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A Comparative Study to Evaluate Regalrez, Nano Regalrez, and Nano Composite for the Consolidation of Pigments used on Ancient Egyptian Wooden Artifacts

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Abstract

The basic goal of a consolidation process is to reach the stage of strengthening the internal structure of the treated material to preserve its structure and authenticity, and to improve its physical and chemical properties. This paper focuses on evaluating the effect of one of the traditional polymers used in the consolidation of painted wooden artifacts (Regalrez 1094) in three different forms: a traditional polymer (R 3%) in white spirit, a composite Nano polymer (Regalrez 1094 with titanium dioxide nanoparticles in different concentrations (1%, 3%, and 5%), and a nano polymer (Nano Regalrez 3%) to reach the best consolidation of the polychrome layer on wood substrates. The properties and crystallization of the pigments and the size of their grains after the application of nanomaterials were studied. Additionally, the efficiency of the nanomaterials in preserving and stabilizing the color degrees applied to the samples before and after (heat and UV) aging and application of the different forms of the polymer by using Transmission Electron Microscope (TEM), color change, USB microscope, Fourier-transform infrared (FTIR) analysis was also evaluated. The results revealed that the traditional polymer Regalrez 3% gave a good result with the least color change occurring in blue, green, and white colors. A composite Regalrez 3% with TiO_2 gave the best result in the two concentrations of TiO_2 (1% and 5%) proving the ability of nano additives to improve the characteristics of polymers and their resistance to aging, while Nano polymers gave bad results, high color change degrees, and clear chemical changes in the chemical components of the pigments and paint media after exposure to aging.

Keywords: Polymeric nanocomposite – Nano polymer - Regalrez 1094- Nano Regalrez 1094- pigments – TEM – color change – FTIR - titanium dioxide nanoparticles.

1- Introduction

Wood is considered the oldest material in the history of humanity, as society realized the importance and value of the material and its characteristics and made tools, furniture, and various pieces out of it. Hence, wood is a multifaceted and versatile material, used since ancient times for many reasons, including its fibrous nature [1]. The ancient Egyptian artist also excelled in the manufacture and composition of materials and various shades of color from the environment in which he lived and developed his industry. The advancement in technology among the ancient Egyptians allowed the artist to develop a wide range of colors by introducing new methods, since ancient times, where he manufactured color materials such as Egyptian blue and green [2]. He was able to develop and mix it with binders to maintain the cohesion of the color granules, achieving a high degree of stability and preservation despite the long periods of time that passed. Therefore, it is necessary to preserve these polychrome artifacts by carrying out various conservation treatments, in particular chemical consolidation processes of pigments.

Consolidation treatment is an important stage in conservation processes, especially when wooden objects are painted with different pigments and have many layers, due to exposure to many deterioration factors that affect their integrity, chemical structure, and mechanical strength [3]. Polymers have undergone multiple developments over time, and the materials used in the treatments have evolved [4]. A consolidation process is applied to restore the cohesive and physical properties, chemical structure, and mechanical strength of the wooden material, whether painted or not, while preserving its originality [5, 6]. The role of consolidation depends on the properties of the consolidated material and its distribution on the surface of the material as a painted wooden sample [7]. However, consolidation materials, especially with painted wood surfaces, may with time and poor preservation conditions, represent many factors of damage and weakness of the artifacts and fail to preserve the color tones

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instead of consolidating them and prolonging the life of the object [5]. Therefore, it is necessary to continue studying the development of these materials and raise their efficiency in terms of their sufficient strength in the consolidation and penetration and the extent of their decomposition when exposed to aging over time especially heat, ultraviolet, or infrared rays, as well as the extent of resistance to high humidity that may lead to exposure to biological infestation [8]. It is also important to improve the consolidation properties of the polymer; therefore, many efforts have been made to improve the quality of different polymers by using nanoparticles [9].

Nanomaterials have particles of size below 100nm, which impart new behaviors and properties. Because of their very small size, they possess different properties, such as improved chemical reactivity, catalyst activity, gas absorbency, and mechanical properties [10]. During the last decades, nanomaterials and nanotechnology have developed strongly, especially in the field of cultural heritage, where various materials have been used and applied in antiquities and works of art [11]. To increase the efficiency of polymers used in consolidation and improve their properties, many studies and researchers developed nanocomposites. The use of some nanomaterials, such as nano titanium dioxide and nano silver oxide, has become common, and their efficiency has been proven, but these studies were conducted on a large scale with many different archaeological materials, including stones and organic materials, for either consolidation or cleaning purposes [12-16]. Additionally, the evaluation of nanomaterials in the treatment of some types of wood has been recently conducted [17,18], however, studies have not expanded widely on the extent to which these nanomaterials affect the consolidation of painted wooden antiquities. Hence, the idea of this research is to study the effect of one of the polymers commonly used in the consolidation of painted wooden objects with one of the nanomaterials, to convert it into a nanomaterial and to study the extent of their effect on each color or pigment separately and the extent of their efficiency in terms of color change and chemical effect on the color properties and its composition. Regalrez 1094, which was chosen for this study, is a hydrogenated hydrocarbon copolymer (2-cyclohexylpropene-co-3-methylcyclohexylethylene) [19]. The nanomaterial used with Regalrez as a copolymer is Nano titanium dioxide (TiO_2), which is one of the most widely used nanomaterials in consolidation processes for organic materials [20-21].

The objective of the study is to conduct a comparative study on the application of traditional Regalrez 3% (R3%) in white spirit, nanocomposite Regalrez with 1%–3%–5% TiO_2, and nano-Regalrez 3% in white spirit in the consolidation of pigments applied on painted wooden samples, to study the properties of the different states of the polymer and the extent of their efficiency and effectiveness in the consolidation of pigments, and to study the extent of their effect on both the chemical composition and the surface color change of colors applied to the wooden surface.

2. Results and discussions

2.1. Measurement of nanoscale size of Regalrez

Morphology and size of the polymeric material of nano Regalrez after physical grinding have been investigated using the transmission electronic microscope (TEM). The polymer was prepared for investigation by suspending the nano-polymer in acetic acid serving with sonication apparatus for 10 min, then in a buffer for a quarter of an hour. This was followed by taking two drops, and placing them on the Cu-grid then allowed drying. Insert the Cu-grid inside the device for imaging [22]. Figure.1 shows the Regalrez crystals with a closed circular shape with bar length as 100nm and magnification as 120K. The crystals appear in nano size ranging from (10.5nm to 15nm).

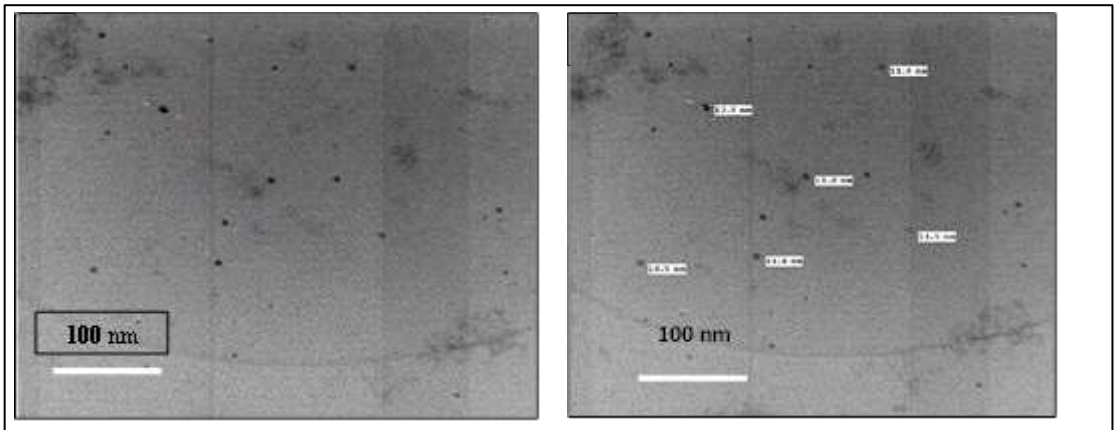


Figure.1: TEM image of Nano Regalrez 3% with Mag., 120K, HV=80.0KV

2.2. Measurement of color change by spectrophotometer

The results of color changes of painted samples after application of polymers and after aging processes (thermal and UV aging), showed different values of the total color changes (ΔE) (Table.1&2). In conservation the differences in color change should not

exceed 5, and less than that is considered a fairly perceptible difference [23-26]. ΔE value was different due to the effect of each polymer on the chemical composition of each pigment.

Based on that, Table (1, A) shows the results of the red samples, that gave the least value of (ΔE = 1.80) after applying (R3% with TiO_2 1%), then it increased after aging to (ΔE = 2.27) indicating that it was affected by aging [15]. A noticeable resistance of the polymer to color change after aging was obtained by adding nano-TiO_2 1%, giving better results than R3% alone, and a moderate color change was caused by other concentrations of nano-TiO_2 (3% and 5%). Nano polymer 3% gave higher values of color change before and after ageing, with ΔE = 4.55, 11.54 respectively. The change occurring in the polymer alone or in its nano form gave the highest color change when the sample darkened in the case of Regalrez as noted in the ΔL, but after ageing a decrease in color change occurred. The value of Δa after treatment was negative in all samples, except for the sample treated with nano Regalrez. After ageing all the Δa values of the samples became positive and redder except for the Regalrez 3%(R 3%).

The results of the blue samples in Table (1, B) showed that all the studied polymers produced a clear color change with blue pigment, but the least noticeable change was with (R3% plus TiO_2 1%, ΔE = 9.27), which decreased after aging (ΔE = 5.13) in spite of its considerable perceptible difference. The polymers used in this study showed less stability and more color change with blue color, as a result of the chemical composition of Egyptian blue ($CaCuSi_4O_{10}$) and its effect on polymers and aging processes. The color change was unacceptable in all cases except for the ΔE of the sample treated with nano Regalrez before ageing. The addition of TiO_2 caused darkening in all cases after treatment, and after ageing the ΔL of the samples changed in the direction of the lighter color, except for the R 3% which darkened. Δa and Δb changed by a large degree in the nano Regalrez sample, and Δa went into the greener direction after ageing in the case of TiO_2 1% and 3%.

Table (1, C) shows the results of green samples, where all polymers produced a clear color change, but the least change was obtained with (R3 %, ΔE = 3.09), which decreased after aging to (ΔE = 2.55). There was no significant color change, but rather a decrease after aging, which indicates that Regalrez resists UV and thermal aging [19] and its compatibility with the nature of green color. R 3% and R3% with TiO_2 5% changed the ΔL to the darker color, and the ΔL remained negative in the sample with 5% TiO_2. However, in the three other treatments the ΔL was positive and gave the sample a lighter color. The Regalrez and TiO_2 1% and 5% changed the Δa to a greener color.

Table (1, D) shows the results of yellow (goethite) samples, and compared to the previous colours the ΔE of goethite was within an acceptable range, except for the sample treated with nano Regalrez before ageing. The sample became lighter and greener in color after treatment, yet darkened after ageing. The best results with the least color change were R3% with TiO2 5%, followed by R3% with TiO_2 1% with a small difference. The sample with TiO_2 3% changed to a greener color after ageing causing an increase in the value of ΔE. As goethite is considered an inorganic oxide, a nanocomposite polymer with nanoparticles of TiO_2 improved the resistance of the polymer to ageing, decomposition of color, and reduced oxidation [11].

According to the results of the yellow (orpiment) samples, as shown in table (1, E), the orpiment samples with various polymers led to a significant color change, as 1% nano-titanium dioxide with Regalrez 3% recorded the highest values of color change before and after ageing., while 3% nano TiO_2 gave less color change values. In the case of TiO_2 5% and nano Regalrez the color change was very high after treatment, but the value decreased after ageing. The Δa of TiO_2 5% was in the direction of the greener color before and after ageing. In the case of nano Regalrez the sample darkened after treatment, but changed to a redder color after ageing.

Table (1, F) shows the results of black samples as it was affected by different polymers in this study and a clear color change by aging (thermal-UV) occurred, where the least values were with (R3% with TiO_2 5%), which was within an acceptable range. However, the highest values were with nano Regalrez, which indicates that nano Regalrez is not efficient on black pigment either.

In all samples were the ΔE was higher than 5, and the main change occurred in the Δb in the direction of the yellow color except for the aged nano Regalrez sample.

The results of white samples showed in Table (1, G) that it was affected by different polymers and a clear color change occurred, the least value was with (R3 %, ΔE = 4.32) which decreased after aging (ΔE = 2.70). This expresses the resistance of Regalrez to aging processes with white color.

The characteristic bands of the colored standards include bands of animal glue used as a binding medium, bands of calcium carbonate used as a preparation layer, and those of the pigment. In treated colored samples, the characteristic bands of Regalrez in addition to the standard bands are present in the spectra. All these bands are clarified in Table.3.

The infrared spectra of the colored samples treated with Regalrez 3%, before and after thermal and UV ageing showed that the stability of this polymer depended on the chemical composition of the pigments. Slight remarkable changes were shown in green and white samples reflecting the good stability of Regalrez with these pigments. While, red, blue, black, yellow orpiment, and yellow goethite showed several spectral changes. To enhance the stability of this polymer with these pigments, nano TiO_2 was added to the polymer and evaluated the role of titanium nanoparticles in improving the polymers stability for the consolidation of the color samples.

2.4.1. Red pigment (Hematite):

The results in Figure (2a) show a slight change of R 3% with TiO_2 1% when applied to red pigment, but no remarkable change was observed in the polymer or medium, and in the ground layer, except for band no. 1. in the range (1465–1415 cm^{-1}), became one peak after application and ageing and a slight shift occurred in some wavenumbers resulting from the applied polymer and the ageing process. This refers to the stability of the polymer towards ageing [27] as the nano titanium dioxide concentration (1%) improved the properties of the polymer and increased its resistance to ageing. However, the results in Figure (2b) show several chemical changes after the application of nano Regalrez to the red sample and after ageing. Various changes in the shape of some bands occurred, the band splitting distinguished to CO_3^{2-} band of calcium carbonate in the standard and after treatment became one peak at 1417 cm^{-1} after ageing [28], C-O stretching of animal glue at 1064 cm^{-1} and carbonyl group stretching

(C=O) at 1786 cm^{-1} disappeared after nano polymer application referring to the influence of nano polymer. These results indicated the effect of polymer and changes in its properties after converting it into nano size.

2.4.2. Blue pigment (Egyptian blue)

Figure (3a) show a very slight change in R3% with TiO_2 nanoparticles 1%, just shifting in some wavenumbers as a result of the ageing process. This result confirmed the stability of the polymer and its suitability to be applied to the Egyptian blue pigment. Stretching vibrations of Si-O-Si in the standard sample of Egyptian blue appeared at 1228 cm^{-1} and 1155 cm^{-1}, while Si-O appeared at 887 cm^{-1} [26, 29]. These bands interacted with those of the polymer in the treated and aged samples, indicating the resistance of this polymer to photo oxidation, as the chemical composition of Egyptian blue is considered a very stable pigment when exposed to light ageing [26, 30]. The presence of titanium dioxide nanoparticles (1%) increased the stability of both pigment and polymer and is suitable with them. While Figure (3b) show several changes when the concentration of titanium dioxide nanoparticles reached 3%, in addition to the change in some wavenumbers, there were some changes in the band shapes and absorption intensities due to the ageing processes: C-H stretching of animal glue and Regalrez was shifted to lower wavenumber from 2987 cm^{-1} to 2956 cm^{-1}; C=O stretching (amide I) of animal glue [31] and C=C stretching of Regalrez shifted from 1631 cm^{-1} to 1614 cm^{-1}; Si-O-Si stretching, which distinguishes Egyptian blue at 1247 cm^{-1} shifted to 1220 cm^{-1}. Band no. (1) at 1043 cm^{-1} corresponding to Si-O asymmetric stretching of the pigment plus C-O stretching of the animal glue and band no. (2) of Si-O symmetric stretching at 875 cm^{-1} disappeared after ageing, reflecting the effect of ageing and polymer on the pigment and binding medium.

2.4.3. Green pigment (Malachite):

Application of R 3% on the green samples showed more acceptable results than that of nano Regalrez or Regalrez with titanium dioxide nanoparticles. The results in figure (4a) show slight changes in the treated sample with R3% after thermal and UV ageing compared with that before ageing confirming the stability of this polymer when used with malachite. The standard spectrum shows the characteristic bands of the green pigment (malachite) [32, 33], the preparation layer (calcium carbonate), and the pigment medium (animal glue), while the spectrum after treatment shows an increase in the absorption intensities of most vibrations due to Regalrez. On contrary, Nano R3% showed various changes after ageing compared with that before ageing and whose spectrum agrees with that of the standard confirming the degradation of the polymer in its nano scale. As shown in figure (4b) band no.1. C=O stretching at 1791 cm^{-1} obviously appeared after treatment, band no.2 small peaks of C-H stretching disappeared after ageing, and band no.3. C-H bending of Nano Regalrez and animal glue at 1487-1375 cm^{-1} changed after ageing in shape, absorption intensity, and in wave numbers.

2.4.4. Yellow pigment (Goethite):

The spectra of yellow (goethite) samples in figure (5a) show slight changes in the treated sample with R 3% + TiO_2 5%, compared with the standard and the aged treated sample. Band no.1 shows that the C-H stretching at 2916 cm^{-1} disappeared after treatment; the intensity of band no.2 corresponding to C-O band at 1136 cm^{-1} decreased; and the small shoulder at 1033 cm^{-1} disappeared after treatment. The spectra in fig(5b) show several changes of R 3% with TiO_2 3%, where the absorbance intensities decreased after the treatment and then increased again after ageing, similar to the standard sample. Band no.1 decreased in absorption intensity and became very weak after treatment, band no.2. at 1633 cm^{-1} assignable to C=C stretching of Regalrez plus amide I of animal glue [34] became broader after treatment, then split into two bands after ageing at 1635 cm^{-1} and 1693 cm^{-1} referring to oxidation and formation of new carbonyl group. The formation of this new band may be due to the ageing process and to the catalytic effect of iron ions present in the pigment composition [35], Band no.3. split in the standard and after ageing but became one peak at 1139 cm^{-1} after treatment with a very small shoulder at 1058cm^{-1}, which indicates that titanium dioxide at 3% is an unsuitable concentration.

2.4.5. Yellow pigment (Orpiment):

The spectra of yellow (Orpiment) samples show obvious changes when R3% with TiO_2 nanoparticles 3% or 1% was applied to the samples. The specialized group of Orpiment at 1039 cm^{-1} disappeared after ageing due to conversion of orpiment to arsenic oxide [30,36,37] , in addition to changes occurring in calcium carbonate and animal glue band at 1417 cm^{-1}. In figure (6a) shows changes in the treated aged sample compared with the treated one, as band no.1. at 1417 cm^{-1} distinct of CO_3^{2-} stretching vibration + C-H bending of animal glue and Regalrez [34, 38] increased obviously in the absorption intensity after ageing, band no.2. at 1062 cm^{-1} decreased after treatment and a new band arose at 1039 cm-1 after treatment related to orpiment pigment and they disappeared after ageing, Band no.3. a new peak appears at 1782 cm^{-1} distinct of the preparation layer $CaCO_3$ after ageing. Also figure (6b) shows the influence of Regalrez 3 % with TiO_2 nanoparticles 1% on orpiment samples after treatment and ageing, as various changes occurred: Band no.1. C-H stretching of animal glue and Regalrez at (2906-2837 cm^{-1}); Band no.2. C=O of calcium carbonate at 1778 cm^{-1} appeared after ageing [46], band no.3. C-H bending of animal glue and Regalrez plus CO_3^{2-} stretching vibration at (1421 cm^{-1}) sharply increased after ageing, Band no.4. C-O of animal glue at 1066 cm^{-1} & 1037cm^{-1} distinct of Orpiment disappeared after ageing [37]. These results concluded that R3% with TiO_2 nanoparticles 3% or 1% is not a suitable material in the treatment of orpiment.

2.4.6. Black pigment (Carbon):

Fig. (7a) shows a slight change occurred in the aged sample compared with that of the treated sample with R3% plus TiO_2 nanoparticles 5%, where the band at 1643 cm^{-1} related to C=O stretching (amide I) of animal glue and C=C of Regalrez sharply decreased after aging [31, 38]. While the spectra in Figure (7b) show more changes in nano R 3%, band no. 1 related to C-H stretching split into three weak bands and became more obvious after ageing, where the absorbance intensities of most bands

increased after ageing, band no. 2 at 1421 cm^{-1} corresponding to C-H bending of Regalrez and animal glue split and increased in intensity. In addition to the appearance of two new bands after ageing at 1066 cm^{-1} and 1024 cm^{-1}(band.no 3) [38, 39]. So these results indicated that Regalrez in nano size is not suitable for the black carbon.

2.4.7. White pigment (Calcium Carbonate):

The spectra in Fig. (8a) shows that no remarkable changes happened in the treated and aged treated white samples with R 3% compared with the standard. These indicated the chemical stability of calcium carbonate and resistance of Regalrez towards ageing process [27]. The spectra in Fig. (8b) show some changes after treatment and ageing process as in band no.1. at 2906 cm^{-1} corresponding to C-H stretching. Bands no.2. of C=C stretching of Regalrez at 1635 cm^{-1} and C-H bending at 1471 cm^{-1} were shifted to lower wavenumbers after aging to 1620 cm^{-1} and 1440 cm^{-1} respectively [40]. While Band no.3. C-O stretching of animal glue at (1149-1072cm^{-1}) disappeared after treatment and ageing [31]. This refers to the change in Regalrez properties after converting it to nano size, which was affected by aging processes.

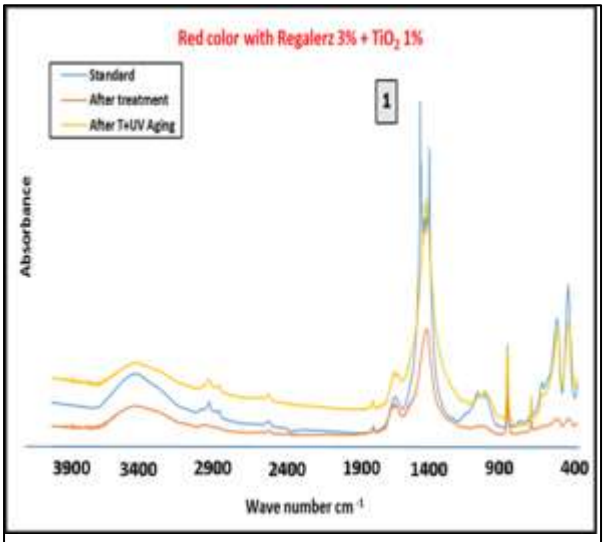


Figure.2a. FTIR spectra of red pigment, standard, after the application with R3% +TiO_2 1% and after ageing.

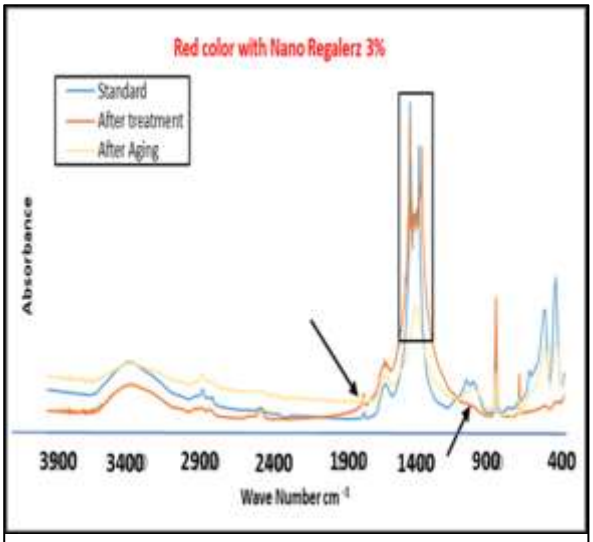


Figure.2b. FTIR spectra of red samples. Standard, after treatment with Nano Regalrez 3%, and after ageing.

Table.1: Changes in the color values of polymers applied on pigment samples after treatment and aging (Heat & UV)

		After treatment				After treatment & Aging (Heat & UV)			
	Polymers	ΔL	Δa	Δb	ΔE	ΔL	Δa	Δb	ΔE
Red pigment	**Regalerz 3%**	-2.76	-4.20	-2.11	**5.45**	-0.91	-0.99	2.58	**2.91**
	Regalerz 3% with TiO_2 (1%)	0.65	-1.29	-1.07	**1.80**	1.04	0.1	2.52	**2.72**
	Regalerz 3% with TiO_2 (3%)	-1.29	-3.02	-2.11	**3.90**	3.27	6.86	2.21	**7.31**
Red pigment	**Regalerz 3% with TiO_2 (5%)**	-0.34	-1.92	-1.89	**2.72**	-0.51	4.58	1.73	**4.92**
	(Nano)Regalerz 3%	-0.05	2.91	3.50	**4.55**	3.07	6.91	8.72	**11.54**
Blue pigment	Regalerz 3%	**7.22**	**3.31**	**5.31**	9.55	**-4.06**	**3.21**	**-3.07**	**8.03**
	Regalerz 3% with TiO_2 (1%)	-8.23	3.72	-2.11	**9..27**	4.35	-2.38	-1.33	**5.13**
	Regalerz 3% with TiO_2 (3%)	-12.8	6.67	-6.40	**15.4**	-7.23	-3.4	-4.99	**9.42**
	Regalerz 3% with TiO_2 (5%)	-7.54	4.83	-1.03	**9.02**	-4.99	3.23	-4.84	**7.67**
	(Nano)Regalerz 3%	-1.92	-1.29	-1.18	**2.59**	1.97	6.88	-3.38	**7.92**
Green pigment	Regalerz 3%	**-1.72**	**-2.51**	**0.58**	3.09	**1.41**	**-1.77**	**1.17**	**2.55**
	Regalerz 3% with TiO_2 (1%)	6.94	-0.84	0.63	**7.02**	1.78	-2.36	-4.61	**5.48**
	Regalerz 3% with TiO_2 (3%)	8.02	0.27	-0.43	**8.04**	8.46	2.28	-6.61	**10.98**
	Regalerz 3% with TiO_2 (5%)	-5.97	-1.50	0.02	**6.15**	-7.55	-1.63	0.32	**7.73**
	(Nano)Regalerz 3%	5.08	-0.43	2.99	**5.91**	10.61	1.54	3.59	**11.31**
Yellow (Goethite) pigment	Regalerz 3%	**0.49**	**0.76**	**0.35**	0.96	**-4.88**	**-0.96**	**-0.17**	**4.97**
	Regalerz 3% with TiO_2 (1%)	0.92	2.11	1.32	**2.66**	1.73	0.24	0.68	**1.88**
	Regalerz 3% with TiO_2 (3%)	1.06	0.92	1.87	**2.34**	2.44	-5.87	3.09	**4.55**
	Regalerz 3% with TiO_2 (5%)	2.08	-1.05	-0.89	**2.49**	-0.95	0.91	0.40	**1.38**
	(Nano)Regalerz 3%	9.02	-3.04	0.83	**9.55**	-1.15	1.54	0.31	**1.95**
Yellow (Orpiment) pigment	Regalerz 3% with TiO_2 (1%)	**9.05**	**-2.96**	**4.69**	10.6	**10.78**	**-1.90**	**-1.33**	**11.03**
	Regalerz 3% with TiO_2 (3%)	1.20	-1.16	0.47	**1.74**	-0.61	3.26	-0.85	**3.42**
	Regalerz 3% with TiO_2 (5%)	5.97	-7.05	1.07	**9.30**	-0.31	-6.21	-1.07	**6.30**
	(Nano)Regalerz 3%	-11.3	0.02	-1.68	**11.42**	2.23	5.68	2.20	**6.49**
Black pigment	Regalerz 3%	**-3.09**	**0.11**	**0.22**	3.10	**-0.43**	**5.26**	**5.38**	**7.54**
	Regalerz 3% with TiO_2 (1%)	-0.01	0.04	0	**0.04**	2.36	4.65	5.56	**7.63**
	Regalerz 3% with TiO_2 (3%)	-0.23	1.05	4.97	**5.08**	2.70	4.54	5.71	**7.78**
	Regalerz 3% with TiO_2 (5%)	1.18	2.04	3.99	**4.69**	-1.53	0	0.07	**1.53**
	(Nano)Regalerz 3%	3.23	0.52	6.12	**6.94**	-7.54	0.25	2.85	**8.06**
White pigment	Regalerz 3%	**4.15**	**-0.28**	**1.17**	4.32	**-2.37**	**-1.29**	**-0.10**	**2.70**
	Regalerz 3% with TiO_2 (1%)	6.16	4.70	0.55	**7.77**	4.17	-2.69	-1.58	**5.21**
	Regalerz 3% with TiO_2 (3%)	7.05	-0.47	0.27	**7.07**	4.21	2.82	-1	**5.16**
	Regalerz 3% with TiO_2 (5%)	4.54	-0.35	-0.15	**4.55**	-2.88	0.18	2.78	**4**
	(Nano)Regalerz 3%	5.22	-4.06	-0.43	**6.63**	7.99	-0.32	1.01	**8.06**

Table .2: USB Microscopy images of pigments, after treatment & after aging processes, different effect of polymers on each color are in agreement with the color change results

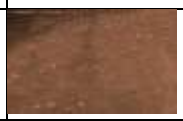
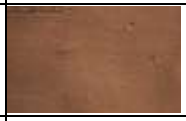
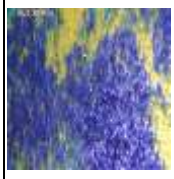
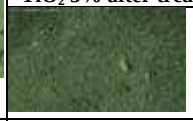
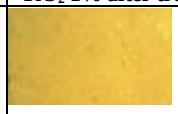
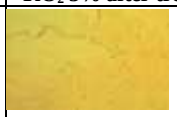
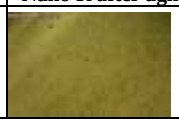
Standard	TiO_2 1% after treatment	TiO_2 1% after aging	TiO_2 3% after treatment	TiO_2 3% after aging
	 Δa= -1.29 ΔE= 1.8	 Δa= 0.1 ΔE= 2.72	 Δa= -3.02 ΔE= 3.90	 Δa= 6.86 ΔE= 7.31
	TiO_2 5% after treatment	TiO_2 5% after aging	Nano R after treatment	Nano R after aging
	 Δa= -1.92 ΔE= 2.72	 Δa= 4.58 ΔE= 4.92	 Δa= 2.91 ΔE = 4.55	 Δa= 6.91 ΔE= 11.54
Standard	TiO_2 1% after treatment	TiO_2 1% after aging	TiO_2 3% after treatment	TiO_2 3% after aging
	 ΔL= -8.23 ΔE = 9.27	 Δa= -2.38 ΔE= 5.13	 ΔL= -12.8 ΔE= 15.4	 Δa= -3.4 ΔE= 9.42
	TiO_2 5% after treatment	TiO_2 5% after aging	Nano R after treatment	Nano R after aging
	 ΔL= -7.54 ΔE = 9.02	 Δb= -4.8 ΔE= 7.67	 ΔL= -1.9 ΔE = 2.59	 Δb= -3.38 ΔE = 7.92
Standard	TiO_2 1% after treatment	TiO_2 1% after aging	TiO_2 3% after treatment	TiO_2 3% after aging
	 Δa= -0.8 ΔE= 7.02	 Δa= -2.36 ΔE= 5.48	 ΔL= 8.02 ΔE = 8.04	 ΔL= 8.46 ΔE = 10.98
	TiO_2 5% after treatment	TiO_2 5% after aging	Nano R after treatment	Nano R after aging
	 ΔL= -5.9 ΔE= 6.15	 ΔL= -7.55 ΔE = 7.73	 ΔL= 5.08 ΔE = 5.91	 ΔL= 10.61 ΔE= 11.31
Standard (orpiment)	TiO_2 1% after treatment	TiO_2 1% after aging	TiO_2 3% after treatment	TiO_2 3% after aging
	 ΔL= 9.05 ΔE= 10.6	 ΔL= 10.78 ΔE = 11.03	 Δa= -1.16 ΔE = 1.74	 Δa= 3.26 ΔE= 3.42
	TiO_2 5% after treatment	TiO_2 5% after aging	Nano R after treatment	Nano R after aging
	 Δa= -7.05 ΔE= 9.30	 Δa= -6.21 ΔE = 6.30	 ΔL= -11.3 ΔE = 11.42	 Δa= 5.68 ΔE = 6.49
Standard (Goethite)	TiO_2 1% after treatment	TiO_2 1% after aging	TiO_2 3% after treatment	TiO_2 3% after aging
	 Δa= 2.11 ΔE= 2.66	 ΔL= 1.73 ΔE = 1.88	 Δb= 1.37 ΔE = 2.34	Δa= -5/87 ΔE = 4.55
	TiO_2 5% after treatment	TiO_2 5% after aging	Nano R after treatment	Nano R after aging
	ΔL= 2.08 ΔE= 2.49	ΔL= -0.95 ΔE = 1.38	Δa= -3.04 ΔE = 9.55	ΔL= -1.15 ΔE = 1.95
Standard (Black)	TiO_2 1% after treatment	TiO_2 1% after aging	TiO_2 3% after treatment	TiO_2 3% after aging
	ΔE= 0.04	Δb= 5.56 ΔE = 7.63	Δb= 4.97 ΔE = 5.08	Δb= 5.71 ΔE = 7.78
	TiO_2 5% after treatment	TiO_2 5% after aging	Nano R after treatment	Nano R after aging
	Δb= 3.99 ΔE= 4.69	ΔE= 1.53	Δb= 6.12 ΔE= 6.94	ΔL= -7.5 ΔE= 8.06

Table .3: The characteristic bands of the colored standards and treated samples

Functional Groups	Wavenumbers cm^{-1}				
	The binding medium animal glue	Preparation layer $Ca\ CO_3$	The treated material Regalrez	The blue pigment Egyptian blue	The green pigment Malachite
Broad O-H stretching band overlaps N-H stretching of animal glue	3400-3200				
O-H stretching (split into two bands)					3394-3304
C-H stretching	3000-2800		2931-2902-2841		
C=O stretching of CO_3^{2-}		1795-1800			
C=O stretching (Amide I) of animal glue + C=C of Regalrez	1660-1600		1695		
Broad band involves: CO_3^{2-} stretching vibration overlapped C-N-H bending band (amide II) + C-H bending of animal glue and Regalrez	amide II 1500- 1565 C-H 1480-1300	Broad band 1370-1490	1436 -1354		1487-1396 split into two bands
Si-O-Si symmetrical stretching vibrations of Egyptian Blue				1228 cm^{-1}	
C-O stretching of animal glue + Si-O Asymmetric vibration of Egyptian Blue	1080			1155	1000-1100
O-C-O bending vibration of carbonate + Si-O symmetric vibration of Egyptian Blue		850-910		887	886
Functional Groups	Wavenumbers cm^{-1}				
	The binding medium animal glue	Preparation layer $Ca\ CO_3$	The treated material Regalrez	The blue pigment Egyptian blue	The green pigment Malachite
Broad O-H stretching band overlaps N-H stretching of animal glue	3400-3200				
O-H stretching (split into two bands)					3394-3304
C-H stretching	3000-2800		2931-2902-2841		
C=O stretching of CO_3^{2-}		1795-1800			
C=O stretching (Amide I) of animal glue + C=C of Regalrez	1660-1600		1695		
Broad band involves: CO_3^{2-} stretching vibration overlapped C-N-H bending band (amide II) + C-H bending of animal glue and Regalrez	amide II 1500- 1565 C-H 1480-1300	Broad band 1370-1490	1436 -1354		1487-1396 split into two bands
Si-O-Si symmetrical stretching vibrations of Egyptian Blue				1228 cm^{-1}	
C-O stretching of animal glue + Si-O Asymmetric vibration of Egyptian Blue	1080			1155	1000-1100
O-C-O bending vibration of carbonate + Si-O symmetric vibration of Egyptian Blue		850-910		887	886

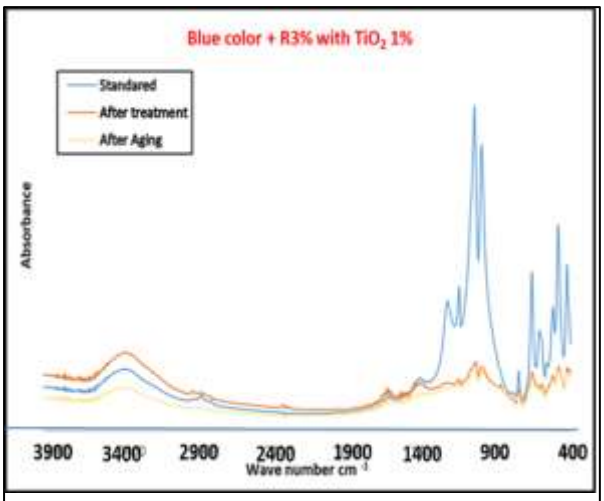


Figure.3a. FTIR spectra of blue samples: standard, after treatment with Regalrez 3% +TiO_2 1%, and after ageing.

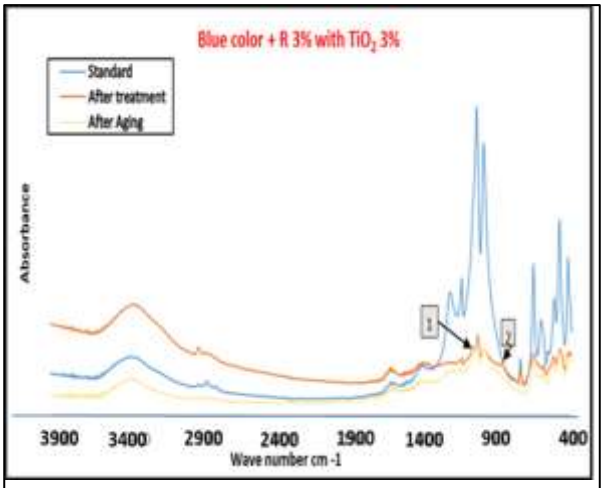


Figure. 3b. FTIR spectra of the blue samples: standard, after treatment with Regalrez 3% + TiO2 3%, and after ageing.

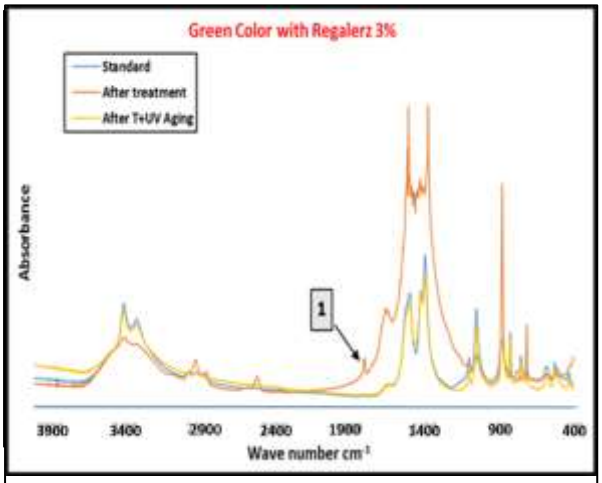


Figure.4a. FTIR spectra of green pigment samples, standard, after treatment with Regalrez 3%, and after ageing

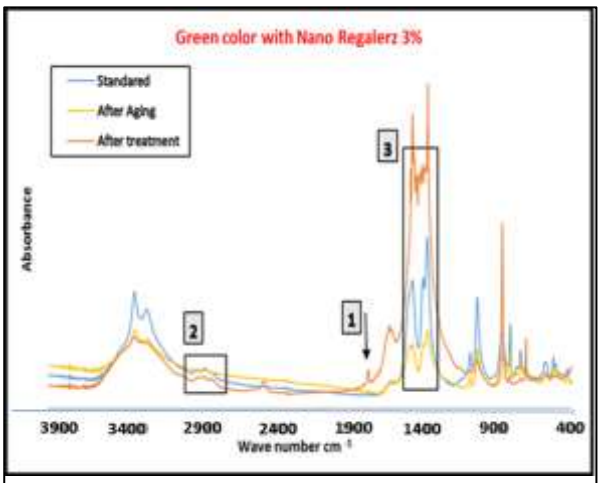


Figure.4b. FTIR spectrum of green samples. Standard, after treatment with Nano Regalrez 3%, and after ageing.

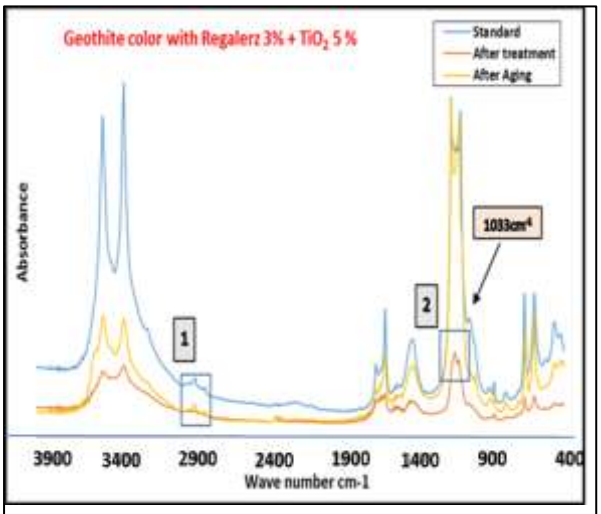


Figure. 5a. FTIR spectra of yellow (Goethite) sample. Standard, after treatment with Regalrez 3% + TiO2 5%, and after ageing.

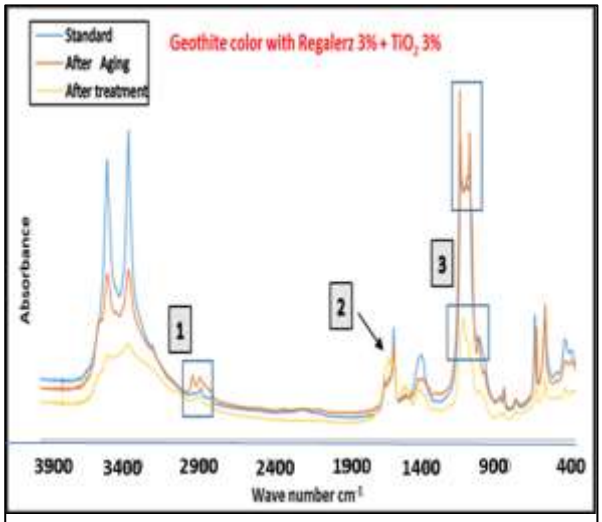


Figure. 5b. FTIR spectra of yellow (Goethite) sample. Standard, after treatment with Regalrez 3% +TiO2 3%, and after ageing.

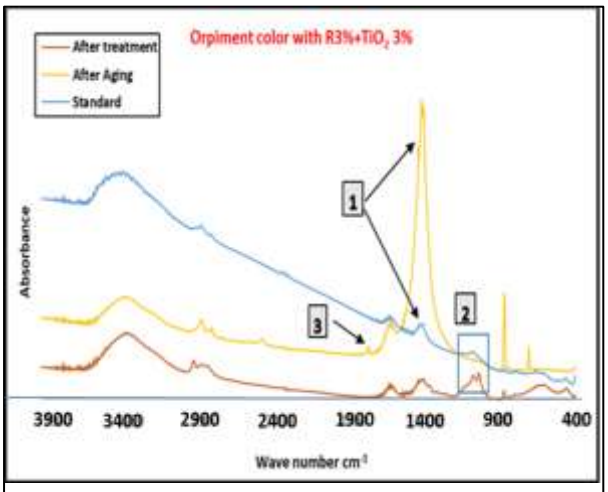


Figure.6a. FTIR spectra of yellow (Orpiment) samples: standard, after treatment with Regalrez 3% +TiO2 nanoparticles 3%, and after treatment and aging.

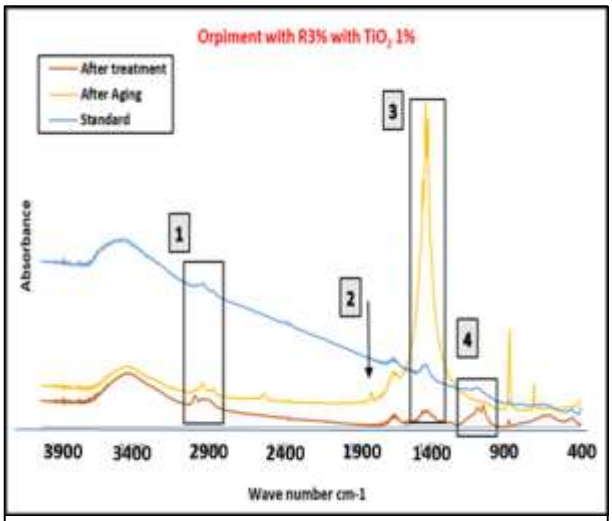


Figure. 6b. FTIR spectra of yellow (Orpiment) samples: standard, after treatment with Regalrez 3% +TiO2 nanoparticles 1%, and after treatment and aging.

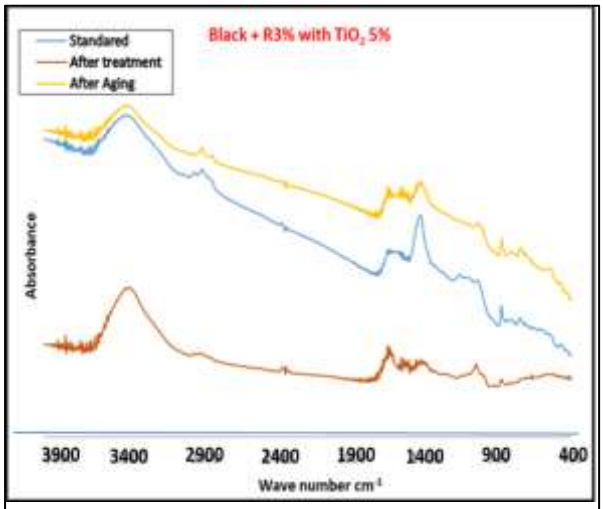


Figure. 7a. FTIR spectra of the black samples: standard, after treatment with Regalrez 3% +TiO2 nanoparticles 5%, and after treatment and aging.

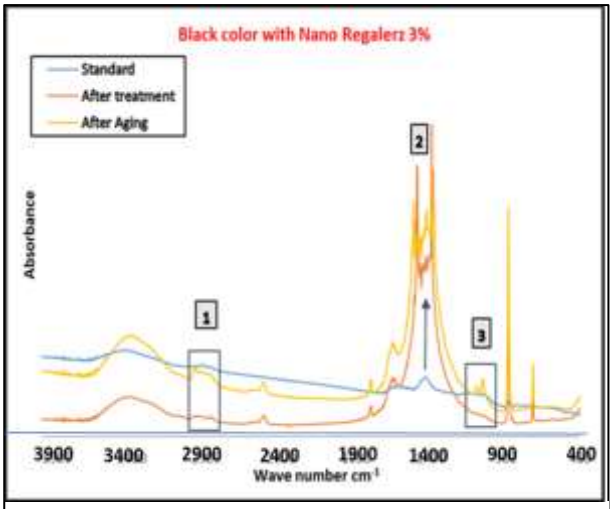


Figure.7b. FTIR spectra of the black samples: standard, treated black sample with Nano Regalrez, and after treatment and ageing.

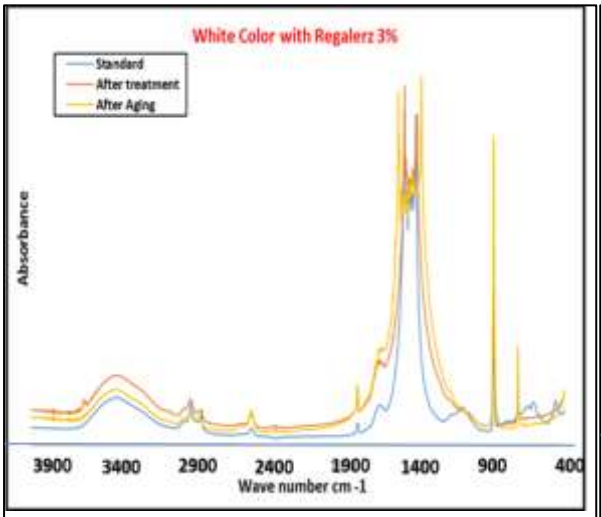


Figure.8a. FTIR spectra of white samples. Standard, after treatment with Regalrez 3%, and after aging.

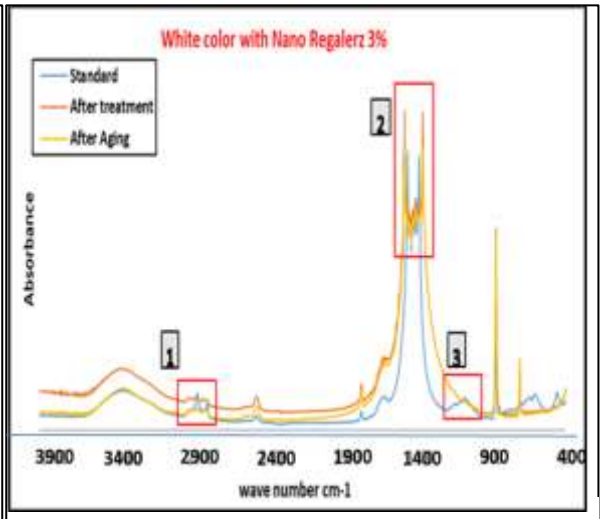


Figure.8b. FTIR spectra of white samples. Standard, after treatment with Nano Regalrez 3%, and after treatment and ageing.

3. Materials and Experiments:

3.1 Materials

Regalerz 1094, produced by TALAS (Brooklyn, NY) company for Conservation and Restoration, a type of thermoplastic polymer resin with low molecular weight was used in this study. It was dissolved in white spirit and titanium dioxide powder nanoparticle with an average particle size of (21nm) -primary particle size (TEM), ≥ 99.5% trace metals basis, supplied from ALDRICH Chemistry was used to improve the properties of polymer.

3.2. Preparation of painted samples

42 experimental samples, which were prepared using sycamore wood (3cm × 3cm × 1 cm), were painted with natural pigments from Kremer Company "Egyptian Blue, Malachite, Goethite, Orpiment, and Hematite". Fine limestone powder was used as a source of calcium carbonate for the preparation layer and white color. Charcoal was used after grinding it well and purifying its grains as a source of black color. Each color had its own distinct chemical composition and nature. Animal glue medium, which was prepared beforehand in a solution (1 glue: 15 water v/v), was used for mixing with calcium carbonate and pigments, which formed the ground and paint layers that were applied to the wood samples, similar to the technique applied in ancient Egypt (Figure.9).

3.3. Preparation of consolidation solution (polymers)

3.3.1. Preparation of Regalrez 3% and Nano composite polymer (Regalrez, TiO_2)

Regalrez solution was prepared with concentration of 3% (wt. /v) in white spirit. Polymeric nanocomposite (Regalrez/ Ti O_2) was prepared as follows: known weight of TiO_2 was dispersed in 100 ml of Regalrez solution aiding with sonication apparatus (Vibra cell, Sonics) for about 10 minutes to complete the mixing process [12,22,23]. The composition was according to (Table 4.).

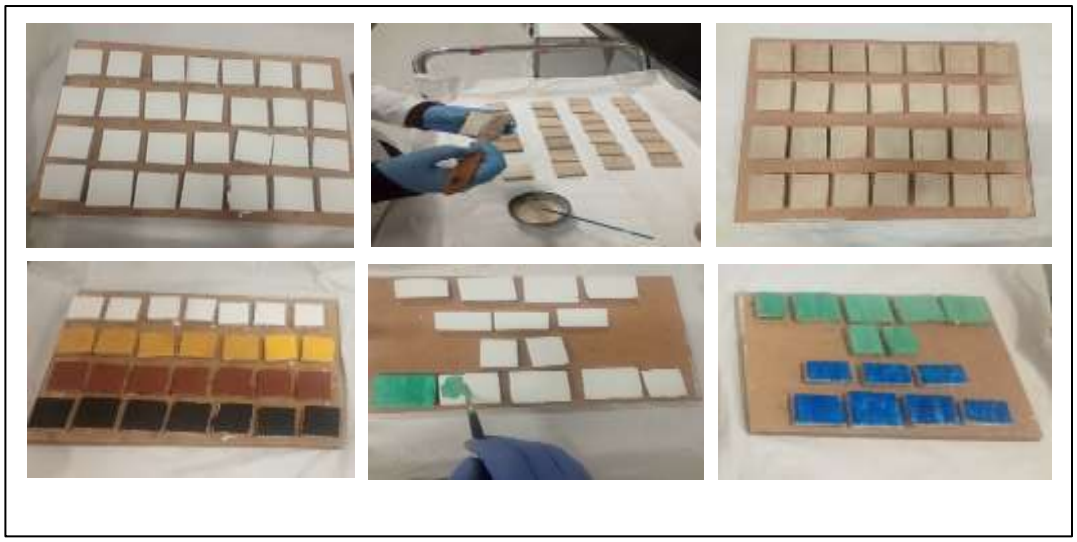


Figure. 9: Stages of applying preparation layers and pigments to wood samples

Table .4: Composition of polymers/ TiO_2 nanocomposite

Concentration of Nano TiO_2	*Concentration of Regalrez*	*Polymer solid content*	*Nano TiO_2 solid content*
1%	**3%**	**3 g**	**0.03 g**
3%	**3%**	**3 g**	**0.09 g**
5%	**3%**	**3 g**	**0.15 g**

3.3.2. Preparation of Nano polymer (Nano Regalrez)

The nano-sized polymer was prepared physically; nanoparticles were prepared using the top-down method, which includes the process of grinding or breaking the particles into fine particles through the so-called mechanical grinding or mechanical milling. Because of its ease of use, low equipment costs, and versatility in producing nearly any kind of material, this technique has gained popularity for creating nanocrystalline materials. The ball mill was used to crush the particles to the target nanosizes by

adjusting several factors. A known quantity of the polymer was ground with a Pulverisette-FRITSCH grinding device with the help of iron balls at a rotation speed of 350 per minute for 4 hours [24] , at the scientific polymer laboratories at the National Research Centre in Egypt.

3.4. Application of consolidation solution and accelerated aging of samples

The consolidation solutions of the polymer in their different concentrations were applied to the painted wooden samples by soft brushes at room temperature. The aging processes for the previously prepared samples were carried out twice. The first one was to perform the aging of the new samples so as to simulate the ancient artifacts. The second aging was conducted after the application of the polymers. The aging process was carried out with two types of aging: thermal and UV aging. The samples were placed inside the convection oven (Type M120-VN/PID System produced by CTS Company) at a temperature of 80 °C and a relative humidity of 65% [25-27] for 10 continuous days, which is equivalent to 50 years under normal circumstances [28]. UV aging was performed on the same samples at an average light intensity of 40 Lux in the UV unit. The UV lamp used was a Luminaire C.T.S. Art Lux 40 with 2 UV. Fluorescent Tubes 5000K, 45 cm long, 30 W., 220 V., with Plexiglas Protection Screen. The samples were exposed to light for 10 continuous days (240 hours), equivalent to fifty years under natural conditions [29].

3.5. Characterization:

3.5.1. Transmission electron microscope (TEM)

The nanoscale size and shape of the polymers were confirmed with Joel transmission electron microscope JEM.14000 Electron Microscope made in Japan at the research laboratories of the Faculty of Agriculture, Cairo University, to investigate the polymeric material of Regalerz that had been converted to the nano-image to confirm its nano-size conversion [30], and to confirm that the polymer had reached the nano-size**.**

3.5.2. Measurement of Color Change by spectrophotometer

Color change in samples was measured using the CIE-L*a*b* system, which is an international system for measuring color change in different samples and is based on the following symbols: Δa-Δb -ΔL - ΔE [31]. And the degree of color change of painted wooden samples was measured before and after aging (thermal and UV) and after application with polymers using a Spectrophotometer CM-700d-Model Japan, ICN Miniscan EZ, Hunter Lab). The total color changes (ΔE*) due to consolidation polymers were calculated based on the following equation: $\Delta E = \sqrt{(\Delta L)2+(\Delta a)2+(\Delta b)2}$. [25][32-33]. Where ΔL*, Δa*, and Δb* are the changes in color according to L*, a*, and b* for the treated and treated aged samples, compared to the control (untreated aged) samples**.**

3.5.3. Digital Light Microscope (USB)

Digital light microscope (Dino Lite) was used for examination of the structure of painted aged samples blue, green, yellow, red and black before and after applying polymers and after the second ageing process to evaluate the distribution and behavior of polymers on treated aged samples, to investigate how the application of consolidated polymers changed the brightness of pigment samples surfaces [30] and to study the effect of the different ageing processes on the polymers.

3.5.4. Fourier transformed infrared spectroscopy (FTIR)

IR Prestige-21 (FTIR spectrophotometer) produced by Shimadzu Company and the IR solution software in the 400–4000 range cm^{-1} with resolution of 8 cm^{-1} using a KBr disc were used and a comparison between the aged samples (control samples) with samples after applying Regalrez (R 3%) in three concentrations and the same samples after the second aging was conducted to study the effect of polymers on pigments; and the extent to which these polymers are affected by thermal and light aging according to the condition of each pigment was evaluated separately.

4. Conclusions

The effect of Regalrez on different pigments varied because of the chemical composition of each color and the different concentrations of nanomaterial which were added to the polymer. The polymer with titanium dioxide in three different concentrations gave less color and chemical changes on all pigments. Green (malachite) and calcite gave the best results with polymer in its original form. It was noted that nano material, when added to the polymer, increased the efficiency and improved the properties and its resistance to aging processes, yet its effect differed from one pigment to the other depending on its chemical composition. Moreover, it was found that the 1% and 5% concentration of titanium dioxide gave best results with many pigments. However, due to the chemical composition of some pigments an increase of oxidative effects of the polymer and binder occurred especially after exposure to light aging.

5. Conflicts of interest

There are no conflicts to declare.

6. Acknowledgements

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