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A. E. Charola

International Centre for the Study of the Preservation and the Restoration of Cultural Property

R. J. Koestler

Metropolitan Museum of Art

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SCANNING ELECTRON MICROSCOPY IN THE EVALUATION OF CONSOLIDATION TREATMENTS FOR STONE

A.E. Charola* and R.J. Koestler

*International Centre for the Study of the Preservation and the Restoration of Cultural Property
Rome, Italy
Objects Conservation Department, Metropolitan Museum of Art, New York, NY 10028

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Abstract

The use of scanning electron microscopy (SEM) examination is shown to be an important tool in the evaluation of the effectiveness of consolidant treatments in stone. This implies the visualization of the attachment of the resin to the stone, the assessment of the degree of penetration and the distribution of the resin in the stone matrix. These factors can then be correlated with the chemical nature of the stone and the resin.

A sample preparation technique for limestone, based on acid etching of the surface, is described. This technique improves the visualization of the resin within the stone.

KEYWORDS: Stone impregnation, limestone, sandstone, silicate-ester, silane, acrylic-silicone resin mixture, consolidation treatment.

*Address for correspondence: ICCROM, 13 Via di S. Michele, 00153 Rome, Italy.
Phone No. (6) 580.9021.

Introduction

The assessment of consolidation treatments applied to stone is of fundamental importance in the area of stone conservation. Usually this assessment is carried out by the determination of the change in some physical parameters of the stone after the consolidant has been applied. The most commonly used ones are: porosity, capillary water absorption and total water absorption. Scanning electron microscopy (SEM) examination can be an extremely useful technique in this assessment as the data obtained by the other methods can be interpreted in the light of the changes in the microstructure of the stone when a given treatment is applied. The visualization of the distribution of the resin in the stone particle surfaces can give a better understanding of the nature of the consolidation obtained.

This study describes the application of SEM in the evaluation of the effectiveness of an acrylic-silicone resin mixture applied to limestones and the changes that occur during the subsequent weathering. This was carried out by examination of specimens from the external, exposed, face of the stone.

An acid-etching technique for limestone specimen preparation was used to enhance the visualization of the resin in the stone. Examination of different commonly used consolidating products are presented. The morphology and the distribution of a given resin within the microstructure of the stone is then correlated to the chemical nature of both the resin and the stone surface.

Experimental

Examination of external, sawn surfaces

For this study, two clastic limestones were chosen: one from Indiana, USA, and a second one from Vicenza, Italy. The oolitic Indiana limestone is more compact than the fossiliferous Vicenza limestone which has a higher open porosity. The rationale behind the choice of these stones is described elsewhere [2].

Cubic (approximately 5 x 5 x 5 cm) samples, sawn from quarry stones, were treated by capillary rise (the bottom two millimeters were

immersed and the system covered to reduce evaporation) with a mixture of 4.5 % w/v Acryloid B72 (Rohm & Haas, Philadelphia, PA 19105) and a 3.4 % v/v Dri-Film 104 (General Electric, Waterford, NY 12188) in organic solvents, mainly 1:1 acetone-1,1,1 trichloroethane. The cubes were left in the mixture for about 18 hours to insure the penetration of the resin mixture throughout the samples. The cubes were then halved, one half was used for SEM examination and other physical measurements, and the second half was subjected to accelerated weathering.

The artificial ageing was carried out in a weathering chamber by repeated cycles of sulphuric acid fog (4 h) followed by drying in a climatic chamber (20 h). Acid fog 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 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 a total of 21 cycles. The side exposed to the weathering agent was the one opposed to that by which the absorption of the resin solution took place.

SEM examination was carried out on specimens from the external faces of the cubes. The specimens were mounted on appropriate stubs and sputter-coated with 10nm of gold. The stone was studied before any treatment was applied (Figure 1), after the impregnation took place (Figure 2), and finally, after the weathering cycles had been completed (Figure 3). The results for both types of limestones were similar and will therefore be illustrated using examples obtained with the Italian limestone.

Examination of acid-etched surfaces

The idea of etching, or dissolving the stone by means of a suitable chemical, so that the distribution of the impregnating agent is made more visible, has been used in the field of stone conservation, not only in macroscopic examination [5,10], but also in microscopic examination [6]. This technique has also been used to assess the protective properties of a given resin *vis-a-vis* the effect of acid air pollutants on these treatments [8].

The technique described here has been applied successfully in previous studies [1,4,9]. Small, about 1-square centimeter surface, specimens were sawn from the treated stone samples. The surface was polished and then lightly etched with 1 M HCl. The etching procedure was followed under a light microscope: when the reaction slowed down, in about half a minute to one minute, the surface was rinsed with distilled water. This procedure was repeated two times.

Discussion

Figure 1 shows the appearance of a sawn surface of Vicenza limestone. Figure 2 shows it after the resin mixture has been applied. The stone particles appear completely covered by a uniform film of the resin mixture. The slight darkening that is observed on the stone surface when the treatment is applied can be explained in view of this SE micrograph: the film covering the

particles changes the light refraction properties of the surface.

Figure 3 shows the surface after subjection to the weathering cycles: the surface has been partly etched by the sulphuric acid where the film did not cover the stone completely. Furthermore, the acid environment induced an *in situ* polymerization of the silicone resin (Dri-Film 104). The polymerization is evidenced by the change of morphology of the film and this hypothesis is supported by the fact that Dry Film 104 has reactive alkoxy groups available for polymerization. Some of the calcium carbonate reacted to form calcium sulfate which crystallized as gypsum, seen in the prismatic crystals that are held in place by the resin strands. The "bonding" of the resin to these new crystals indicates that these reactions are taking place simultaneously. Further discussions on the nature of the *in situ* polymerization and the crystallization of gypsum can be found in previous reports [13,14].

Figure 4 shows a SE micrograph of an etched specimen from the interior of a sample of the Vicenza limestone treated with the resin mixture. It shows that the penetration of the resin is uniform throughout the stone. It also shows that the stone is not completely protected by this treatment, as could have been supposed from the examination of Figure 2. Some areas are still exposed and when acid comes in contact with them, the limestone will be dissolved. This SE micrograph demonstrates that the etching technique is not altering the nature of the resin (compare with Figure 3) but is merely revealing the areas susceptible to acid attack and those protected by the resin.

Some of the most frequently used treatments for stone consolidation at the present time are based on silicate esters or on mixtures of these and silanes. Figure 5 shows an Egyptian limestone (Dendera) treated with a commercial product based on a silicate ester-silane mixture (Wacker-H). The three-dimensional network that is seen is a result of the *in situ* crosslinking of the silanes and the etching away of the calcite grains (compare with the network obtained with the acrylic-silicone resin after weathering, Figure 3). The reason that no calcite grains are seen in this SE micrograph is due to the fact that the Egyptian limestone is a much finer grained limestone than the other ones studied.

Figure 6 shows a French limestone (Lavoux) treated with a product based just on a silicate ester (Wacker-OH). Clumps of sponge-like masses of silica are deposited interstitially between the calcite grains. The reason that individual clumps are formed can be explained by the fact that the polymerization of this product is carried out in the presence of a catalyst. Wherever a catalyst molecule is present, the polymerization reaction starts. Thus several nuclei for polymerization form simultaneously and the reaction continues around them until all the silicate ester molecules in the neighborhood have reacted.

The effect of the chemical nature of the stone on the distribution of the resin, for the case of these last two mentioned types, is

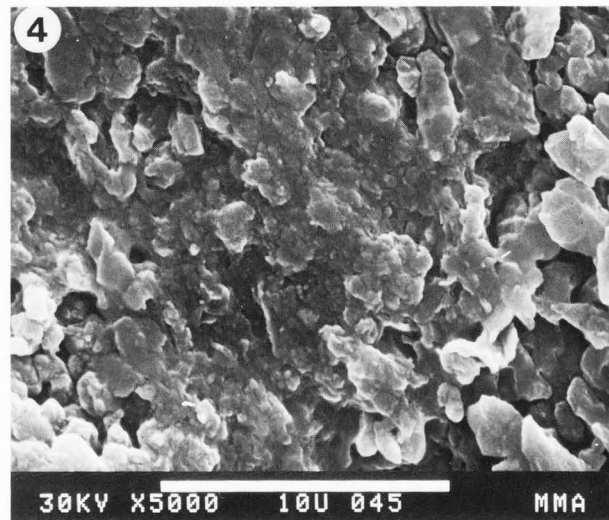
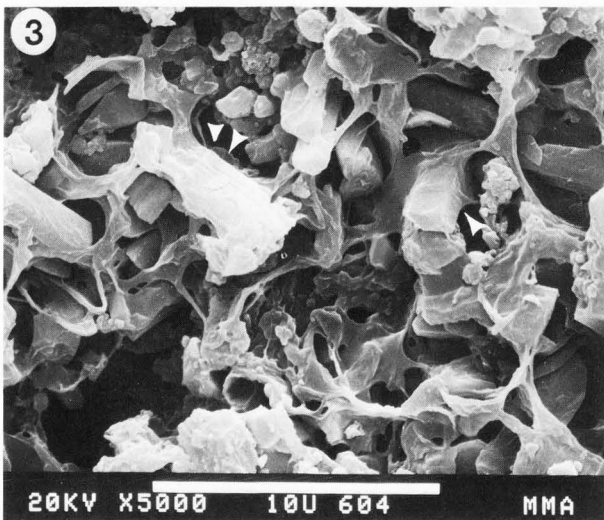
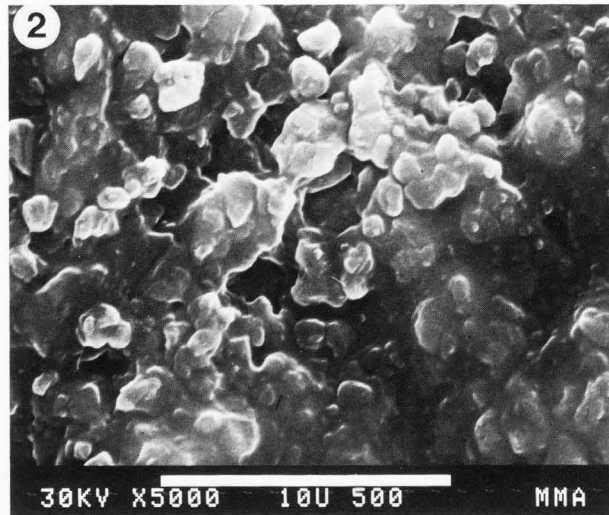
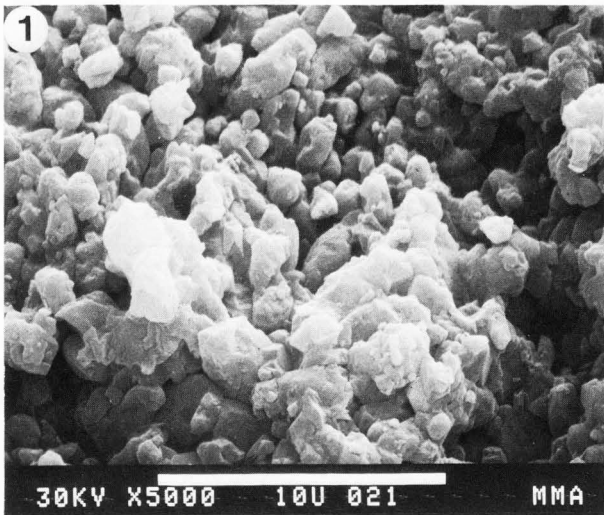


Figure 1 SE micrograph of a sawed surface of Vicenza limestone.

Figure 2 Appearance of an external, sawed, surface of Vicenza limestone after treatment with an acrylic-silicone resin mixture. The resin forms a uniform film that coats the stone particles.

Figure 3 Appearance of an external, sawed, surface of Vicenza limestone that was treated with an acrylic-silicone resin and after artificial ageing. The surface has been etched by the sulphuric acid which has also induced the *in situ* polymerization of the silicone resin producing a network which bonds the particles together. The arrows point to the prismatic gypsum crystals that formed as a consequence of the acid etching.

Figure 4 Appearance of an internal, polished and etched surface of Vicenza limestone treated with an acrylic-silicone resin mixture. The acid has etched the stone in the places where the resin film coating was not sufficiently adherent (lower right and left corners).

illustrated in Figures 7 and 8. Figure 7 corresponds to an external, sawn, face of a sandstone (Ohio), treated with a silicate ester-silane mixture (Wacker-H). It shows that due to the chemical affinity between the resin and the silica surface of the grains, uniform bonding occurs. This is evidenced by the even film that is deposited on the surface of the grains. A similar film is also formed for the case of the

silicate ester resin (Wacker-OH) seen in Figure 8. To be especially noted are the cracks in the film which are due to the shrinking that occurs as the condensation part of the polymerization reaction takes place. That less cracking occurs in the case of the silicate ester-silane mixture could be explained in terms of the presence of the silane, which, being only a trifunctional monomer, as opposed to the tetrafunctional

silicate ester, could possibly produce a more "elastic" network.

Conclusions

Scanning electron microscopy has proved to be an extremely powerful technique in obtaining insight into the manner consolidation occurs according to the type of resin and the nature of the stone treated.

Mixtures of acrylic-silicone resins, even though they weather and change superficially, remain essentially unchanged in the depth of the stone matrix [3,14]. These observations agree with the empirical field experience that has been obtained with this treatment [11,12].

The important role that the chemical nature of the stone plays in the distribution of the resin in its matrix can be appreciated for the case of the silicate esters and its mixtures with silanes. These products were developed in the first place for use on sandstones, but have also been found to be effective on calcareous stones [7].

SEM, through the visualization of the changes in microstructure after a treatment is applied, or after its weathering, helps in the elucidation of the nature of the reactions taking place.

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Discussion with Reviewers

J. Twilly: I believe that it is quite important to quantify the content of clay and siliceous matter in a "limestone" and it is necessary to locate these concentrations via petrography before drawing conclusions about the significance of views such as those in figures 5 and 6.

Authors: All the limestones that were studied had a uniform distribution of clays and silica. It would appear to be that in these cases the distribution of the resins in the matrix of the stone is also uniform and not affected by the siliceous matter content in them. Similar distributions of resin were obtained regardless of the concentration of these materials. For the particular cases illustrated, the content of siliceous matter was about 10% for the Egyptian stone (Figure 5), and about 1% for the Lavoux stone (Figure 6).

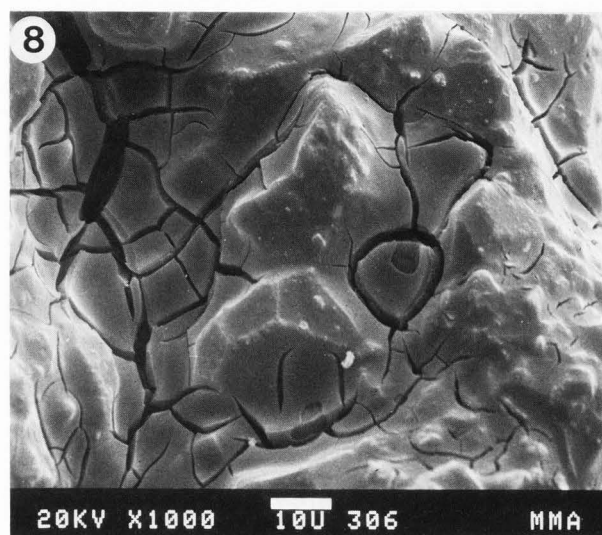
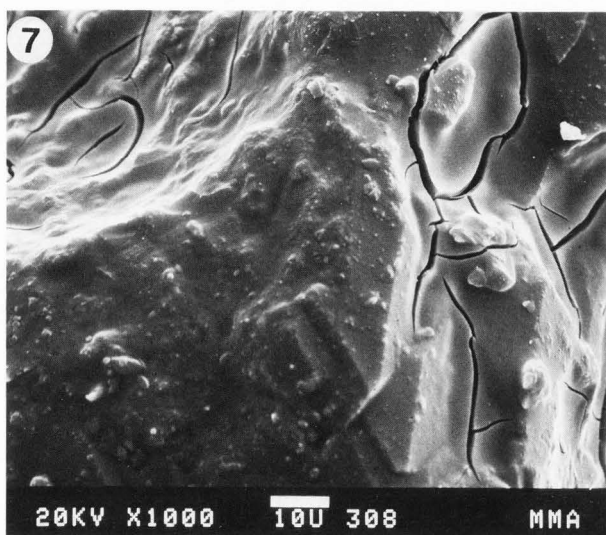
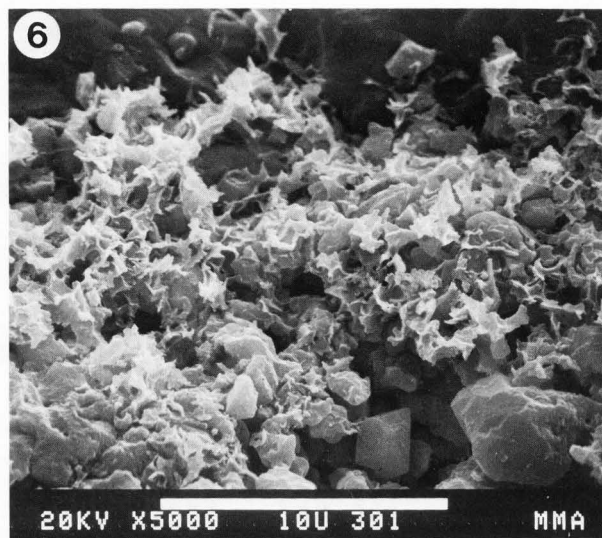
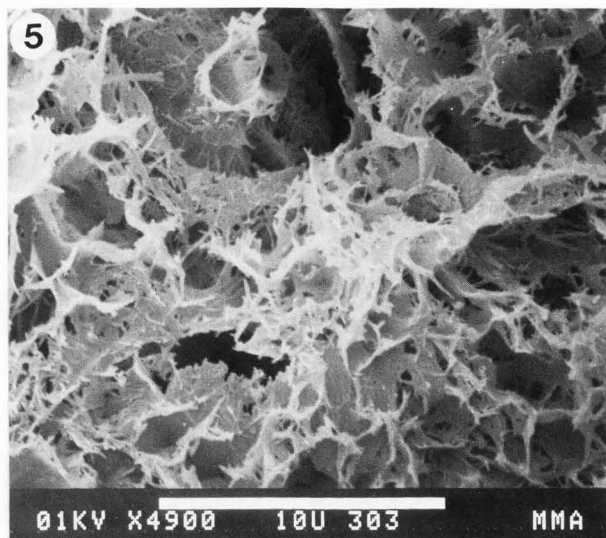


Figure 5 SE micrograph of a polished and etched surface of Egyptian limestone treated with a silicate ester-silane mixture (Wacker-H). The resin forms a network that is characteristic of the *in situ* polymerization of silanes. As this is a very fine-grained limestone, the etching has removed all of the surface grains.

Figure 6 Appearance of a polished and etched surface of a French limestone treated with a silicate ester (Wacker-OH). As there is no chemical affinity of the resin for the stone, the resin can only react with itself. This occurs in spongy-looking masses that apparently originate around a catalyzing nucleus where the polymerization reaction starts.

Figure 7 SE micrograph of a sawed surface of sandstone treated with Wacker-H. The chemical affinity of the resin for the stone matrix is apparent in the uniform coating obtained.

Figure 8 Appearance of a sawed surface of sandstone treated with Wacker-OH. The uniform coating of the sand grains by the resin can be explained by their chemical affinity. The cracking of the coating could be explained by the shrinking and/or induced stress that occurs during the condensation phase of the polymerization reaction.

J.Twilly: Why was the "drying" cycle conducted at the relatively humid condition of 70% RH?

Authors: This relatively humid condition was chosen because it was considered to be a severe weathering factor for the resin.

J.Twilly: The effect of monomer loss and solvent evaporation (subsequent to the gelation stage of curing) in causing shrinkage seems to be neglected.

Authors: In our experience, monomer loss has not induced cracking but this phenomenon has been observed to depend upon the rate of the polymerization reaction (see A.E. Charola, G.E. Wheeler, and G.G. Freund. 1984. The Influence of Relative Humidity in the Polymerization of Methyltrimethoxysilane. Preprints of the Paris IIC Congress "Adhesives and Consolidants", International Institute for Conservation of Historic and Artistic Works, London, 177-181). In other experiments, carried out with silicate esters in solvent but without a catalyst, no cracking was observed.

J.Twilly: Should the "in situ" polymerization due to silane cross-linking shown in Figure 5 be differentiated from that shown in Figure 3?

Authors: No, the same phenomenon is illustrated.

M.Montoto: Have you measured the water permeability in the non-treated Ohio sandstone in the treated ones? The shrinking phenomenon developed in the sandstone after the treatments (Figs. 7 and 8) seems to dramatically affect the stone permeability, a physical property very significant in stone conservation.

Authors: These types of measurements have been published in another report (see K.J.H. Zinsmeister, N.Weiss and F.Gale. 1985. Evaluation of Consolidation Treatments of an American Sandstone. *Bautenschutz und Bausanierung* 2, 79-85).

G.Simmons: Figure 3 caption says that gypsum formed as a product of the etching. The material may be $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ but it is absolutely not gypsum. Gypsum is a mineral and can be formed only in nature. The compound $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is geologically not gypsum even though it has the same composition. Secondly, how do you know that the composition is that of gypsum and not anhydride?

Authors: The mineral composition was determined by x-ray powder diffraction. In the field of conservation the compound $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, formed "naturally" on limestone or marble surfaces due to the effect of air pollutants and/or biological action, has always been called gypsum by general consensus of scientists [geologists, chemists, biologists, and physicists] working in this field.