27394

THE INFLUENCE OF ACID RAIN AND UV RADIATION ON THE AGEING OF ACRYLIC AND SILICONE RESINS

A. TUCCI
Centro "Cesare Gnudi", Bologna, Italia

R. J. KOESTLER, A. E. CHAROLA
Metropolitan Museum of Art, New York, USA

R. ROSSI-MANARESI
Centro "Cesare Gnudi", Bologna, Italia

Abstract

Indiana and Vicenza limestone samples were treated with a mixture of an acrylic resin (B72) and a silicone resin (DF104). The samples were then aged artificially by subjecting them to cycles of acid rain alternating with UV exposure. Because of the change in the appearance of the resin when examined by scanning electron microscopy it was decided that a more detailed study was necessary to understand the mechanisms involved in the ageing process.

To carry out this study, samples of both types of stone were treated with each resin independently, and also in a mixture. They were then aged by either UV or acid rain exposure. One set of samples was subjected to 400 hours in a climate chamber at 50°C, 70% RH, and was irradiated by UV light with an emission maximum at 280-380 nm and 125 W intensity. The second set of samples was subjected to 80 hours of acid rain, using 0.02 M H_2SO_4 in a weathering chamber so that the acid solution would bathe the face of the samples at a rate of 0.01 ml per hour per cm^2.

Specimens from each type of sample were examined by scanning electron microscopy to study how each factor influenced each type of resin independently and when in a mixture. The information obtained is discussed as a function of the actual ageing that can be expected when this treatment is applied to outdoor sculpture and monuments.

1. INTRODUCTION

The treatment for stone studied in this paper, a mixture based on an acrylic resin (Acryloid B72) and a silicone resin (DriFilm 104) has been in use successfully for the past ten years. It has been used in the restoration of several important monuments in Italy [1-4], and has proved to be useful both as a consolidant and as a water-repellent treatment.

In a previous study on the effect of accelerated weathering on limestones treated with this mixture, it was found that the appearance under scanning electron microscopic (SEM) examination of the applied resin mixture changed significantly upon ageing [5].

The present study evaluates the influence of each of the factors used in the accelerated weathering test: the UV radiation and acid rain, on each resin separately and when applied in a mixture.

2. EXPERIMENTAL

Two kinds of clastic limestones were used for this study: Indiana and Vicenza limestones. Detailed discussion as to the change in porosity and water absorption characteristics when treated with the resin mixture was given in a previous study [5,6].

Samples (5 cm x 5 cm x 5 cm) of both limestones were treated by capillary rise (the bottom two millimeters were immersed and the system covered to reduce evaporation) with the following solutions:

A. DriFilm 104

B. 10% w/v of Acryloid B72 in a mixture of solvents:
66.7% v/v acetone:1,1,1-trichloroethane::1:1
33.3% v/v toluene:xylene::1:1

C. 15% v/v of 30% w/v Acryloid B72 in 1:1 toluene-xylene
5% v/v of 70% v/v DriFilm 104 in white spirit
40% v/v 1,1,1-trichloroethane
40% v/v acetone

The treated samples were sawed in half and each half subjected to either one or the other following treatment:

1. 400 hours in a climate chamber at 50°C and 70% RH with irradiation from a 125-W lamp with a wavelength emission maximum of 280-380 nm.
2. 80 hours in an accelerated weathering chamber with acid fog. This was obtained by means of a 0.02 M H_2SO_4 solution such that the exposed side of the sample received 0.01 ml/cm² per hour.

The side exposed to the weathering agent (either the UV or the acid fog) was the one opposed to that by which the absorption of the resin solution took place.

A parallel set of untreated samples of the two limestones, subjected to either one of these two treatments, were used as controls.

Specimens of the exposed surfaces of each of these samples and also of their side surfaces (perpendicular to the exposed face), were examined by SEM. All specimens were sputter coated with 10 nm of gold.

3. RESULTS

The results are similar for both type of limestones. For reason of space, only photographs of the Indiana limestone samples will be presented.

The appearance of the microstructure of limestone treated with B72, DriFilm or a mixture of both resins, is very similar under SEM examination [6]. The resin or resin mixture coats the grains of the limestone fairly uniformly. This appearance does not seem to be affected by UV irradiation. Figure 1 shows the appearance of the resin mixture after UV exposure.

Significant changes in the microstructure appear after the samples are subjected to acid fog. Each resin presents a different appearance, and differences can also be observed depending on whether

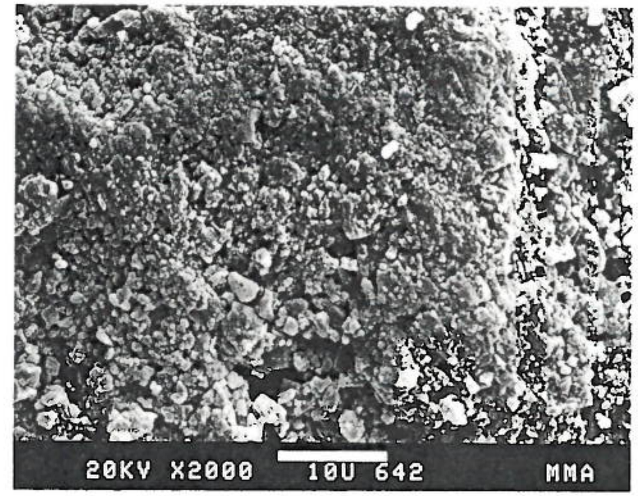

Figure 1: Indiana limestone treated with acrylic-silicone resin mixture and exposed to UV radiation for 400 hrs in a climate chamber. The appearance of the resin has not changed from that of the control samples.

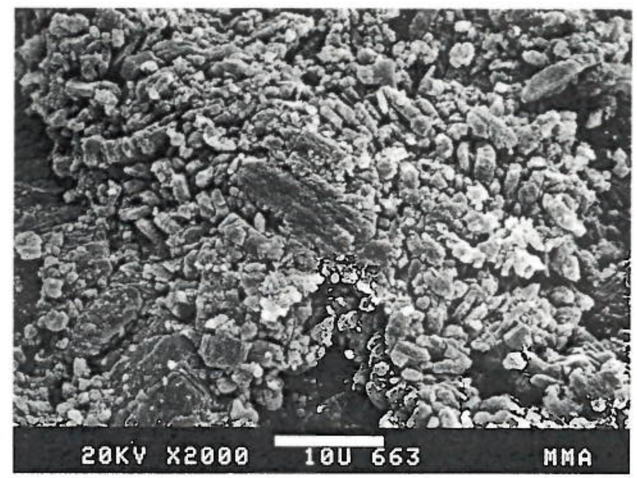

Figure 2: Side face of block treated with acrylic resin and exposed to 80 hrs. of acid fog in an accelerated weathering chamber. The resin is broken up into islands of consolidated agglomerates of grains.

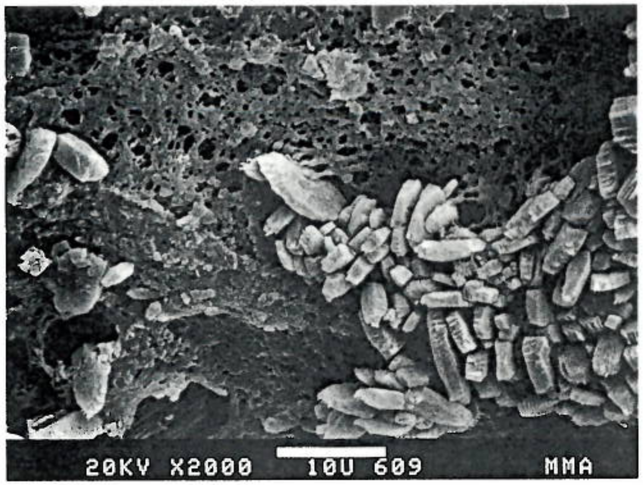

Figure 3: Top surface of block treated with acrylic resin and exposed to 80 hours of acid fog. Note the gypsum crystals held in the residual network of the resin.

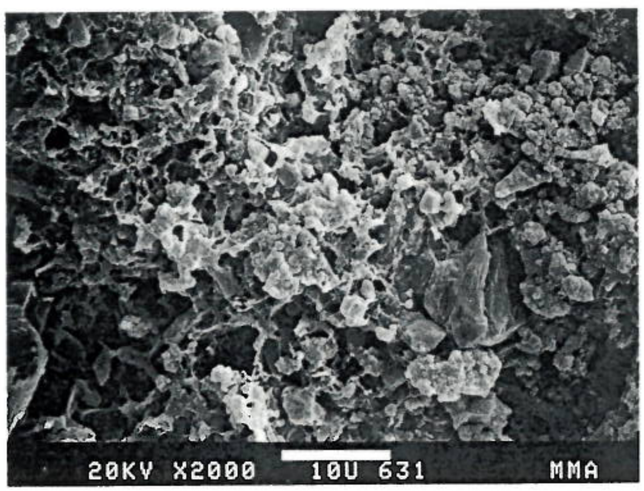

Figure 4: Top surface of block treated with silicone resin and exposed to 80 hours of acid fog. Note the three dimensional network of resin formed.

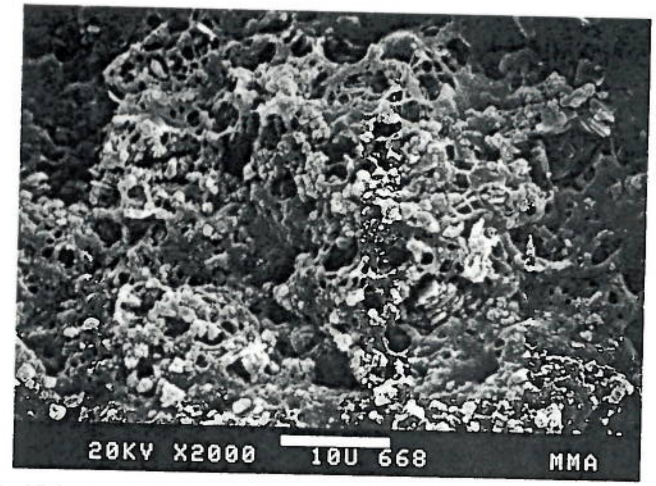

Figure 5: Side face of block treated with the resin mixture and exposed to 80 hours of acid fog. Note that the appearance of the network is a combination of that produced by the individual resins.

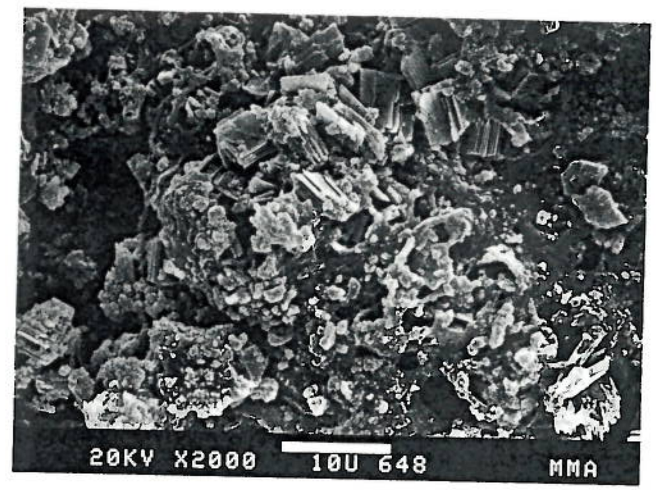

Figure 6: Top face of block treated with resin mixture and exposed to 80 hours of acid fog. Note the abundance and the change of habit of the gypsum crystals formed in this case.

the acid fog fell directly on the face of the sample (top exposed surface) or whether the surface was at right angles to the exposed top (side face).

The appearance of a side face of a sample treated only with the acrylic resin is illustrated in Figure 2. It can be seen that the resin is now broken into islands of consolidated agglomerates of limestone grains due to the etching of the acid that attacks any exposed limestone. When the attack of the acid is a direct one, as in the case of the exposed top surface, the appearance is dramatically different. The resin is now left behind as a net that holds the gypsum crystals formed during the acid attack in place. This can be seen in Figure 3.

The effect of acid fog on the appearance of the silicone resin is somewhat different. Figure 4 shows the three-dimensional network that can be observed on the exposed top-surface.

The appearance of the surface microstructure of a limestone treated with the resin mixture after being subjected to acid fog is represented in Figure 5, for the side face, and in Figure 6, for the top exposed surface. The overall appearance is a combination of the appearance of both resins: a network with smaller cells. This network is obscured by the abundance of gypsum crystals in the case of the top surface illustrated in Figure 6.

It is interesting to note that the habit under which the gypsum crystals grow changes depending on the type of resin applied to the stone. In the case of the untreated limestone, prismatic crystals formed rather than the platy ones seen in Figure 3 for the sample treated with the acrylic resin. In the case of the resin mixture, (Figure 6) the crystals appear again with a prismatic shape, composed of thinner plates and with sharper angles than those formed on the untreated stone. For the case of the silicone resin treatment by itself, the crystals are prismatic, similar to those in Figure 6, but without the "exfoliation".

4. DISCUSSION AND CONCLUSIONS

The SEM examination of the surface microstructure of limestone samples treated with different resins and subjected to different ageing factors has permitted the evaluation of the effect these factors have on the micromorphology of the resin in the stone.

UV radiation does not alter the "visual" appearance of these resins as seen by SEM, within the exposure times studied. This does not imply that the resin has not altered, but only that the morphology has not changed significantly. The acrylic resin could be expected to depolymerize under UV irradiation but this reaction does not occur easily as long as the irradiation takes place at room temperature [7]. Experiments carried out on thin films of B72 showed that it took some 3000 hours of continuous irradiation with a high intensity light source, reproducing daylight, to significantly decrease the molecular weight average of the polymer [8].

The effect of acid fog on the samples is obvious when examined by SEM. In the case of the acrylic resin, the flat network observed is produced by the etching away of the calcite crystals leaving the resin behind. This phenomenon also occurs in the case of the silicone resin, but in this case a second reaction is added: in situ polymerization of

the silicone resin. This reaction can proceed via the remaining alkoxy groups which are still present in the pre-polymerized product, as demonstrated by IR analysis [6]. The hydrolysis of these alkoxy groups is favoured by the catalytic action of the acid fog and the subsequent condensation continues the polymerization [9]. The resulting tridimensional network formed in situ provides protection for the treated stone by physically holding the loosened grains of the stone in place. Bonding of the resin to the calcareous stone surfaces is not likely because of their difference in chemical nature. In the case of the resin mixture, a combination effect of both resins is observed resulting in a thicker tridimensional network with smaller cells.

The deterioration effect of acid fog is dependent on whether the treated stone surface is directly exposed to it or not. If directly exposed, the damage to the surface of the stone is quite pronounced, though at depths of less than a centimeter the resin mixture was not affected. Treatment with the resin mixture diminishes the overall deterioration of the stone by preventing excessive absorption of water, acid solution and/or resulting salt solution, due to the hydrophobic nature of these resins. Furthermore, the network formed prevents the detachment of the loosened surface grains.

The acrylic-silicone resin treatment slows down the damaging effects of acid fog on calcareous stones due to its hydrophobic nature. In addition it has the capability of continuing protection as deterioration proceeds due to the fact that the in situ polymerization of the silicone moiety in this mixture is triggered by the weathering itself.

5. REFERENCES

1. ROSSI-MANARESI, R., Scientific and Technical Research, in Jacopo della Quercia e la Facciata di San Petronio, Centro per la Conservazione delle Sculture all'Aperto, Bologna (1981) 225-277

2. ROSSI-MANARESI, R., Treatments for Sandstone Consolidation, in The Conservation of Stone I, Centro per la Conservazione delle Sculture all'Aperto, Bologna (1975) 547-571

3. ROSSI-MANARESI, R., Effectiveness of Conservation Treatments for the Sandstone Monuments in Bologna, in The Conservation of Stone II, Centro per la Conservazione delle Sculture all'Aperto, Bologna (1981) 665-688

4. NONFARMALE, O., A Method of Consolidation and Restoration for Decayed Sandstone, in The Conservation of Stone I, Centro per la Conservazione delle Sculture all'Aperto, Bologna (1975) 401-410

5. ROSSI-MANARESI, R., CHAROLA, A.E., TUCCI, A., KOESTLER, R.J. and WHEELER, G.E., Study of Accelerated Weathering of Limestones Treated with and Acrylic-Silicone Mixture, in Proceedings of the 7th Triennial Meeting at ICOM, Copenhagen (1984) Vol. I, Section 10, 1-4

6. CHAROLA, A.E., ROSSI-MANARESI, R., KOESTLER, R.J., WHEELER, G.E. and TUCCI, A., SEM Examination of Limestones Treated with Silane or Prepolymerized Silicone Resin in Solution, in Preprints of the IIC Congress "Adhesives and Consolidants", Paris (1984) 182-184

7. KELEN, T., Polymer Degradation, Van Nostrand Rheinhold, New York, 1983, pp. 137-151

8. DE LA RIE, R., Personal communication

9. EABORN, C., Organosilicon Compounds, Academic Press, New York, 1960, pp. 255-264 and 301-304

MATERIALS

Acryloid B72, Rohm & Haas, Philadelphia, PA 19105, USA; is a methylacrylate-ethylmethacrylate copolymer.

Dri-Film 104, General Electric, Waterford, NY 12188, USA; is a prepolymerimed methyl trialkoxy silane.

ACKNOWLEDGEMENTS

The authors wish to thank C. Blair for help in SEM sample preparation and for photographic reproduction of the SEM micrographs.

CHANGES IN VAPOUR WATER TRANSMISSION OF STONE MATERIALS IMPREGNATED WITH SILICON AND ACRYLIC RESINS

A. VALLE, G. DRIUSSI, G. BISCONTIN
Departement of Chemistry, University of Venice, Italy

Abstract

In a previous paper we dealt with the permeability to the vapour of various kind of stone materials, treated with polymeric protectives and consolidants. Permeability, like a function of resin's concentration, has been studied. As a general trend, it was observed that the permeability decreases as resin's concentration increases up to a limit value corresponding to a limit concentration (saturation of the system). Overcoming this concentration, permeability shows no more changes.
In this paper we have studied resins solutions in various solvents and in low concentration, that are the most used in restauration, with the aim to better define the behaviour of the treated materials.
Porosity's measurements have been carried out in order to explain how resin arranges itself inside the pores' walls, that is when and what resin covers and when and what obstructs them.
Evaluations of permeability's changes after artificial aging are going to be completed, in order to determine the resistance of the applied resins.

1. INTRODUCTION

This paper is fitted in an investigation of which our group takes care for some time, in order to study the behaviour of products used in stone materials conservation.

The general characteristics these products must have, are know [1], [2], and are reported by various indications of UNESCO. Among these ones, it is foundamental that treatment permits water passage in the vapour form from the interior to the exterior of stone, but that it doesn't allow the entrance of free water, coming from the exterior.

By the way, besides the suitable solvents, the choice of the quantity of the product to apply is important: it has to be just enough to cover pores of material with a hydrorepellent system, without obstructing them [3].

In a previous paper [4], an investigation on permeability varation of samples treated with resins in various concentrations were done in order to state the concentration limit to which partial obstruction of pores occurs.

It was observed that vapour permeability decreases while resin concentration increases, with great variations in a little concentration range, generally a little above the 30%, a value which depends from the used resin-solvent system, besides from the treated stone. Overcoming this value, permeability decreases no more: being indicative of the attainment of the "saturation" limit of stone.

In this paper, investigation is focused on the behaviour of low concentred resins, that are the most used in conservation and that do not completely obstruct pores of material.

Laboratoire de conservation de la pierre
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

ACTES PROCEEDINGS

V^e CONGRÈS INTERNATIONAL SUR L'ALTÉRATION ET LA CONSERVATION DE LA PIERRE

V^th INTERNATIONAL CONGRESS ON DETERIORATION AND CONSERVATION OF STONE

Lausanne, 25-27.9.1985

VOLUME 2

Textes rassemblés par
G. Félix

PRESSES POLYTECHNIQUES ROMANDES