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SEM EXAMINATION OF LIMESTONES TREATED WITH SILANES OR PREPOLYMERIZED SILICONE RESIN IN SOLUTION

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1 INTRODUCTION

Two limestones were chosen for this study: Indiana, an oolitic limestone, and Vicenza, a fossiliferous one. Neither of these limestones is prone to decay. The main concerns in the study are the possibility of characterizing a given resin by its appearance under the scanning electron microscope (SEM), visualization of the attachment of the resin to the stone, degree of penetration and the possibility of linking this type of data to the aging and performance of a given resin.

The stones were treated with methyl trimethoxy silane (MTMOS) or Dri-Film 104, and mixtures of either with Acryloid B72. The choice of treatments was based on previous field experience with them: MTMOS with and without addition of Acryloid B72 had been used to treat some Egyptian limestone bas-reliefs [1,2] and the mixture of Dri-Film 104 with Acryloid B72 was used extensively in the restoration of the Church of San Petronio in Bologna [3] and other monuments in Italy [4-6].

2 SAMPLE PREPARATION

Cubic samples (4cm x 4cm x 4cm) of parallel specimens of both limestones were treated by capillary rise (the bottom two millimeters were immersed and the system covered to reduce evaporation) in one of the following mixtures:

1. Methyl trimethoxy silane (Dow Corning Z-6070 or T-4-0149)
2. 4.5% w/v Acryloid B72 (Röhm & Haas) in methyl trimethoxy silane
3. Dri-Film 104 (General Electric)
4. 15% v/v of 30% w/v Acryloid B72 in 1:1 toluene-xylene mixture
   5% v/v of 70% v/v Dri-Film 104 in white spirit
   40% v/v 1,1,1-trichloroethane
   40% v/v acetone

The Vicenza limestone was totally wetted after about three hours of contact with the mixtures while the Indiana limestone needed about 18 hours. This is in accordance with their different capillary water absorption coefficients [7]: $0.17 kg/m^2s^{0.5}$ for the Vicenza stone and $0.07 kg/m^2s^{0.5}$ for the Indiana one.

Specimens (3cm x 2cm x 1cm) were cut from the cube, leaving out the top centimeter as in some cases the impregnant had not reached that area. The inner surface was polished and lightly etched with 1M HCl. The etching procedure was monitored under a light microscope: the surface was wetted with the acid and when the bubbling diminished (from half a minute to a minute), a new drop was added and this treatment repeated twice more. The surface was carefully washed to remove the excess acid and left to dry. The samples were mounted on appropriate stubs and sputter-coated with 10nm of gold [8].

3 RESULTS AND DISCUSSION

All treatments satisfy one of the primary requirements for any stone treatment: the macroscopic appearance of the stone itself is not altered by it. The degree of penetration as assessed by low-magnification SEM observation is similar in both stones and for all the four treatments considered. The addition of B72 in the amounts that were studied (approx 5%) does not seem to change the appearance of the impregnant significantly when viewed by SEM. Therefore the discussion will be essentially limited to the differences between DF-104 and MTMOS and illustrated only with photomicrographs of Indiana limestone, though a set of similar photomicrographs could be shown for the Vicenza stone.

The difference between DF-104 and MTMOS is that the first is a partially prepolymerized silicone resin in solution while the latter is a pure monomer that polymerizes *in situ*. This difference is readily observable under the SEM in the way the resin attaches itself to the stone. Figure 1a shows the appearance of a polished and etched surface of Indiana limestone treated with MTMOS. Note that the covering of the stone by the resin is not completely uniform but is

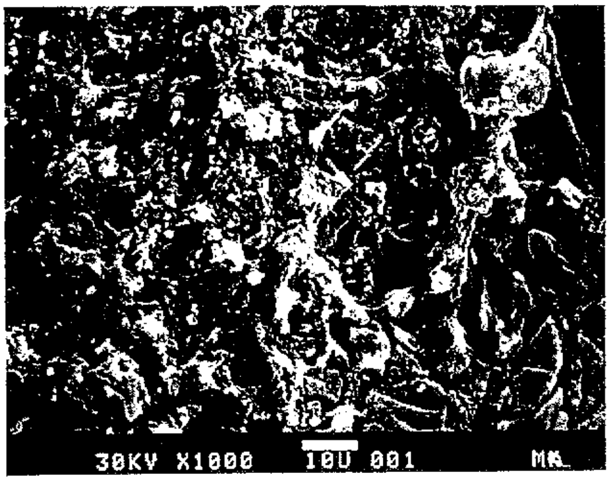

Fig. 1a SEM photomicrograph of Indiana limestone treated with MTMOS, in a polished and etched surface. The MTMOS forms a network that covers and holds the particles in place. The lower left-hand side has a thicker layer of the resin than the upper right-hand side where the outline of the etched calcite crystals is readily visible.

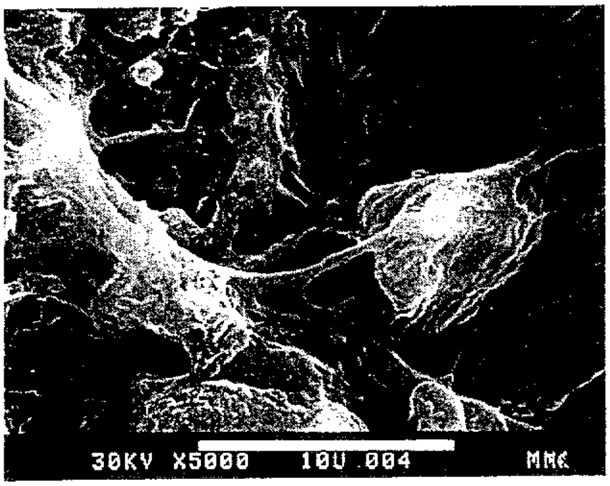

Fig. 1b Detail of the previous photomicrograph showing the resin covering the calcite crystals and the network formed.

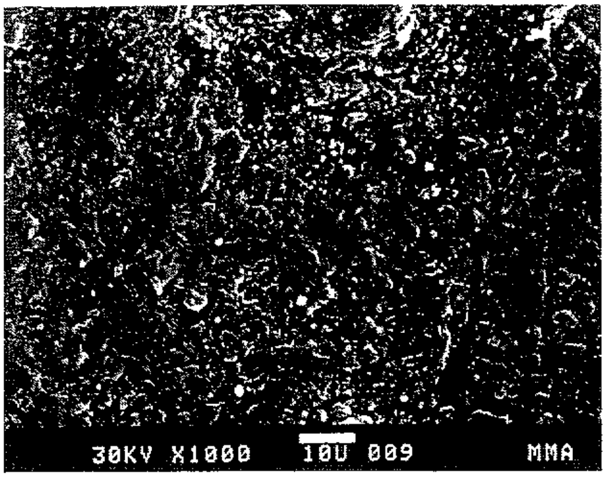

Fig. 2a SEM photomicrograph of Indiana limestone treated with DF-104, in a polished and etched surface. The pre-polymerized resin forms a film as the solvent that covers the calcite grains evaporates.

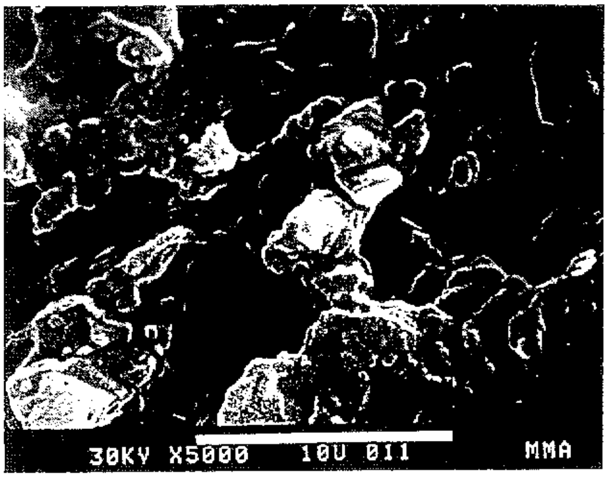

Fig. 2b Detail of the previous photomicrograph showing the film deposited on the calcite grains.

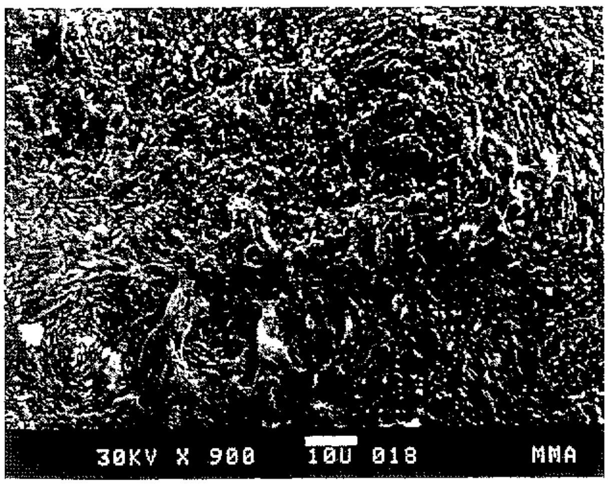

Fig. 3a SEM photomicrograph of Indiana limestone treated with DF-104 and B72 in a mixture of solvents (treatment 4), in a polished and etched surface. The amount of resin deposited is less, and only forms a thick film locally.

heavier on the left side of the photomicrograph. The white nodules are thicker masses of resin which, being raised above the general surface, allow for a larger signal, more

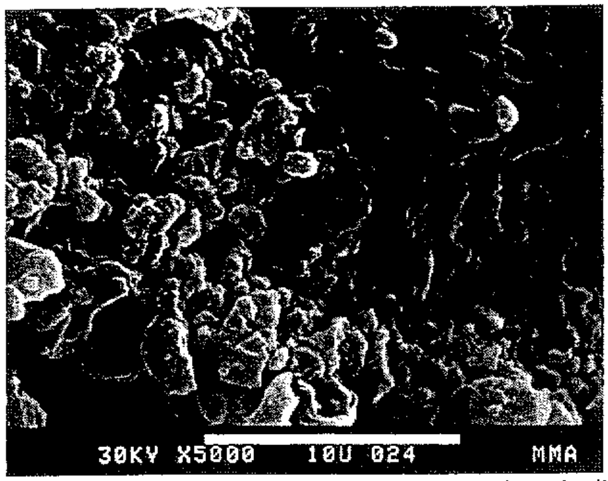

Fig. 3b Detail of the previous photomicrograph showing a detail of a thicker film of resin (top right corner) which fades into a thinner film (lower right-hand side) characteristic of the appearance of this treatment, and a non-impregnated part of Indiana limestone (bottom left corner).

electrons, to be collected from them. Figure 1b is a detail at higher magnification of the previous photomicrograph. The network of strands that attach the resin to the stone is readily visible. Note the thin film partially covering the large crystal in the top right-hand corner. Figures 2a and 2b are views of the stone treated with pure DF-104 (treatment 3). The resin forms a fairly uniform and heavy coating on the stone particles. Figures 3a and 3b show the appearance of the DF-104 resin when it is applied with more solvents (treatment 4). The coating in this case is not as uniform. Figure 3a shows areas with heavier coating at lower center, but the rest of the stone is covered with a thinner film, which can be seen at higher magnification, in the lower right-hand side of Figure 3b. This thinner film is characteristic for this type of treatment. Figure 3b also shows how this resin is only deposited on the crystal grains, without forming an evident attachment to them. The left side of this same photomicrograph shows the appearance of etched limestone in an area that was not covered with resin. It also shows, to some extent, the range of crystal sizes that can be found in this limestone. The lower magnification micrographs (Figs 1a and 3a) show that the treatments in actual use do not form an absolutely uniform coating on the stone particles at microscopic level, even though the impregnation obtained was homogeneous.

DF-104 does not appear to form the network that seems to be characteristic of MTMOS, which can be explained by the fact that it is already partially polymerized and that essentially it is deposited in place as the solvent evaporates so that little bonding will take place between it and the stone. This also explains why, even after four years in place, it can be removed by solvents [3]. MTMOS, on the other hand, penetrates as a monomer into the stone and polymerizes in place, forming a network around the stone particles during polymerization. This treatment has not been shown to be reversible.

ACKNOWLEDGEMENTS

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MATERIALS

Methyl trimethoxy silane: Dow Corning Z-6070 or T-4-0149 (the numbers refer to the same chemical compound but with different marketing purposes). Dow Chemical, Midland, MI 48640, USA.
Acryloid B72, Röhm & Haas, Philadelphia, PA 19105, USA.
Dri-Film 104, General Electric, Waterford, NY 12188, USA.

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