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## The Influence of Nano-Materials in Presence of Vinyl Acetate Copolymer ( Beva 371) for Consolidation of an Egyptian Coptic Fresco Painting

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### Abstract

Nano-lime dispersed in propanol was extensively used for consolidation of mural paintings. Current result pointed out the effect of using different nano-dispersed materials (nano silica, nano calcium hydroxide and carbonate) with Beva 371 soluble in toluene/ethanol to consolidate models of an Egyptian Coptic fresco. Scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and spectrophotometer were used to determine the visual properties, morphological and physical properties of the treated models. The influence of treatment on various mechanical characteristics of consolidated models were also, tested in detail by means of tests on specimens of the treated models. The treatment was carried out in presence of the nano-materials with or without the polymeric material. The mechanical characteristics of the treated models were improved. This can be attributed to nano-calcium hydroxide was turned into calcium carbonate and both of nano- silica and nano-calcium carbonate appeared as filler. The high impact of nano-materials remind even in presence of polymeric material (Beva 371).

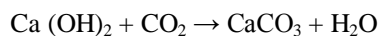
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**Keywords:** Beva371; Nano-lime; Nano-silica; Nano- Calcium carbonate; Hardness.

## **1. Introduction**

Many kinds of polymers are synthesized for the conservation field [1]. One of the most largely applied is vinyl acetate copolymers (Beva 371). It was developed by Berger 1984 and proved to be successful in consolidation of mural paintings as it is resist yellowing by aging easy to prepare and apply. Beva 371 using by brush or spray with an 8-10% solution in toluene (1:3 or 1:4.) and allow to dry overnight [2]. The structure of Beva 371 is Elvax (ethylenelvinyl acetate [EVA] copolymer), ketone resin N (polycyclohexanone), A-C copolymer (EVA), Cellolyn 21 (phthalate ester of hydroabietyl alcohol), and paraffin [3]. Carritti has studied the performance of nano- lime in the presence of Paraloid for consolidation a lime stone and proved that the behavior in terms of mechanical properties by the application of  $\text{Ca}(\text{OH})_2$  nanoparticles remained excellent even in the presence or absence of Paraloid [4]. Currently the nano- materials in combined with the polymeric material are studied in consolidation of mural painting and to notice the effect of nano-materials in the presence or absence of polymeric materials. According to the disadvantages of using polymers, salt crystallization occurs within the pores of the wall paintings, generating strong mechanical stress [1]. All polymers such as Paraloid B 72 are turn to yellow in a few years which turning to yellow after 20 years at least [5] In the last decades, in order to avoid these disadvantages, a new way for consolidation appeared using of nano-lime dispersions (usually 2-propanol) has been developed by the Florence unit of the CSGI [6]. This new method has been mainly used to support the mechanical properties. It is exhibit a good mechanical properties due to the nano-lime companied with the carbon dioxide in the surrounded air to produce new calcium carbonate which filled the gaps and connected the compounds each other [7] , as the following reaction:



This technique considered very useful in cases of surface color powdering for mural paintings, consolidation and preconsolidation treatments. Once the  $\text{Ca}(\text{OH})_2$  nanoparticles penetrate easily into the porous matrix, of the objects (lime stone or in mortars) without any cares of the water content [8]. The high retention of this absorbed water favors the correct carbonation with formation of a new  $\text{CaCO}_3$  crystal network that embeds the detached quartz grains [9]. In the present work the interactions between nano-materials and Beva 371 by preparing some mixture of Beva 371 with  $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$  and  $\text{SiO}_2$  nanoparticles is homogeneously dispersed were studied. Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were used to characterize the influences of nano-materials in presence of polymer matrix for consolidation of an Egyptian Coptic fresco painting.

## **2. Material and Methods**

### **2.1. Materials**

All the chemicals were of analytical grade and were used without further purification. The materials required for the synthesis of nano-lime are calcium chloride, sodium hydroxide and Triton 100 were obtained from Aldrich. Whereas, the materials required for the synthesis of silica nanoparticles are Tetraethyl orthosilicate (TEOS 98%,

Fischer), ammonium hydroxide solution (31.5%, Aldrich) and Absolute ethanol 99 % from ADWIC Company. Calcium oxide was purchased from Aldrich and used for preparation of calcium carbonate. BEVA 371 is a thermoplastic, elastomeric polymer mixture. It is composed of Elvax (ethylenelvinyl acetate [EVA] copolymer), ketone resin N (polycyclohexanone), A-C copolymer (EVA), Cellolyn 21 (phthalate ester of hydroabietyl alcohol), and paraffin. It is an opaque gel at room temperature and has a melting point of 50-55 °C. It is soluble in naphtha, toluene, acetone, and alcohol. BEVA produces a matte [3], waxy finish and is used as a consolidated for paintings and textiles and it was purchased from Arts Conservation Agency (local company). Water was purified by a Millipore Elix 3 apparatus: the resistance of the ultra-pure water was 18 MΩ.cm.

## 2.2. Synthesis of nano-materials

The nano lime was synthesized by preparing two initial aqueous solutions of 100 mL containing 3.33 g of CaCl<sub>2</sub> (corresponding to 0.3 mol/L of CaCl<sub>2</sub>) and 2.40 g of NaOH (corresponding to 0.6 mol/L of NaOH), respectively. Then Triton X-100 was added to calcium chloride initial aqueous solution, which is later mixed simultaneously to the aqueous sodium hydroxide one, at the fixed temperature of 90 °C. [10] Silica nanoparticles were prepared by hydrolysis and condensation of TEOS in ethanol and in presence of ammonia as catalyst. First, solution containing appropriate quantities of absolute ethanol, ammonia and deionized water were stirred for 5 min. to ensure complete mixing. Then a proper amount of TEOS in absolute ethanol was added to the above solution and the reaction proceeded at ambient temperature for 24 h according to reactants concentrations. Thereafter the colloidal solution was separated by high-speed centrifuge, and the silica particles were washed by absolute ethanol for three times to remove undesirable particles, followed by drying in oven at 100 °C for 2 h [11] CaCO<sub>3</sub> nano-particles were prepared by using the reaction system Ca(OH)<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> as described in our previous work Bulk CaO was firstly calcined at 1000 °C for 2 h then slaked into lime milk in mono-distilled water at 80 °C. The lime milk was cooled to room temperature (20 °C). At this temperature, the CO<sub>2</sub> gas was injected into the lime milk (1000 mL min<sup>-1</sup> flow rate and 1 M CaO concentration) with vigorous stirring. The pH recorded on-line with a pH-meter (Jenway 3305) and a conductometer (Jenway 4510). When the pH value decreased from 14 to 9 and the electric conductivity showed a sharp decrease, this was an indication that the reaction was completed, the CO<sub>2</sub> flow was stopped. CaCO<sub>3</sub> particles were obtained and dried at 120 °C in a drying oven for at least 24 h [12].

## 2.3. Preparation of the mixed nano-materials polymer liquid system

**Table 1:** The composition and the appearance of the obtained mixed system

Component	With Polymeric material			Without Polymeric material		
	gm			gm		
Nano-	SiO <sub>2</sub>	CaCO <sub>3</sub>	Ca(OH) <sub>2</sub>	SiO <sub>2</sub>	CaCO <sub>3</sub>	Ca(OH) <sub>2</sub>
Ethanol	80	80	80	98	98	98
Toluene	16	16	16	-	-	-
Beva 371 solution	2	2	2	----	----	----
Nanomaterial	2	2	2	2	2	2

Preparation of the mixed nano-materials /Beva 371 system was carried out as follows. 2gm opaque gel of Beva 371 was added dropwise to ethanol / toluene mixture (80:16 by weight) at room temperature then 2 gm of nano-

material (initial concentration 20 g/L). The composition and the appearance of the obtained mixed system are listed in **Table 1**. Then to compare the effect of polymeric materials on the role of nano-materials in the consolidation of the models, the nano-materials were used without polymeric materials to define the difference between the presence and absence of polymeric materials.

### **2.3.1. The fresco painting condition**

The pictorial layer suffered from severe loss and color change around the lost areas [13] and the whole fresco painting suffered from weakness as there were a vital cracks. The three models of Egyptian Coptic fresco were exposed to artificial aging to create a similar circumstances for the original fresco painting then they were treated with three different system described in **Table 1**:



**Figure 1:** the Egyptian Coptic fresco painting

- 1) Beva 371 with  $\text{Ca(OH)}_2$  nanoparticles.
- 2) Beva 371 with  $\text{SiO}_2$  nanoparticles
- 3) Beva 371 with  $\text{CaCO}_3$  nanoparticles.

The models of Coptic fresco paintings were treated with the previous components and three other models were treated with nano-materials in ethanol without polymeric material using brushes through Japanese paper [14] The models were subjected to different accelerated ageing test to simulate the most Common outdoor heritage deterioration processes due to weathering agents. so they were exposed to temperature 25 °C for 12 h then up gradually to 60 °C for 8 h then left them in room temperature for 24 h this round repeated 10 times to define the state of models after exposing for changing in temperature [15].

### **2.4. Characterization**

The morphology was examined by scanning electron microscope model Quanta 250 FEG Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses with accelerating voltage 30 K.V., magnification 14x up to 1000000 and resolution for Gun. In .FEI company, Netherlands ). Sample preparation consisted of application of a superficial gold film by sputtering to prevent electro-static charge. X-ray diffraction were obtained using PAN analytical X-Ray Diffraction equipment model X' Pert PRO with Monochromator, Cu-radiation ( $\theta 1.542\text{\AA}$ ) at 50 K.V., 40 M.A. and scanning speed 0.02o/sec. were used. The reflection peaks

between  $2\theta=2\theta_0$  and  $60^\circ$ , corresponding spacing ( $d$ , Å) and relative intensities ( $I/I_0$ ) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files. IR spectra were obtained using a FT-IR Thermos Nicolet 760. The resolution is of: 4 cm<sup>-1</sup> (Region 4000: 400 / Absolute threshold 0.002 /Sensitivity: 50). The sample preparation process without grinding as it is connected to ATR unit.)

#### **2.4.1. 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) cm<sup>2</sup>. 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  $\Delta E^*$  between two color stimuli  $\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2}$  [16].

#### **2.4.2. Hardness and Bursting**

The Shore D scale is based on ASTM D2240. The test involves the use of a hardened steel rod 1.1 mm - 1.4 mm diameter, with a 30° conical point, 0.1 mm radius tip. This exerts 44.64 N of force [17] The measured hardness is determined by the penetration depth of the indenter under the load maximum penetration for each scale is 2.5-2.54 mm, the amount of penetration is converted to hardness reading on scale of 100 units maximum hardness value 100 shore corresponds to zero penetration which can be converted in to newton to be 44.45 N [18]

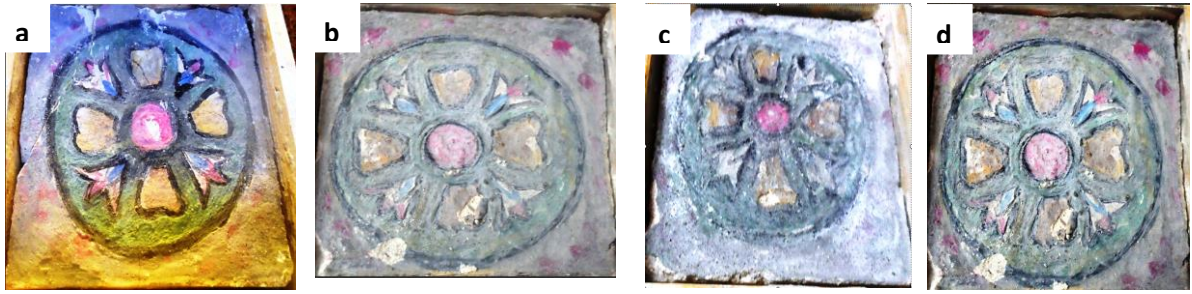
**Tinius Olsen H5KT machine** was designed for using in Research and Quality Control to measure material's strength and performance. All tests are designed and implemented by Tinius Olsen in accordance with key international testing standards including ISO, ASTM, EN and other industrial standards. The load measurement accuracy: +/- 0.5% of applied load from 2% to 100%, and position measurement accuracy: +/- 0.01% of reading or 0.001 mm [19].

### **3. Results and discussion**

The application of the three nano-materials with or without the polymeric material caused changes in the visual properties, such as changes in colors of the treated models which can be tested by using spectrophotometer. On other hand, the nano-materials improved the mechanical properties of the treated models, as the nano-materials increase the models strength to the exogenous factors as the mechanical properties were tested using the hardness tester and the bursting strength detector, The polymeric material showed no effect on the role of nano-materials as the results are the same even in presence or absence the polymeric material.

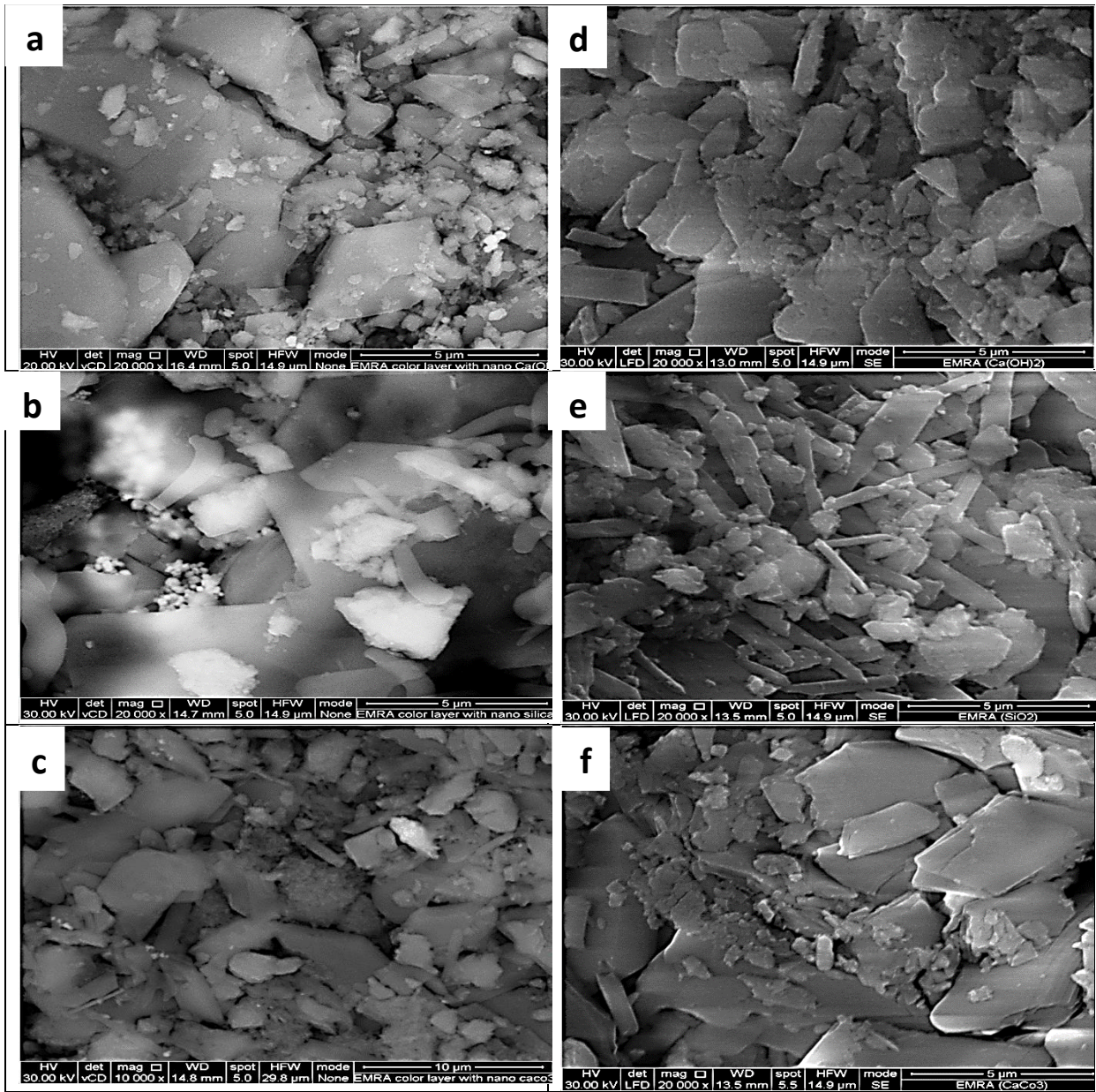
#### **3.1. The visual properties and the changes of colors after treatment**

The purpose of comparison the changes of visual colors before (2a) and after treatment (2b-c) to detect a little change of colors caused by treatment. The models after treatment in presence of polymeric material (solution of Beva 371) with nano-materials are an opaque layers appeared on the treated models as shown in Figure 2 (b-c.)



**Figure 2:** a) untreated model and the three models after treatment with solution of conc. 2 % Beva 371: b) nano-calcium hydroxide c) nano-silica d) nano-calcium carbonate

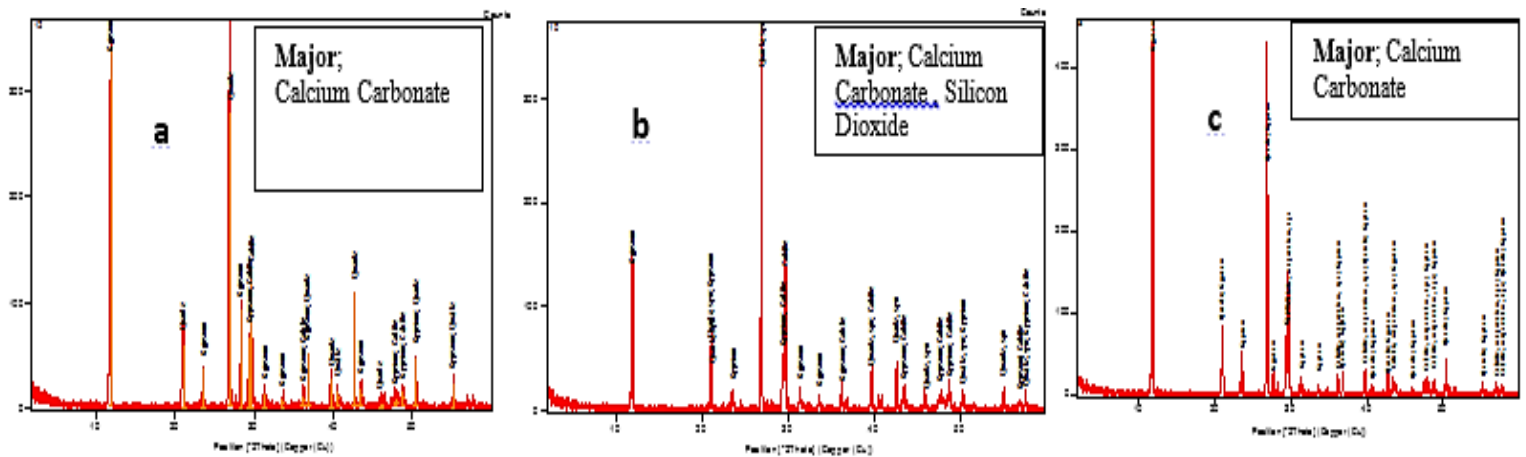
### 3.2. Scanning Electron Microscope



**Figure 3:** SEM images of pure nano-materials without Beva 371 a) Ca(OH)<sub>2</sub> during the carbonation process, b) nano-silica c) nano-calcium carbonate and, nano-materials with Beva 371 a) Ca (OH)<sub>2</sub> b) nano-silica c) nano-calcium carbonate.

### 3.3. X-Ray Diffraction

Figure a-c shows the x-ray Diffraction (XRD) of the treated samples with the three nano- materials + Beva 371. The XRD data revealed that the calcite and gypsum are more major components in samples from models treated with three nano-material in presence or absence of Beva 371. From Fig. 4a it was noticed that the intensities of calcium carbonate XRD peaks which converted from calcium hydroxide is higher than the intensities of the nano-calcium carbonate Fig. 4c which means the size are increased of as seen in SEM image Fig. 3a. On the other hand, it was observed that the samples treated with nano-silica Fig. 4b revealed that the intensities of original calcium carbonate of the model sample is less than other nano-carbonate samples .

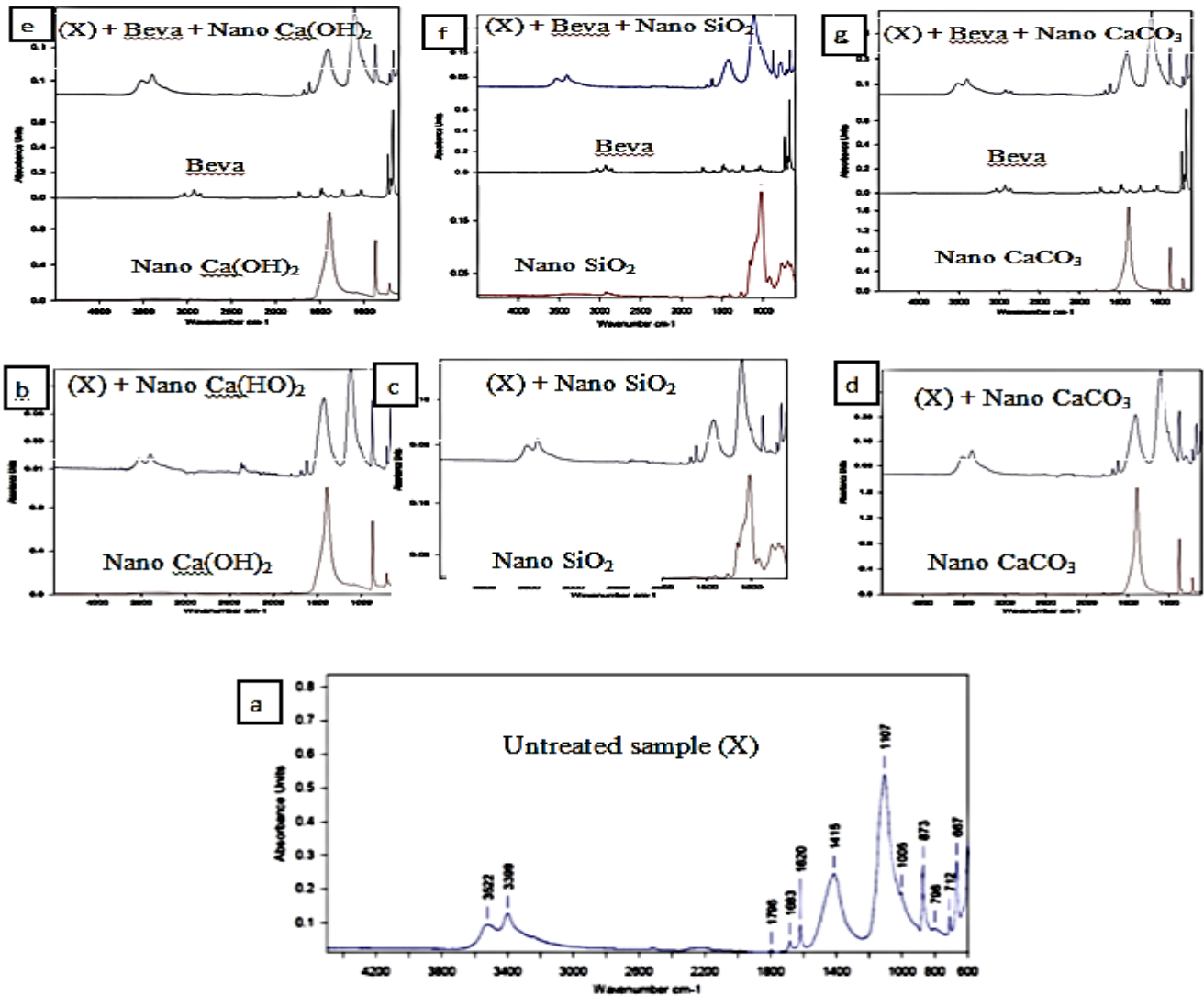


**Figure 4:** X-ray Diffraction (XRD) of the treated samples with the three nano-materials + Beva 371.

### 3.4. Fourier transform infrared

Figure 5a-f shows FTIR spectra of a) untreated sample and addition of nano-materials to untreated sample b) Ca(OH)<sub>2</sub>, c) nano-silica, d) nano-calcium carbonate, and nano-materials with Beva 371 to untreated sample e) Ca(OH)<sub>2</sub>, f) nano-silica, g) nano-calcium carbonate. The FTIR of untreated sample (Fig. 5a) revealed that at least one strong absorption band from C-O stretching at 1415 cm<sup>-1</sup> calcite, the band is smooth, symmetrical, and broad. Carbonate bending vibrations produce sharp bands in the region of 900-650 cm<sup>-1</sup>. These bands show measurable frequency deviations corresponding to the attached cation. For example, the out-of-plane bending vibration for calcium carbonate (calcite) occurs at 873 cm<sup>-1</sup>, SO<sub>4</sub> bending and stretching band at 667, 1107cm<sup>-1</sup>, anti-symmetric and symmetric O-H stretching bands of gypsum at 3522, 3399 cm<sup>-1</sup>. Fig. 5b, d represents the FTIR spectra of calcium hydroxide and nano-calcium carbonate before and after loaded to untreated sample in absence of Beva 371, respectively. The spectra shows at least one strong absorption band from c-o stretching in the region of 1550-1350 cm<sup>-1</sup> calcite, the band is smooth, symmetrical, and carbonate bending vibrations produce sharp bands at the region of 900-650 cm<sup>-1</sup> indicates the presence of calcium carbonate, stemming from the reaction of lime with carbon dioxide in the air and nano-calcium carbonate. The intensity of pure nano-calcium carbonate is higher than calcium carbonate converted from calcium hydroxide. On the other hand, when the nano-calcium hydroxide and carbonate added to the untreated sample, the peaks of untreated sample were appeared in expense of nano-materials. This is due to the present of nano-materials are low compared to the untreated sample. Moreover, Fig. 5e, g represents the FTIR spectra of calcium hydroxide and nano-calcium

carbonate before and after loaded to untreated sample in presence of Beva 371, respectively. Beva 371 spectrum shows a strong absorption of C-H stretching bands on 2850,2919,3028  $\text{cm}^{-1}$ , C=O stretching band on 1712,1736 $\text{cm}^{-1}$ , C-H bending bands on 1462  $\text{cm}^{-1}$ , C-O stretching bands on 889  $\text{cm}^{-1}$  and C-H torsion band on 728 $\text{cm}^{-1}$  [20] From Fig. 5e, g, it is observed that a similar untreated sample peaks are revealed with increasing of peaks intensities in presence of Beva 371 and nano-materials. Whereas, Fig. 5c, f represents the FTIR spectra of silicon dioxide before and after loaded to untreated sample and absence and presence of Beva 371, respectively. FTIR spectrum of silica reveals that asymmetric Si-O-Si stretching band on 1108  $\text{cm}^{-1}$ , show strong absorption band from c-o stretching on 1411 $\text{cm}^{-1}$ , while the crystalline silica mineral quartz has the same primary absorption band near 950  $\text{cm}^{-1}$ , but small doublet band near 692  $\text{cm}^{-1}$  that is very characteristic [21]. The spectrum of untreated sample are similar in presence and absence of Beva 371 and nano-silica. But it noticed that the peak represented to silica after loaded to untreated sample in presence Beva at 692  $\text{cm}^{-1}$ . FT-IR data are in a good agreement with XRD data.



**Figure 5a-f:** FTIR spectra of a) untreated sample (X) and addition of nano-materials 371 to untreated sample b)  $\text{Ca}(\text{OH})_2$ , c) nano-silica, d) nano -calcium carbonate, and nano-materials with Beva 371 to untreated sample e)  $\text{Ca}(\text{OH})_2$ , f) nano-silica, g) nano-calcium carbonate.



### 3.5. Spectrophotometer

**Table 2** shows the color variation promoted on the models after treatment with nano-lime, nano-silica and nano-calcium carbonate  $\Delta L^*$  is the variation in luminosity,  $\Delta a^*$  is the variation in the red–green parameter,  $\Delta b^*$  is the variation in the blue–yellow parameter and  $\Delta E^*$  is the total color difference. Displays the color variations of the treated models for the tested treatments, the most important contribution came from  $L^*$   $a^*$   $b^*$  where  $L^*$  represents lightness (0% black, 100% white),  $a^*$  redness-greenness, and  $b^*$  yellow-blueness. For this work the values of  $a^* > 0$  and  $b^* > 0$  which represent the colors red and yellow, respectively. The yellow color of untreated models falls within the range:  $L^*$  -9.88,  $a^*$  3.24 and  $b^*$  0.062. In general, treatments of nano-material led to a darkening of the models surfaces. For nano-calcium hydroxide for example, the  $L^*$  dropped by -10.37 while nano-calcium hydroxide loaded Beva 371 by -37.3 .

**Table 2:** coordinate of color obtained by using spectrophotometer

Color	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E^*$	observations
Yellow Untreated	-9.88	3.24	0.0062	10.42	<b><math>10 &gt; \Delta E &gt; 5</math> In the untreated samples.</b>
Black untreated	-0.76	-0.08	2.22	2.35	
Red untreated	1.60	0.87	1.09	2.12	
Yellow Ca(OH) <sub>2</sub> + Beva 371	- 37.3	-2.22	-17.66	41.34	<b>The results showed that Beva 371 tended to lighten <math>\Delta E &gt; 12</math> This value Increased because of the presence of polymeric material</b>
black Ca(OH) <sub>2</sub> + Beva 371	- 5.21	-0.49	-0.20	5.24	
Red Ca(OH) <sub>2</sub> + Beva 371	-5.99	-1.09	-36.42	13.93	
Yellow SiO <sub>2</sub> + Beva 371	-40.46	-2.01	-18.72	44.63	
black SiO <sub>2</sub> + Beva 371	-3.885	1.20	-21.44	10.22	
Red SiO <sub>2</sub> + Beva 371	-6.07	1.05	-0.03	6.16	
Yellow CaCO <sub>3</sub> + Beva 371	-5.48	1.01	- 6.85	8.83	
Black CaCO <sub>3</sub> + Beva 371	2.47	-0.77	3.04	36.93	
Red CaCO <sub>3</sub> + Beva 371	-3.89	0.92	6.81	7.90	
Yellow Ca(OH) <sub>2</sub>	- 10.37	2.14	-1.56	10.70	<b><math>\Delta E</math> values indicated that this variation is the same of the treatments with Beva 371 but it is slight</b>
Black Ca(OH) <sub>2</sub>	10.55	0.05	0.39	10.56	
Red Ca(OH) <sub>2</sub>	8.09	0.56	10.46	13.24	
Yellow SiO <sub>2</sub>	- 25.86	1.08	-12.85	28.90	
Black SiO <sub>2</sub>	- 16.88	1.15	-4.47	17.50	
Red SiO <sub>2</sub>	-38.78	-0.17	-8.08	39.61	
Yellow CaCO <sub>3</sub>	- 28.74	0.64	-12.53	31.36	
Black CaCO <sub>3</sub>	-1.58	0.21	-10.09	3.99	
Red CaCO <sub>3</sub>	-3.26	1.67	6.47	7.43	

The color of models treated with nano-materials were observed to alter slightly after the treatment,  $\Delta E$  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 colors

In this respect yellow, red and black colors in the treated models with nano-materials before and after aging have no acceptable  $\Delta E$  values where it ranges between 2.12 and 10.42. Other colored samples treated with nano-materials in presence of Beva 371 were not fitting in these limits i.e., have  $\Delta E$  values between 44.63 and 5.42 depending on their chemical composition. These values indicate that Beva 371 induced chromatic variations resulting from its thermal oxidative decomposition. The completed data are listed in **Table 2**, a clear change in surface color was observed visually. The average  $b^*$  and  $a^*$  values increased and the models appears red-orange colored after the treatment. This discoloration very probably results from the accumulation of nano-materials on the surfaces [22].

### 3.6. Hardness and bursting

#### A-The Hardness Tests using Shore D

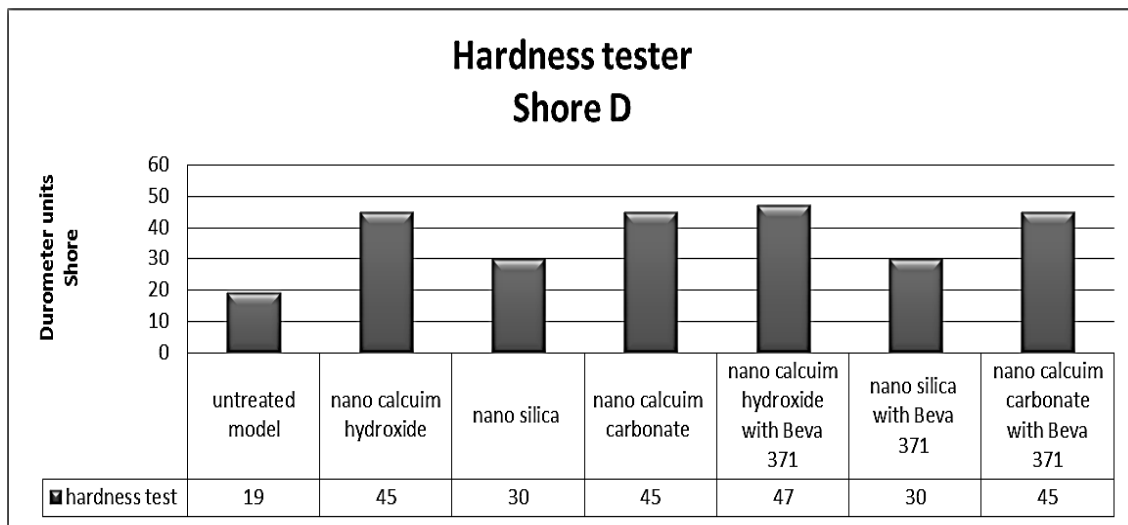
The Shore D scale is based on ASTM D2240. The test involves the use of a hardened steel rod 1.1 mm - 1.4 mm diameter, with a 30° conical point, 0.1 mm radius tip. This exerts 44.64 N of force (Fig. 6).[23] The measured hardness is determined by the penetration depth of the indenter under the load maximum penetration for each scale is 2.5-2.54 mm, the amount of penetration is converted to hardness reading on scale of 100 units maximum hardness value 100 shore corresponds to zero penetration which can be converted in to Newton to be 44.45 N.[19] Hardness tests for untreated model and treated models with the three nano-materials in presence and absence of Beva371 are presented in **Figure 7** and **Table 3**. Differences in surface hardness values were minimal between the different treatments, but some trends were noted. In all cases, the hardness results of treated models increased over the untreated model. Hardness values of models treated with nano-materials loaded-Beva 371 showed very similar hardness values of models treated with nano-materials. The improvement happened due to the application of nano-materials fill the gaps and connected the compounds each other according. On the other hand, calcium hydroxide acts as its nature through the carbonation process for the combination of layers of mural paintings in presence or absence of Beva 371.

**Table 3:** shore D models surfaces hardness results

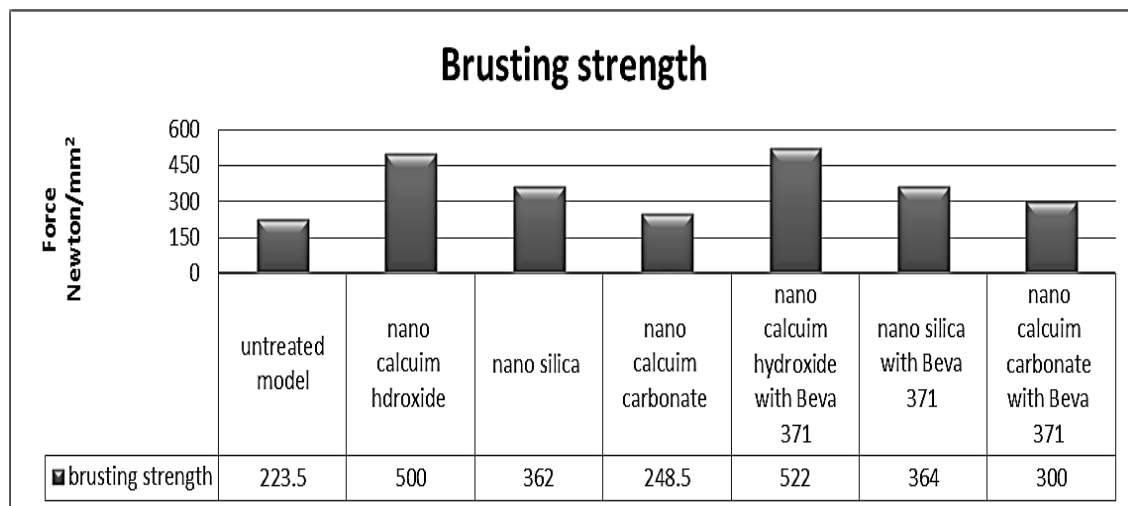
Sample	Average hardness shore D	Shore D (Newtons)
Untreated model	19 ± 0.5	13 N
Nano-calcium hydroxide with Beva 371	47± 0.5	22 N
Nano-silicon dioxide with Beva 371	35± 0.5	18 N
Nano-calcium carbonate with Beva 371	40± 0.5	18 N
Nano-calcium hydroxide	47± 0.5	22 N
Nano-silicon dioxide	35± 0.5	18 N
Nano-calcium carbonate	40± 0.5	18 N



**Figure 6:** Testing samples for Hardness using Shore D and bursting strength test using Tinuis Olsen



**Figure 7:** Hardness tests for untreated model and treated models with the three nano- materials in presence and absence of Beva 371



**Figure 8:** Bursting strength for untreated model and treated models with the three nano-materials in presence and in absence of Beva 371.

### ***B-The bursting strength Tests or compressive strength using Tinuis Olsen***

Bursting strength or compressive strength express the ability of samples to bear compressive strength to be broken (Fig. 6) [24] Bursting strength for untreated model and treated models with the three nano-materials in presence and in absence of Beva 371 are presented in **Table 4**. The results proved that there is an improvement happened in the presence of Beva 371 or absence. This is due to the application of nano-materials which fill the gaps and led to all materials are unity and increase the bursting strength as the calcium hydroxide turned in to calcium carbonate which increase the ability of resistance and the other two nano-materials used as filler to fill the gaps inside the structure of the models. On other hand the role of polymeric material appeared in a limited results and can' be concerned because the concentration of Beva 371 was only 2 %.

**Table 4:** Bursting strength of models results

<b>Sample</b>	<b>Bursting strength (Newton /mm<sup>2</sup>)</b>
<b>Untreated model</b>	224 N/mm
<b>Nano-calcium hydroxide with Beva 371</b>	522 N/mm <sup>2</sup>
<b>Nano-silicon dioxide with Beva 371</b>	450 N/mm <sup>2</sup>
<b>Nano-calcium carbonate with Beva 371</b>	249 N/mm <sup>2</sup>
<b>Nano-calcium hydroxide</b>	500 N/mm <sup>2</sup>
<b>Nano-silicon dioxide</b>	362 N/mm <sup>2</sup>
<b>Nano-calcium carbonate</b>	300 N/mm <sup>2</sup>

### ***4.Conclusions***

This study focused on the interactions between Beva 371 which represented the polymer used in the consolidation of mural paintings and nano calcium hydroxide, nano-silica and nano and calcium carbonate. The nano-calcium hydroxide turned into calcium carbonate as the known carbonation in presence or absence of Beva 371. Both nano silicon dioxide and nano-calcium carbonate used as filler as they filled the gaps inside the structures of the models even in presence of polymeric material as SEM images showed. The application of those materials on the models caused a visual difference in compared with untreated model. Although, the success of the application of nano-materials in the consolidation of the models, they caused an obvious change in colors as the spectrophotometer results showed. This can be attributed probably to the residues of the solvents and Beva 371 with the three nano-materials. Finally, the mechanical properties studied by the shore D and the results revealed that the treatment of nano-materials and even in presence of Beva 371 improved the mechanical properties and the bursting strength tested to assure that the treatment of the nano-materials increase the models strength to the exogenous factors.

### ***Recommendations***

In conservation field the nano- materials proved the effectiveness and success as the particles are in nanometer size can penetrate through the surfaces of the objects easily.

**The following recommendations are offered to the people who worked in conservation field:**

- 1- The treatment with nano- materials didn't affected by the presence of polymeric materials or absence so the polymeric material can be laminated in the conservation due to wide disadvantages.
- 2- The nano-lime improved the mechanical properties for the treated models of the mural painting even in presence of polymeric material by the formation of calcium carbonate through carbonation process.
- 3- Nano- materials can be used as filler such as nano-silica and nano-calcium carbonate instead of the polymeric material in consolidation as unfortunately still use in the conservation field
- 4- Although all the success the nano-materials achieved they caused changes in colors of the treated models tested by spectrophotometer so during the application of nano-materials must be applied through two layers of Japanese paper to laminate the accumulation on the surface.

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**Reference**

- [1]. **Giorgi R., Baglioni M., Berti D., Baglioni P.,** New Methodologies for the Conservation of Cultural Heritage: Micellar Solutions, Microemulsions, and Hydroxide Nanoparticles, *Account of Chemical Research*, 2009, pp.605-704.
- [2]. **Berger G. A.,** Heat-Seal Lining of a Torn Painting with BEVA 371”, *Studies in Conservation*, 20(3), 1975, pp.51-125.
- [3]. **Derrick M.,** *Infrared Spectroscopy In Conservation Science, Scientific Tools For Conservation*, The Getty Conservation Institute, Los Angeles, 1995, pp.198.
- [4]. **Carretti E., Chelazzi D., Rocchigiani G., Baglioni P.,** Interactions between Nanostructured Calcium Hydroxide and Acrylate Copolymers, *Implications in Cultural Heritage Conservation*, 2013, pp. 9881-9890.
- [5]. **Dietemann P., Higgitt C., Kalin M., Edelmann M.J., Knochenmuss R., Zenobi R.,** Aging and yellowing of triterpenoid resin varnishes e Influence of aging conditions and resin composition, *Journal of Cultural Heritage*, 2009, pp.30-40.
- [6]. **Baglioni P., Giorgia R., Chelazzia D.,** nano materials or the conservation and preservation of movable and immovable art works , *Progress in cultural heritage Preservation , EUROMED*, 2012, pp313-318.
- [7]. **Brajer I.,** Problems with past conservation treatments on the wall church paintings in and lose in a research and development report from the workshop November 2-3, 2007, Österbybruk , Upland, Sweden,pp.1-72.
- [8]. **Blee A., Martin J.G.,** Nanoparticles and the conservation of cultural heritage, *Materials Forum*, 32, 2008, pp.121-128.
- [9]. **Baglioni P., Giorgi R.,** Soft and hard nano-materials for restoration and conservation of cultural heritage, *Soft Matter*, 2006, pp. 293-303.
- [10]. **Daniele V., Taglieri G.,** Synthesis of Ca(OH)<sub>2</sub> nanoparticles with the addition of Triton X-100.

- Protective treatments on natural stones: Preliminary results, *Journal of Cultural Heritage*, 2012, pp.40-46 .
- [11]. **Ibrahim I.A.M, Zikry A.A.F., Sharaf M.A.**, Preparation of spherical silica nanoparticles: Stober silica, *Journal of American Science*, 6(11), 2010, pp.986-989.
- [12]. **Morsy F.A., El-Sheikh S. M., Barhoum A.**, Nano-silica and SiO<sub>2</sub>/CaCO<sub>3</sub> nano composite prepared from semi-burned rice straw ash as modified papermaking fillers, *Arabian Journal of Chemistry*, in press, 2014, pp.1-11.
- [13]. **Casadio F., Colombo C., Toniolo L.**, Detaching Methodology for fresco Painting, (in) 9th International Congress on Deterioration and conservation of stone, Venice June 19- 24, *Journal of Cultural Heritage*, 2000, pp. 739-747.
- [14]. **Natali I., Saladino M.L., Andriulo F., Martino C., Caponetti E., Carretti E., Dei L.**, Consolidation and protection by nanolime: recent advances for the conservation of the graffiti, Carceri dello Steri Palermo and of the 18th century lunettes, SS. Giuda e Simone Cloister, Carniola (Emboli) , *Journal of Cultural Heritage*, 2014, pp.151–158.
- [15]. **Batterham I., Rai R.**, A comparison of artificial aging with 27 years of natural aging 2008 AICCM Book, Paper and Photographic Materials Symposium, 2008, pp.1-9.
- [16]. **Darwish S.S.**, Evaluation of the effectiveness of some consolidates used for the treatment of the Sixth century Egyptian cemetery wall painting, *International Journal of Conservation Science*, 4(4), 2013, pp.413-422.
- [17]. **Sophie M.B.**, Emmanuel S. and Daniel V., TEOS based consolidates for Maltese globigerina limestone effect of hydroxyl conversion treatment , in 12th international Congress on the Deterioration and Conservation of Stone, 24 October 2012 ,Session x: 1:15 – 3:00 , pp.1-10.
- [18]. **Kopeliovich D.**, Requirements to engine bearing materials, [www.substech.com](http://www.substech.com).
- [19]. <http://www.tiniusolsens.com/products/bench-machines/bench-h5k-t.html>
- [20]. **Stuart B. H.**, Analytical Technique in Materials Conservation, Wiley, 2007, pp.1-423.
- [21]. **Derrick M.**, Infrared Spectroscopy in Conservation Science, Scientific Tools for Conservation, The Getty Conservation Institute, Los Angeles, 1995, pp.1-252.
- [22]. X-rite.com, A guide to understand color communication, x-rite in corporate., 2007, p.1-26.
- [23]. **Slišková Z., Drdacky M.**, Testing of treatment effects of nano sols on selected porous historic materials, *Journal of Cultural Heritage*, 2014, pp.1- 4.
- [24]. **Slišková Z., Drdacky M.**, Consolidation of weak lime mortars by means of saturated solution of calcium hydroxide or barium hydroxide, *Journal of Cultural Heritage*, 2014 , pp.1-9.