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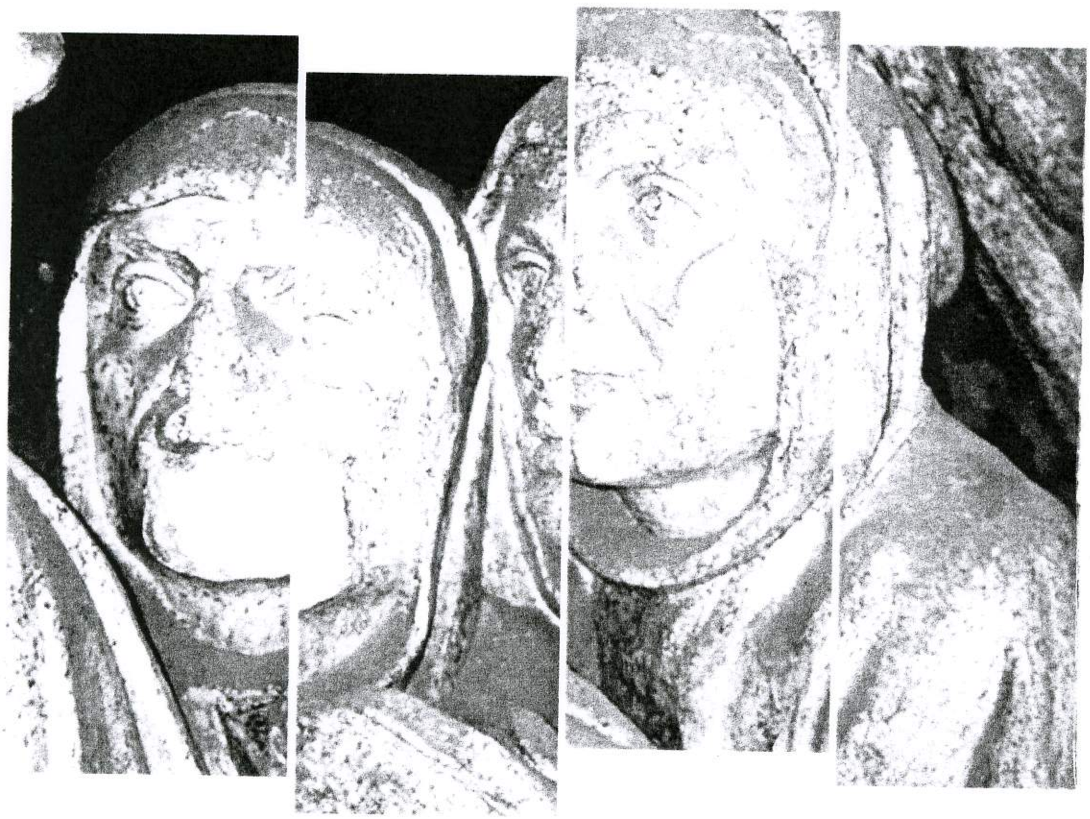

Stone consolidation in cultural heritage
research and practice

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Influence of the application methodologies on the distribution of consolidant products within a porous material

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SUMMARY: The aim of this study is to estimate the distribution of several consolidants into brick samples in relation to the product application methodology. Samples were treated by total immersion, by capillarity and by vacuum impregnation. Several commercial consolidants were used, namely Acryl 33, Paraloid B72, Akeogard CO, Akeogard ME and an ethyl silicate in isopropyl alcohol. Mercury intrusion porosimetry was used to determine the total open porosity, pore size distribution before and after treatment and to assess the product distribution inside the material. The study concludes that products tend to distribute in specific ranges of the pore size in relation to their application methodology and chemical - physical characteristics.

KEY- WORDS: consolidant, porosity, conservation, penetration depth, stone conservation.

INTRODUCTION

The decay process of historical buildings exposed outdoors is the direct consequence of numerous solicitations caused by external factors (such as natural agents or anthropic activities), which determine the loss of many specific characteristics of the material like hardness, stability and particle cohesion [1, 2, 3]. The deterioration condition of the material often requires protective or consolidation operations in order to withstand the alteration processes. The consolidation procedure has the fundamental function of re-establishing the particle cohesion and the physical properties; therefore the indispensable consolidant requirements are related to the depth of penetration, the effect on the porosity of the consolidated material, the changes of water vapour permeability of the treated stone, the chromatic variation and the durability of the treated material [4, 5].

Certainly the success of a consolidating operation depends above all on the capability of the consolidant penetration in depth, which is correlated to its viscosity, solvent evaporation rate, surface tension, product application condition and methodology and, finally, to the porosity and pore size distribution of the weathered material [6].

This study considers the influence of the application methodology on both the consolidating efficacy and the product distribution into a brick material treated with different categories of consolidants available in commerce.

MATERIALS AND METHOD

In this study four typologies of consolidant products were tested: Acryl 33 (Bresciani srl, Italy), an ester acrylic copolymer in aqueous dispersion (5% dispersion), Paraloid B72 (Rohm and Hass, USA), an ethylmethacrylate/methacrylate copolymer in ethyl acetate (5% solution), Akeogard ME (Syremont, Italy), a thetrafluoroethylene hexafluoropropene vinylidene fluoride copolymer in aqueous microemulsion (5% microemulsion) and ethyl silicate (Phase, Italy) in isopropyl alcohol (47% solution) [7, 8, 9, 10, 11].

Brick samples characterized by homogeneous porosity were cut to cubes of 5x5x5 cm^3 dimensions, dried in an oven for 24 h and then weighed (P0). Subsequently, each consolidant was employed to treat five brick samples using three different application methodologies: total immersion into product solution/dispersion for 16 hours, product capillarity absorption from a filter paper pad constantly imbibed with the consolidant for 16 hours and vacuum impregnation for 16 hours (the samples were out-gassed under vacuum in the desiccator at about 3·10-2 mbar for 45 minutes prior to impregnation). Immediately after polymer treatment samples were weighed (Pu) and left in desiccators for 20 days at room temperature and at relative humidity of 50%. The time of solvent evaporation was considered finished when the sample weight (Ps) variation between two following weighings realized in a 24 hours interval was lower than 0.1%.

The quantities ΔPu %= (Pu – P0)·100/ Pu and ΔPs %= (Ps – P0)·100/ P0 were taken into account in order to evaluate the amount of humid product absorbed (polymer + solvent or dispersed phase + continuous phase) and the real amount of polymer (or dispersed phase) inserted into the material, respectively.

The determination of the product distribution into brick specimens was carried out by mercury intrusion porosimetry (MIP) [12] evaluating the changes of the total cumulative volume and the pore size distribution before and after treatment [13, 14]. Since this measure did not show relevant cumulative volume variations beyond 5 mm in depth the analyzed samples correspond to the superficial layers with this thickness value.

RESULTS AND DISCUSSION

The comparison between ΔPu % and ΔPs % allows evaluating which imbibition technique results more efficacious in what concerns the polymer amount really absorbed by the material. Table 1 and Table 2 show ΔPu % and ΔPs %, respectively, and also report densities and relative viscosities of the employed products. The observed ΔPu % reveal that in all cases, except for the ethyl silicate one, the larger amount of absorbed consolidant is achieved by the vacuum impregnation method, as it was only to be expected. The application of ethyl silicate and Akeogard ME by immersion and capillarity methods respectively shows similar ΔPu% values, differently from what happened with the Acryl 33 and Paraloid B72 products, for which the immersion impregnation gave better results in comparison to the capillarity. Moreover, for a given consolidant its absorption appears almost independent of the specific application technique.

Table 1: Mean percentage weight variation of humid treated samples and physical properties of the used products

Product	ΔP_u% (by total immersion)	ΔP_u% (by capillarity)	ΔP_u% (by vacuum impregnation)	Density* (gr/cm³)	Viscosity* (20°C, cP)
ACRYL 33 (5%)	15.81 ± 1.20	13.84 ± 1.20	16.61 ± 1.10	1.00	1.21
PARALOID B72 (5%)	15.49 ± 1.50	14.12 ± 0.90	16.58 ± 1.20	0.80	1.20
ME (5%)	14.82 ± 1.10	14.56 ± 1.50	15.89 ± 1.20	1.36	1.15
ETHYL SILICATE (47%)	15.89 ± 1.40	15.37 ± 0.75	15.07 ± 1.20	0.95	1.01

*= measured with densimeter and Ostwald viscosimeter

Table 2: mean percentage weight variation of dry treated samples and physical properties of the used products

Product	ΔPs% (by total mmersion)	ΔPs% (by capillarity)	ΔPs% (by vacuum impregnation)	Density* (g/cm³)	Viscosity* (20°C, cP)
ACRYL 33 (5%)	0.15 ± 0.05	0.46 ± 0.09	0.29 ± 0.1	1.00	1.21
PARALOID B72 (5%)	0.67 ± 0.20	0.53 ± 0.25	0.78 ± 0.18	0.80	1.20
ME (5%)	0.43 ± 0.13	0.26 ± 0.16	0.57 ± 0.12	1.36	1.15
ETHYL SILICATE (47%)	6.88 ± 0.19	6.78 ± 0.15	7.37 ± 0.22	0.95	1.01

*= measured by densimeter and Ostwald viscosimeter

The comparison of the ΔPs% data (table 2) revealed that the amount of polymeric residue in specimens is greater by vacuum impregnation, confirming the previous hypothesis that this method should be the best one. Acryl 33 reveals an exception because it shows an anomalous behaviour. In fact the ΔPs% gained by the vacuum method is lower than by the capillarity one although the ΔPu% obtained by the vacuum procedure is larger than the value achieved by the capillarity. Another anomalous behaviour is evident also in the case of Akeogard ME product. In fact, the ΔPs value obtained by the total immersion treatment results approximately one and half times the amount of the ΔPs% coming from the product capillarity application, although the corresponding ΔPu% are similar. The particular behaviour of Acryl 33 and Akeogard ME could be ascribed to a specific mechanism of absorption due to the particular nature of these types of polymers that belong to water dispersion and microemulsion categories [15].

Table 3 regards the untreated brick material data achieved by porosimetric analysis and it reports the values of the total cumulative volume, the cumulative volume distribution in specific ranges of the pore radius and the corresponding percentage values. The data point out that the majority of brick pores has radius between 0.6 – 0.2 μm while the remaining pore radii resulted homogeneously distributed in the other ranges.

Table 3: total cumulative volume of untreated brick and distribution values of cumulative volume and percentage cumulative volume in fixed ranges of pore radius

Pore radius range (μm)	Cumulative volume (mm^3/gr)	Cumulative volume %
20 - 0,6	16.7 ± 5.6	8.7 ± 2.9
0,6 – 0,4	60.8 ± 3.4	31.8 ± 1.8
0,4 – 0,2	72.3 ± 0.7	37.9 ± 0.4
0,2 – 0,1	20.1 ± 0.1	10.5 ± 0.1
< 0,1	18.6 ± 2.9	9.7 ± 1.5
Total cumulative volume (mm^3/gr)	191.0 ± 7.4	

Tables 4 - 7 show the average values of the cumulative volumes achieved by porosimetric analysis on five samples treated employing the three dissimilar methodologies. Table 4 reports the Acryl 33 data. Even though the samples treated by the different procedures absorbed quite different ΔPs% amount, the porosimetric results reveal a similar distribution of the product within the material and comparable variations of cumulative volume both in immersion, capillarity and vacuum impregnation. In all cases, the product not only tends to permeate the largest pores, but also favours the creation of many pores with size lower than 0.4 μm The vacuum impregnation is distinguished from the other two methods because by this procedure the percentage of pores with radius lower than 0.1μm results nearly fourfold (twofold) the same value obtained by immersion (capillarity).

Table 4: total cumulative volume of brick treated with Acryl 33, ΔPs% and distribution values of percentage cumulative volume in pore radius fixed ranges.

Pore radius range (μm)	Cum. Volume% (Untreated)	Cum. Volume% (by total immersion)	Cum. Volume% (by capillarity)	Cum. Volume% (by vacuum impregnation)
20 - 0.6	8.7 ± 2.9	2.6 ± 0.3	2.0 ± 0.4	1.4 ± 0.4
0.6 – 0.4	31.8 ± 1.8	30.1 ± 0.1	24.4 ± 5.7	16.5 ± 7.7
0.4 – 0.2	37.9 ± 0.4	42.8 ± 0.2	45.5 ± 6.8	48.7 ± 10.2
0.2 – 0.1	10.5 ± 0.1	11.4 ± 0.8	11.1 ± 0.4	10.8 ± 2.1
< 0.1	9.7 ± 1.5	13.1 ± 3.3	16.6 ± 3.6	22.1 ± 5.8
Total cumulative volume (mm^3/gr)	191.0 ± 7.4	177.1 ± 3.9	176. 8 ± 7.5	170.0 ± 2.5
ΔP_s%	---	0.2 ± 0.1	0.5 ± 0.1	0.3 ± 0.1

Table 5: total cumulative volume of brick treated with Paraloid B72, $\Delta P_s\%$ and distribution values of percentage cumulative volume in pore radius fixed ranges.

Pore radius range (μm)	Cum. Volume% (Untreated)	Cum. Volume% (by total immersion)	Cum. Volume% (by capillarity)	Cum. Volume% (by vacuum impregnation)
20 - 0.6	8.7 ± 2.9	2.4 ± 0.2	2.1 ± 0.7	2.6 ± 1.0
0.6 - 0.4	31.8 ± 1.8	27.2 ± 1.5	25.6 ± 1.4	34.7 ± 2.7
0.4 - 0.2	37.9 ± 0.4	32.6 ± 4.2	49.5 ± 3.2	44.2 ± 2.5
0.2 - 0.1	10.5 ± 0.1	13.3 ± 0.3	12.4 ± 0.3	9.5 ± 1.2
< 0.1	9.7 ± 1.5	24.5 ± 2.3	9.8 ± 1.3	8.4 ± 4.1
Total cumulative volume (mm³/gr)	191.0 ± 7.4	168.9 ± 1.2	164.2 ± 5.9	155.0 ± 9.2

Table 6: total cumulative volume of brick treated with Akeogard ME, $\Delta P_s\%$ and distribution values of percentage cumulative volume in pore radius fixed ranges.

Pore radius range (μm)	Cum. Volume% (Untreated)	Cum. Volume% (by total immersion)	Cum. Volume% (by capillarity)	Cum. Volume% (by vacuum impregnation)
20 - 0.6	8.7 ± 2.9	2.6 ± 0.7	2.3 ± 0.4	1.9 ± 0.1
0.6 - 0.4	31.8 ± 1.8	21.8 ± 2.9	21.2 ± 4.8	20.9 ± 5.9
0.4 - 0.2	37.9 ± 0.4	38.3 ± 3.1	47.8± 2.8	50.1 ± 4.6
0.2 - 0.1	10.5 ± 0.1	17.4± 0.1	13.6 ± 1.0	12.9 ± 0.3
< 0.1	9.7 ± 1.5	19.0 ± 4.5	15.1 ± 0.5	13.8 ± 1.2
Total cumulative volume (mm³/gr)	191.0 ± 7.4	181.1 ± 7.9	183.2 ± 5.7	178.8 ± 1.0
$\Delta P_s\%$	---	0.4 ± 0.1	0.3 ± 0.2	0.6 ± 0.1

The Paraloid B72 applied with the different methodologies (table 5) seemed to have different distributions in the brick specimens. In all cases, the product reduces the pores with radius dimension between 20 – 0.6 μm. The immersion and the capillarity methodologies cause a further decrease of the pores with radius dimension between 0.6 – 0.4 μm and the consequent increase of the pore radii in the range 0.4 – 0.2 μm in the case of the samples treated by the capillarity procedure. The immersion methodology seems to favour a better product depth penetration, increasing the pores with dimension lower than 0.2 μm. The vacuum impregnation involves a reduction of the pores with radius larger than 0.6 μm and the increase of the lower ones. The cumulative volume seems out of line with the $\Delta P_s\%$. Perhaps the product spread differently into the samples; in particular, the vacuum impregnation appears to obstruct the product depth penetration while the immersion procedure seems to facilitate it. Probably porosity measurements carried out with more sensitive systems could give more information (considering also the substantial standard deviation value obtained by the vacuum impregnation porosity measures).

Table 7: total cumulative volume of brick treated with ethyl silicate, $\Delta P_s\%$ and distribution values of percentage cumulative volume in pore radius fixed ranges.

Pore radius range (μm)	Cum. Volume% (Untreated)	Cum. Volume% (by total immersion)	Cum. Volume% (by capillarity)	Cum. Volume% (by vacuum impregnation)
20 - 0.6	8.7 ± 2.9	2.8 ± 0.1	2.9 ± 0.3	3.5 ± 0.1
0.6 – 0.4	31.8 ± 1.8	29.2 ± 16.3	23.9 ± 8.4	38.2 ± 9.3
0.4 – 0.2	37.9 ± 0.4	37.7 ± 10.9	50.3 ± 7.8	38.8 ± 1.6
0.2 – 0.1	10.5 ± 0.1	4.8 ± 0.2	5.6 ± 0.8	4.4 ± 0.7
< 0.1	9.7 ± 1.5	25.6 ± 2.4	17.7 ± 1.7	15.2 ± 2.6
Cumulative volume (mm^3/gr)	191.0 ± 7.4	88.5 ± 2.8	95.9 ± 2.8	92.1 ± 13.1
$\Delta P_s\%$	---	6.9 ± 0.2	6.8 ± 0.2	7.4 ± 0.2

The Akeogard ME porosimetric data (table 6) put in light a similar distribution of the product in the material and comparable percentage variation of cumulative volume in the immersion, capillarity and vacuum impregnation cases. In fact, in all cases, the product penetrates and permeates the pores with radius dimension between 20 – 0.4 μm, it reduces the section of the pores and it creates a predominant and homogeneous amount of pores characterized by radius dimension smaller than 0.4μm. The capillarity and vacuum methodologies appear to favour the creation of pores with radius dimension between 0.4 – 0.2μm, whereas the immersion procedure seems to facilitate the formation of pores with dimensions lower than 0.2μm.

Finally, the results obtained by porosimetric analysis of the specimens treated with ethyl silicate (table 7) indicate that the product distributes into the porous material in three different ways. In fact the total immersion impregnation procedure seems to produce the permeation of almost all pore radius ranges, generating many pores with dimension lower than 0.1μm. The capillarity impregnation method promotes the pore permeation with the reduction of pore radii both between 20 – 0.4μm and 0.2 – 0.1μm, but in this case the mechanism of distribution of the polymer favours not only the formation of pores with dimensions lower than 0.1 μm but also the generation of pores within 0.4 – 0.2 μm; moreover it is ascertained that the ethyl silicate tends also to fill or to block many pores. The vacuum impregnation treatment causes the permeation of the largest pores and of the pores of 0.2 – 0.1 μm, and it produces mainly the increase of the smallest pores and partially the growth of pores with dimension between 0.6 – 0.2 μm. As it has been just observed, the ethyl silicate shows different behaviours depending on the chosen application method, as it was observed also in the Paraloid B72 case.

CONCLUSION

The tests made on the specimens point out how 5 mm superficial layers of bricks treated with different consolidants (Acryl 33, Paraloid B72, Akeogard ME, ethyl silicate) and distinct application methodologies (total immersion, capillarity, vacuum impregnation) were modified. Apart from the application methodologies all products show a similar amount of humid absorbed product (ΔPu %). Instead, the dry polymer amount that remained within the materials is different, generally being lower than the theoretical value (in particular in the cases of Akeogard ME and Acryl 33 water solvent products). The amount of humid absorbed product by immersion is comparable to the quantity obtained by the capillarity procedure; these values result not much higher in the case of vacuum impregnation.

The investigation of the 5 mm superficial layers of the treated samples highlights that:

- The water dispersion products (Akeogard ME and Acryl 33) tend to reduce the section of the pores with radius dimension higher than 0.4 μm and to increase the pores with radius lower than 0.2μm. The two products do not show substantial differences although Acryl 33 is a macrodispersion (particle size = 150 nm) and Akeogard ME is a microdispersion (particle size = 15 nm).
- The product application methodology influences the distribution of Paraloid B72: the immersion procedure reduces the pore section with radius higher than 0.2 μm and it increases the pores with lower dimension. The capillarity method involves the reduction of the pore size larger than 0.4 μm and the increase of the pores with radius dimension 0.4 - 0.1 μm. The product seems not to cause a further pore increase. The vacuum impregnation seems to cause a similar behaviour: the product produces the reduction of the pore with radius dimension larger than 0.6 μm and it leaves unchanged the distribution of the pore radius lower 0.2 μm.
- As in the Paraloid B72 case, the ethyl silicate seems to feel the effect of the application methodology even if the presence of the product leads to the increase of pores with dimension lower than 0.1 μm.

The cumulative volume difference does not appear to be in relation to the amount of product present in the material: the supposition that a certain amount of product penetrates over 5 mm in depth could explain this fact. The measurements carried out on deeper layers do not show considerable cumulative volume variations and so they do not give important information.

The vacuum impregnation, carried out in accordance with the described methodology, does not appear more efficacious: the comparison of the cumulative volume data and the dry polymer amounts reveals that this treatment does not produce a better product penetration in depth.

The application of the water dispersion products feels the effect of their peculiar nature; in particular, the Akeogard ME vacuum treatment causes a ΔPs% higher than the same value obtained by the other two methods. Instead, in the Acryl 33 case, the higher ΔPs% is obtained with the capillarity treatment. This means that the methodology application is strictly connected to the product nature and the systems considered in general more effective for the traditional solvent products application are not so much efficacious for emulsion and dispersion products.

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