

EVALUATION OF THE EFFECTIVENESS OF SOME CONSOLIDANTS USED FOR THE TREATMENT OF THE XIXTH CENTURY EGYPTIAN CEMETERY WALL PAINTING

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Abstract

A large number of wall paintings suffer from many aspects of deterioration such as cracking, surface powdering, losing painted layers and forming colored stains due to biological or salt effects. Surface consolidation, directed to achieve cohesion and stability, is based on the use of materials with aggregating properties. Two products (Paraloid B-72 and SILRES® BS OH 100) were selected to evaluate their efficiency for consolidation treatments of painted surfaces of Hawsh al- Basha courtyard dating back to Mohammed Ali's family period (1805-1952) in Egypt. Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy with Attenuation Total Reflection (FTIR-ATR) and Colorimetric measurements were used in performing the study. The results showed that the stability of the consolidants depended on the chemical composition of the pigments.

Keywords: wall painting; Hawsh al- Basha; consolidation; SEM, FTIR-ATR; colorimetric measurements.

Introduction

Various deterioration phenomena can be seen within the painted layers of the chamber wall of Khediew Tawfik's mother, Nour Shafaq, in the Hawsh al-Basha graveyard dating back to Mohammed Ali's family period (1805-1952) in Egypt. Cracks in different forms and depths are distributed all over the painted layer but they appeared obviously in the lower part. Large areas of the painted layer are very fragile and completely detached from the background lime stone wall. Exfoliation from the priming and ground layer and powdering of the superficial layer of the paint are associated with the previous deterioration phenomena (Fig. 1).

These indoor wall paintings are exposed to uncontrolled environmental conditions. Salty ground water rising in the walls, in addition to rainfall which enters through the broken windows in the upper part of the walls raising the interior relative humidity. These factors led to the different forms of previously mentioned decay.

The aim of this work is to evaluate the effectiveness of acrylic and silica-based products commonly used for preservation of painted layers in order to find the best product to preserve the pigments, which are composed of various chemical compositions from further weathering and degradation. These products were selected according to their commercial availability on the market of stone materials conservation both as consolidants and water repellents to preserve the artifacts from further deterioration [1]. Paraloid B72 and SILRES®BS OH 100 were selected for the same purposes in this research. Paraloid B72 is a well-known and studied acrylic resin which has been and still is extensively used as an adhesive and consolidant for stone materials

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[2-4]. It is composed of two monomers, ethylmethacrylate - methylacrylate copolymer. SILRES® BS OH 100 (solventless mixtures of ethyl silicates) was used as supplied. Once SILRES® BS OH 100 is applied; it reacts with the water in the capillary pores to form a silica- gel- based mineral binder (SiO_2aq). The binder stabilizes the building material by way of covalent Si-O- Si bonds [5, 6]. After their application on wall painting specimens detached from Hawsh Al-Basha building, they were submitted to artificial thermal aging. The chemical and physical transformations were evaluated to define their suitability for wall painting treatment. Investigation of the materials and painting techniques used in wall paintings of Hawsh Al-Basha courtyard has been already discussed before by Darwish, 2013 [7]. Pigments including white zincite, earth green, blue synthetic ultramarine, yellow massicot, black a mixture of magnetite & graphite, brownish red lead and golden brass (Cu + Zn) were identified. The binding medium in the painting was determined as animal glue. Two preparation layers were identified: the inner coarse ground layer composed of gypsum as a major with calcite and small amounts of quartz and the outer fine ground layer composed of calcite only.



Fig. 1. Deteriorated wall paintings: various deterioration phenomena which can be seen within the painted layers in the chamber wall of Khediew Tawfik's mother Nour Shafaq in Hawsh al- Basha building.

Materials and Methods

Painted layers samples

Representative samples were collected from the detached parts of painted layers with different colours in the chamber wall of Khediew Tawfik's mother Nour Shafaq in Hawsh al-Basha graveyard (Table 1). The samples were prepared for protective products evaluation.

Table 1. Samples treated by Paraloid B 72 and SILRES® BS OH 100

Sample Colour	Pigment	Chemical name	Chemical formula	Average dimensions of the treated samples (cm ²)
yellow	massicot	Lead(II) oxide	PbO	1.7X1.1
green	green earth	Complex aluminosilicate	$\text{K}[(\text{Al,FeIII}),(\text{FeII,Mg})](\text{AlSi}_3\text{Si}_4\text{O}_{10}(\text{OH})_2)$	1.4X1.2
blue	Synthetic Ultramarine	A complex sulfur-containing sodium aluminum silicate	$\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$	1.3X1.4
white	zincite	zinc oxide	ZnO	1.5X1.2
black	Magnetite + graphite	iron(II,III) oxide + carbon	Fe_3O_4 + C	1.6X1.4
brownish red	minium	lead tetroxide	Pb_3O_4	1.3X 1.1

Protective products treatment

The protective products tested in this work were: Paraloid B72 and SILRES® BS OH 100. Paraloid B72 was applied 5% diluted in toluene. SILRES® BS OH 100 (solventless mixtures of ethyl silicates) was used as supplied by Wacker 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 cure for 15 days. Some of the treated samples were submitted to investigation methods and others were

submitted to the artificial aging and then to investigation methods to monitor the changes of protective materials after accelerated aging test.

Thermal - aging method

Thermal-aging was selected to simulate the natural conditions in which the historical paints exist. The treated samples were put in a temperature-controlled oven "Herous-Germany" on special frames. The samples were thermally aged separately at a temperature of 100°C for 50 hours according to Feller, 1999 [8].

Scanning electron microscopy

The microstructure of treated samples and treated aged samples were observed by scanning electron microscopy (SEM) Philips (XL30). This examination was performed 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).

Colorimetric measurements

Color changes induced by protective products and samples degradation were evaluated by spectrophotometer Optimatch 3100® from the SDL Company. The dimension of the measured area of each sample equals to (1X1) cm². The colors are given in CIE Lab coordinates, L* corresponding to the brightness (100 = white, 0 = black), a* to the red–green coordinate (positive sign = red, negative sign = green), and b* to the yellow–blue coordinate (positive sign = yellow, negative sign = blue). The total color difference ΔE^* between two color stimuli $\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2}$ [9-11].

Fourier transformed infrared spectroscopy

The changes of molecular structure occurring in the treated samples upon aging procedures were monitored by BRUKER'S VERTEX 70 – Attenuated total reflection infrared spectroscopy (ATR -FTIR spectrometer) in the 650 – 4000cm⁻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.

Results and Discussions

Visual and SEM microscopy observation

The morphology of the surface of treated and treated aged samples with both products was investigated using Scanning Electron Microscope (SEM).

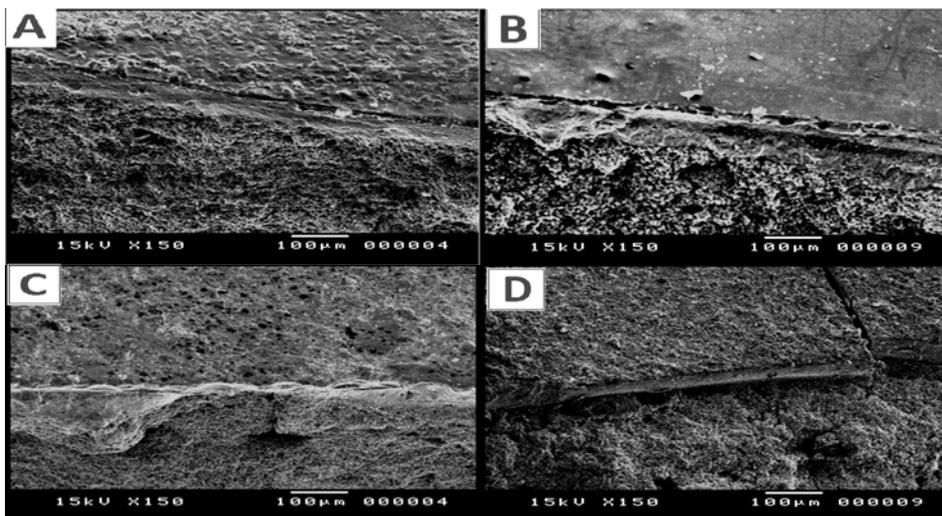


Fig. 2. SEM photomicrographs of the treated yellow pigment: A - SEM photomicrograph (150X) of the treated samples with B72 shows the blistered film of the polymer on yellow pigment with priming layer and binding medium; B - SEM photomicrograph (X150) of the aged treated samples with B72 shows that due to the low T_g of B-72, better distribution of the polymer within the pigment layer was evident; C - SEM photomicrograph (150X) of treated samples with SILRES® BS OH 100; D - SEM photomicrograph (150X) of the aged treated samples with SILRES® BS OH 100 shows a crack in the paint layer with the fine preparation layer underneath.

Scanning electron micrographs were taken of selected samples to study the type of coating, film-forming capacity, adherence to material, continuity of treatments or cracking. Some types of damaged aspects were identified in most of the studied samples with examples shown in figures 2, 3 and 4.

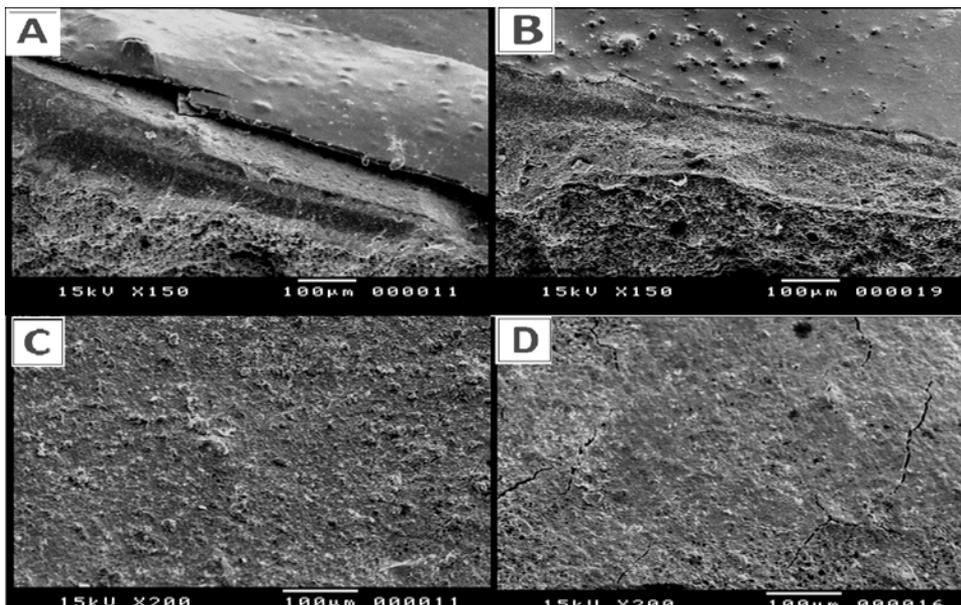


Fig. 3. SEM photomicrographs of the treated white pigment: A - SEM photomicrographs (150X) of the treated samples with B72 shows detachment of the paint layer from the fine preparation layer as a result of surface tension effect.; B - SEM photomicrographs (150X) of the aged treated samples with B72 shows that thermal effect decreases the viscosity of B72 and this permits penetration of the polymer and good attachment results with formation of blistering. Reduction in the viscosity is explained that chain scission is dominant reaction in the degradation of B-72 rather than cross linking [10]; C - SEM photomicrographs (200X) of the treated samples with SILRES® BS OH 100 shows that adhesion of pigments with priming layer and binding media are quite well; D - SEM photomicrographs (200X) of the aged treated samples with SILRES® BS OH 100 shows the formation of blistering and micro-cracks on the surfaces of the paintings.

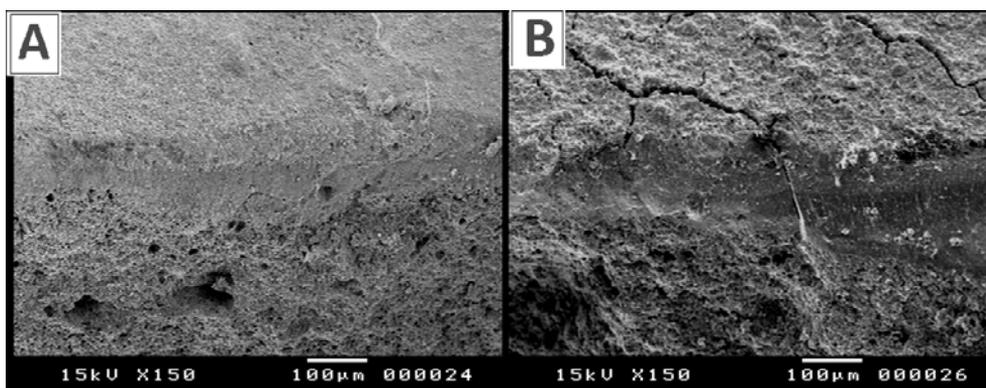


Fig. 4. SEM photomicrographs of blue pigment treated with SILRES® BS OH 100: A - SEM photomicrograph (150X) of the treated samples shows that adhesion of pigments with priming layer and binding media are quite well; B - SEM photomicrograph (150X) of the aged treated samples shows the formation of blistering and micro-cracks on the surfaces of the paintings.

Colorimetric test

In this research, colorimetric test was used first for the determination of the natural pigment color parameters. The following step was the investigation of the color changes induced by the treatment of the painted surfaces with the protective products. Finally, this technique was used for the assessment of the pigment color changes that intervened during the artificial accelerated aging tests. Based on color parameters measurements, the ΔE values were calculated. These values indicate the registered color differences between the natural and the treated or treated/aged pigment samples. The colour changes that might intervene following the treatment of painted surfaces with chemical products have to be reduced to a maximum extent in order to alter as little as possible as compared to the untreated samples. According to Italian guidelines for the restoration of stone buildings, the ΔE value must be < 5 ; other authors state that this threshold value should be < 10 [9-14]. According to Limbo and Piergiovanni, 2006 [15] ΔE scale in stone materials conservation is as follow:

- $\Delta E < 0.2$: not perceptible difference
- $0.2 < \Delta E < 0.5$: very small difference
- $0.5 < \Delta E < 2$: 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

In this respect, black and blue samples treated with paraloid B72 before and after aging have acceptable ΔE values where it ranges between 1.83 and 2.61 for black samples and between 1.15 and 2.33 for blue samples. Other coloured samples treated with B72 are not fitting in these limits i.e., have ΔE values between 8.62 and 22.31 depending on their chemical composition. These values indicate that B72 induced chromatic variations resulting from its thermal oxidative decomposition. The completed data are listed in Table 2.

The results in Table 3 showed that colour variations of black, brownish red lead and blue samples treated with SILRES® BS OH 100 decreased after the thermal aging where ΔE values were 0.94, 6.30 and 3.67 respectively and fitted the acceptable ΔE values. On contrary, consolidation of both white and yellow samples by SILRES® BS OH 100 produced different colours where ΔE became 14.69 and 27.26 respectively after thermal aging.

Table 2. Color measurement of B72 treated and treated aged samples

Sample	Comp.	ΔL	Δa	Δb	ΔE	Observations
Black pigment	B72	-1.65	-0.16	-0.02	2.61	$\Delta E < 5$, i.e., acceptable changes were obtained. ΔL values proved that when the surfaces of these pigments were moistened with B72 they darkened, but after aging, the darkness of the black surfaces decreased and lightening of blue surfaces resulted.
	B72 AG*	-0.49	-0.11	-1.76	1.83	
Blue pigment	B72	-1.14	0.05	-0.14	1.15	$10 > \Delta E > 5$, i.e., slight difference was obtained between untreated and treated samples. After aging $\Delta E > 12$: different colour was produced as a result of thermal oxidative decomposition and generation of ketone and acid groups which were confirmed by FTIR (see figure 8).
	B72 AG*	1.53	-1.14	-1.33	2.33	
Brownish red lead pigment	B72	-0.26	4.77	7.18	8.62	ΔE value between treated and untreated green samples was close to the threshold value, while whose value increased after the thermal aging and produced another colour. The results also showed that B72 tended to lighten these samples especially after aging.
	B72 AG*	-0.49	10.52	8.16	13.32	
Green pigment	B72	5.87	-3.03	6.32	9.14	The results showed that B72 tended to lighten these samples and produced another colour where, $\Delta E > 12$. This value decreased after the thermal aging.
	B72 AG*	10.86	-2.22	12.00	16.34	
White pigment	B72	19.10	0.10	6.35	20.13	
	B72 AG*	17.88	0.33	8.19	19.67	
Yellow pigment	B72	10.15	4.16	19.43	22.31	
	B72 AG*	6.54	2.86	13.66	15.41	

AG* – after aging

Table 3. Color measurement of SILRES® BS OH 100 treated and treated aged samples

Sample	Comp.	ΔL	Δa	Δb	ΔE	Observations
Black pigment	SILRES® BS OH 100	-4.65	0.12	-2.87	5.47	Color variations decreased after the thermal aging where, ΔE became 0.94 and acceptable changes were obtained. ΔL results also showed that the treatment increased the darkness but after aging, the darkness of the black surfaces decreased and lightening took place.
	SILRES® BS OH 100 AG*	0.54	0.22	0.74	0.94	
Reddish brown pigment	SILRES® BS OH 100	2.65	1.72	6.58	7.30	ΔL values showed that treatment caused lightening of these samples but after aging it tended to darken them. ΔE value < 10 and referred to induction of slight chromatic variations within the accepted range.
	SILRES® BS OH 100 AG*	-4.08	3.36	3.43	6.30	
Green pigment	SILRES® BS OH 100	-1.57	-2.43	2.13	3.59	Thermal aging increased the lightness of the samples and induced accepted slight colour difference.
	SILRES® BS OH 100 AG*	3.81	-3.63	5.94	7.94	
Blue pigment	SILRES® BS OH 100	-0.52	-0.11	-6.80	6.82	ΔL values showed that SILRES® BS OH 100 tended to darken these samples. Color variations decreased after the thermal aging and acceptable changes were obtained.
	SILRES® BS OH 100 AG*	-3.42	-0.01	1.33	3.67	
White pigment	SILRES® BS OH 100	10.40	-0.08	3.22	10.89	ΔL values proved that treatment of White and yellow pigments by SILRES® BS OH 100 increased the lightness. ΔE values indicated that this product induced strong chromatic variations and produced another colour especially after aging.
	SILRES® BS OH 100 AG*	13.53	0.05	5.72	14.69	
Yellow pigment	SILRES® BS OH 100	3.18	0.71	0.28	3.27	
	SILRES® BS OH 100 AG*	13.55	5.08	23.10	27.26	

AG* – after aging

FTIR-ATR analysis

The infrared spectra of the samples treated with Paraloid B72 before and after thermal aging showed that the stability of this consolidant depended on the chemical composition of the pigments. No remarkable changes were shown in blue, green and yellow samples reflecting the good stability of B72 with these pigments (Fig. 5). Black, white and brownish red lead samples showed several spectral changes. Intensity of the absorption bands which demonstrates existence of long polymer chain in black samples have decreased. In the spectral region between 3100 and 2800 cm^{-1} the absorption bands, corresponding to stretching vibration of C-H, CH₂, CH₃, have decreased as long with the bands corresponding to vibration of skeleton CH₂ in longer chains at 712 cm^{-1} . The absorption band at 1434 cm^{-1} corresponding to vibration of methyl and methylene groups, has disappeared. Carbonyl band at 1721 cm^{-1} of ester groups decreased. This particular sample's degradation may be considered due to the presence of iron ions in the pigment composition (mixture of graphite and magnetite) which catalyzed polymer oxidation (Fig. 6) [16].

In white samples, the presence of oxidized structures is detectable after thermal aging with the appearance of hydroxyl groups centered at about 3400 cm^{-1} which can be assigned to the stretching vibrations of bonded acid OH groups and the decreasing the intensity and broadening of the carbonyl peak (1733 cm^{-1}) on both sides resulting from the generation of ketone and acid groups. In addition to the disappearance of the band at 1080 cm^{-1} corresponding to C-O vibration with growing of a small absorption at ca. 1547 cm^{-1} . These changes may result from bond scission of main-chain and elimination of side groups (Figure 7). FTIR results

confirmed the colour measurement results, where $\Delta E > 12$. This means that according to ΔE scale different colours were obtained. From these results, we can suggest that the chemical composition of white pigment (zincite, ZnO) plays an important role in catalyzing oxidative decomposition of B72.

Brownish red pigment is identified as brownish red lead which is an oxidizing agent. The PbO_2 functions as an oxidising agent within the whole structure of $PbO_2 \cdot 2PbO$ resulting in the change in hue over time [17]. Infrared analysis in figure 8 showed formation of oxygen-containing functional groups. Multiple modifications occurred in $1000\text{--}1200\text{cm}^{-1}$ region due to formation of new C–O bonds in addition to increasing and slightly broadening of C=O stretching band at 1722cm^{-1} resulting from oxidation effect.

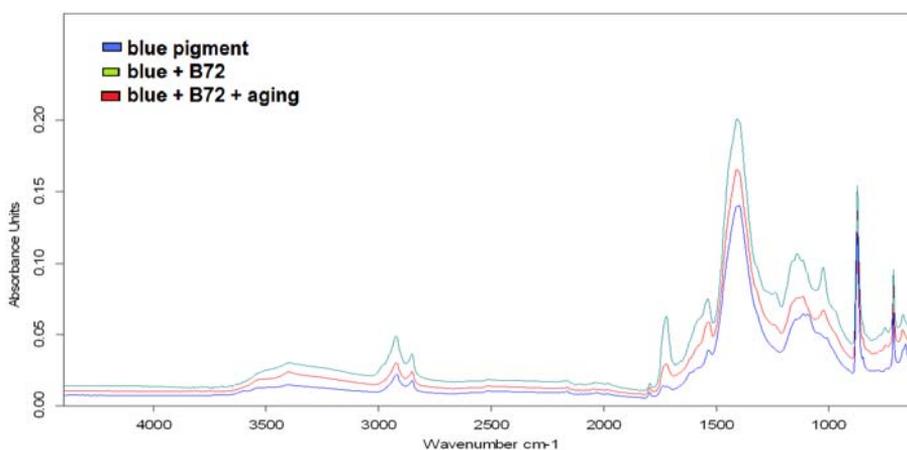


Fig. 5. FTIR-ATR spectrum of the treated blue painted layer with B72: The spectrum shows that no remarkable changes were observed in treated and treated aged samples compared with untreated samples.

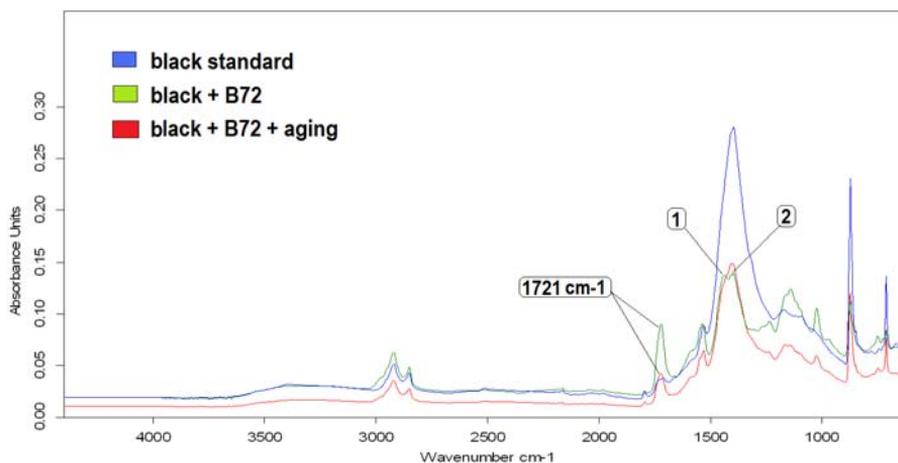


Fig. 6. FTIR-ATR spectrum of the treated black painted layer with B72: The spectrum shows the effect of thermal aging on treated black sample with B72: the intensity of C=O stretching band of B72 at 1721cm^{-1} decreased, band no.1 at 1434cm^{-1} of B72 disappeared reflecting the degradation of this polymer, band no. 2 at 1397cm^{-1} assignable to CO_3^{2-} group of $CaCO_3$ (the outer fine ground layer), unchanged.

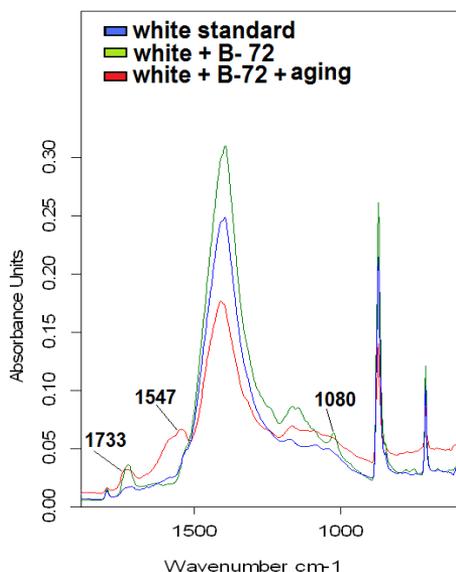


Fig. 7. FTIR-ATR spectrum of the treated white painted layer with B72: The spectrum shows the effect of thermal aging on treated white sample with B72: The broadening of the carbonyl peak at 1733cm^{-1} on both sides resulting from the generation of ketone and acid groups; disappearance of C-O stretching band at 1080cm^{-1} ; appearance of a new band at 1547cm^{-1} .

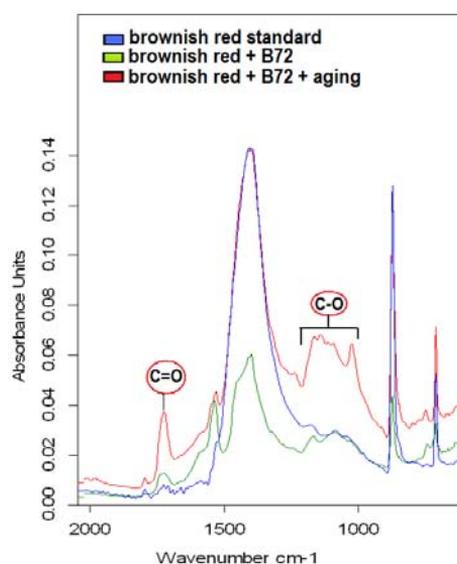


Fig. 8. FTIR-ATR spectrum of the treated brownish red painted layer with B72: The spectrum shows the effect of thermal aging on treated brownish red sample with B72: Multiple modifications occurred in $1000\text{-}1200\text{cm}^{-1}$ region; increasing and broadening of C=O stretching band at 1722cm^{-1} .

The FTIR spectra of black, white and brownish red samples treated with SILRES® BS OH 100 before and after thermal aging showed no significant changes in all major signals. Spectra of blue, green and yellow samples showed a slight modification of the intensities of the bands in the $1000\text{--}1300\text{cm}^{-1}$ region (Figs. 9, 10 and 11) i.e., Si – O – Si, Si – O – C and Si – C₂H₅ ($1000\text{--}1200\text{cm}^{-1}$) are affected by the thermal aging. These changes are most probably due to the chain-scission of Si – O – Si and Si – O – C bonds.

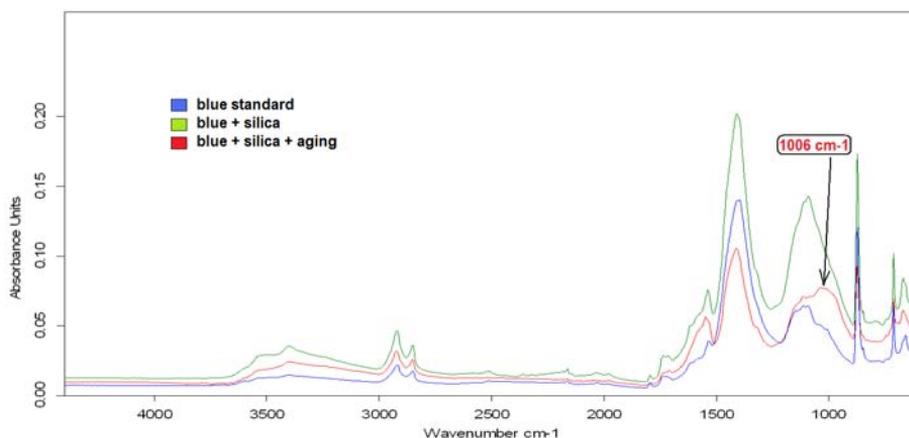


Fig. 9. FTIR-ATR spectrum of the treated blue painted layer with SILRES® BS OH 100: The spectrum shows the appearance of a new band at 1006cm^{-1} after thermal aging of treated sample.

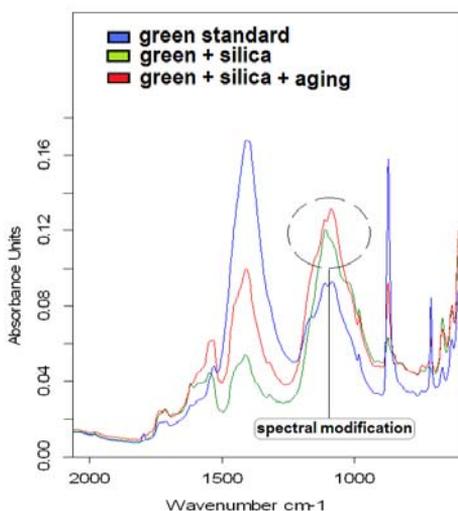


Fig. 10. FTIR-ATR spectrum of the treated green painted layer with SILRES® BS OH 100: The spectrum shows the effect of treatment of sample with SILRES® BS OH 100 before and after thermal aging.

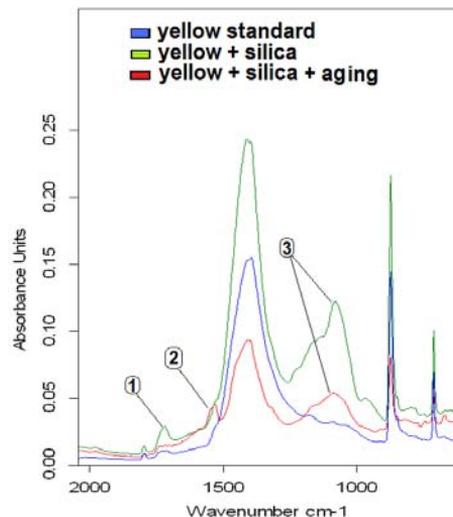


Fig. 11. FTIR-ATR spectrum of the treated yellow painted layer with SILRES® BS OH 100: The spectrum shows the effect of thermal aging on treated yellow sample with SILRES® BS OH 100: disappearing of band no.1 at 1718cm^{-1} ; growing a new band no.2 at 1529cm^{-1} ; the intensity of band no.3 at 1068cm^{-1} decreased.

Conclusions

The paper showed the importance of studying the interactions between consolidation products and pigment. In particular, we tested the effectiveness of two products (Paraloid B72 and SILRES® BS OH 100) on the painted surfaces, in order to find the best product to preserve the pigments from further weathering and degradation. The selected products were tested under thermal aging. The results obtained by SEM, colorimetric test and FTIR-ATR showed the differences in efficiency of the two products.

According to the results obtained, painted surfaces with brownish red lead and black (a mixture of magnetite and graphite) can be safely treated with SILRES® BS OH 100 where, no significant changes are found in all major FTIR signals and also they have acceptable total colour difference. On the contrary, painted surfaces with blue synthetic ultramarine can be safely treated with B72 as no remarkable FTIR changes were shown and ΔE fit the acceptable value.

It is found that even if the acceptable chromatic variation is considered to be $\Delta E < 10$, some painted samples don't fit within these limits no matter which treatment was applied, and that is due to their composing minerals. This appears to be the case of white zincite and yellow massicot samples, which registered total color change values higher than 10 irrelevant of the chemical and physical properties of the polymer applied. In the case of earth green samples, B72 induced strong colour variations ($\Delta E > 10$) especially after thermal aging, although FTIR showed no chemical bonds changes. Whereas, when they were treated with SILRES® BS OH 100, accepted ΔE values were obtained and slight FTIR spectral modification took place.

From these results, we can suggest that no ideal consolidant can be used for treating all pigments. Therefore before using pigment consolidant we have to determine first which chemical composition is involved in the pigment, and then select the polymer that will give good stability and durability. On this basis, it is concluded that stability of both B72 and SILRES® BS OH 100 depends on the chemical composition of pigments. A further study is

needed to evaluate various consolidation products for all important pigments used in Egyptian wall paintings.

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