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EXPERIMENTAL STUDY ON THE EFFICACY OF CLEANING SYSTEMS FOR THE REMOVAL OF PREVIOUS CONSERVATION TREATMENTS FROM TUTANKHAMUNS' GILDED WOODEN BED

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Abstract

The aim of this paper is to identify the best and most appropriate method to soften and remove three previous intervention materials (paraffin wax, rosin + paraffin wax, rosin + bees wax) and dirt layers applied on gilded wooden experimental samples, which were prepared on the basis of the information inferred from both chemical and physical analyses carried out on the gilded wooden bed of King Tutankhamun. Successful removal of previous intervention materials was determined by several scientific and analytical measures including ultraviolet induced luminescence (UVL), optical microscopy (OM), colorimetric measurements, X-ray fluorescence spectroscopy (XRF), and Fourier transform infrared spectroscopy (FTIR). Results indicate that it is possible to soften and easily remove previous intervention materials and dirt layers from gilding surface by using carbopol surfactant gels, which were extremely effective for solubilizing and removal of previous intervention materials from the studied bed without causing harm on the original gilding and offering essential data for the follow-up treatment and conservation works of the other gilded objects of King Tutankhamun.

***Keywords**: Tutankhamun; Gilding; Cleaning; Solvent gel, Paraffin wax; Rosin; UVL; FTIR.*

Introduction

The investigation of Tutankhamuns' gilded wooden bed (Carter. No 377, GEM 14276) showed that the use of different organic materials during several restoration interventions since the discovery of the tomb included paraffin wax, mixture of rosin and paraffin wax and also mixture of rosin and bees wax [1, 2]. Unfortunately, their applications induced a drastic alteration of the interfacial properties of the object and lead to increased degradation as well as prevented the application of other materials for conservation [1, 3-5]. These previously added organic materials had to be removed, yet that had to be achieved without affecting the original gilding materials. The complete removal of these added materials is often a delicate problem, not only due to the lack of reversibility for resins or waxes, but also because of the poor cohesion of the gilded layer and its water sensitivity, as well as the thin thickness of gold leaves used in the bed. An important challenge for us is to find highly selective agents that act only on the deleterious layers, do not damage chemically or mechanically the gilded layer that is to be cleaned, and do not leave residues on the surface after removal of the cleaning agents. Carbopol solvent surfactant gels [6] and microemulsions [7] are the present cleaning systems used by

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conservators for removal of previous consolidation materials and dirt layers from artifacts [8-13] as these systems avoid penetration of the dissolved previous treatment layers into the support base, avoid the presence of residues from the products used and minimize the use of pure solvents. Therefore, this paper describes an experimental study using traditional and current cleaning systems with the aim of evaluating the most effective material that has the ability swell and remove previous restoration materials and dirt layers from gilded experimental samples without causing any harm on the gilding.

Materials and methods

Materials

Acacia wood, calcium carbonate, linen, carbon black, gold leaf (Composition: 95% Au, 4%Ag, 1%Cu; thickness: 3μm) were used for preparing the experimental gilded samples, similar to the structure of Tutankhamuns' bed. Paraffin wax, bees wax and rosin were added to the gilded samples for simulation of old treatments. Carbopol Ultrez 21, Ethomeen C12, Ethomeen C 25, iso- propanol, acetone, sodium dodecyl sulphate (SDS) (purity 99%), 1-pentanol (purity 98.5%), ethyl acetate (purity 99.5%), xylene (purity > 99.5%), white spirit, 1-vinylimidazole, 1-Bromooctadecane, N,N′-Methylenebis acrylamide, acrylamide, potassium persulfate, $Fe(NO_3)_3{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ (99%, Aldrich), urea (99, Merck) and purified water were the cleaning materials chosen for evaluation.

Preparation of experimental gilding samples

To evaluate the effectiveness of the prepared cleaning systems, gilded experimental samples were prepared based on the information inferred from both chemical and physical analyses carried out on the gilded wooden bed of King Tutankhamun [1] following its stratigraphic structure. The preparation of these experimental samples involved the covering of acacia wood surface with a black layer made of carbon bound with glue, followed by a woven linen layer adhered to a white preparation layer made of calcium carbonate bound with animal glue to obtain a smooth surface for gilding process. On top of these layers, a layer of gold leaf was attached by animal glue. The gilded experimental samples were coated by three consolidation materials commonly used in previous conservation treatments detected during the investigation and analysis of the gilded wooden bed of King Tutankhamun: namely paraffin wax, mixture of paraffin wax and rosin and mixture of beeswax and rosin. To simulate the natural aging process of 90 years exposure in the Egyptian Museum at Cairo, experimental samples were submitted to artificial UV aging using UV-ageing box for 265 hours as described in the literature [14, 15]. This box was designed to include two UV lamps; the first lamp (CTS) with two Black Light Blue tubes, which peak at 385nm, while the second lamb (Vilber Lourmat) has two UV tubes, peaking at 365nm.

Preparation of the cleaning systems

A total of six "traditional and new" cleaning systems were applied on the experimental samples for evaluating their effectiveness in the removal of previous intervention materials (Table 1).

Criteria for selection of solvents

Organic solvents were selected by Trisolv system, which is online interactive software that reproduces the Teas Chart and its parameters and allows the user to calculate a precise volume percentage for solvent mixtures with low toxicity and retention time, created by three different solvents (alcohols, aliphatic hydrocarbons and ketones).

Synthesis of surfactant solvent gel

Surfactant solvent gels based on carbopol were synthesized as reported in the literature [6, 16]. These surfactant gels cleaning systems were applied by means of brushes with the presence of a barrier of Japanese paper on the experimental surface and were left on the sample for a maximum of 40 minutes. To avoid the fast evaporation of the solvents, the solvent gels were covered with a polyethylene foil.

Table 1. A summary of the cleaning systems used here to evaluate their effectiveness in the removal of previous interventions materials

	Cleaning systems	Barrier (Japanese paper)	Contact period (Minutes)
1st cleaning system	**Free solvent mixtures composed of**: Xylene + white spirite + iso propanol Perfected with cotton swab.	No	-
2nd cleaning system	**Hot air tool** perfected with cotton swab.	No	-
3rd cleaning system	**Carbopol solvent gel composed of:** Carbopol Ultrez 21 (2g)+ ethomeen c 25 (20ml)+ acetone / ethyl acetate (60ml)+ white spirit (40ml)+ water (10ml)	Yes	40
4th cleaning system	**Carbopol solvent gel composed of:** Carbopol Ultrez 21 (2g)+ ethomeen c 12 (20ml)+ xylene / white spirit (80ml)+ iso propanol (20ml)+ water (1.5ml)	Yes	40
5th cleaning system	**Carbopol solvent gel composed of:** Carbopol Ultrez 21 (2g)+ ethomeen c 25 / ethomeen c 12 (20ml)+ iso propanol / ethyl acetate (60ml)+ white spirit (40ml)+ water (8ml)	Yes	40
6th cleaning system	**Magnetic nano gel with microemulsion composed of** Water (84.4%), SDS (4.1%), pentanol (PeOH) (7.9%), xylene/white spirit (3.6%)	No	240

Synthesis of microemulsion

Oil in water microemulsion (classical system) was made with sodium dodecyl sulfate (SDS), 1-pentanol (PeOH) as a co-surfactant, and a small amount of a mixture of xylene and white spirit were slowly added under constant stirring [17-19].

Synthesis of magnetic polyacrylamide nanogel

Synthesis of *magnetic* polyacrylamide nanogel was prepared as reported by [13]. The nano magnetic gel was immersed in a closed flask containing the microemulsion for three days on a magnetic stirrer in normal room temperature. The prepared gel was applied directly on the experimental surface by means of a spatula and left there for a maximum of 4 hours covered with a polyethylene foil.

Methodology

To evaluate the effectiveness of the prepared cleaning systems in the removal of previous intervention materials from the surface of gilded experimental samples, different analytical techniques were used.

Ultraviolet-induced visible luminescence imaging (UVL)

The setup required for the imaging technique included a digital modified camera Nikon D90 (CMOS sensor) equipped with a Nikon Nikkor 60 mm lens. Visible (Vis) images were acquired by using two sources of fluorescent lamps and a X-Nite CC1 digital UV/ IR blocking filter in front of the camera lens. UVL images were acquired by using two sources of UV 365 nm LED lamps and a combination of the UV/ IR Baader and X-Nite CC1 filters in front of the camera lens to cut both reflected ultraviolet and the possible infrared stray radiation generated by the lamps [20, 1]. This technique is commonly used to reveal the distribution of luminescent organic materials; hence it can be used to characterize and evaluate the gilding surface before and after cleaning [21, 22].

Optical Microscopy (OM)

To evaluate the gilding surface before and after cleaning systems, a Keyence VHX – 900F digital microscope (Japan) equipped with aVHX – 5020 digital camera VH-ZST with Dual-objective zoom lens of 20 up to 2000×. The images were taken at 100× magnification.

Colorimetric measurements

For measuring color of the gilded experimental samples before and after cleaning methods, Konika Minolta spectrophotometer CM-700d (Japan) was used. This portable device is equipped with a 5mm diameter integrating sphere. It works in the d/8 illumination-viewing geometry and its spectral sensitivity ranges from 400 to 740nm. Each color measurement was replicated three times before and after cleaning, and the average was recorded. The total color difference ΔE* was evaluated before and after each application indicating the cleaning efficacy. The magnitude of the colour change is calculated by the color difference (Euclidian) distance expressed as: $\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$, Where L* is the lightness difference, a* the red/green difference, b* is the yellow/blue difference [23, 24].

X-ray fluorescence spectroscopy (XRF)

The measurements were directly performed with a Niton™ XL3t GOLDD handheld XRF spectrophotometer instrument using the NITON XL3t x-ray tube-based analyzer with Ag anode, 50kV and 0-200Ma max in order to evaluate the efficacy of the cleaning systems in removing the dirt layers. The instrument head was placed in contact with the selected area and the irradiated area had ca. 3mm radius. All points were exposed for a minimum of 120s. XRF spectra were produced using ™ Niton Data Transfer (NDT) software.

Total reflectance Fourier Transform Infrared Spectroscopy (FTIR)

Reflectance FTIR spectra were recorded using a portable ALPHA Bruker spectrophotometer equipped with the external total reflectance module for a contactless acquisition and a 0/0 geometry. Spectra were obtained from 200 scans in the range of 4000–400cm^1 at a resolution of 4cm^1. We elaborated the acquired spectra using the OPUS software by Bruker, by means of Kramers–Kronig transformation in order to verify the presence or absence of previous treatment materials on the gilding surface after application of cleaning systems [25-27].

Results

Removal of rosin and paraffin wax mixture

Results of analytical techniques used to evaluate the cleaning systems for removal of rosin and paraffin wax mixture, are summarized in Table 2. In figure 1, by comparing VIS and UV images, it was clear that 1st cleaning system (free solvents) gave fair results with partial swelling and irregular cleaning, causing damage to the gilding surface that was visible with UVL imaging and at high magnification using digital microscopy. Very good results were achieved using cleaning system no 3 and 5, which resulted in the complete softening and removal of paraffin wax and rosin mixture from the gilding surface, without damaging to the gilding layer as illustrated in figure 1. Good results were also achieved using cleaning system no 4 in a similar manner to remove rosin and paraffin wax mixture from the same surface, as illustrated in figure 1, but some parts of wax and rosin remained. In contrast, the 6th cleaning system was unsuccessful in removing rosin and paraffin wax mixture, although it was very effective in softening the rosin and paraffin wax mixture, yet harmful to the gilding surface due to the long contact period of 4 hours that was required. Moreover, the use of hot air tool resulted in the partial redistribution of the rosin and paraffin wax mixture on the gilding surface.

By interpreting the results obtained through the three-color coordinates in Table 2, it appears that lightness (L*) was reduced in all samples after cleaning, as well as a* and b* coordinates, indicating that samples became yellow. The greatest ΔE value was obtained with the 5th cleaning system, followed by 3rd and 4th cleaning systems; the 6th cleaning system was the least effective. Swab application was the least efficient in comparison to gel solvent applications. These results appear to correspond with UV imaging and microscopy. According to the FTIR analysis results before and after cleaning, the 5th cleaning system was most effective in the removal of rosin and paraffin wax, because of absence of any bands attributed to rosin and paraffin wax (Fig. 2) and also absence of any bands attributed to the residues of the gel. Although the 3rd cleaning system showed the complete softening and removal of paraffin wax and rosin mixture from the gilding surface under UVL imaging, FTIR spectra showed bands at 2916, 1462 and 729cm^{-1}, which attributed to the presence of paraffin wax. The 1st and 6th cleaning systems appear to have the lowest cleaning efficacy for removal of rosin and paraffin wax, because bands of rosin (1695, 1379, 1273 and 1173cm^{-1}) and paraffin wax (2916, 1462 and 729cm^{-1}) were detected with high intensity (Fig. 2) confirming that they are still present on the gilding surface. These results appear to correspond with colorimetric measurements, where ΔE^* value was high for the 5th cleaning system, followed by 3rd and 4th cleaning systems.

Table 2. A summary of analytical techniques results used to evaluate the cleaning systems for removal of rosin and paraffin wax mixture

Cleaning systems for the removal of rosin and Paraffin wax mixture	Results of analytical techniques				
	Colorimetric measurements				IR bands (cm^{-1})
	L*	a*	b*	ΔE*	
Gilding surface	70.89	3.42	40.55	-	-
No treatment	77.97	6.60	56.38	7.32	1695, 1379, 1273, 1173, 1051–2916, 1462, 729
1st cleaning system	78.08	4.18	45.96	5.60	1695, 1379, 1273, 1173, 1051–2916, 1462, 729
2nd cleaning system	77.58	3.25	47.32	5.44	1695, 1379, 1273, 1173, 1051–2916, 1462, 729
3rd cleaning system	72.23	2.12	42.40	1.58	2916, 1462, 729
4th cleaning system	75.52	3.32	45.06	3.79	1695, 1379, 1273, 1173, 1051–2916, 1462, 729-
5th cleaning system	70.77	2.61	43.05	1.11	-
6th cleaning system	76.84	3.96	44.18	4.58	1695, 1379, 1273, 1173, 1051–2916, 1462, 729

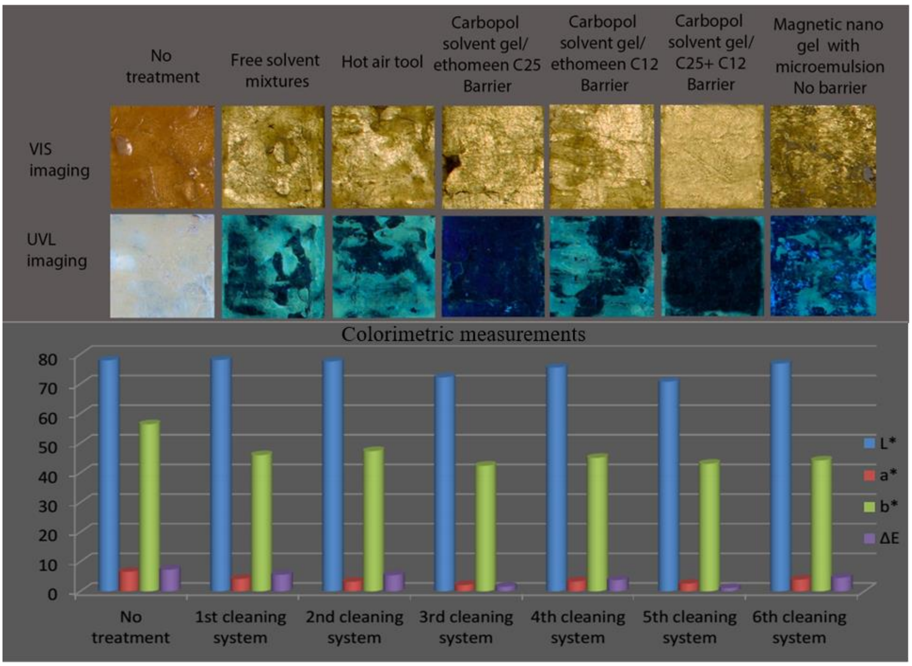

Fig. 1. VIS, UVL imaging and colorimetric measurements for experimental cleaning systems on gilded experimental samples treated with rosin and paraffin wax mixture

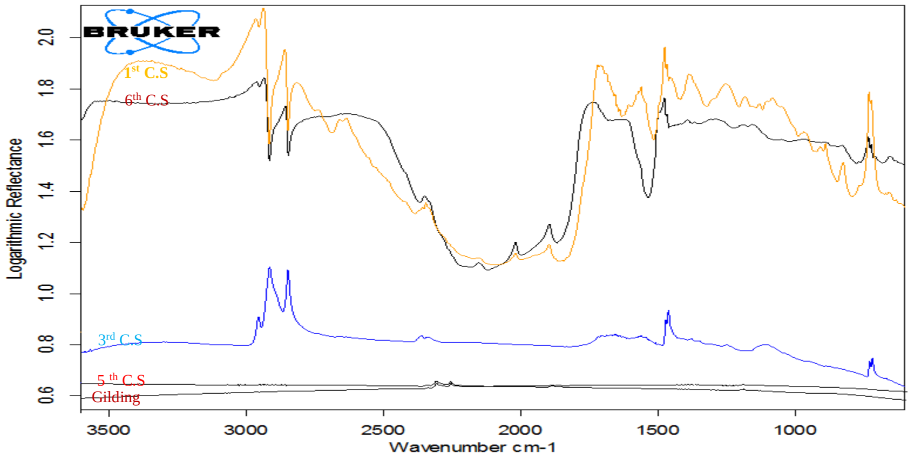

Fig. 2. FTIR spectra for experimental cleaning systems on gilded experimental samples treated with rosin and paraffin wax mixture

Removal of rosin and bees wax mixture

The traditional and new cleaning systems used here to evaluate their effectiveness in the removal of rosin and bees wax mixture, are summarized in Table 3. In figure 3, by comparing VIS and UV images, it was clear that the 1st cleaning system (free solvents) gave fair results with partial swelling and irregular cleaning. It also caused damage to the gilding surface, which was visible with UV imaging and at high magnification under digital microscopy.

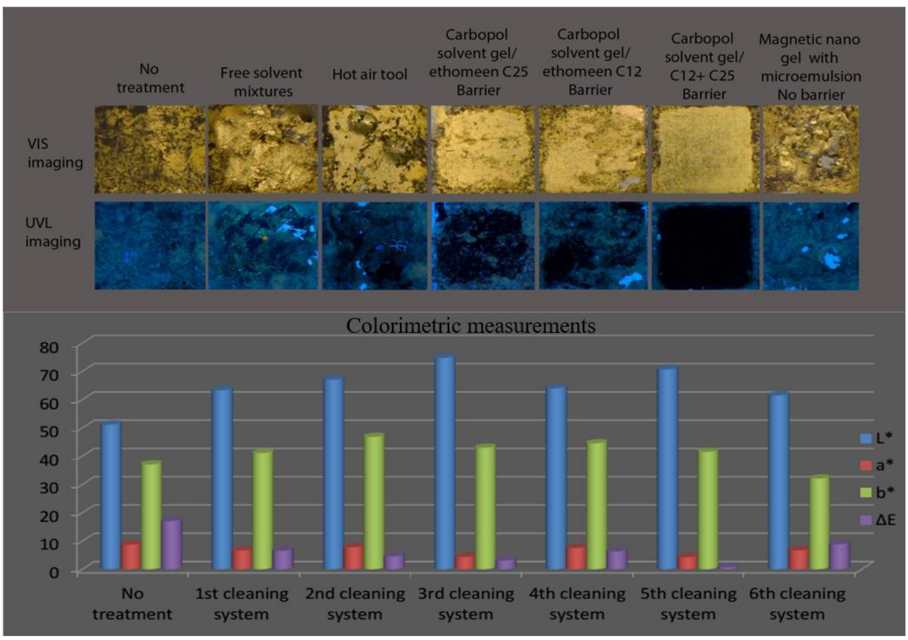

Fig. 3. VIS, UVL imaging and colorimetric measurements for experimental cleaning systems on gilded experimental samples treated with rosin and bees wax mixture with dirt

Cleaning system no 5 proved to be very effective in the complete softening and removal of paraffin wax and dirt layers without damaging the gilding surface. Good results were achieved using cleaning system no 3 in a similar manner to remove rosin and bees wax mixture and dirt layer from the same surface, as illustrated in figure 3, without damaging the gilding layer, but little spots of wax and dirt layer remained. Good results were also achieved using cleaning system no 4 without any damage to the gilding layer, but considerable amount of rosin and wax mixture and dirt layer remained on the samples. In contrast, the 6th cleaning system was unsuccessful in removing the wax layer and dirt layer, although it was very effective in softening the rosin and bees wax mixture and dirt layer but proved to be harmful to the gilding surface due to the long contact period of 4 hours that was required. In addition, 2nd cleaning system (hot air tool) caused bulking of the gilded gesso layer due to the high temperature and limited cracks only visible with UV imaging and high magnification under microscope, as well as considerable amount of the mixture was observed.

Table 3. A summary of analytical techniques results used to evaluate the cleaning systems for removal of rosin and bees wax mixture with dirt

Cleaning systems for the removal of rosin and bees wax mixture with dirt	Results of analytical techniques					
	Colorimetric measurements				Elements detected by XRF	IR bands (cm^{-1})
	L*	a*	b*	ΔE*		
Gilding surface	70.89	3.42	40.55	-	Au, Ag, Cu, Ca, Fe	-
No treatment	51.17	8.70	37.10	17.05	Au, Ag, Cu, Ca, Fe, Si, Al, K, Ti	1695, 1379, 1273, 1173, 1051–2916, 1735, 1462, 729
1st cleaning system	63.30	6.62	41.07	6.51	Au, Ag, Cu, Ca, Fe, Si, Al, K, Ti	1695, 1379, 1273, 1173, 1051–2916, 1735, 1462, 729
2nd cleaning system	5thC.S 67.08	7.84	46.84	4.57	Au, Ag, Cu, Ca, Fe	1695, 1379, 1273, 1173, 1051–2916, 1735, 1462, 729
3rd cleaning system	74.79	4.33	43.01	3.09	Au, Ag, Cu, Ca, Fe	2916, 1735, 1462, 729
4th cleaning system	64.02	7.51	44.57	6.25	Au, Ag, Cu, Ca, Fe	1695, 1379, 1273, 1173, 1051–2916, 1735, 1462, 729
5th cleaning system	70.66	4.29	41.51	0.70	Au, Ag, Cu, Ca, Fe	-
6th cleaning system	61.49	6.70	32.09	8.86	Au, Ag, Cu, Ca, Fe, Si, Al, K, Ti	1695, 1379, 1273, 1173, 1051–2916, 1735, 1462, 729

By interpreting the results obtained through the three-color coordinates in table 3, it appears that lightness (L*) increased in all samples after cleaning, as well as the b* coordinate, indicating that samples became yellow. In contrast, a* was reduced due to the removal of the dirt layers. The greatest ΔE* value was obtained with the 5th cleaning system, followed by 3rd and 4th cleaning systems; the 6th cleaning system was the least effective. Swab application was the least efficient in comparison to gel solvent applications. Comparison of XRF results before and after the application of rosin and bees wax mixture with dirt layer detected high intensity of iron and silicon with a small amount of aluminium and potassium. According to the XRF results before and after cleaning, the 3rd and 5th cleaning systems were most effective in the removal of dirt layer, since the intensity of detected iron and silicon were reduced with the absence of aluminium and potassium. The 1st and 6th cleaning systems appear to have the lowest cleaning efficacy for removal of dirt layer, because iron and silicon were detected with high intensity confirming that the dirt layers were still present on the gilding surface. These results appear to correspond with colorimetric measurements, where ΔE* value was high for 5th cleaning system, followed by 3rd and 4th cleaning systems. According to the FTIR analysis results before and after cleaning, the 5th cleaning system was most effective in the removal of rosin and bees wax, because of absence of any bands attributed to rosin and bees wax (Fig. 4) and also absence of any bands attributed to the residues of the gel. FTIR spectra of the 3rd cleaning system showed absence of any bands attributed to rosin, but bands at 2916, 1735, 1462 and 729cm^{-1}, which are attributed to bee's wax were detected confirming that this system was most effective in the removal of rosin, but little amount of bee's wax was still present on the gilding surface. The 1st and 6th cleaning systems have the lowest cleaning efficacy for removal of rosin and paraffin wax, because bands of rosin (1695, 1379, 1273, 1173 and 1051cm^{-1}) and bees wax (2916, 1735, 1462 and 729cm^{-1}) were detected with a high intensity (Fig. 4) confirming that they are still present on the gilding surface. These results appear to correspond with colorimetric measurements, where ΔE^* value was high for the 5th cleaning system, followed by 3rd and 4th cleaning systems.

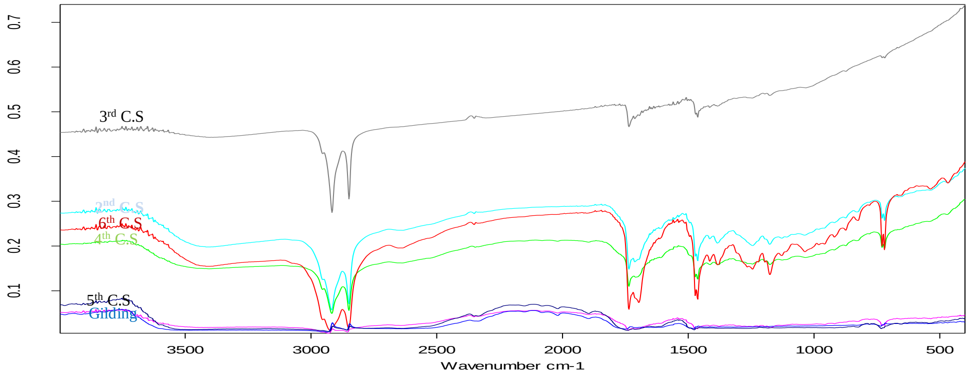

Fig. 4. FTIR spectra for experimental cleaning systems on gilded experimental samples treated with rosin and bees wax mixture

Removal of paraffin wax mixed with dirt layers

The results of the cleaning systems used here to evaluate their effectiveness in the removal of paraffin wax mixed with dirt layer are summarized in Table 4. In figure 5, by comparing VIS and UV images, it was clear that 1st cleaning system (free solvents) gave fair results with partial swelling and irregular cleaning, as well as causing damage to the gilding surface which was only visible with UV imaging and with high magnification under digital microscopy.

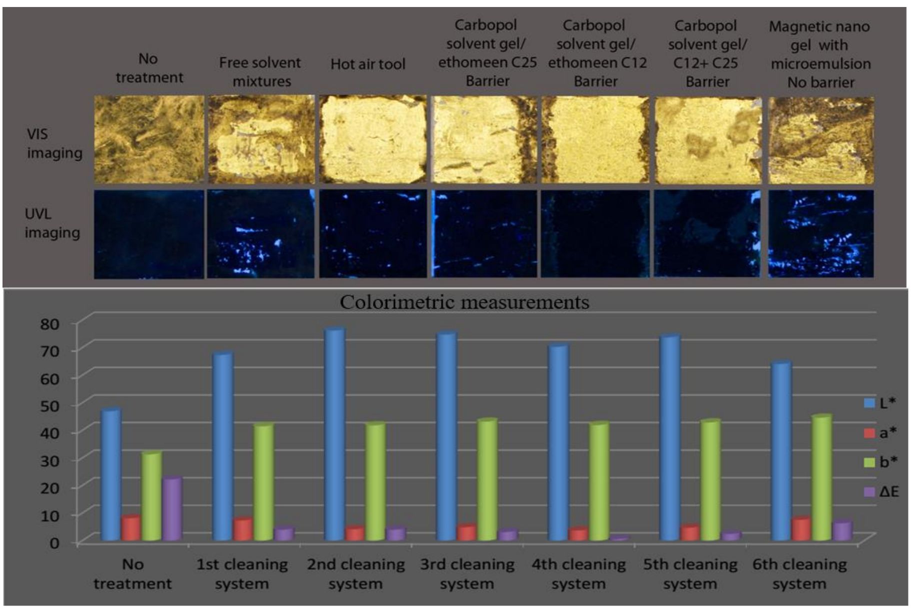

Fig. 5. VIS, UVL imaging and colorimetric measurements for experimental cleaning systems on gilded experimental samples treated with paraffin wax with dirt layers

While cleaning system no 4 is very effective in the complete softening and removal of paraffin wax and dirt layers without damaging the gilding surface. Good results were achieved using cleaning system no 5 in a similar manner to remove paraffin wax and dirt layer from the same surface, as illustrated in figure 6a, without any damage to the gilding layer, but some spots of wax and dirt layer remained. Good results were also achieved using cleaning system no 2 and 3, but these systems showed limited scratching only visible with UV imaging and high magnification under microscope, as well as some spots of wax were observed under microscope. In contrast, the 6th cleaning system was unsuccessful in removing the wax layer and dirt layer and caused loss for the gilded layer.

By interpreting the results obtained through the three color coordinates in Table 4, it appears that lightness (L*) increased in all samples after cleaning, as well as the b* coordinate, indicating that samples became yellow. In contrast, a* was reduced due to the removal of the dirt layers. The greatest $\Delta E*$ value was obtained with the 4th cleaning system, followed by 5th, 3rd and 2nd cleaning systems; the 6th cleaning system was the least effective. Swab application was the least efficient in comparison to gel solvent applications. Comparison of XRF results before and after the application of paraffin wax mixed with dirt layer showed that a high intensity of iron and silicon was detected with a small amount of aluminium and potassium. According to the XRF results before and after cleaning, the 2nd, 3rd, 4th and 5th cleaning systems were most effective in the removal of dirt layer, since the intensity of detected iron and silicon were reduced with the absence of aluminium and potassium. The 1st and 6th cleaning systems appear to have the lowest cleaning efficacy for removal of dirt layer, because iron and silicon were detected in a high intensity confirming that the dirt layers were still present on the gilding surface. These results appear to correspond with colorimetric measurements, where $\Delta E*$ value was high for 4th cleaning system, followed by 5th, 3rd and 2nd cleaning systems. According to the FTIR analysis results before and after cleaning, the 4th cleaning system was the most effective in the removal of paraffin wax, because of absence of any bands attributed to paraffin wax. The 1st and 6th cleaning systems appear to have the lowest cleaning efficacy for removal of paraffin wax and dirt layers, because the bands of paraffin wax at 2916, 1462 and 729cm^{-1} and the stretching vibrations of Si−O− Si bands at 1099, 1043 and 796cm^{-1} were detected with high intensity confirming that they are still present on the gilding surface. These results appear to correspond with colorimetric measurements, where $\Delta E*$ value was high for the 4th cleaning system, followed by 5th and 3rd cleaning systems.

Table 4. A summary of analytical techniques results used to evaluate the cleaning systems for the removal of Paraffin wax with dirt layer

Cleaning systems for removal of Paraffin wax and dirt layer	Results of analytical techniques					
	Colorimetric measurements				Elements detected by XRF	IR bands (cm^{-1})
	L	a*	b*	ΔE*		
Gilding surface	70.89	3.42	40.55	-	Au, Ag, Cu, Ca, Fe	-
No treatment	46.89	8.09	31.28	22.18	Au, Ag, Cu, Ca, Fe, Si, Al, K, Ti	2916, 1463, 728-1099, 1043, 796
1st cleaning system	67.33	7.30	41.44	3.95	Au, Ag, Cu, Ca, Fe, Si, Al, K, Ti	2916, 1463, 728-1099, 1043, 796
2nd cleaning system	76.17	4.09	41.78	3.96	Au, Ag, Cu, Ca, Fe	2916, 1463, 728
3rd cleaning system	74.69	4.85	43.14	3.12	Au, Ag, Cu, Ca, Fe	2916, 1463, 728
4th cleaning system	70.30	3.64	41.92	0.57	Au, Ag, Cu, Ca, Fe	-
5th cleaning system	73.72	4.67	42.85	2.40	Au, Ag, Cu, Ca, Fe	2916, 1463, 728
6th cleaning system	64.02	7.51	44.57	6.25	Au, Ag, Cu, Ca, Fe, Si, Al, K, Ti	2916, 1463, 728-1099, 1043, 796

Discussion

These results show that free solvents are not effective for complete removal of previous interventions with organic materials, when used in the traditional manner, applied by cotton swab, and are also harmful to the gilding surface. Unfortunately, the use of hot air tool can result in bulking and cracking of the gilded gesso layers and the partial redistribution of the unwanted substances through the cracks. After the application of solvent gels, these materials were swollen and softened and could be easily removed with a spatula without any mechanical force, followed by clearance with white spirit without causing any damage to the gilding surface in accordance with previously published data [8, 10, 28, 29]. The 5th cleaning system which was composed of carbopol Ultrez 21 (2g), ethomeen c 25/ethomeen c 12 (20mL), iso propanol/ethyl acetate (60mL), white spirit (40mL) and water (8mL), was the most appropriate gel in removing mixtures of rosin with paraffin wax or bees wax because its swelling action was more effective and rapid than free solvent mixtures tested by swab or with other types of gels without damaging the gilding surface. The 4th cleaning system, which was composed of carbopol Ultrez 21 (2g), ethomeen c 12 (20mL), xylene/white spirit (80mL), iso propanol (20mL) and water (1.5mL), was the most appropriate gel in removing paraffin wax mixed with dirt because its swelling action was more effective and rapid than free solvent mixtures tested by other types of gels; most probably because the wax was highly soluble in xylene and white spirit. Although the nano gel loaded with the microemulsion proved to be very effective in removing previous wax spots from mural painting surfaces [13], it proved to be unsuccessful in removing previous treatments with organic materials and caused loss of gilding layer as the interaction of water with gilded gesso layers dissolved the ancient glue used to adhere the gold leaf with gesso layer leading to the detachment of the pictorial layer.

Based upon the favourable results obtained from this experimental study, which basically aimed at seeking out the best cleaning system for removal of previous intervention materials that had been used in the gilded bed of King Tutankhamun, the 5th cleaning system, which was composed of carbopol Ultrez 21 (2g), ethomeen c 25/ethomeen c 12 (20mL), iso propanol/ethyl acetate (60mL), white spirit (40mL) and water (8mL), was applied on the outer surface of the foot board of the studied bed (Fig. 6), which had a layer of rosin and paraffin wax mixture applied in the previous restoration intervention. In figure 6a and b, UV-induced luminescence revealed the presence of a greenish emission from rosin and paraffin wax mixture on the gilded surface around the cracks and separations, and its presence is much more extensive than was discernible with the naked eye. The UVL image in figure 6c, taken after cleaning clearly shows that the removal of rosin and paraffin wax mixture was efficiently achieved as seen in UVL imaging and does not produce apparent UV emission in the regions where the gel was applied.

Fig. 6. Gilding surface of the outer region of the foot board from the studied bed covered with a layer of rosin and paraffin wax mixture: a- Visible image before gel application; b- UVL image before gel application; c- UVL image after gel application

Figure 7a is a photo of a "drum" decoration (of the left front leg of the studied bed), where the gel application (4th cleaning system) was conducted based upon the results obtained from this experimental study to remove a layer of paraffin wax and dirt. After application of the gel, this layer was swollen, softened and easily removed without any mechanical force, followed by clearance with white spirit without any damage to the gilding surface. Figure 7b shows how a layer of paraffin wax and dirt was efficiently removed.

For reassurance of how successful these applications were, this region was analyzed before and after the gel treatment by colormetric measurements (Fig. 7c), where lightness (L*) was increased after cleaning, as well as the b* coordinate, indicating that samples became yellow. In contrast, a* was reduced due to the removal of the dirt layers. This conclusion was confirmed more quantitatively by analyzing this region before and after the gel treatment by handheld XRF, which showed a strong reduction of the intensity of all the peaks from the dirt layer (Fig. 7d).

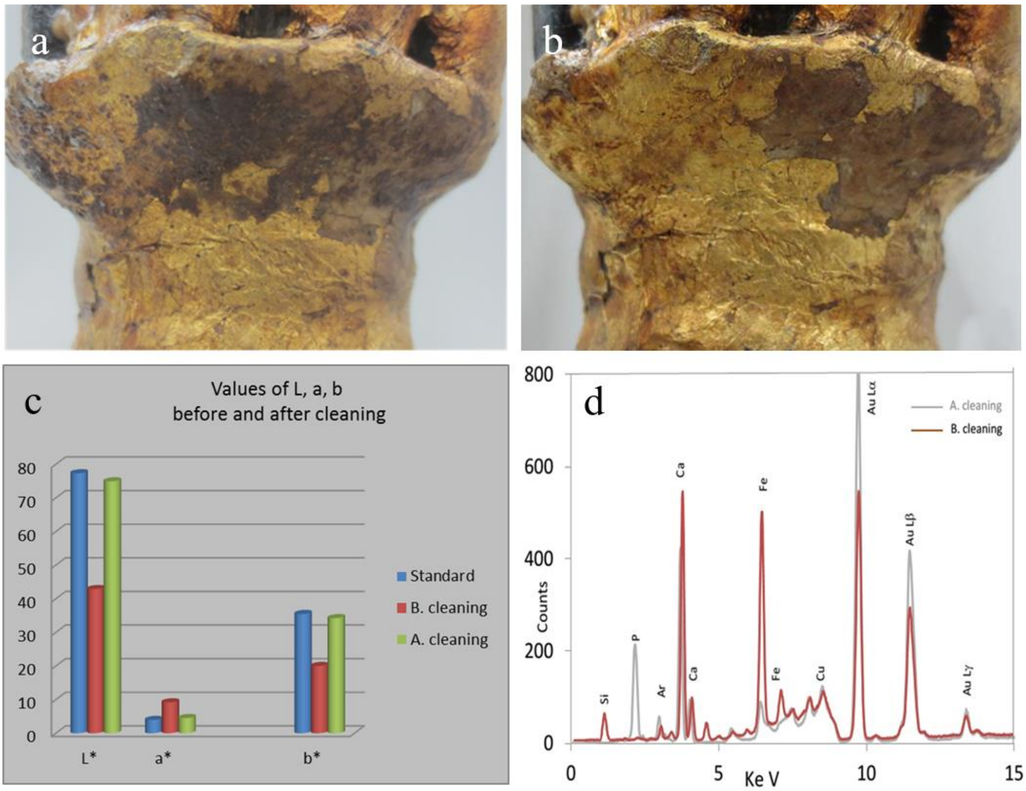

Fig. 7. Gilding surface of drum region of the front left leg with layer of paraffin wax and dirties: a-Before; b- After the gel application; c- Results of colorimetric measurements; d- XRF spectra before and after cleaning

The 4th cleaning system on the gilding surface of the figure *Bes* (on the right head end corner of the frame of the studied bed) (Fig. 8a) was applied to remove a dark layer of paraffin wax. After application of the gel, this dark layer of paraffin wax was easily removed without any mechanical force, followed by clearance with white spirit without any damage to the gilding surface.

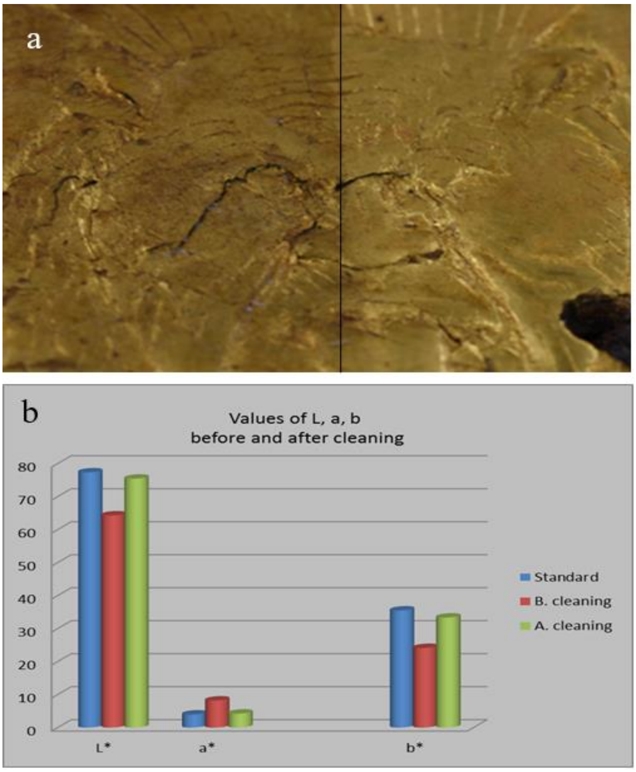

Fig. 8. Gilding surface of figure *Bes* region (on the right head end corner of the frame of the studied bed) with dark layer of paraffin wax: a-Before (left) and after (right) the gel application; b- Results of colorimetric measurements

The untreated area (left part) still had a dark surface of paraffin wax; while the treated region did not and appeared visually to have been cleaned. This conclusion was further confirmed by analyzing this region before and after the gel treatment by colormetric measurements (Fig. 8b), in which the lightness (L*) was increased after cleaning, as well as the b* coordinate, indicating that samples became yellow. In contrast a* was reduced due to the removal of the dirt layers.

Conclusions

The experimental results indicate that carbopol solvent gels are very effective in solubilizing previous interventions with organic materials (such as paraffin wax, mixture of bee's wax and rosin and mixture of paraffin wax and rosin) and dirt from gilding surfaces and aid in their removal in comparison to free solvent mixtures tested by swabs or with micro emulsion. These had been confirmed by different analytical techniques including ultraviolet induced luminescence (UVL), optical microscopy (OM), Colorimetric measurements, X-ray fluorescence spectroscopy (XRF), and Fourier transform infrared spectroscopy (FTIR) considering the balance between effectiveness, control, and the period of application of the different cleaning systems. It is also important to note that the selection criteria controlling the choice of one cleaning system over another are closely associated with the chemical nature of the hydrophobic material that is to be removed and the most suitable organic solvent for solubilizing it in order to achieve the best performance. Based upon the results obtained from this experimental study, the solvent gels that had been applied were extremely effective in solubilizing previous intervention materials from the studied bed without causing harm on the original gilding surface during removal of the previous treatments and the bed was successfully conserved. Treatment could not be accomplished using standard methods but required a search for an ideal solution based on the condition and composition of the artifact. Moreover, the obtained results provide essential data for the follow-up treatment and conservation works of other gilded objects of king Tutankhamun.

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References

[1] A. Abdrabou, N. M. E Hadidi, S. Hamed, M. Abdallah, *Multidisciplinary approach for the investigation and analysis of a gilded wooden bed of King Tutankhamun*, **Journal of Archaeological Science: Reports , 21**, 2018, pp. 553–564.

[2] L. Notes, *The Griffith Institute, Tutankhamun: Anatomy of an Excavation, Alfred Lucas's Notes on Conservation of Objects from the Tomb of Tutankhamun*, [Online]. Available: http://www.griffith.ox.ac.uk/discoveringTut/conservation/4lucasn6.html.

[3] P. Hatchfield and R. Koestler, *Scanning electron microscopic examination of archaeological wood micro structure altered by conservation treatments*, **Scanning Microscopy,** 1, 1987, pp. 1059–1069.

[4] T. Jaeger, *Removal of paraffin wax in the re-treatment of archaeological iron*, **Journal of the American Institute for Conservation**, **47**(3), 2008, pp. 217–223.

[5] A. Unger, A. Schniewind, W. Unger, **Conservation of Wood Artifacts**, **Hand Book**, Springer-Verlag, Berlin Heidelberg, 2001.

[6] R. Wolbers, **Cleaning painting surfaces: aqueous methods**, London: Butterworths, 2000.

[7] E. Carretti, B. Salvadori, P. Baglioni, L. Dei, *Microemulsions and Micellar Solutions for Cleaning Wall Painting Surfaces*, **Studies in Conservation**, **50**(2), 2005. pp. 128-136.

[8] R. Keppler, A. Schlotter, V. Johanneke, *From brown to bright: Removing several varnish and dirty layers from a 17th – century ceiling painted on wood*, **Gels in the Conservations of Art** (Editors: L.V. Angelova, B. Ormsby, J.H. Townsend, R. Wolbers), Archetype publications, London, 2017, pp. 184-186.

[9] P. Mezzadri, G. Sidoti, M.C. Gaetani, *The case of carpogrossi in Rome: trials and tests using gels for the cleaning of contemporary wall painting*, **Gels in the Conservations of Art** (Editors: L.V. Angelova, B. Ormsby, J.H. Townsend, R. Wolbers), Archetype publications, London, 2017, pp. 337-342.

[10] S.M. Ortego, A.B. Gine, *The removal of dirt and coatings from heavily restored medieval painted ceramic socarrats from Vlencia, Spain, using gelled system*, **Gels in the Conservations of Art** (Editors: L.V. Angelova, B. Ormsby, J.H. Townsend, R. Wolbers), Archetype publications, London, 2017, pp. 372-375.

[11] M. Baglioni, R. Giorgi, D. Berti, P. Baglioni, *Smart cleaning of cultural heritage: a new challenge for soft nanoscience*, **Nanoscale**, **4**, 2012, pp. 42–53.

[12] G. Pizzorusso, E. Fratini, J. Eiblmeier, R. Giorg, D. Chelazzi, A. Chevalier, P. Baglioni, *Physicochemical Characterization of Acrylamide/Bisacrylamide Hydrogels and Their Application for the Conservation of Easel Paintings*, **Langmuir, 28**, 2012, pp. 3952-3961.

[13] K.K. Salama, M.F. Ali, M. El-Sheikh, A.A. Nada, M.A. Betiha, *A new way in synthesizing magnetic nano gel for cleaning an egyptian coptic fresco painting*, **Mediterranean Archaeology and Archaeometry**, **17(**1), 2017, pp. 189-195.

[14] C.H. Thuer, **Scottish Renaissance Interiors: Facings and adhesives for size tempera painted wood**, Historic Scotland Technical Paper 11, 2011.
[15] R.L. Feller, **Accelerated Aging– Photochemical and Thermal Aspects, Research in Conservation 4**, The Getty Conservation Institute,1994.
[16] D. Stulik, H. Khanjian, V. Dorge, A. d. Tagle, *Scientific investigation of surface cleaning processes: quantitative study of gel residue on porous and topographically complex surfaces*, ***ICOM Committee for Conservation***, 2002, pp. 245-251.
[17] E. Carretti, L. Dei, C. Mililani, F. Rosi, *Monitoring of pictorial surfaces by mid FTIR reflectance spectroscopy: efficiency of innovative colloidal cleaning agents*, **Spectroscopy Letters, 38**, 2005, pp. 459-475.
[18] P. Baglioni, R. Giorgi, L. Dei, *Soft condensed matter for the conservation of cultural heritage*, **C. R. Chimie**, **12**, 2009, pp. 61-69.
[19] E. Carretti, L. Dei , P. Baglioni, *Solublization of acrylic and vinyl polymers in Nanocontainers solutions: Application of Microemulision and micelles to cultural heritage conservation*, **Langmuir**, **19**, 2003, pp. 7867-7872.
[20] A. Cosentino, Practical notes on ultraviolet technical photography for art examination, **Conservar Património**, **21**, 2015, pp. 53-62.
[21] E. Carretti, I. Natali, C. Matarrese, P. Bracco, R. G. Weiss, P. Baglioni, A. Salvini, L. Dei, *A new family of high viscosity polymeric dispersions for cleaning easel paintings*, **Journal of Cultural Heritage**, **11**, 2010, pp. 373-380.
[22] I. Brajer, M. F.-L. Rouzic, Y. Shashoua, M. Taube, D. Chelazzi, M. Baglioni, R. Giorgi, P. Baglioni: *The removal of aged acrylic coatings from wall paintings using microemulsions*, **17th Triennial Conference of ICOM. CC**, Melbourne, 2014.
[23] S. Acquaviva, E. D'Anna, M.D. Giorgi, A. D. Patria, L.P. Pezzati, L. Vicari, F. Bloisi, V. Califano, *Laser cleaning of gilded wood: A comparative study of colour variations induced by irradiation at different wavelengths*, **Applied Surface Science**, **253**, 2007, pp. 7715-7718.
[24] S. Rapti, S. Boyatzis, S. Rivers, A. Velios, A. Pournou, *Removing iron stains from wood and textile objects: assessing gelled siderophores as novel green chelators*, **Gels in the Conservations of Art** (Editors: L.V. Angelova, B. Ormsby, J.H. Townsend, R. Wolbers), Archetype publications, London, 2017, pp. 343-348.
[25] E. Carretti, L. Dei, R. G. Weiss, P. Bracco, P. Baglioni, *A new class of gels for the conservation of painted surfaces*, **Journal of Cultural Heritage**, **9**, 2008, pp. 386-393.
[26] L. Rampazzi, B. Rizzo, C. Colombo, C. Conti, M. Realini, *Use of LA-ICP-MS technique with SEM-EDS analysis in the study of finishing layers*, **Lasers in the Conservation of Artworks**, Taylor & Francis Group, London, 2008.
[27] I.C.A. Sandu, C. Luca, I. Sandu, V. Vasilache, M. Hayashi, *Authentication of the ancient easel paintings through materials identification from the polychrome layers - II. Analysis by means of the FT-IR spectrophotometry*, **Revista de Chimie, 59**(4), 2008, pp. 384-387.
[28] K. de Ghetaldi, B. Baade, Z. Voras, E. Wroczynski, *Resurrecting a giant: using solvent gels and agueous systems to restore Villanova University's Triumph of David*, **Gels in the Conservations of Art** (Editors: L. V. Angelova, B. Ormsby, J. H. Townsend, R. Wolbers), Archetype publications, London, 2017, pp. 157-164.
[29] C. Mckibbin, L. A. Jones, E. Verveniotou, *Giant seguoia: an extraordinary case study involving carbopol gel*, **Gels in the Conservations of Art** (Editors: L.V. Angelova, B. Ormsby, J.H. Townsend, R. Wolbers), Archetype publications, London, 2017, pp. 172-176

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