THE MECHANISM OF SOME CONSOLIDATES MIGRATION IN POROUS STONE "LIME STONE"

Mohsen M. Saleh*, M. M El-Sankary**, Ali T. Omar and Giussepe Fan Foni***

Abstract:

The present paper is a result of investigation on migration of some consolidates – Thermoplastic resins to the surface pores of impregnated stone which are reported.

The causes of migration were evaluated as well as the conditions which allow reducing these undesirable effects. It has been stated that the effect of resin molecules, solution viscosity, stone structure and the conditions of drying after impregnation. This investigation are applied on lime stone samples as a porous stone which widely used as building materials in Egypt.

Different analytical and investigation methods were applied to study the stone samples such as polarizing microscope, X-ray diffraction analysis (XRD) and scanning electron microscope (SEM) equipped with (EDX) microanalyzer.

1. Introduction

The main idea of this paper is derived from (Domasłowski et al., 1976). The principal aim of structural consolidation of porous stone is implied by the necessity of obtaining homogeneous physical and chemical properties of stone. Numerous examples are known where stone objects consolidated superficially are subjected to further deterioration. However, numerous difficulties are met, especially in the case of application of the so-called reversible products as e.g. thermoplastic synthetic resin

It is difficult to obtain satisfactory depth of penetration and to reduce migration to the surface pores of stone, which results from solvent evaporation during the process of drying.

Concerning consolidation, difficulties are mainly due to the too high viscosity of the applied solutions of thermoplastic resins which exceeds the viscosity of silicone and epoxy resins. The viscosity depends on the molecules dimension, solutions concentration, the quality of solvent, etc. The process of migration to the surface pores of stone has not been sufficiently known and valued, neither by the conservators nor by the scientists).

* Cairo Univ., Faculty of Archaeology, Conservation Dep.
** Nuclear Materials Authority, El-Kattamiya, Cairo
*** Italian Egyptian Center for restoration and Archaeology [CIERA]

The conservators usually evaluate the depth of the consolidated stone layer on the basis of the depth of penetration of solution, which might be incorrect in the majority of cases. On the other hand, some scientists stated that the difference between the depth of penetration of solution and the depth of consolidation is related to application through the so-called bad solvents. These bad solvents resulted in polymers of a too high viscosity, which are not able to penetrate into the stone pores.

Stone acts as a molecular sieve, it lets the solvent pass and retains the polymer. Investigation on the effect of resin migration and solution penetration capacity as related the properties of the treated stone samples has been performed in the Conservation Department, Faculty of Archaeology Cairo University, Egypt.

2. Materials and Methods

Consolidant applied comprise solution of Thermosetting resins [Ethyl silicate (silicic acid + alcohol)] and Thermoplastic resins [Paraloid B-72 from Rohm and Haas, USA] dissolved in different solvents [Toluene, acetone and thinner].

Limestone from Tura was used for consolidants application. This limestone was the finest and whitest of all the Egyptian quarries. So, it was used as facing stones for the richest tombs, as for the floors and ceilings of mastabas (Grimal, 1988).

Different methods were used to investigate the limestone samples before and after treatment, such as X ray diffraction analysis (XRD), optical microscopy, Scanning electron microscope (SEM) equipped with energy dispersive X-ray fluorescence (EDX) microanalyzer.

3. Methodology of Stone Impregnation and Determination of Resin Distribution in The Pores of Stone

Cubic samples [5 x 5 x 5 cm] were immersed in the respective solution to a depth of 1 cm and impregnated by capillary rise. After the solution had risen to its upper surface, the samples were dried under the normal condition and a 3 mm thick slice was cut horizontally across each sample, at right angle to the direction of capillary rise.

The resin distribution was determined by etching the slices with a 5% solution of hydrochloric acid for 0.5 to 2 hours, till the reaction quenching [fig.1]. Calcium carbonate was decomposed in the zones where the resin did not penetrate. Characteristic stone 'frames' were observed as a result of differential consolidate migration.

Fig.1 Etching the limestone slice by HCl 5%

The consolidant material distribution was determined on the surfaces by measuring their hydrophobic properties by the time of absorption of drops of water (~50 µl in volume), put in 1 cm distance. An immediate absorption of water drop proved the absence of resin. A reduced rate of infiltration or no infiltration at all provided information on the accumulation resin [fig.2].

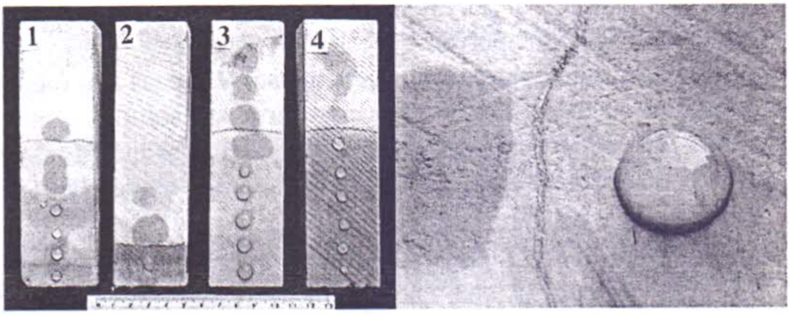


Fig.2 Measuring the hydrophobic properties of samples by the time of absorption of drops of water 50 µl in volume, [1] paraloid B.72 in toluene , [2] paraloid B.72 in acetone , [3] paraloid B-72 in Thinner , [4] Ethyl silicate

4. Results

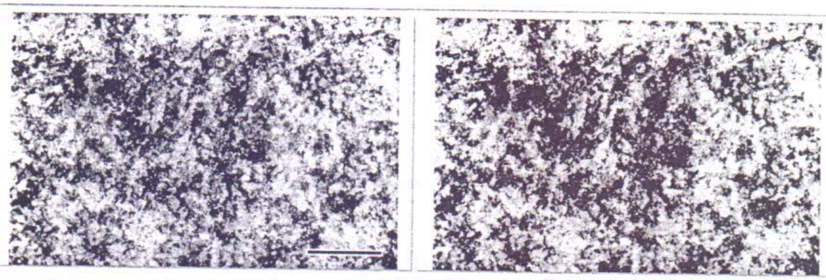
When investigating the process of resin accumulation in the surface pores, the following factors should be taken into account: stone characteristics, type of resin and solvent, and the ambient conditions during of the treated stone. Porous stones represent different types of materials as far as porosity, pore size distribution and pore shape, specific surface and wet ability are concerned.

The movement of solutions towards the core of the stone and the behavior of resin in the pores may be affected by all the above factors. Taking this into account, it could be supposed that fine-porous stones would either from a kind of sieve for macro-molecular resins, or cause phase separation of solvents due to a well developed specific surface. The latter effect is very often observed in the course stone impregnation by a capillary method.

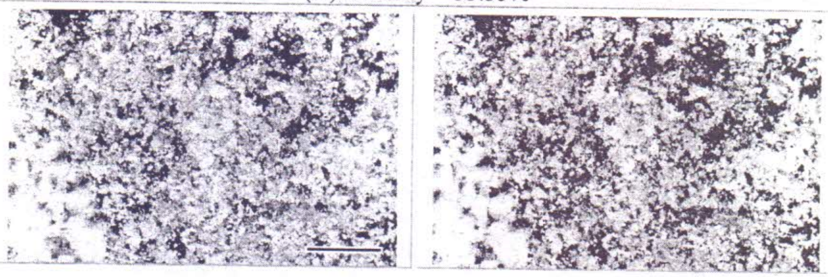
3.1. Polarized Microscope Result

Thin sections were prepared from the studied samples, then petrographical examination and photography was carried out under the polarizing microscope. Mineralogical composition, pore structure and percentage were characterized. The total void areas were determined (as plane area %) in the different thin sections by planimetery using the computer program (Sigma Scan Pro.5 of SPSS Inc.) for image analysis.

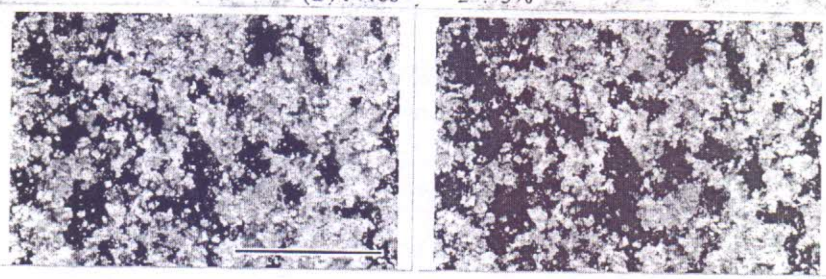
Petrographical investigation reveal that the studied limestone samples are heterogeneous concerning their micromorphology and microtextural characteristics (Fig. 2). Their fine granular calcite (micrite) shows different degrees of clotting and coagulation probably inherited from their biochemical environment of deposition. Fine pores are distributed as interconnected network with different shape and density.



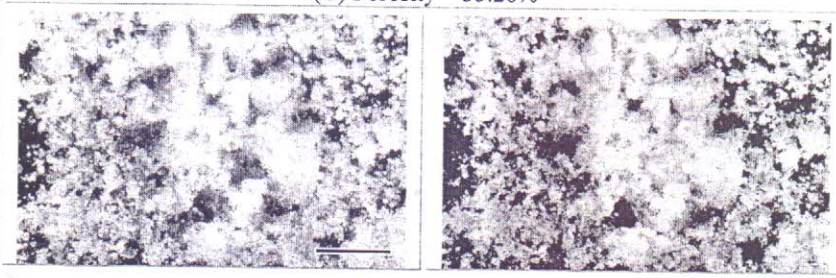
(A) Porosity = 33.35%



(B) Porosity = 25.33%



(C) Porosity = 35.26%



(D) Porosity = 18.50%

Fig.2. Photomicrographs of representative limestone samples showing different degrees of micrite clotting and coagulation; their corresponding porosity false images are located to the right. The estimated porosity values are indicated. Bar scale equals 200 µm.

The total porosity as plane as plane area% was estimated, which ranges from 18.5 to 35.3%. This inter-growing diversified porosity and granulometry are considered to play an effective role concerning consolidant materials penetration.

3.2. X-Ray Diffraction Analysis (XRD)

Mineralogical investigation was carried out through X-ray diffraction analysis, which is an effective tool to identify the mineralogical constituents of the building materials comprising stones, mortar, plaster and different painting materials. Representative powdered samples of these materials were studied using x-ray diffractometer (Philips, PW 1840) with Ni-filtered CuKα radiation at operating conditions of 40 kV/30 mA and a scan speed of 2° (2θ)/min. The results indicated that the studied samples are composed of low Mg-calcite with trace amount of dolomite (Fig. 3).

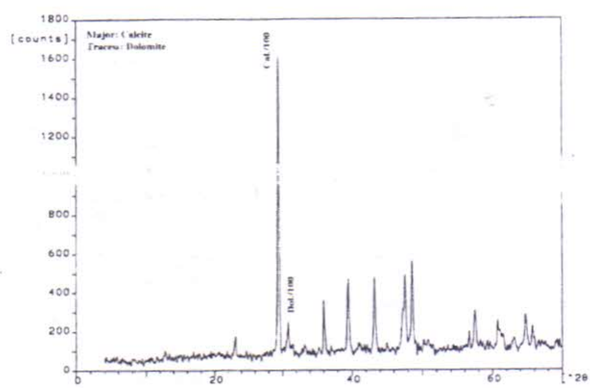


Fig.3. Representative (XRD) Pattern of the studied limestone.

3.3. Scanning Electron Microscope (SEM/EDX) Results

The FEI Quanta 200- Environmental SEM Equipment was used for investigate the untreated limestone and treated limestone samples to identify their micro-morphological, microtextural characteristics and the consolidant penetration on the surface pores, that treated samples were left for two months because of completely setting. The SEM-EDX analysis indicated that:

3.3.1 Untreated Limestone

Untreated limestone samples were characterized by scanning electron microscope (SEM) to identify their micro-morphological and microtextural characteristics. In addition, several (EDX) semi-quantitative microanalyses by spot and area scan modes were carried out and their results are listed in Table (1).

Table (1) (EDX) analytical results of untreated limestone samples

Sample No.	Analytical results (Wt. %)							
	CO_2	Cl	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	CaO
1	53.15	-	00.42	01.97	00.72	02.74	00.24	40.76
2	56.17	00.22	00.71	01.39	00.54	01.82	00.55	38.60
3	50.04	-	-	02.23	00.87	03.50	0042	42.94
4	61.88	01.03	02.23	01.96	01.07	03.02	-	28.81

In addition, the SEM images show that the studied limestone samples are composed of tiny micrite to microspar rhombic crystals tightly attached to each other (Fig. 4). They show regular to semi-regular orientation. The observed bright batches are due to differential reflection due to micro-relief.

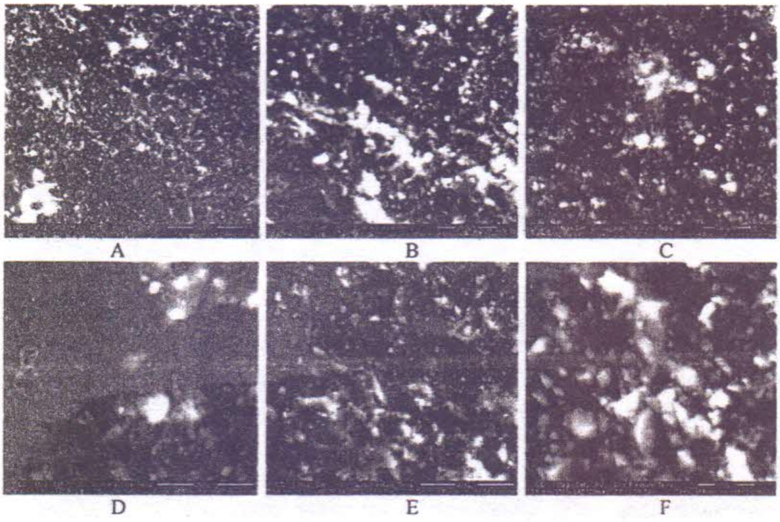


Fig.4 (SEM) images of the investigated untreated limestone samples.

3.3.2 Limestone treated with Paraloid B.72 in toluene 5%

Limestone samples which treated with paraloid B.72 dissolved in Toluene wer investigated by the SEM to identify their micro-morphological , microtextural characteristics and the consolidant penetration on the surface pores, the SEM images indicated that the studied samples: were penetrated with paraloid resin in the stone surface pores and banded the losing grains [fig.5. A, B. C].

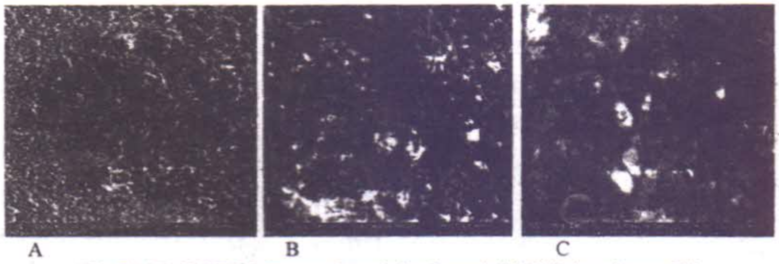


Fig.5.A.B.C (SEM) images (results) of paraloid B.72 in toluene 5%

4.3.3 Limestone treated with Paraloid B.72 in acetone 5%

Limestone samples which treated with paraloid B.72 dissolved in Acetone were investigated by the SEM, which indicated that: thin paraloid film coated some surface parts of the limestone sample this thin coated film is varied in thickness. (fig.5. A, B, C, D, E and F)

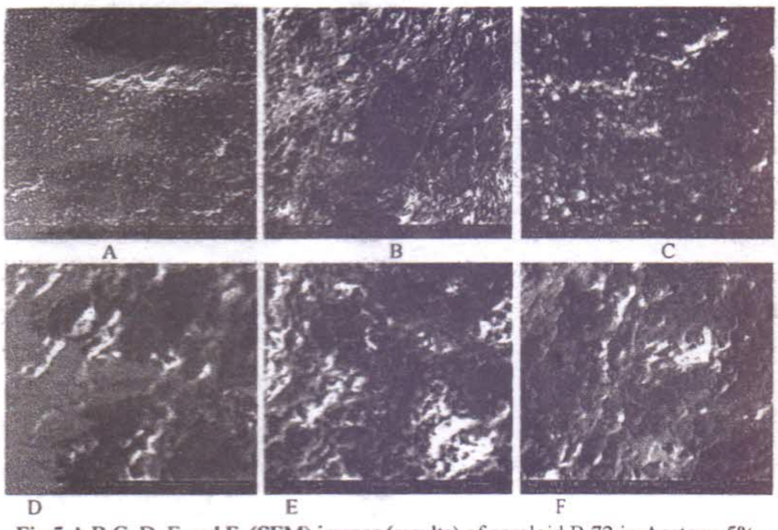
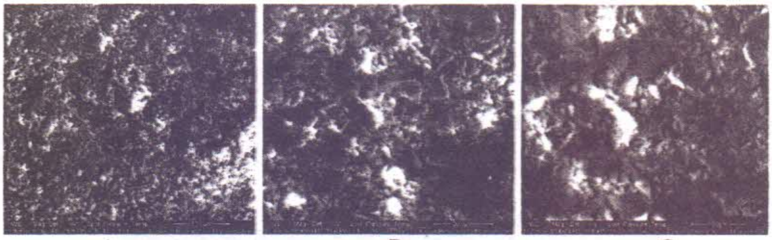


Fig.5.A,B,C, D. E and F, (SEM) images (results) of paraloid B.72 in Acetone 5%.

4.3.4 Limestone treated with Paraloid B-72 in Thinner 5%

Limestone samples that treated with paraloid B.72 dissolved in thinner at room temperature were investigated by the SEM, images observed that, scales of paraloid were formed on the pore surface of the limestone samples especially at the weakness parts. (fig.6. A, B and C)

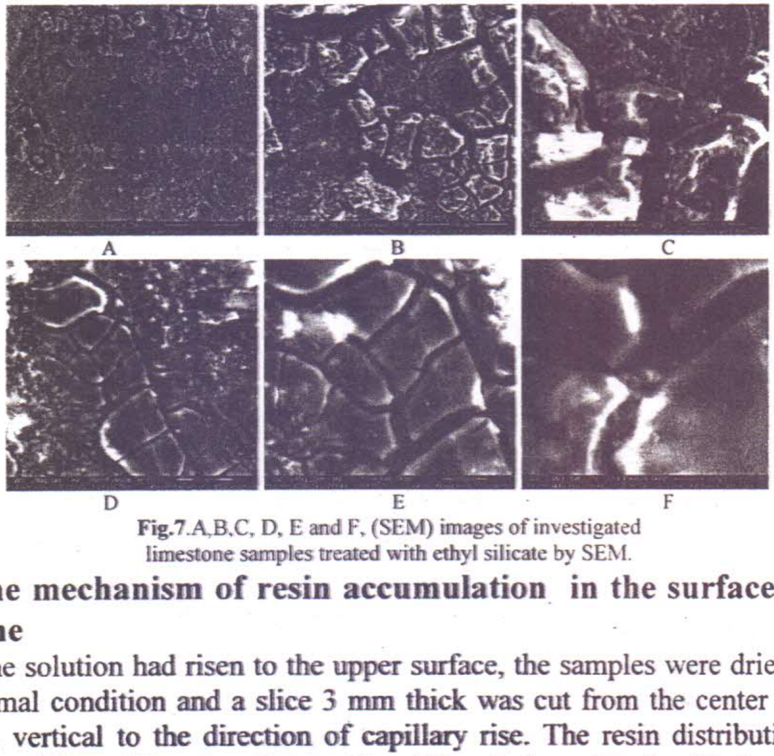


A B C

Fig.6.A,B and C, (SEM) images (results) of paraloid B.72 in thinner 5%

4.3.5 Limestone treated with Ethyl silicate

Limestone samples which treated with ethyl silicate were investigated by the SEM, that indicated the following observation a silica gel deposit between the grains of limestone surface jointing the friable calcite grains. [fig.5. A, B, C, D, E and F].



A B C

D E F

Fig.7.A,B,C, D, E and F, (SEM) images of investigated limestone samples treated with ethyl silicate by SEM.

4.4 The mechanism of resin accumulation in the surface pores of stone

After the solution had risen to the upper surface, the samples were dried under the normal condition and a slice 3 mm thick was cut from the center of each sample, vertical to the direction of capillary rise. The resin distribution was determined by etching the slices with a 5% solution of hydrochloric acid for 0.5, 1or 2 hours Calcium carbonate was decomposed in the zones where the resin did not penetrate. Characteristic stone 'frames or etching the edges' were observed as a result of consolidate migration. The following results were obtained for each consolidate materials as follows.

4.4.1 Limestone treated with Paraloid B.72 in toluene 5%

After drying, thin slices were cut off and etched with acid. The results depicted in [fig.8 A, B]

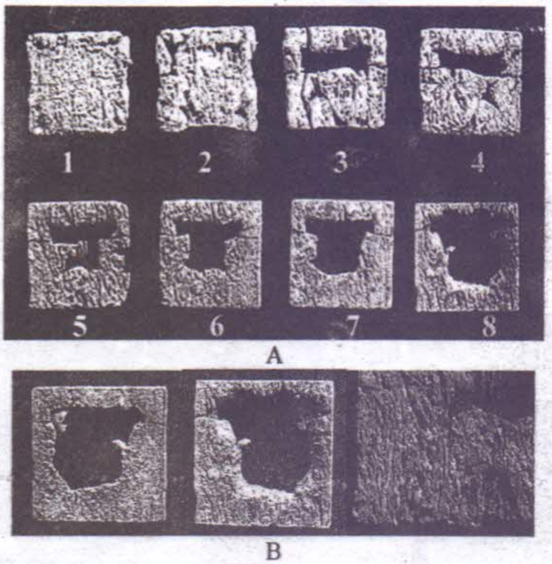


Fig.8.A,B limestone slices cut out of cubes [5 X 5 X 5 cm] treated with paraloid B.72 in toluene 5%. A, upper and lower rows shows the gradually precipitation of resin on the outer surface of the samples proves that the process is due to resin migration during the evaporation of solvent. B, close up for the last slice shows the etching of inner parts with acid that did not consolidate with paraloid B.72 in toluene 5%.

4.4.2 Limestone treated with Paraloid B-72 in Acetone 5%

After drying, thin slices were cut off and etched with acid. The results depicted in [fig.9 A, B, C]

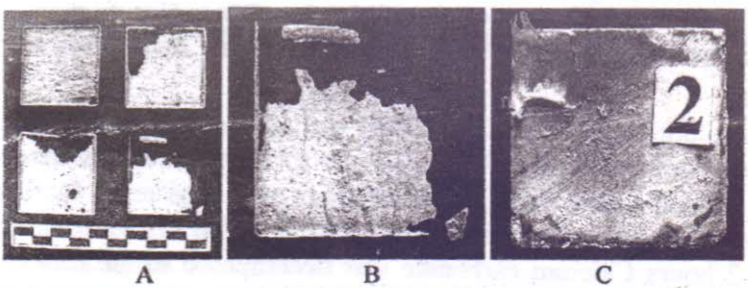


Fig.9.A, B, C. limestone slices cut out of cubes [5 X 5 X 5 cm] treated with paraloid B.72 in acetone 5%. A, the gradually precipitation of resin on the outer surface proves that the process is due to resin

migration during the evaporation of solvent. B, close up for the last slice shows the etching of corner part with acid that did not consolidate with resin, C, thin paraloid film coated some surface parts.

4.4.3 Limestone treated with Paraloid B-72 in Thinner 5%

After drying, thin slices were cut off and etched with acid. The results depicted in (fig.10)

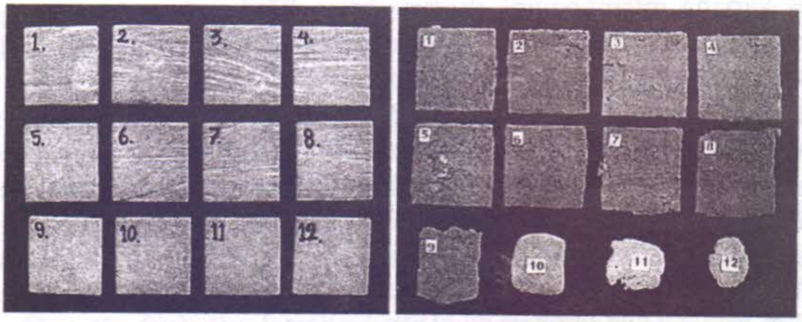
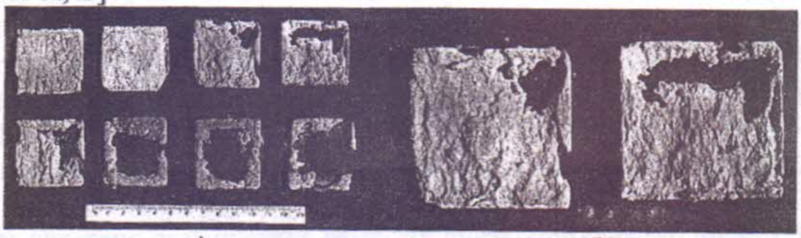


Fig.10. Limestone slices cut out of cubes [5 X 5 X 5 cm] treated with paraloid B.72 in thinner 5%. A, the slices before etching with acid. B, gradually precipitation of resin on the inner surface proves that the process is due to resin migration during the evaporation of solvent B, close up for the 5th and 11th slices shows the etching edges parts with acid that did not consolidate with resin.

4.4.4 Limestone treated with Ethyl silicate

After drying, thin slices were cut off and etched with acid. The results depicted in [fig.11 A, B]



A B

Fig.11.A, B, limestone slices cut out of cubes [5 X 5 X 5 cm] treated with Ethyl silicate A, the gradually precipitation of resin on the outer surface proves that the process is due to resin migration during the evaporation of solvent. B, close up for some slice shows the etching of inner parts with acid that did not consolidate with resin.

5. Discussion and Conclusion

The consolidate distribution was determined on the surfaces by measuring their hydrophobic properties by the time of absorption of drops of water 50 µl in volume, put in 1 cm distance. An immediate absorption of water drop proved the absence of resin. A reduced rate of infiltration or no infiltration at all provided information on the accumulation resin. The Ethyl silicate obtained the best result about 60% of the total stone sample surface area then paraloid B-72

in Thinner obtained 40% of the total stone sample surface area, paraloid B.72 in toluene obtained 30%, but paraloid B.72 in acetone obtained 10% of the total stone surface area, this low rate of consolidate distribution (P. in Acetone) considered as indication for a rapid evaporation of Acetone.

X-Ray Diffraction (XRD) Result proved that the studied limestone samples are composed mainly of low-Mg Calcite as major constituents with traces of dolomite.

Petrographically, the studied fine-grained limestone samples are heterogonous, show varying microtextural characteristics. Their micron-sized calcite grains are clotted and coagulated to form different micromorphological features. Correspondingly, their porosity values are variable but pores are well connected to each other. These criteria permit the penetration of the applied consolidant materials. Considerable modification due to digenetic processes are not observed except the small extent of recrystallization of micrite to microspar. SEM characterization reveals that the micrite is not homogenous but has areas of finer or coarser crystals.

Limestone samples which treated with (Paraloid B.72 that dissolved in, toluene, acetone and thinner) and [Ethyl silicate] were investigated by the SEM in order to identify the deep penetration of the consolidate resin on the stone surface after two months of consolidation process. Paraloid in Toluene 5% was penetrated in the stone surface pores and externally banded the loosing grains. Limestone samples which treated with paraloid B.72 dissolved in Acetone 5% have a thin paraloid film coated some surface parts of the limestone sample this thin coated film is varied in thickness. Paraloid had inhomogeneous coated film probably due to rapid solvent evaporation.

Limestone samples which treated with Paraloid B.72 dissolved in thinner showed a scales of paraloid were formed on the surface of the limestone samples especially at the friable surface parts. So it is recommended that using of toluene solvent with paraloid shows a better surface penetration than acetone and thinner solvents.

According to the pervious result of SEM investigation methods it can be deducted that the choice of solvent is extremely important as the solutions should be characterized by a low viscosity in order to penetrate easily through the pores and should not be subjected to the effect of phase separation which could reduce the penetration of resin into the deeper pores. The solvent should show an easy capillary rise which depends on the ratio of the surface tension to viscosity. The volatility, on the contrary, should be reduced, as by capillary rise into fine-porous stones the solution may be subjected to concentration due to rapid solvent evaporation.

Limestone samples which treated with ethyl silicate (Silicic acid + Alcohol) was showed a silica gel deposit between the calcite grains of limestone surface jointing the friable calcite grains. Silica gel can be obtained resulting to the following equations:

$Si(OH)_4 + 4\,C_2H_5OH \longrightarrow Si(OC_2H_5)_4 + 4\,H_2O$

Silicic acid   Alcohol   Ethyl Silicate   Water

$Si(OC_2H_5)_4 + 4\,H_2O \longrightarrow SiO_2 + 4\,C_2H_5OH$

Ethyl Silicate   Water   Silica gel   Alcohol

Silica gel is deposited as a binder between the calcite grains. This silica gel is a pure mineral, random and amorphous.[Mayer H. 1999],[Bradley, S and others 1999],[Łukaszewicz, J. W 1996]

Limestone slices treated with paraloid B.72 in toluene 5%. shows the gradually precipitation of resin on the outer surface proves that the process is due to resin migration during the evaporation of solvent, the etching inner parts with acid that did not consolidate with paraloid B.72 in toluene 5%. The etching with acid begin from the first slice gradually till etching 50% of volume in the last slices.

Limestone samples treated with paraloid B.72 in acetone 5%, were etched from one corner till completely etching of this corner. The paraloid B.72 in acetone 5%, was achieved the lower consolidation ratio comparing with the other solvent, probably due to rapid solvent (Acetone) evaporation.

Limestone slices treated with paraloid B.72 in thinner 5%. showed the etching edges parts with acid that did not consolidate with resin. But the internal parts were completely consolidate on the contrary of paraloid B.72 with acetone and toluene, this mean that the behavior of consolidate materials depends on the kind of solvent. But in this case [Paraloid B.72 in thinner] needs a deeply study to determine the relationship between resin, solvent, stone and the condition of applying the consolidate.

Limestone slices cut out of cubes [5 X 5 X 5 cm] treated with Ethyl silicate shows, the gradually precipitation of resin on the outer surface proves that the process is due to resin migration during the evaporation of solvent, it is observed that slices etched from inner parts with acid that did not consolidate with resin.

6. References

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