

Usage of Nanoparticles in Consolidating Painted Wooden Ceilings

Assist. Prof. Dr. Rehab Fathy Hammam Aly

Assistant Professor of Paintings Conservation

Head of Monuments Restoration Department High Institute of Tourism and Monuments

Restoration – Abu Qir – Alexandria

Rehabfathey99@gmail.com

1. Abstract

Wood ceilings with colorful decorations are one of the distinctive architectural characteristics of Islamic homes. Islamic architecture used wood widely in building ceilings, so that they are built in the form of prominent wood beams interspersed with a low area called the truss, provided that they were decorated with plant or engineering units that could be colored or gilded. In addition, ceilings were often inscribed in the middle with colorful decorative light lanterns. Despite the heritage and aesthetic values of these ceilings, most of them, if not all, are exposed to many factors and conditions that caused their deterioration discoloration. One of the topics presented for research and discussion is how to find the best materials and methods that can be applied for the treatment and consolidation of these valuable colored decorations. In light of the recent scientific revolution of the success of Nano-scale applications that have been addressed in most areas of science and technology in addition to the field of restoration, the research aims to try using nanotechnology so that the nanometer sized materials can be obtained and used in the treatment and consolidation of the colors applied to wood ceilings.

Therefore, this paper aims at applying the Nano technology, specifically (Primal AC33/TiO₂ nanoparticles), practically to the field of restoration in terms of treating and consolidating deteriorated colored wood ceilings.

Primal AC33 5% is applied with TiO₂ Nano compounds to consolidate the color layers on the wood ceilings. Then, their physical, mechanical and optical properties are evaluated after the applying the aging processes. The results concluded that the compound (Primal AC33 / Nano TiO₂) can be considered as a new factor in the field of preserving color layers of wood surfaces.

2. Keywords;

Painted wood, consolidation, Primal AC33, TiO₂ nanoparticles

الملخص

تعد الاسقف الخشبية ذات الزخارف الملونة من الخصائص المعمارية المميزة للبيوت الإسلامية، فقد استخد المعمار المسلم الأخشاب على نطاق واسع في الأسقف، بحيث يتم تنفيذها على هيئة براطيم خشبية بارزة تتخللها منطقة منخفضة تسمى الطليبية، على أن يتم زخرفتها بوحدات نباتية أو هندسية ملونة أو مذهبة وغالبا ما كان يتوسط السقف خشبية أو ملقف منقوش بوحدات زخرفية ملونة أيضا، وبالرغم مما تتمتع به هذه الأسقف من قيم تراثية وجمالية إلا ان أغلبها إن لم يكن جميعها يتعرض للعديد من العوامل والظروف التي أدت بدورها إلى تدهور تلك الأخشاب بما تحمله من زخارف وألوان، لذا أصبح من الموضوعات المطروحة للبحث والمناقشة هو كيفية إيجاد أفضل المواد والأساليب التي يمكن تطبيقها في علاج وتقوية تلك الزخارف الملونة ذات القيمة، ونظرا لما شهدته الأونة الأخيرة من ثورة علمية بخصوص نجاح تطبيقات

النانو التي تم تناولها في أغلب مجالات العلوم والتكنولوجيا، وكذلك مجال الترميم فقد جاءت فكرة البحث التي تهدف إلى محاولة إستخدام تكنولوجيا النانو بحيث يمكن الحصول على المواد المستخدمة في حجم النانوميتر وذلك لتطبيقها في علاج وتقوية الألوان المنفذة على أخشاب الأسقف.

في هذا السياق، تهدف هذه الورقة في المقام الأول إلى التطبيق العملي لتقنية النانو على وجه التحديد (الجسيمات النانوية الأولية $AC33 / TiO_2$) كمادة مقوية للأسقف الخشبية الملونة المتدهورة والمتهاكلة.

هذا وقد تم تطبيق تركيز 5% Primal AC33in مع مركبات TiO_2 Nano لتقوية طبقات الألوان المنفذة على الأسقف الخشبية، ثم تم تقييم خصائصها الفيزيائية والميكانيكية والبصرية بعد إجراءات عمليات التقادم الزمني، هذا وقد خلصت النتائج إلى أن المركب ($Primal AC33 / nano TiO_2$) يمكن اعتباره عاملاً جديداً في مجال حفظ طبقات الالوان باستخدام اسلوب الطلاء أو التسقية المباشرة للأسطح الخشبية الملونة.

الكلمات المفتاحية:

3. Aim

The research aims primarily to suggest new consolidation materials that can be used to treat and consolidate the weakness and fragility of the painted layers in the decoration of wood ceilings, without any color alteration or Blanche.

4. Introduction

It is broadly believed in the field of art history that painted decoration of wood ceilings is one of the prime artistic features of Islamic domestic architecture, especially in Egypt. However, numerous examples of those colored wooden ceilings in various historic Egyptian Islamic houses have been subjected to harsh conditions, by natural or human means, which resulted in their deteriorations in different degrees and levels.

After decades of exposure to climatic conditions, painted wood exhibits several forms of deterioration including water staining, soiling, termite and other insect damage, paint loss, severe abrasion, the formation of crusts probably associated with the dissolution and re-deposition of manure in addition to the over-application of paint and other coatings^[1]. Most often, old wood objects present evidence of active infestation, besides historical biological degradation by insects or fungi, which affects their structural integrity, as well as other physical and mechanical properties. The authenticity of the object is threatened. Therefore, conservation of wood objects is a complex process as a result of wood's faulty defects that occur by time. In this respect, conservators are being confronted with a myriad of puzzling issues^[2].

In this paper, a preliminary study is carried out to select samples taken from buildings as examples to represent Cairo's historic domestic architecture, identify the adequate technique, and determine the proper materials which are examined and analyzed by X-rays, SEM, EDX, and Digital Optical Microscope (Fig. 1). Then, some samples are prepared according to the same original objects, materials, technique and decorative style. This required artificial aging in two steps; the first step is conducted before consolidation and the second is after consolidation. The criteria used to evaluate ($Primal AC33/TiO_2$ nanoparticles) as

consolidation material for painted wood is the mechanical and visual properties, SEM scans, digital Optical microscope and colorimeter for degree of color change.

5. Experimental

Small samples of painted wood ceilings are taken from different buildings; (al-Set Wasila's house, Zainab Khatoun's house and al-Harawy's house). Then, they are prepared to be examined and analyzed in lab, by Scanning Electronic Microscope (SEM) with edex, x-ray diffraction (XRD), digital microscope. The results are complemented by Fourier Transform Infrared Spectroscopy (FTIR) and Ultraviolet wave (UV). The results indicate the following:

5.1. Analyses and Examination

5.1.1. Identification of the wood

Three painted wood samples are taken from the wood ceilings, and examined in the wood technology department labs - Faculty of Agriculture - Alexandria University. 20 μ m is obtained in the three principal anatomical directions, transverse (TS), tangential (LS) and Radial (RLS). The histological sections are observed by optical microscope in transmitted light (Olympus BX40) with a digital camera under 40-60X magnification. Finally, it turned out that the samples are all types of pine wood. As shown in (Fig. 2)

5.1.2. Analysis using X-Ray diffraction

A tiny small sample from original painted layers of wood ceilings is taken for laboratory analysis X-ray diffraction in order to determine their components, which is a well-known and long used method for obtaining the lattice spacing of crystalline samples. The condition for the diffraction of x-rays by crystal lattice can be expressed in the form of Bragg's law ^[3] $[n\lambda=2d_{(hkl)} \cdot \sin\theta]$. The aim of the present study is to obtain chemical and mineralogical compositions of the samples, in order to elucidate some details of the painting process as indicated in (Table 1).

5.1.3. Analyses using Ultraviolet spectrum

Ultraviolet (UV) spectroscopy is a technique used to quantify the light that is absorbed and scattered by a sample (a quantity known as the extinction, which is defined as the sum of absorbed and scattered light). In its simplest form, a sample is placed between a light source and a photo detector where the intensity of a beam of light is measured before and after passing through the sample. These measurements are compared at each wavelength to quantify the sample's wavelength dependent extension spectrum. The data is typically plotted in an extension similar to a wavelength function.

Each spectrum is background corrected using a "blank" a cuvette filled with only the dispersing medium to guarantee that spectral features from the solvent are not included in the sample extension spectrum ^[4]. **Three samples are analyzed (Fig.3) to show the following results:**

- The medium used in decorative paint is animal glue.
- The type of wood might be juniper or pine wood.
- In one of the samples, a layer of linen textile which is found between the wood surface and the decorative layer has been treated by madder dye

5.1.4. Fourier transforms infrared spectral analysis (FTIR)

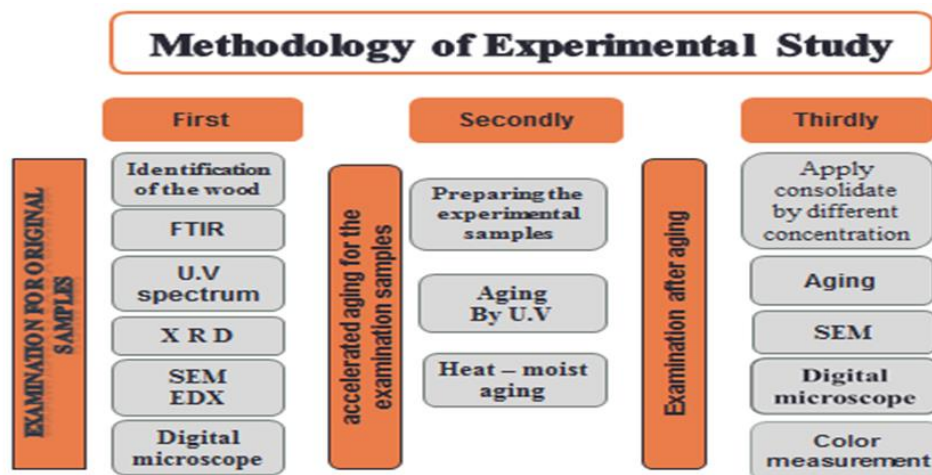
The chemical structural changes that occur in the original samples of painted wooden ceiling is analyzed by Fourier Transform Infrared spectral analysis (FTIR) which is used for the characterization of the materials of polychrome. The various methods proved to be very effective in characterizing both the inorganic and organic constituents in addition to pinpointing the analytical data within a precise layer of the stratigraphy of the cross-sectioned samples. To avoid any interference while studying all possible bands from the reference samples, appropriate embedding media free preparation techniques had to be applied [5]. The spectra were recorded in transmission mode to ensure comparability with thin section data. Based on the results, the medium of paint turned out to be animal glue, as shown in (Fig. 4)

5.1.5. Examination using Digital microscope and SEM with EDX

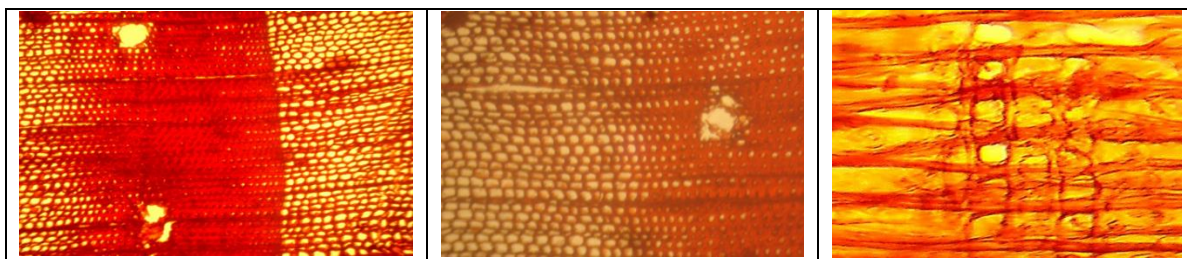
Three samples are observed using Optical Digital Microscope and Scanning Electron Microscope (SEM). Optical microscope enables the observation of the structure of individual layers (stratigraphic analysis) while (SEM) is a technique used for topological examination. Electron microscopy combined with Energy Dispersive X-ray spectroscopy (EDX) provides spectra of X-ray frequencies that are used to identify constituent elements, as shown in (Fig. 5). The global chemical compositions of all the samples determined by SEM-EDX are indicated in (Table 2).

5.1.6. Identification pigments and preparatory layer

The compounds of painting and preparatory layers are identified in accordance with the results of XRD EDX analysis. For all samples, the bands associated with the presence of calcite and quartz are detected. The characteristic peaks of gypsum are also identified in samples 1 and 2. The presence/absence of sulfur gives the indication of the appearance or absence of gypsum. The author can identify the presence of iron oxides in the form of goethite (FeOOH or Fe₂O₃·H₂O), the bands due to hematite, Fe₂O₃, the main reason for the reddish hue. The presence of (Pb) is related with the pigment white lead (2PbCO₂·Pb (OH)₂) present in the bolus and the red pigment (Pb₃O₄), associated with the red paint. Iron, which appears in almost all the samples, is responsible for the red coloration of some preparatory layers. Calcium is related with the presence of calcium carbonate or calcium sulfate in the preparatory layer. The presence of Malachite is also the reason behind the green pigment.



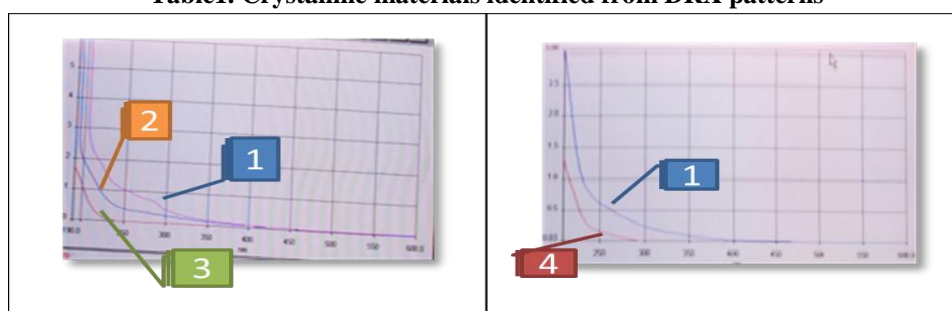
(Fig.1) methodology of the experimental section



(Fig. 2) Cross section of wood sample

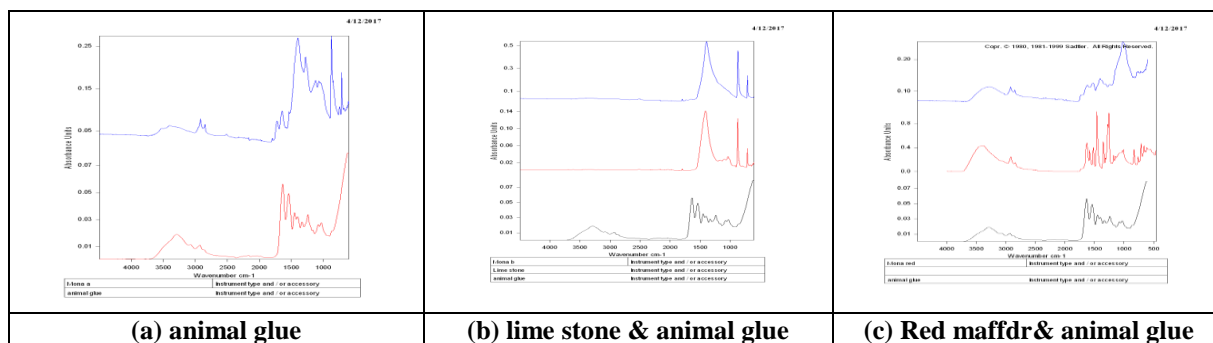
Sample	Chart	Crystalline materials	
<p>1</p>		<p>Calcite Quartz Magnetite Gypsum.</p>	<p>$CaCO_3$ SiO_2 Fe_3O_4 $CaSO_4 \cdot 2H_2O$</p>
<p>2</p>		<p>Quartz Calcite Gypsum. Goethite</p>	<p>SiO_2 $CaCO_3$ $CaSO_4 \cdot 2H_2O$ $Fe_2O_3 \cdot H_2O$</p>
<p>3</p>		<p>Hematite Calcite Gypsum Sodium chloride Malachite</p>	<p>Fe_2O_3 $CaCO_3$ $CaSO_4 \cdot 2H_2O$ NaCl $CuCO_3 \cdot Cu(OH)_2$</p>

Table1. Crystalline materials identified from DRX patterns



(Fig. 3) 1-UV curve for unknown sample
3- U.V curve for animal glue

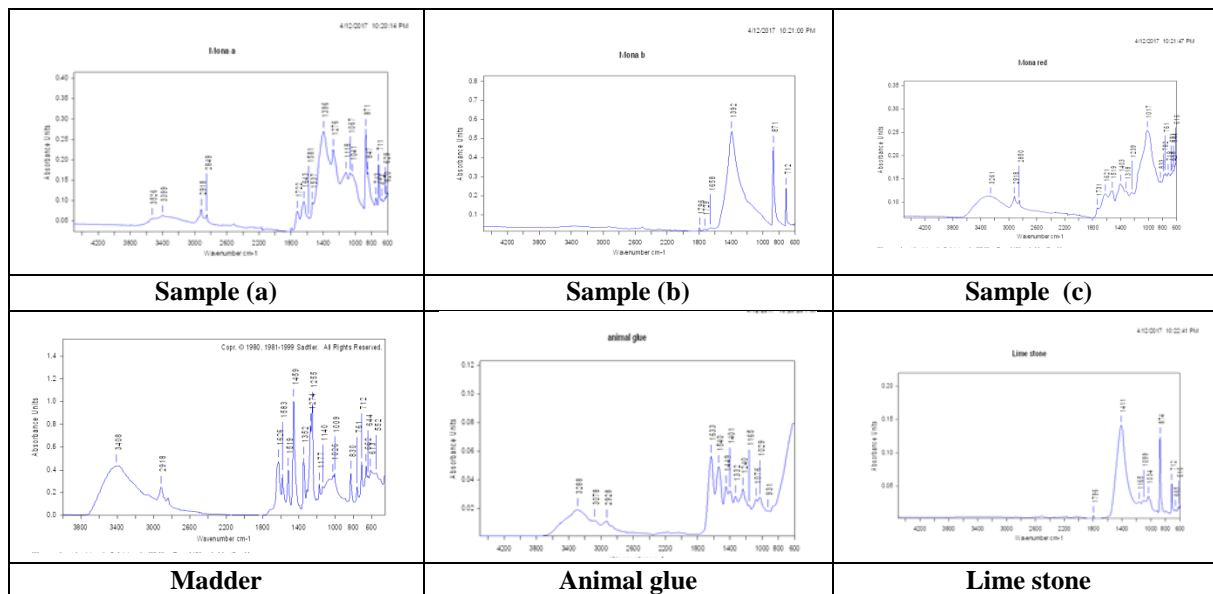
2- U.V curve for the red madder
4- U.V curve for Juniper plant extract



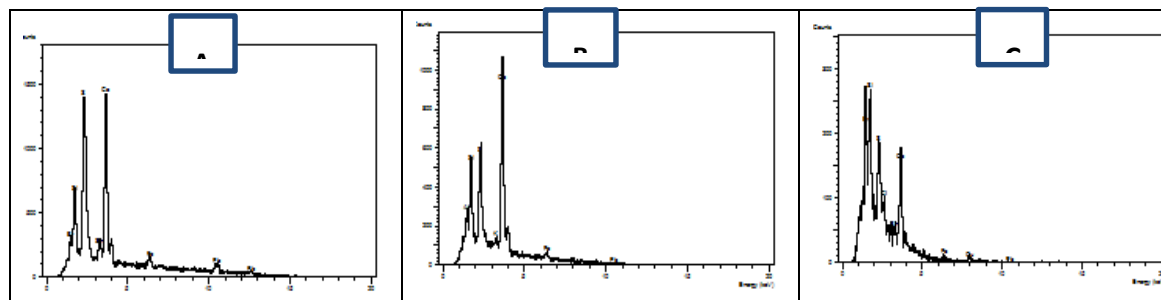
(a) animal glue

(b) lime stone & animal glue

(c) Red maffdr & animal glue



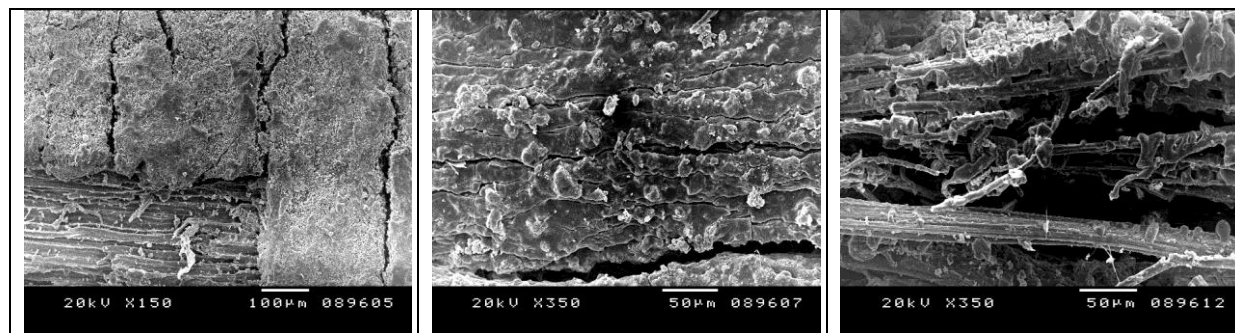
(Fig. 4) Fourier transforms infrared spectroscopies FTIR of: (a) sample, (b) sample and (c)



(Fig. 5) EDX patterns of three samples of painted wood components

Sample	Elements									
	Br	Si	S	Sn	Ca	Fe	Pb	Cl	Cu	Na
A	2.2	7.3	35.5	5.6	42.7	3.6	2.5			
B	3.6	11.3	24.8	2	55.4	2.5	0.4			
C	20.9	14.8	25.1	2.6	25.5	1.5	0.1	7.3	2.3	0.9

(Table2) Global chemical elements (mass %)



(Fig. 6) SEM of the original samples 1 to 3 respectively



(Fig. 7) Optical micrographs of samples from (1) to (3), respectively

5.2. Sample preparation

Based on the previous data obtained from the results of the examination and analysis, some samples are prepared. Three pieces of pine wood are spread, a preparatory layer is applied, and then layers of paints are drawn according to the Islamic style of decorative designs comparable to the original designs, as shown in (Fig. 8)

5.3. Accelerated aging

The accelerated aging experiments are performed on experimental painted wood. The aging method is selected for the purpose of imitating an average deterioration, which is observed on historical building. In artificial or accelerated aging methods, a material is exposed in a climate chamber to extreme conditions in terms of temperature and humidity for a certain period of time, during which the changes in the material are measured. Artificial aging tests are often used to determine the permanence of painted wood ceilings and their rate of degradation and to predict the long-term effect of a conservation treatment. Accelerated aging regime is used in:

5.3.1. Aging by UV lamps

The effect of accelerated UV-aging on properties of wood-fiber composites has been studied where wood-fibers are subjected to accelerated UV-aging in a QUV weather meter for up to 8 weeks. Without any consolidation, stabilization degradation is made [6]. For UV aging, a Fade-O-Meter instrument is used at room temperature for 144 h (6 consecutive days) [7]. The temperature and humidity were at about 22°C and 40%, respectively. The UV light is generated by a carbon arc light source and the wavelength range of emitted light was 350–430 nm, Mercury-ARC Lamp (E40-Mix F 500 W). The samples are exposed to UV radiations by putting them in a closed box of Bulbs & Tubes under Ultra Violet radiations, in two steps. The first step is conducted before applying the consolidation while the second is after application. Exposure lasted all day round, as shown in (Fig. 9).

5.3.2. heat moist aging

Heat treatment improves the dimensional stability and decay resistance of wood, both of which are of great importance in wood applications. However, it is shown that strength properties decrease as a result of thermal treatment which causes considerable color changes [8]. The process of decay is simulated by immersion in water (Fig. 10), then heating and drying in oven at a temperature of 90±3°C, respectively in constant relative humidity 40% inside an accelerated aging chamber. The aging period lasted for 30 days. (Fig. 11)

5.4. Materials

Primal AC33 nanoparticles dissolved in Ethanol, starting with 3% concentration and up to 5%, in addition to Titanium dioxide (TiO_2) nanoparticles are used. In this case, reinforcement materials (TiO_2) are added to the polymer matrix (Primal AC 33 in Ethanol). Thus, it is mixed to obtain homogeneous composite nanomaterial. The previous experiments indicated that nanoparticle of titanium dioxide (TiO_2) were useful in the consolidation processes for wood, due to UV protection, fire resistance, water resistance (super hydrophobic surfaces), bio-protection^[9]. Primal, which is an acrylic resin, is widely used in the field of preservation and conservation as it has proved its successes in consolidation and adhesion^[10]. Polymeric Nanocomposites are prepared using different composition ratios of MMA and BuA in the presence of different weights of TiO_2 nanoparticles (0.1, 0.3 and 0.5 gm.) using emulsion polymerization technique by irradiation ultrasonic initiation doses for different time intervals. The polymerization is carried out according to the following procedure: in a 250 ml flask, 1 gm. of SDS is dissolved in distilled water (90 ml), 10 gm. of monomers mixture according to the selected BuA percentage (1, 3 and 5%), were added and well irradiated using 400 watts ultrasonic irradiation as initiation system for different times (5, 10 and 15 min)¹¹. The consolidate is applied with Sprayer without damaging the very fragile pigments and wood. The condition of the wood was such that it needed to absorb a large amount of consolidation.



(Fig. 8) Sample preparation



(Fig. 9) Aging by UV lamps



(Fig. 10) Moist aging



(Fig. 11) Heat aging

5.5. Examination using Digital microscope and SEM

The experimental samples are re-examined by scanning electronic microscope and digital microscope before and after treatment and aging, as shown in (Fig.13, 14)

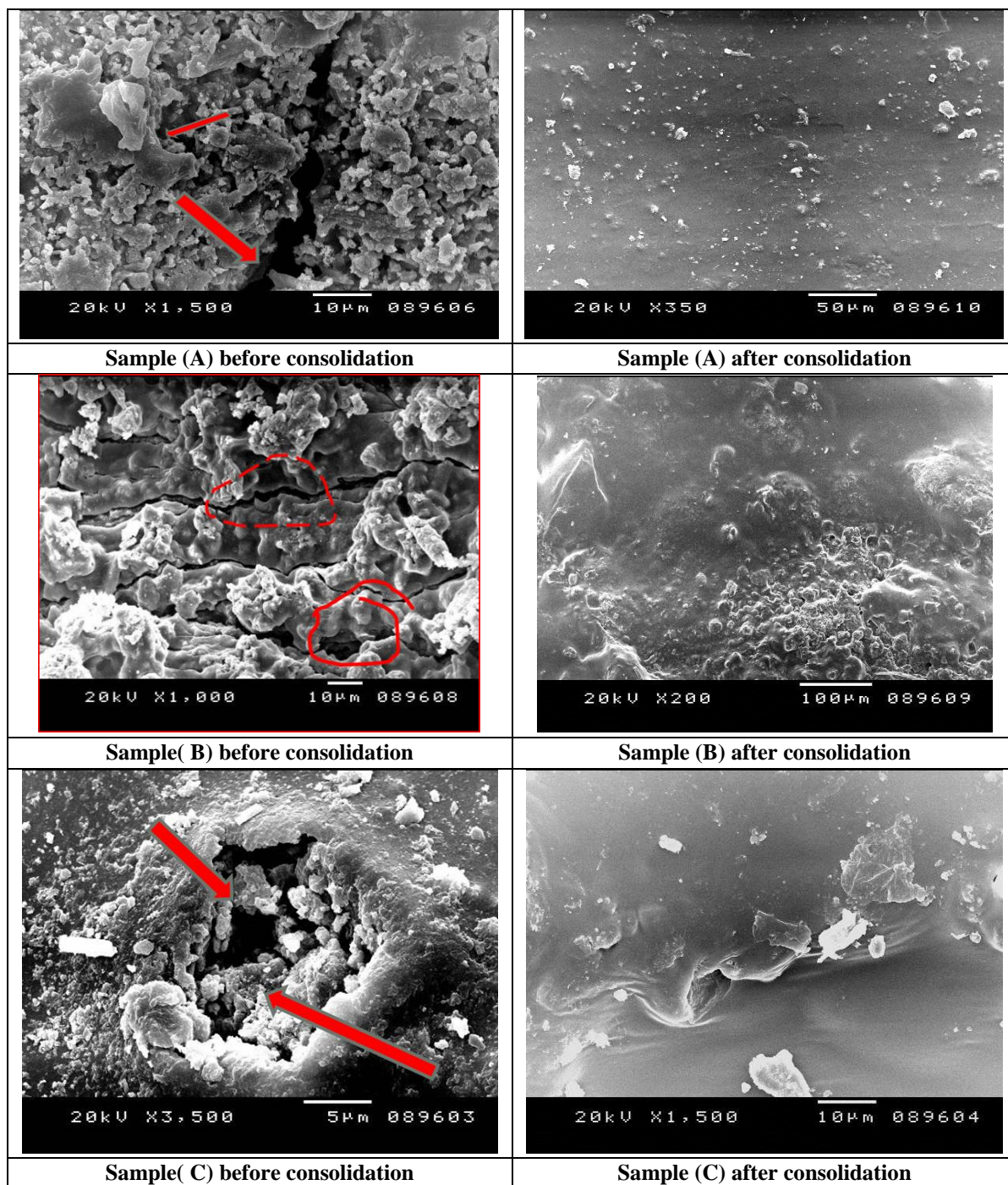
5.6. Color measurement

A colorimeter is a device used in measuring the absorbance of particular wavelengths of light by a specific solution. Color difference parameter (ΔE^*ab) is measured by using Optimatch

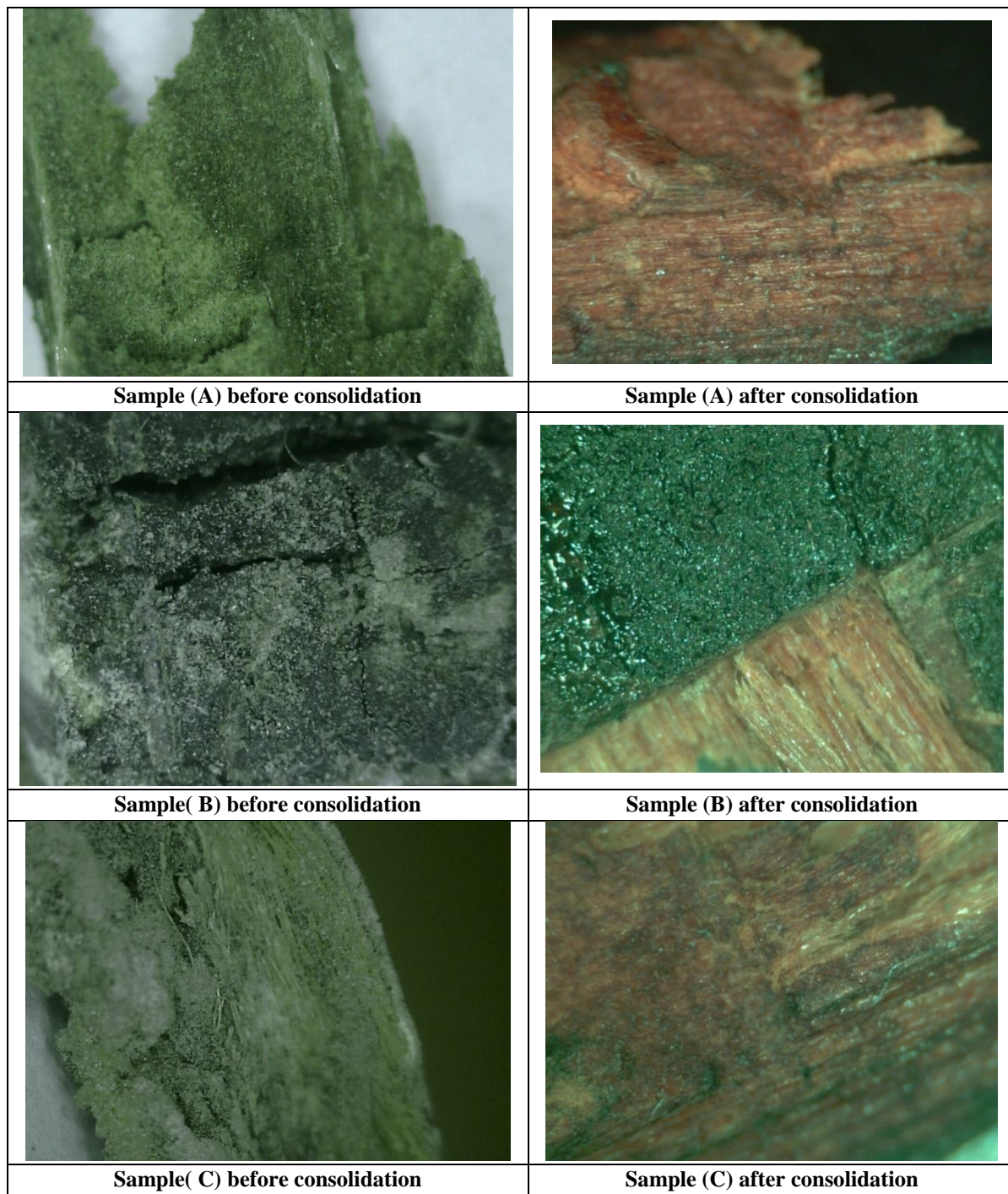
3100 spectrophotometer. For each sample the average of three measurements is recorded. In order to have a relative evaluation of the induced damage degree on color changes, the overall color differences (ΔE^*ab) between reference and aged samples are calculated using the (CIE Standard, 2007) ($L^*a^*b^*$) equation. The results are shown in table (3)

5.7. Aging after consolidation

The second stage of accelerated aging is carried out on experimental painted wood samples after consolidation, using the same methods, in order to compare their properties before and after treatment.



(Fig. 12) SEM of experimental samples before and after treatment 1 to 3, respectively



(Fig. 13) Digital microscope of experimental samples before and after treatment 1 to 3, respectively

Sample	measurements before aging			measurements after aging			The difference between before and after			Square number of difference			Sum of squaring	Sqrt of the sum of (E)
	L	A	B	L	A	B	L	A	B	L	A	B		
(A)	47.45	2.04	1.94	47.66	2.001	1.88	-0.21	0.039	0.06	0.044	0.001	0.003	0.0486	0.22
(B)	52.01	1.36	3.52	51.47	1.98	4.43	0.54	-0.62	-0.91	0.291	0.384	0.828	1.503	1.22
(C)	78.84	4.34	18.67	78.77	3.32	18.0	0.07	1.02	0.66	0.004	1.04	0.43	2.13	1.45

Color alteration in panting layers after consolidation

Table (3) calculations of color alteration in panting layers after consolidation

6. Discussion of Results

According to the result of the microscopic examination, it is clear that the untreated fibers are completely separate from each other. However, in the case of the treated sample, full fibers might be integrated and interrelated. This is due to the formation of wood fiber bundles and the polymer matrix where these fibers have increased their bonding and integration by increasing polymer concentration. As noted in samples without consolidation, a separation of the layers of paint, frailty and weakness in untreated samples is observed. Whereas, the samples treated by consolidation indicate that all layers of paintings and wood support are compacted in one unit, which is a good evidence for the success of (Primal AC33/TiO₂ nanoparticles) in the consolidation process. For the painted layers on wood treated with the polymer after thermal and light aging, it can be observed that there is a slight color alteration of the painted wood which is not visible to the naked eye, and that its properties has fairly improved.

7. Conclusions

With the aim of treating painted wood using the Primal C33/TiO₂ nanoparticles, reinforcement materials (TiO₂) are added to the polymer matrix (Primal AC 33 in Ethanol). Thus, the mixture is used to obtain homogeneous composite nanomaterial. The previous experiments indicated that the use of nanoparticle of titanium dioxide to treat the weakness of wood ceilings of historic buildings has helped to improve the properties of wood and paint layer. It has been investigated using different experimental techniques and evaluated using color change measurement and SEM with EDX. After using UV heat and light to accelerate the aging methods, the conclusions drawn from this research can be summarized as follows:

- Some samples are taken from three buildings. Then, examination and analyses are carried out to identify the technique and the materials .
- Based on the previous data, some samples are prepared according the same original techniques, materials and decorative design style.
- After aging acceleration is carried out, the treatment using Primal C33/TiO₂ nanoparticles is applied.
- After aging, the experimental samples are examined to evaluate the success of the treatment.
- Based on the results of the examination, the author is able to acknowledge the success of using the present consolidation material. Therefore, the author recommends using Primal C33/TiO₂ nanoparticles in the treatment of weaknesses in antique painted wood.

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