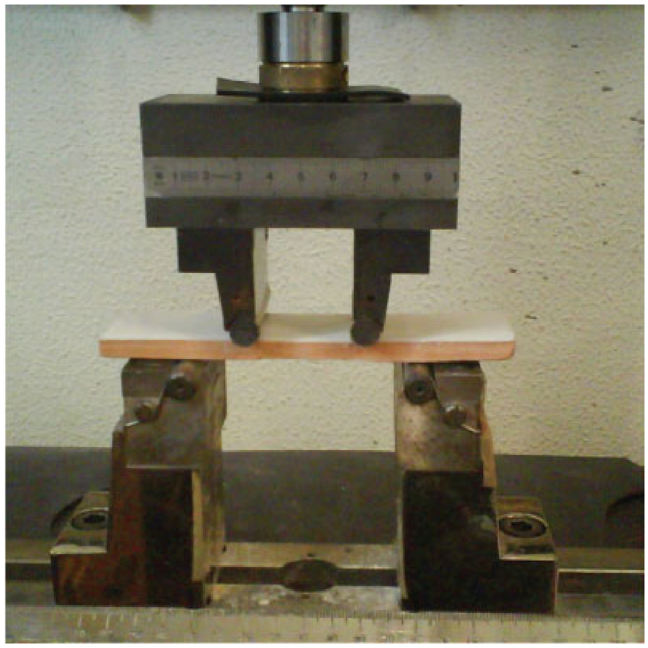

Figure 2 Four point bending test of a ceramic tile. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The fracture load $F_{\max}$,, *i.e.* the maximum load attained by one sample, is used to determine the bending strength σ_f with equation:

$$\sigma_f = \frac{3}{2}\frac{F_{\max}L}{bh^2} \quad (2)$$

where L is the distance between support points and b and h are the cross-sectional dimensions of the tile. In Table I the average and the standard deviation of the bending strength σ_f for each treatment are indicate.

As a considerable number of untreated samples were tested, the application of the Weibull statistical analysis was possible. As for other brittle materials, the bending strength varies from specimen to specimen and it is more precisely described with a statistical measure of its variability, i.e., the Weibull modulus, *m*.[27,28] The parameter P is considered to be the probability of failure at a stress σ_f. P values are assigned, after ranking the strength data from the smallest to largest, according to

$$P = \frac{i - 0.5}{N} \quad (3)$$

where i is the rank and N the total number of specimens. Weibull analysis may assume a relatively simple power-law stress function for the survival of the elements in the group:

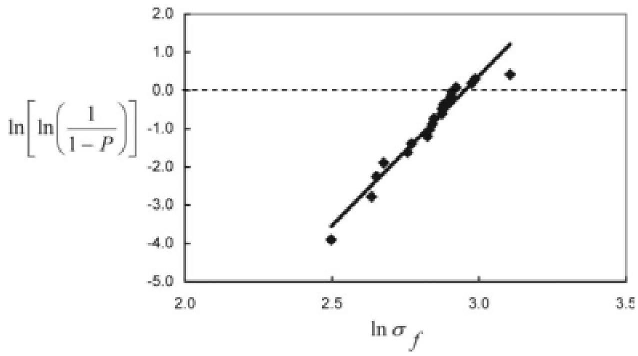

Figure 3 Weibull statistical analysis for untreated samples, with $y = \ln[\ln(\frac{1}{1-P})]$ as a function of $x = \ln\ \sigma_f$. A best fit (—) to the data (◆) gives $m = 7.835$.

$$P = 1 - \exp\left\{-\left(\frac{\sigma_f}{\sigma_0}\right)^m\right\} \quad (4)$$

where, σ_0 and m are, respectively, the scale parameter and the shape parameter.[14] Equation (4) may be linearised in the form $y = A + Bx$ where $y = \ln\left[\ln\left(\left(\frac{1}{1-P}\right)\right)\right]$, $A = -m \ln \sigma_0$, $B = m$, and $x = \ln \sigma_f$. Figure 3 represents $y = \ln\left[\ln\left(\left(\frac{1}{1-P}\right)\right)\right]$ as a function of $x = \ln \sigma_f$ for the untreated samples tested. As a result of the best fit to the data, a Weibull modulus of 7.835 could be found. The value of this modulus shows a small variation in measured bending strengths.

As a consequence of conservation treatments an improvement of the mechanical resistance is usually observed, as the result of the porosity decrease. Nevertheless, the results of Table I shows that with the exception of the tiles submitted to immersion treatment with Paraloid B-72, all the other treated samples have almost the same flexural resistance as the untreated tile, in spite of showing identical porosity (measured as *op* from the water absorption essay) as Paraloid B-72 immersed tiles. Even following different impregnation strategies the inefficiency of TEOS for pore blocking is referred in the literature. For instance the results reported in Ref. 11 permitted to conclude that TEOS appear to be deposited as surface coating.[11] In general, ethylsilicates, like TEOS, polymerize inside the tile and amorphous silica is formed, which may lead to an increase of the flexural strength.[3] However gel shrinkage may cause the appearance of cracks inside the tile, as happens with stone,[18] which will not improve the mechanical resistance.

In this work, it seems that with the exception of the immersion in Paraloid B-72, all the treatments resulted only in a surface coating, and no penetration inside the tile was achieved. It must be also stressed that the increase of the bending strength attained with the second immersion treatment of the Paraloid-10-I-a and b samples is negligible.

CONCLUSIONS

This study was focused on tiles' conservation, an important cultural heritage issue, particularly for South Europe where tiles have been widely used in building constructions for several centuries. The efficiency of the coating treatments was investigated with three different products aiming to combine the protection of cultural heritage artefacts with a more sustainable development, reducing the amount of organic compounds used in the treatments.

The experimental results obtained allow concluding that the improvement of both water absorption and mechanical properties was achieved only when immersion treatments with Paraloid B-72 were used. Nevertheless, the second immersion treatment on Paraloid B-72 solution, followed by the museums restoration departments, does not confer any significant increase in the hydrophobic or mechanical properties of the tiles. As a consequence, the elimination of this second step can be envisaged with time and economical benefits but, above all, turning the process more environmentally friendly. On the other hand, if the purpose of the treatment is only the increase of the water repulsion properties, the use of small volumes of Paraloid B-72 solution applied by brush, or IN2210 sprayed can be an option that allies environmental benefits with reductions in cost and time.

Concerning the use of TEOS, it was applied as received following the procedure described for stones where *in situ* hydrolysis and condensation reactions are promoted.[5,19] The results obtained show that the polymerization occurred to some extent as some improvement in the hydrophobic properties of the samples was observed.

This article is a first step of a deeper study focused on the use of several polymeric coatings for tiles protection. Different forms of application intending to minimize the amount of organic solvent will continue to be essayed. Besides the characterization described in this article, the determination of pore size distributions, either by structural characterisation with SEM either with mercury porosimetry is foreseen. Also, other mechanical tests which include scratch and hardness tests will be done. The effects on the weathering conditions will be evaluated by changing the humidity and temperature conditions.

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References

1. Carretti, E.; Dei, L. Prog Org Coat 2004, 49, 282.
2. Ferreira Pinto, A. P.; Delgado Rodrigues, J. J Cult Herit 2008, 9, 38.
3. Cnudde, V.; Dierick, M.; Vlassenbroeck, J.; Masschaele, B.; Lehmann, E.; Jacobs, P.; Van Hoorebeke, L. J Cult Herit 2007, 8, 331.
4. Tsakalof, A.; Manoudis, P.; Karapanagiotis, I.; Chryssoulakis, I.; Panayiotou, C. J Cult Herit 2007, 8, 69.
5. Sadat-Shojai, M.; Ershad-Langroudi, A. J Appl Polym Sci 2009, 112, 2535.
6. Camaiti, M.; Bugani, S.; Bernardi, E.; Morselli, L.; Matteini, M. Appli Geoche 2007, 22, 1248.
7. Bracci, S.; Melo, M. J. Polym Degrad Stab 2003, 80, 533.
8. Zoghlami, K.; Gómez-Gras, D.; Álvarez, A. In Proceedings of the 6th International Symposium on the Conservation of Monuments in the Mediterranean Basin. Aires De Barros, L., Zezza, F., Eds.; Oceanus: Lisbon, 2004; 501.
9. Favaro, M.; Mendichi, R.; Ossola, F.; Russo, U.; Simon, S.; Tomasin, P.; Vigato, P. A. Polym Degrad Stab 2006, 91, 3083.
10. Favaro, M.; Mendichi, R.; Ossola, F.; Simon, S.; Tomasin, P.; Vigato, P. A. Polym Degrad Stab 2007, 92, 335.
11. Ribeiro Carrott, M. M. L.; Farinha Antunes, J. L.; Carrot, P. J. M. In Proceedings of the 4th International Symposium on the Conservation of Monuments in the Mediterranean Basin. Rhodes, A., Moropoulou, F., Zezza, E., Kollias, I., Eds.; Technical Chamber of Greece: Athens, 1997; p 79.
12. Vaz, M. F.; Pires, J.; Carvalho, A. P. J Cult Herit 2008, 9, 269.
13. Farinha Antunes, J. L. Caracterização de azulejos do século XVII. Estudos para a sua consolidação, MSc Thesis, Instituto Superior Técnico, Lisbon, 1992.
14. Cocca, M.; D'arienzo, L.; D'orazio, L.; Gentile, G.; Martuscelli, E. Polym Test 2004, 23, 333.
15. Price, C. A. Stone Conservation: An Overview on Current Research; The Getty Conservation Institute: Santa Monica: California, 1996. Available at: http://www.getty.edu/conservation/publications/pdf_publications/stoneconservation.pdf.
16. Milliani, C.; Velo-Simpson, M. L.; Scherer, G. W. J Cult Herit 2007, 8, 1.
17. Mosquera, M. J.; Pozo, J.; Esquivias, L.; Rivas, T.; Silva, B. J. Non-Cryst Solids 2002, 311, 185.
18. Mosquera, M. J.; Pozo, J.; Esquivias, L. J. Sol-Gel Sci Technol 2003, 26, 1227.
19. Rao, A. V.; Wagh, P. B.; Haranath, D.; Risbud, P. P.; Kumbhare, S. D. Ceram Int 1999, 25, 505.
20. Rao, A. V.; Bhagat, S. D. Solid State Sci 2004, 6, 945.
21. Bandyopadhyay, A.; Sarkar, M. D.; Bhowmick, A. K. J Mater Sci 2006, 41, 5981.
22. Torrisi, A. J Cult Herit 2008, 9, 135.
23. Baglioni, P.; Giorgi, R.; Dei, L. C R Chem 2009, 1261.
24. Baglioni, P.; Giorgi, R. Soft Matter 2006, 2, 293.
25. D. Arienzo, L.; Scarfato, P.; Incarnato, L. J Cult Herit 2008, 9, 253.
26. International Standard UNI 10921:2001., Cultural Heritage - Natural and Artificial Stones - Water Repellents - Application on Samples and Determination of their Properties in Laboratory, Milan, 2001.
27. ASTM C 1239-06A. Standard Practice for Reporting Uniaxial Strength Data and Estimating Weibull Distribution Parameters for Advanced Ceramics (2007).
28. Weibull, W. J Appl Mech 1951, 18, 293.
29. International Center for Diffraction Data. Power Diffraction File Alphabetical Index; International Center for Diffraction Data: Swarthmore PA, 1988.
30. Sanjad, T.; Angelica, R.; Oliveira, M.; Costa, W. R Esc Minas Ouro Preto 2004, 57, 255.