ICOM 7th Triennial Meeting Copenhagen 1984 pp. 84-10-1 to 84-10-4

STUDY OF ACCELERATED WEATHERING OF LIMESTONES TREATED WITH AN ACRYLIC-SILICONE MIXTURE

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SUMMARY

Vicenza and Indiana limestones treated with an acrylic-silicone resin mixture were studied to determine the behaviour of the impregnant. The specimens were studied before treatment, after treatment, and after simulated aging in the laboratory. Water imbibition and the water absorption coefficient decrease after the application of the treatment. The open porosity decreases somewhat, especially for the larger pores, but does not change significantly even after aging. Scanning electron microscopy examination of the samples show that the mixture provides a fairly uniform coating on the stone particles. After aging the silicone resin (which is a prepolymerized methyl alkoxy silane) polymerizes further and forms a network that holds the covered particles together.

Introduction

Treatments for stone usually must provide two functions, a consolidating one, in the case where cohesion between the stone particles has decreased, and a protecting one, to prevent further damage. Rendering the stone surface and the pore structure hydrorepellent is one of the best protections against further damage [1].

The treatment discussed in this paper has proved efficient not only as a consolidant but also as a hydrorepellent [2,3,4,5] and has given good results in the treatment of extended surfaces of monuments [6,7,8].

The aim of this study was to examine the appearance of the resin in situ by scanning electron microscopy (SEM). The samples were examined before and after treatment, and also after simulated aging in the laboratory. The treatment was applied to stones that are not very susceptible to weathering so that the results obtained would not be obscured by changes in the stone due to the simulated aging process. The efficacy of the treatment was assessed by techniques such as porosity measurements and water imbibition tests.

Treatment

For this study the treatment was applied to two limestones: one from Vicenza, Italy, and the other from Indiana, USA. Both are clastic limestones: the first is fossiliferous and the second oolitic. Their structure is unhomogeneous and they differ with respect to compactness and porosity: Vicenza limestone has more of an open porosity than Indiana limestone which is more compact. 5 cm) and from Indiana (6 x 4.5 x 6 cm) were treated by capillary absorption with a mixture of 4.5 % w/v Paraloid B 72 and 3.5 % v/v Dri-Film 104 in organic solvents, mainly 1:1 acetone-1,1,1 trichloroethane. Due to its lower porosity, Indiana limestone needed more time than Vicenza limestone to be completely wetted. Both stones were left in the mixture for about 18 hours to insure the penetration of the resin throughout the samples.

After evaporation of the solvent the increase in weight for the samples of Vicenza stone was 1.5% and 0.6% for those of Indiana stone.

Experimental

The degree of water imbibition and the water absorption coefficient were determined by following the procedures recommended by RILEM 25 PEM [9] with some modifications [2]. The measurements were carried out before and after treatment.

The water imbibition was determined by 48 hour immersion at atmospheric pressure and the water absorbed expressed as percentage of the dry mass of the sample. The results are given in Table I.

Table I - Water absorption

	Water Imbibition mass %		Water Abs. Coeff. $(kg/m^2s^{0.5}) \times 10^3$	
	untreated	treated	untreated	treated
Vicenza	10.8	9.7	174.0	4.0
Indiana	5.8	5.1	72.5	2.3

The water absorption coefficient was calculated from the experimental curve obtained by measuring the water absorbed by capillary acrion (through the same face through which the mixture was absorbed) as a function of the square root of time. Data are from the initial slope of the curve. Results are reported in Table I.

After these determinations, the samples were halved, one half was used for porosity measurements and for SEM examination, and the other half was subjected to accelerated weathering. The weathering test was carried out by repeated cycles of sulphuric acid fog (4 hours) followed by drying in a climatic chamber (20 hours). Acid fog was obtained by means of a 0.02 M H_2SO_4 solution and about 1 ml of acid solution collected in each cycle on the horizontal face of the sample (the absorbing face). The climatic chamber was equipped with a 125 W UV lamp, with highest emission at 280-380 nm which was left on during the length of the exposure in the chamber at 50°C and 70% RH. The samples were subjected to 21 cycles.

Results

Total open porosity and distribution of the volume of the pores as a function of their radius was determined by means of a mercury porosimeter. The mean values of the porosity are given in Table II.

Table II - Porosity (vol %)

	untreated	treated	treated, aged
Vicenza	37.2	25.5	26.0
Indiana	22.6	19.7	20.3

The porosity of the untreated specimens are the case of the treated and aged specimens, the mean was obtained from a larger number of determinations. To assess the homogeneity of the treatment, measurements were carried out on specimens taken at different distances from the absorbing face. The values obtained fall within the range of the results obtained due to the unhomogeneity of the stones themselves. In the case of the aged specimens the measurements were taken from the face exposed directly to the acid fog (absorbing face). The distribution of pore sizes for the Vicenza limestone are shown in Figure 1 and for the Indiana limestone in Figure 2. These are typical of the results obtained from all the measurements taken.

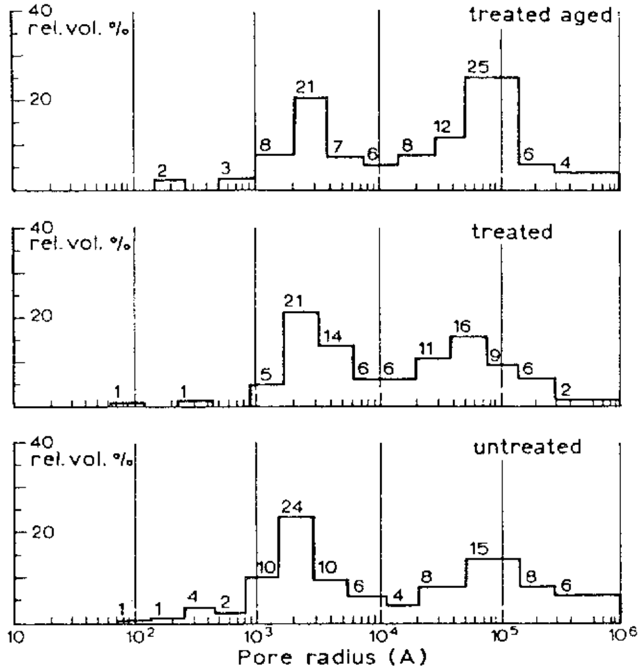

Figure 1. Relative pore volume distribution as a function of pore radius for Vicenza limestone.

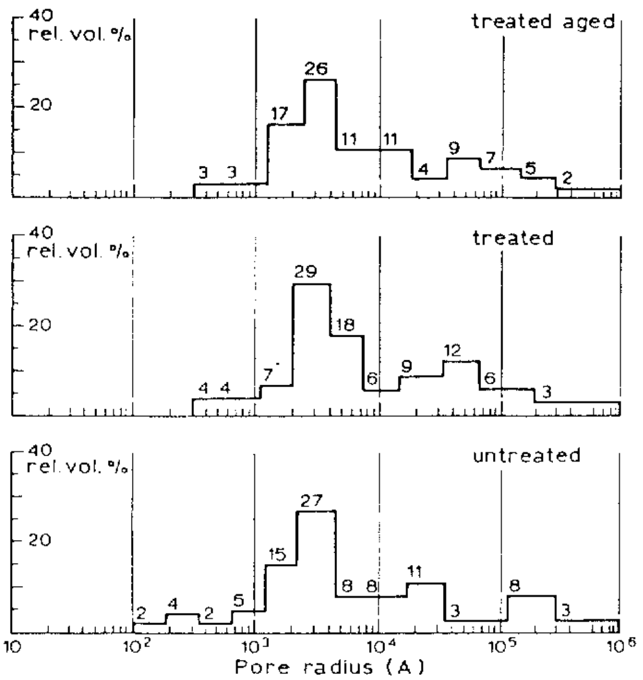

Figure 2. Relative pore volume distribution as a function of pore radius for Indiana limestone.

SEM examination was carried out on specimens from the external faces of the samples that were perpendicular to the absorbing face of the block. Both types of stone showed similar results due to the treatment and also due to the accelerated weathering process. The photomicrogaphs presented will be only of the Vicenza stone, but a similar set could be produced for the Indiana stone.

Through SEM examination of specimens from the interior of the samples it could be established that the penetration of the resin was fairly homogeneous throughout the stone [10]. The appearance of the exterior surface of the stone before and after treatment can be seen in Figures 3 and 4 respectively. Figure 5 shows the appearance of the stone and resin after the accelerated weathering process.

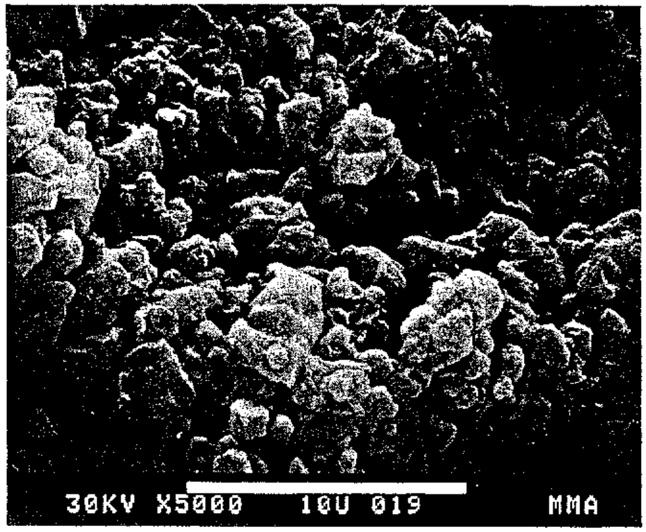

Figure 3. SEM photomicrograph of an external (sawed) surface of Vicenza limestone before the application of the treatment.

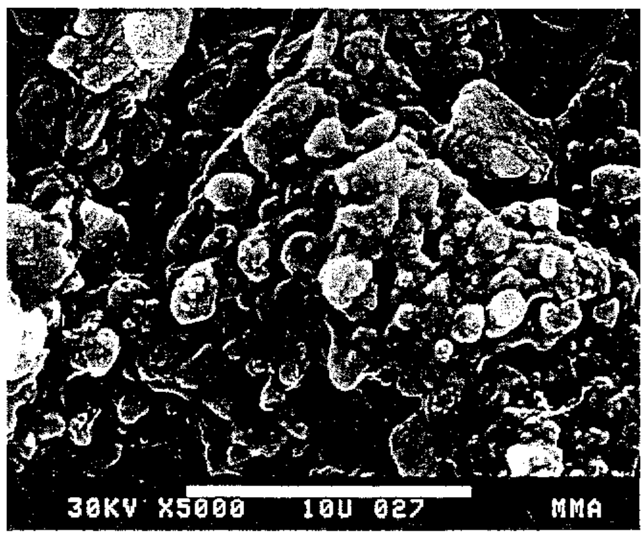

Figure 4. SEM photomicrograph of an external (sawed) surface of Vicenza limestone after treatment with the acrylic-silicone mixture. Note the homogeneous coating of the stone particles by the resin. The appearance of this film is characteristic of the Dri-Film 104 silicone resin.

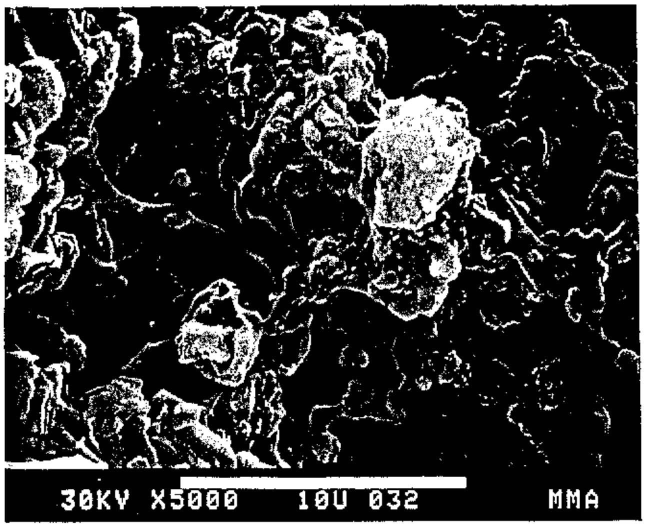

Figure 5. SEM photomicrograph of an external (sawed) surface of Vicenza limestone after treatment and after accelerated weathering. The larger pore space is due to the etching effect of the acid fog. Note that a network of resin has developed as a result of the weathering process. This type of network seems to be characteristic of in situ polymerization of silanes.

Discussion and Conclusions

The diminution of total porosity after the treatment and the fact that the relative distribution of pore sizes remains practically unchanged suggest that the distribution of the resin in the stone is fairly homogeneous. This conclusion can be substantiated by SEM examination [10]. Even though the total porosity is still high, the water absorption is reduced drastically. This can be explained by the hydrophobic nature of the Dri-Film 104. The appearance of this silicone resin in the stone is shown in Figure 4. The influence of the Paraloid B 72 in the mixture is not evident by SEM examination [10]. Dri-Film 104 deposits a film of the prepolymerized silicone resin as the solvent evaporates. The deposit on the outer faces is somewhat thicker than in the interior of the samples, which can be explained by the "carrying" effect of the solvent as it evaporates.

The effect of the accelerated weathering brings about a network formation in the resin which seems to be a characteristic of the in situ polymerization of silanes [10,11]. The appearance of the resin in the stone after the accelerated weathering is shown in Figure 5 which also shows in part the etching of the stone by the sulfuric acid fog. The change in appearance of the resin can be explained by the fact that Dri-Film 104 still has reactive alkoxy groups available for polymerization. The infrared spectrum of Dri-Film 104, shown in Figure 6, prove these to be mainly methoxy groups (850 cm^{-1}) [12]. Under the influence of the weathering agents, especially the acid fog, it is likely that these methoxy groups would hydrolyze and condense thus carrying further the polymerization reaction. Therefore it would appear to be that this silicone resin, whose first function is as a hydrorepellent, could also contribute towards the consolidation of the stone as the weathering process continues.

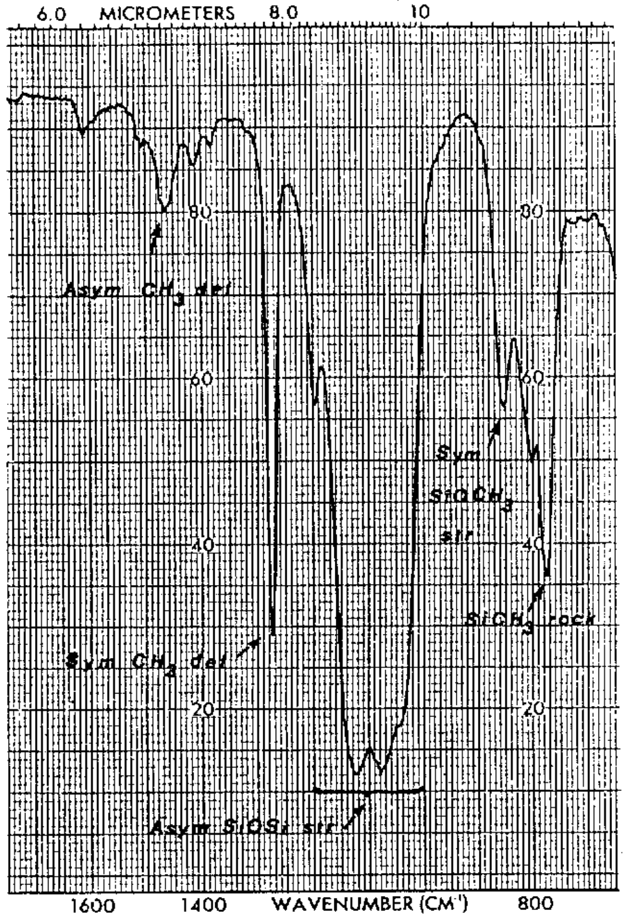

Figure 6. Detail of the infrared spectrum of the liquid Dri-Film 104.

Materials

Paraloid B 72, Röhm & Haas, is a methylacrylate ethylmethacrylate copolymer.

Dri-Film 104, General Electric, is a prepolymerized methyl alkoxy silane, presumably methyl trimethoxy silane, in solution.

Instrumentation

Fog Test Chamber: Weiss type S 400
Climatic Chamber: Weiss type T 240 + ZAB/20J
Porosimeter: Carlo Erba model 220 + Macropore Unit model 120

Acknowledgements

This study was partly supported by the National Museum Act Smithsonian Institution Grant No. FC-306156. Thanks are extended to Richard Sheryll for the help in SEM sample preparation and for the photographic reproduction of the SEM micrographs. Thanks are also due to Gregory Freund for the infrared spectrum of the Dri-Film 104.

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