Evaluation of the reliability and durability of some chemical treatments proposed for consolidation of so called-marble decoration used in 19th century cemetery (Hosh Al Basha), Cairo, Egypt.

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Abstract

The conservation of so called-marble ornaments is a very important cultural heritage issue, since this kind of decoration was widely use for casing stone buildings during 19th and beginning of 20th centuries in Egypt. The wide variation of materials and techniques used for imitating natural marble is a really big challenge for conservators. Actually most of so called- marble decorations are subjected to several degradation agents which can lead to the loss of material cohesion mostly caused by alteration phenomena that often produce the detachment of large areas of imitated marble ornaments. Surface consolidation, directed to achieve cohesion and stability, is based on the use of materials with aggregating properties. This study started with characterization of the yellow veined imitated marble stucco used in Hosh Al Basha courtyard dating back to Mohammed Ali's family period (1805-1952) in Egypt. The imitated marble stucco consists of two main layers. The outer finishing layer, yellow paint veined with brown color, composed mainly of yellow zincite (ZnO). Gypsum ($CaSO_4.2H_2O$), halite (NaCl) and calcite ($CaCo_3$) were detected in this layer also. The mineral composition of the subsurface layer (prime layer) shows the presence of gypsum (major mineral), zincite (ZnO), anhydrite ($CaSO_4$) and halite (NaCl) were also detected. Two products (Paraloid B-72 and SILRES® BS OH 100) were selected to evaluate their efficiency for consolidation

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treatments of imitated marble stucco. The selected products were tested under thermal ageing. Polarizing microscope (PLM), scanning electron microscopy with the energy dispersive X-ray (SEM-EDX), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR-ATR) and colorimetric measurements were used in performing the study.

Keywords: Stucco marble, Hosh Al Basha courtyard, Characterization, Consolidation, SEM-EDX, XRD, FTIR-ATR, Colorimetric measurements

1. Introduction:

The so called-marble decoration is one of the ornamentation techniques that were obviously used in the 19th and 20th centuries architectures in Egypt. This kind of ornamentation was used to decorate the interior and exterior wall of many palaces, public fountain and the cemetery dating back to Mohammed Ali's family period (1805-1952) in Egypt. The artisan tried to get the best appearances of various kind of natural marble by using different materials and techniques. Each kind of so called-marble decoration need to perform separated study to determine materials and techniques used in its execution aiming to chose the suitable materials that should be used in its conservation process. This paper has two main aims. The first is the characterization of the materials and technique used in execution of veined yellow so called-marble used for casing the interiors walls of Hosh Al Bash building in the southern Cemetery of Cairo. The second is the evaluation of reliability and durability of acrylic and silica-based products used as preservatives for decorative elements under thermal aging to determine their suitability for preservation of veined yellow imitated marble used in Hosh Al Bash. In this paper, these products have been selected according to their commercial availability on the market of stone materials conservation. Acrylic polymers and silica-based products have been widely employed for the treatment of stone materials both as consolidants and water repellents to preserve the artifacts from further deterioration[1,2,3,4,5]. Paraloid B-72 and SILRES®BS OH 100 were selected for investigation. After their application on veined yellow imitated marble stucco specimens from Hosh Al Bash building, they were submitted to artificial thermal aging. The chemical and physical transformations have been evaluated to define their suitability for imitated marble stucco treatment.

1.2 historical background

Hosh al Basha is an Arabic name meaning, 'courtyard of the Pasha', which was given to the Royal family graveyards and more specifically, the descendents of Mohammed Ali's family. The graveyards were built on a rectangular area located behind the tomb of Al-Imam al-Shafei dating back to the 12th century, south of Cairo Citadel. The graveyard is dating back to 1815 but it was reported that Mohammed Ali bought this courtyard in 1805 [6]-[7]. At first he built a simple graveyard consists of two domes that was completed later to be six-domed complex [Fig.1]. The tomb complex was built for burial his family members and his distinguished statesmen. The interiors of the main central chambers were richly decorated with

[1] L. Toniolo, A. Paradisi, S. Goidanich, G. Pennati, Mechanical behaviour of lime based mortars after surface consolidation, J. Construction and Building Materials 25, 2011, 1553–1559.

[2] M. Favaro, R. Mendichi, F. Ossola, U. Russo, S. Simon, P. Tomasin, P.A. Vigato, Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: Photo-oxidative weathering, J. Polymer Degradation and Stability 91 (2006) 3083,3096.

[3] S. Bracci, M.J. Melo, Correlating natural ageing and Xenon irradiation of Paraloid B72 applied on stone, J. Polymer Degradation and Stability 80, 2003, 533–541

[4] G.M. Crisci, M.F. La Russa, M. Macchione, M. Malagodi, A.M. Palermo, S.A. Ruffolo, Study of archaeological underwater finds: deterioration and conservation, J. Applied Physics A 100, 2010: 855–863

[5] Wheeler G. Alkoxysilanes and the consolidation of stone: where we are now. In: Proceedings of the international symposium on stone consolidation in cultural heritage, Lisbon, Portugal; 2008. p. 41–52.

[6] Williams, Caroline, Islamic Monuments in Cairo: The Practical Guide, American University of Cairo Press, Cairo, 2002.

[7] Fadya A. Mostafa, Cairo cemetery architectures in 19th century, archeological and architectural study, MA thesis, faculty of archaeology, Cairo University, 2003.

inscriptions, precious marbles and amazingly detailed colorful paintings. The veined yellow imitated marble stucco is occupied the upper parts of walls and ceilings [Fig. 2a, b, c]. Various deterioration phenomena can be seen within the imitated marble stucco. Cracks in different depths and forms are distributive all over the stucco but they appeared obviously in the lower part of the stucco (about 2 meters high from the ground). Large areas of stucco layer are very fragile and they are completely detached from the background lime stone wall [Fig.3a, b, c]. Powdering of the superficial layer of the stucco and exfoliation of the veined yellow layer from the priming and ground layer is association the previous deterioration phenomena.

2. Experimental procedure

2.1 stucco samples, protective products treatment and thermal-aging method.

Some of representative samples were collected from the detached parts of yellow stucco veined with brown color occupied the ceiling of the main central chambers of Tuson, Ismail and Ibrahim Basha (the sons of Mohammed Ali Basha) in Hosh al Basha graveyard. The samples were first observed by digital optical Microscopy to investigate their stratigraphic sequence. Some of samples were prepared for characterization studies and the others were prepared for protective products evaluation.

The protective products tested in this work were: Paraloid B-72 and SILRES® BS OH 100. Paraloid B-72 is a well-known and studied acrylic resin[8,9, 10] which has been and still is extensively used as an adhesive and consolidant for stone materials. It is

[8] M.F.Vaz, J. Pires, A.P. Carvalho, Effect of the impregnation treatment with Paraloid B-72 on the properties of old Portuguese ceramic tiles, Journal of cultural heritage 9 (2008) 269–276.
[9] L. Yang, L. Wang, P. Wang, Investigation of photo-stability of acrylic polymer Paraloid B72 used for conservation, Sciences of conservation and archaeology 19 (2007) 54–58.
[10] S. Chapman, D. Mason, Literature review: the use of Paraloid B72 as a surface consolidant for stained glass, Journal of the American Institute for Conservation 42 (2003) 381–392.

composed of two monomers, ethyl methacrylate - methylacrylate copolymer. It was applied 5% diluted in toluene. SILRES® BS OH 100 (solventless mixtures of ethyl silicates) was used as supplied. It is commercialized by Wackrer Silicons (Germany). The products were applied by brushing at room pressure and temperature. The operation was repeated three times within half hour between each application and the treated samples were left to dry off for 15 days. Some of treated samples were submitted to investigation methods and the others were submitted to the artificial aging and then to the investigation methods to monitor the changes of protective materials after accelerated aging test.

Thermal-aging was selected to simulate the natural conditions in which the historical yellow veined stucco exists. The treated samples were put in a temperature-controlled oven "Herous-Germany" on special frames. The samples were thermally aged separately at temperature of 100^{o}C for 50 hours concerning the mineral composition of stucco.

2.2 Investigation methodologies

2.2.1. Optical microscopy

Preliminary morphological observation of the yellow veined stucco samples were carried out using digital optical light microscopy attached with the computer. Thin section of the crushed yellow paint was examined using polarized transmitted light microscopy model Nikon opti photo x23 equipped with photo camera S23, under 10x and 20x magnification in plane-polarized light.

2.2.2. Scanning electron microscopy

The microstructure of the untreated samples, treated samples and treated aged samples were observed by scanning electron microscopy (SEM) Philips (XL30), equipped with EDX micro-analytical system. This examination was performed to detect the element contents of the untreated samples and to evaluate the distribution and behavior of the protective materials on the treated samples and treated aged samples. Images were acquired in backscattered mode (BSE).

2.2.3. X-ray diffraction

The mineralogical composition of the yellow stucco veined with brown color was obtained by XRD analysis. Fine powders of the brown veins, yellow area and subsurface layer were analyzed with a diffractometer (PW 3071) Philips (CuKα 40 kV, 30 mA). The scanned 2theta range was 5 to 60 degrees.

2.2.4. Fourier transformed infrared spectroscopy

The changes of molecular structure occurring in the treated samples upon ageing procedures were monitored by BRUKER'S VERTEX 70 – Attenuated total reflection infrared spectroscopy (ATR -FTIR spectrometer) in the 650 – 4000 cm^{-1} range with resolution of $4cm^{-1}$. The vibrational bands that appear in the infrared spectra provide information about the chemical functional groups of a sample which leads to study the changes in characterization of the materials.

2.2.5. Colorimetric measurements

Color changes induced by protective products and samples degradation were evaluated by spectrophotometer Optimatch 3100® from the SDL Company. Chromatic values are expressed in CIE L*a*b* space, where L* defines lightness, which can vary from 0 (black) to 100 (white), a* denotes red/green values, and b* yellow/blue ones, i.e., + a is red, – a is green, + b is yellow and – b is blue. The ΔL, Δa, and Δb values listed in the table indicate how much a standard and a sample differ from one another in L*, a*, and b*. The ΔE indicated the total color difference was calculated using ΔL, Δa, and Δb.

which can vary from 0 (black) to 100 (white),

a* and b* are the chromatic coordinates, i.e., + a is red, – a is green, + b is yellow and –b is blue

3. Results and discussion

3.1 Characterization of the yellow veined stucco marble.

The preliminary observation of the collected samples revealed the presence of two main layers: primer white layer and outer finishing layer, which is yellow paint veined with brown color imitated the appearance of the natural marble.

The examination of the thin section of the crushed yellow paint under polarizing light microscope (PLM) displayed the aggregates of opaque brown and yellow particles (Fig.4a) No more physical and optical characteristics were observed most probably due to the well grinding of the used pigments.

The SEM was used both on the paint layer and on the individual yellow and brown pigment particles (grains) that were separated from the prime layer and mounted on a carbon stub. The SEM exhibited disintegrated cracked surface of the paint layer (Fig.4b). The total EDX analysis of the yellow veined layer showed that zinc (Zn), carbon (C) and sodium (Na) are the dominant elements; their values are 20%, 30% and 16% respectively. The value of zinc rise to 36% in some areas that contain brown veins. Small amount of sulfur (S), calcium (Ca) and chlorine (Cl) were recorded. EDX spot measurements were also taken of individual pigment particles of yellow and brown paint (Fig.4c) The gathered data showed that (Zn) is the dominant element besides (C) and (O). Some grains consisting mainly of sulfur (S) and calcium (Ca) representing gypsum were also observed.

The XRD analysis was performed on the separated layers samples. The XRD analysis of the yellow surface layer veined with brown color showed that the major mineral is zincite (ZnO) (Fig.5). Gypsum ($CaSO_4.2H_2O$), halite (NaCl) and calcite ($CaCo_3$) are the following minerals in percentage. Anhydrite ($CaSO_4$) is the minor mineral in this layer. The XRD analysis of the subsurface layer (back ground layer) indicated that the major minerals are gypsum ($CaSO_4.2H_2O$). Small amount of zincite (ZnO), anhydrite ($CaSO_4$) and halite (NaCl) were also detected (fig.6).

The mineralogical compositions of the studied samples showed that the used stucco consists of two main layers. The outer finishing layer, yellow paint veined with brown color, composed mainly of zincite (ZnO). It is called red, orange and yellow zinc oxide mineral that was mined and crushed to produce various color of zinc paints during 1830 to 1850 in Europe and America. Welsh[11] reported that The New Jersey Zinc Company not only mined the ore but also manufactured the zinc oxide pigment and the paints at their plant in Newark starting in the late 1840s. In addition, they experimented with manufacturing paints made with the crushed ore, franklinite and zincite, and they successfully marketed them in a variety of colors including orange, stone-color, light brown, brown, dark brown, black, and delicate blue. The historical information about the manufacture of zinc paints indicate that the imitated marble stucco was probably added to the courtyard later after its first construction from 1805 to 1816. Many architectural extensions were added to Hosh Al Basha courtyard during his rule and his successors' rules.

The mineral composition of the subsurface layer indicates that gypsum was used as background layer. The anhydrite detected in both layers could be primarily present in the initial material with gypsum or a byproduct of gypsum dehydration. Transformation

[11] Welsh, S.F., 2008. Identification of 1850s Brown Zinc Paint Made with Franklinite and Zincite at the U.S. Capitol, APT Bulletin, **39**, pp. 17-30.

between gypsum and is a delicate process and can proceed in reverse depending on the climatic (RH and T) conditions, in which the transformation of calcium sulphates occurs has been studied by several authors[12]. Changes in calcium sulphates can take place in hot and humid climates. The dehydration of gypsum begins at approximately 80°C, although in dry air, some dehydration will take place already at 50°C[13]. The presence of significant amount of halite, which is generated in the background limestone wall due to the height of ground water in courtyard area, can accelerate the transformation process. It has been shown that the transition temperature for dehydration of gypsum is significantly reduced to around 18°C in the presence of sodium chloride[14]. All of the mentioned conditions are attained in Hosh Al Basha courtyard. The transformation of gypsum causes volume changes and degradation of the imitated marble stucco components which clarify the reasons for cracks, exfoliation and powdering of the yellow veined stucco. Recovering the internal cohesion of the stucco materials is very essential demand to stop losing of large parts of the imitated marble stucco. Surface consolidation, directed to restore cohesion and stability, is the first step in the conservation process.

3.2 evaluation of selected consolidation materials for imitated marble conservation.

The treated samples with consolidation materials were examined by colorimetric test, SEM microscopy and FTIR analysis; and after the thermal aging the samples were examined by the same instruments to assess the reliability and durability of the selected materials used with the stucco.

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12 F.Mees, G.Stoops, Circumgranular bassanite in a gypsum crust from eastern Algeria, J. Sedimentology 50 (2003) 1139- 1145.

13 S. Azam, Influence of mineralogy on swelling and consolidation of soils in eastern Saudi Arabia, J. Can. Geotech, 40 (5), 2003, 964- 975.

14 Hardie, L. A., The gypsum-anhydrite equilibrium at one atmosphere pressure, Am. Miner., **52,** 1967, 171–200.

3.2.1 Colorimetric test

Color alterations in the examined samples after product application are expressed by the ΔE parameter, which indicates the difference between each chromatic coordinate (ΔL*, Δa* and Δb*) in untreated, treated and treated aged samples. According to Italian guidelines for the restoration of stone buildings, the ΔE value must be < 5[15]. In this respect, samples treated with paraloid B 72 have ΔE values between 9.44 and 5.82 and those treated with SILRES® BS OH 100 have ΔE values between5.52 and 5.15. These values indicate that both products induced chromatic variations, visible to the naked eye, which are greater than the acceptable limit (ΔE = 5) but the ΔE values of samples treated with SILRES® BS OH 100 are still more acceptable than those treated with paraloid B 72 since they are near to 5. The completed data listed in (Table 1) showed that the value ΔL of the samples treated with Paraloid B72 is - 3.05 which indicate the decrease in lightness. It is worth to clear that ΔL value = the difference between the L value of treated sample and the L value of standard sample; ΔL*=L*2-L*1. So when the value of ΔL is negative this means that the value of treated sample is less (near to 0 values) than the value of standard samples. A rise in lightness was observed in the samples treated with SILRES® BS OH 100 indicating that this product tended to lighten the sample. It is worth noting that these color variations decreased after the thermal aging with both products. In general the total chromatic variation values ΔE of the two products after aging are not far from the allowable color change in stone materials conservation since the

[15] Mauro F., La Russ, Germana Barone, Application of protective products to ‘‘Noto’’ calcarenite (south-eastern Sicily): a case study for the conservation of stone materials, J. Environ Earth Sci.62, 201, 1263 – 1272.

value of 5 and value of 6 are laying in the same rang of ΔE scale as follow[16]:

- $\Delta E < 0.2$: not perceptible difference
- $0.2 < \Delta E < 0.5$: very small difference
- $0.2 < \Delta E < 0.5$: small difference
- $2 < \Delta E < 3$: fairly perceptible difference
- $3 < \Delta E < 6$: perceptible difference
- $6 < \Delta E < 12$: strong difference
- $\Delta E > 12$: different colours

3.2.2 Visual and SEM microscopy observation

Visual observations indicated that the consolidation treatment changed the color of the samples. When the surfaces of the samples were moistened with consolidant, they darkened, but after drying, the darkness of the surfaces decreased. The SEM examination of the treated samples with both products were performed to study the type of coating, film-forming capacity, adherence to material, continuity of treatments, or cracking. The SEM examination of the samples treated with Paraloid B-72 show that the consolidant filled most of the pores and obscured many of particles (Fig. 7 a, c). No visible cracks are seen in the film coating. The SEM examination of the samples treated with SILRES® BS OH 100 showed a homogeneous coating of the particles more than the coating with Paraloid B-72(Fig.7 b, d). This may be due to the fact that the

[16] Limbo, S., Piergiovanni, L., Shelf life of minimally processed potatoes Part 1. Effects of high oxygen partial pressures in combination with ascorbic and citric acids on enzymatic browning. *Postharvest Biology and Technology*, 39, 2006, 254–264)

chemicals structure of SILRES® BS OH 100 can construct longer chains that lie on the surface of the particles and coating them. After aging no significant changes were observed in the consolidants film which indicate that microstructure of both products are stable under the effect of the artificial thermal aging (fig.7 e, f).

3.2.3 FTIR-ATR analysis.

The infrared spectra of the sample treated with Paraloid B72 before and after aging show small change of the chemical structure (Fig. 8) and (table 2). The change happened at the main absorption

peak 3000 ~ 3600 cm^{-1} corresponding to OH group. No remarkable

changes at the 1727 cm^{-1} (corresponding to C =O bond), at 2917 cm^{-1} (corresponding to CH_3), and 2849 cm^{-1} (corresponding to CH_2) were recorded, suggesting the stability of these bonds under the thermal aging. The disappear of the C = C unsaturated bonds, evidenced by the absorption at around 1682 cm^{-1}, is a consequence of the polymerization of the unsaturated bonds under the thermal aging. The intensity increase of the absorption peaks at 1540 cm^{-1}, 1414 $cm^{-1}$and 1318 cm^{-1}(corresponding to C-H and C-O-C bonds) is most probably a consequence of the polymerization increasing resulting of the condensation under the thermal aging. The modification and decreasing observed at the 1000 – 1200 cm^{-1} area is most probably due to the chain-scission of Si – O – C and Si – O – Si bonds. In general, the Paraloid B72 showed good stability towards the thermal aging because of the absence of new cross-linking (new compound)[17].

[17] M. Lazzari, O. Chiantore, Thermal-ageing of paraloid acrylic protective polymers, J. Polymer 41, 2000, 6447–6455.

The FTIR spectra of the sample treated with SILRES® BS OH 100 show significant changes in all major signals which all decrease in their intensity (Fig.9) (table2). Considering the attribution of the typical absorption bands and their variation during degradation it appears that the major chemical groups CH3 (2921cm-1), CH_2 (2851 cm-1), Si – CH_3 (874 cm-1and 797 cm-1) and Si – O – Si, Si – O – C, Si – CH_3 (1000 – 1200 cm-1) are affected by the thermal degradation. As a consequence, one can conclude that the environmental stability of SILRES® BS OH 100 is somewhat lower as compared to this of Paraloid B72.

4 Conclusions

This study was focused on stucco so called-marble conservation as it is an important cultural heritage issue, particularly for 19th century in Egypt where the imitation of marble has been widely used in building decorations. The first step in the imitated marble conservation is to characterize the materials and techniques used for execution of imitated marble because of their amazing variety. The results obtained in this study showed that the yellow veined stucco marble (imitated marble) used in Hosh Al Basha courtyard consists of two main layers. The outer finishing layer, yellow paint veined with brown color, composed mainly of yellow zincite (ZnO) that was used during 1830 to 1850. The date of using zinc paint indicates that the imitated marble stucco was probably added to the courtyard later after its first construction from 1805 to 1816. The subsurface layer (prime layer) is composed mainly of gypsum. The yellow veined stucco marble is exposed to high rate of deterioration as the presence of significant amount of halite and anhydrite detected in the studied samples.

The study showed the importance of studying interactions between consolidation products and imitated marble materials. In particular, we aimed at testing the effectiveness of two products (Paraloid B-

72 and SILRES® BS OH 100) on yellow veined stucco marble, in order to find the best product to preserve the stucco from further weathering and degradation. The selected products were tested under thermal aging. The result obtained by SEM, colorimetric test and FTIR-ATR showed the differing efficiency of the two products. In particular, SILRES® BS OH 100 is less stable than Paraloid B72, although it did not cause any great variations in original color after treatment. Paraloid B72 showed good stability, although it produced evident changes in color of the yellow veined stucco after treatment, a detail which may relate to the interference between brown veins and the yellow paint in various degrees in one studied sample. However, it is worth noting that these color variations decreased to the allowable range during thermal degradation. Therefore, protective treatment with Paraloid B72 may be proposed to preserve the imitated marble stucco with consideration of humidity in the surrounding environment. A deeper study focusing on the efficiency of the selected products under the salt crystallization and changing of the humidity and temperature conditions is needed. Also other mechanical tests which include scratch and hardness tests will be done.

Fig. 1 shows the tomb complex of Hosh Al Basha courtyard in Al-Imam Al-Shafei

Fig. 2 shows the interiors of the main central chambers decorated with imitated marble occupied the upper parts of walls and ceilings

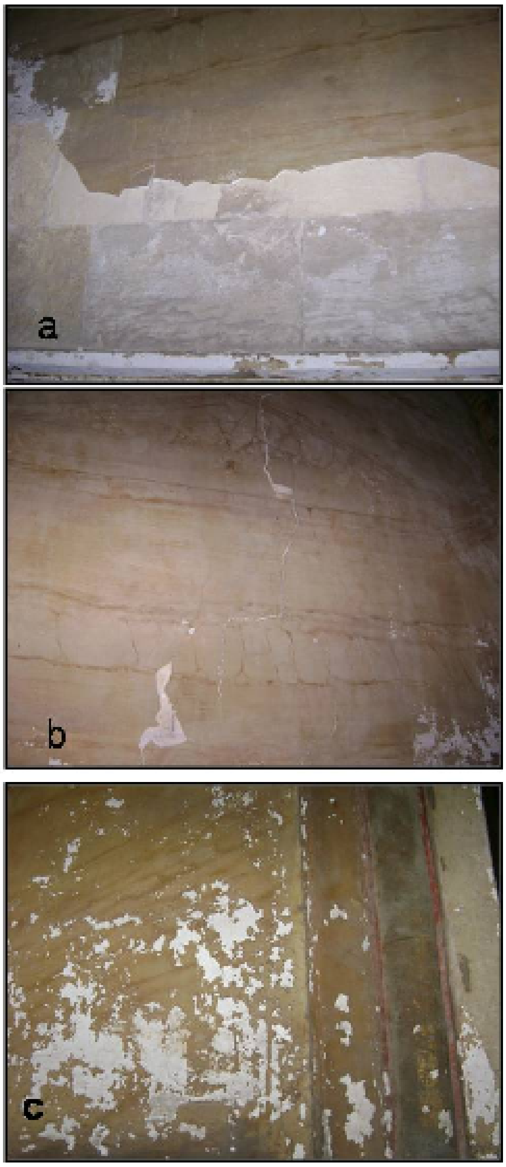

Fig. 3 shows the deterioration phenomena of the imitated marble, (a) shows the missing parts, (b) the arrow points to the crack and (c) shows the exfoliation of the veined layers

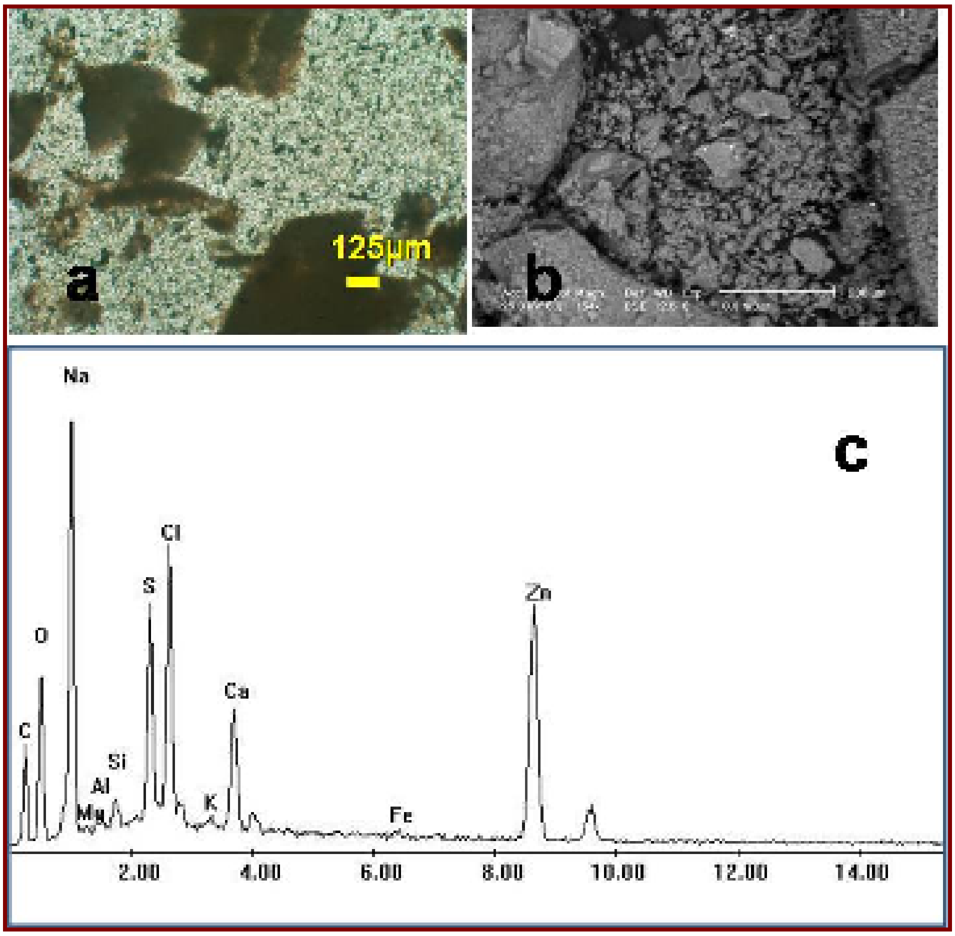

Fig. 4: (a) Photomicrograph of crushed yellow pigments in the yellow veined paint. 20X, (b) SEM image of yellow and brown grains, (c) EDX spot analysis from image (b).

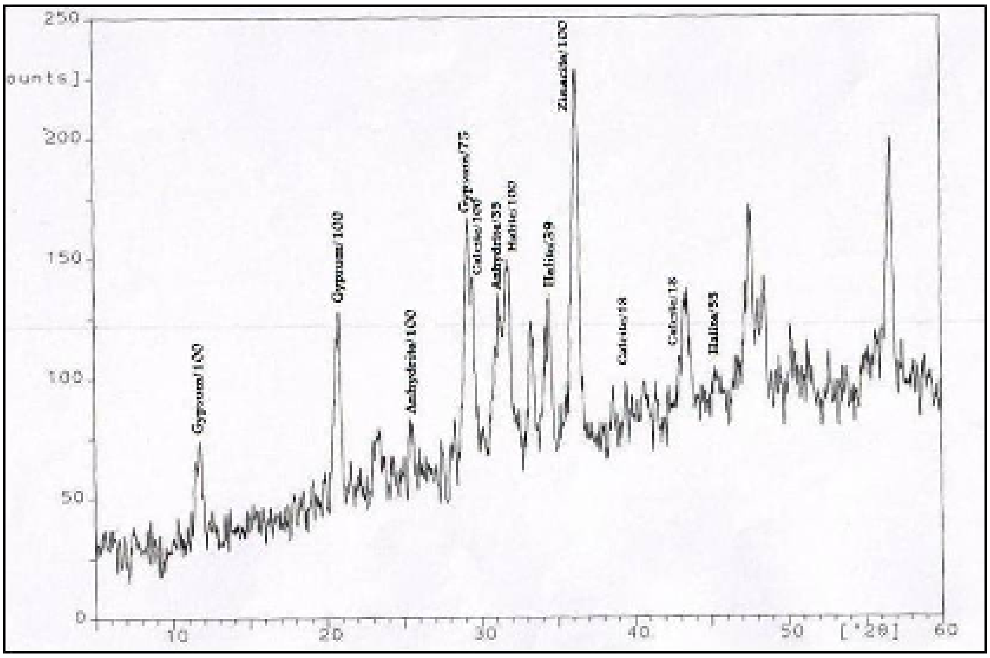

Fig. 5 the XRD patterns of the yellow veined layer

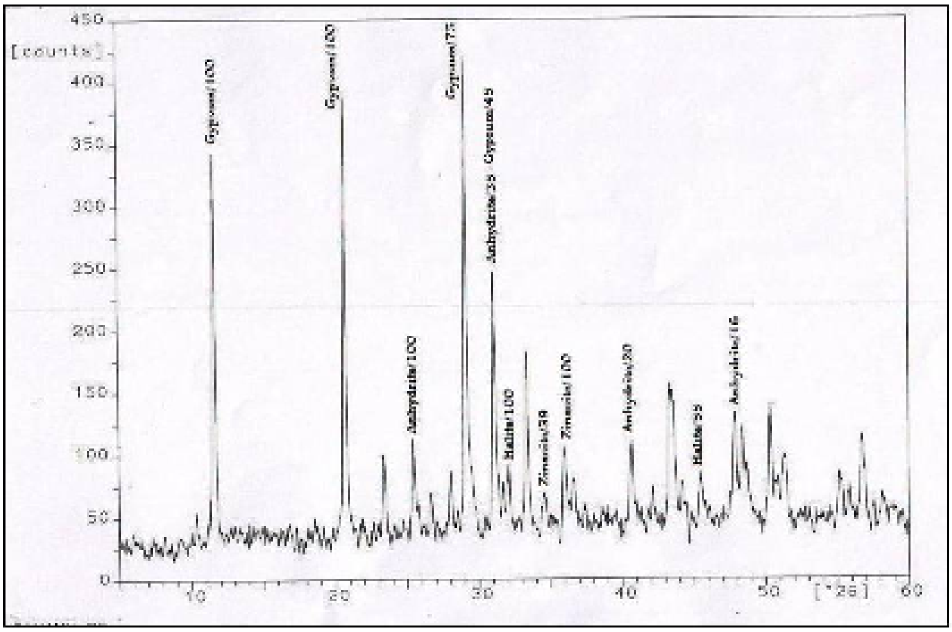

Fig. 6 the XRD patterns of the subsurface layer

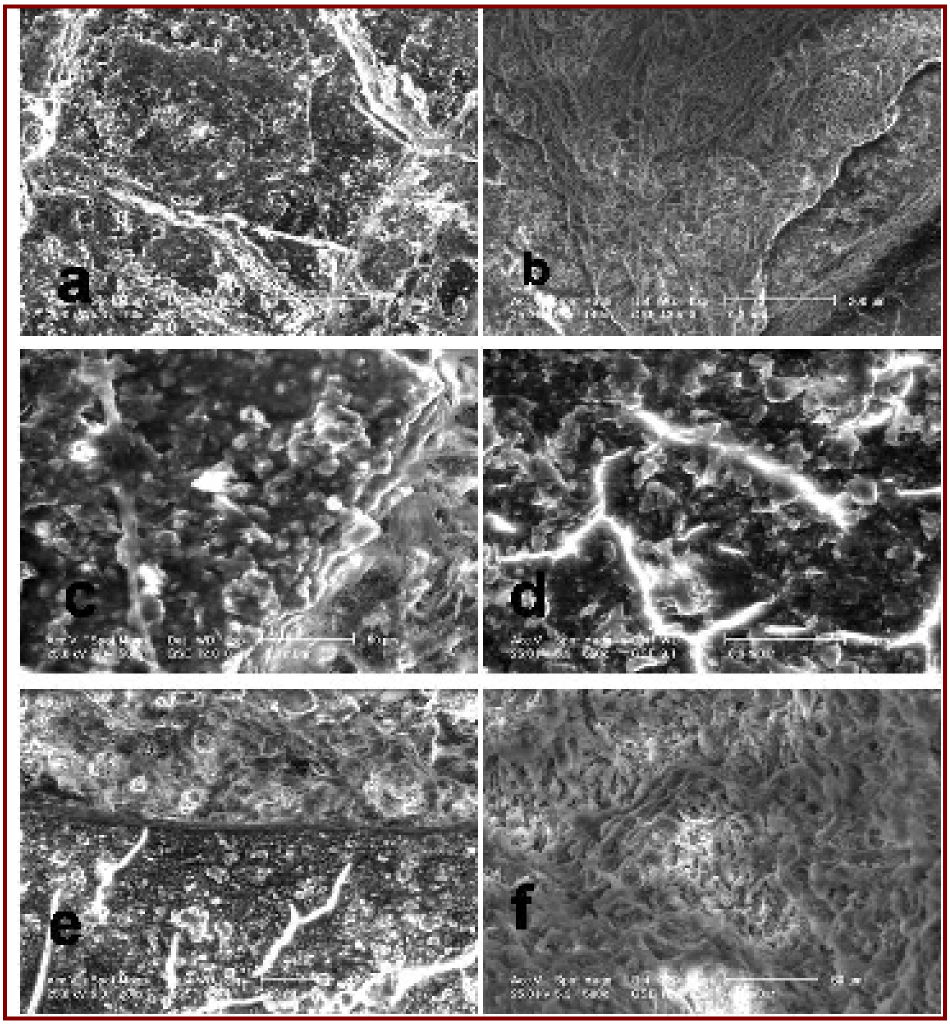

Fig.7 (a) and (c) show the SEM image of the sample treated with Paraloid B 72 before aging under different magnification, (b) and (d) show the SEM image of the sample treated with SILRES® BS OH 100 before aging. Images (e) and (f) show the SEM image of the samples treated with Paraloid B 72 and SILRES® BS OH 100 respectively.

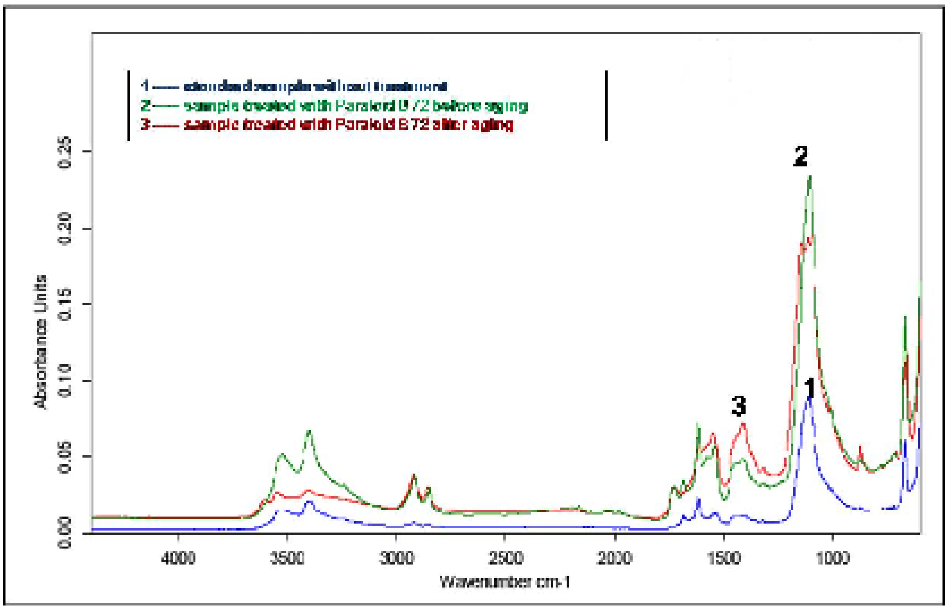

Fig. 8 shows the FTIR- ATR spectra of the sample untreated (1), treated with Paraloid B72before aging (2) and after aging (3)

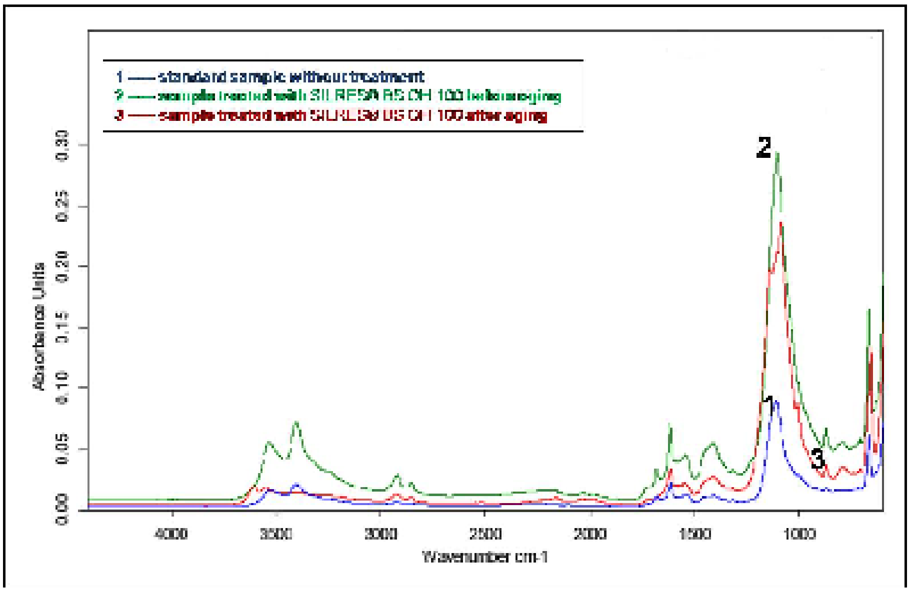

Fig. 9 shows the FTIR- ATR spectra of the sample untreated (1), treated with SILRES® BS OH 100 before aging (2) and after thermal aging (3)

Table 1 color measurement in treated and aged samples

Applied protective materials	Δ (treated and untreated samples)				Δ (aged and untreated samples)			
	Δ*L**	Δ*a**	Δ*b**	Δ*E*	Δ*L**	Δ*a**	Δ*b**	Δ*E*
Paraloid B72	-3.05	1.57	8.80	9.44	-2.07	1.78	5.14	5.82
SILRES® BS OH 100	1.42	0.57	5.30	5.52	0.51	1.61	4.87	5.15

Table 2. FTIR of treated samples before aging and after aging.

FTIR-ATR of sample treated with Paraloid B72 before aging		FTIR-ATR of sample treated with Paraloid B72 after aging		FTIR-ATR of sample treated with SILRES® BS OH 100 before aging		FTIR-ATR of sample treated with SILRES® BS OH 100 after aging	
Wavenu-mber	Rel. intensity	Wavenu-mber	Rel. intensity	Wavenu-mber	Rel. intensity	Wavenu-mber	Rel. intensity
3524	0.017	3604	0.003	3531	0.020	3605	0.016
3399	0.058	3544	0.005	3401	0.064	3551	0.004
2918	0.024	3404	0.015	2922	0.014	2924	0.006
2850	0.010	2924	0.029	2851	0.005	2853	0.002
1727	0.010	2852	0.008	1683	0.010	1619	0.021
1683	0.010	1734	0.010	1620	0.052	1549	0.006
1620	0.055	1618	0.006	1547	0.012	1411	0.013

1574	0.003	1549	0.038	1412	0.028	1090	0.214
1540	0.027	1410	0.042	1319	0.002	1009	0.009
1414	0.023	1318	0.003	1109	0.256	874	0.010
1318	0.002	1145	0.009	874	0.017	778	0.001
1110	0.203	1113	0.008	797	0.006	660	0.090
875	0.004	1008	0.006	668	0.089		
667	0.073	874	0.017				
		713	0.006				
		660	0.062				