



## Experimental and comparative studies for evaluation of green solvents in cleaning the aged dammar varnish from oil paintings

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### Abstract

Recently, the pursuit of green cleaning practices has been induced with the aim of the replacement of the toxic materials with safer ones for the conservators' health and environment. This study aims to investigate the efficiency of using the green solvents as alternatives to the toxic solvents commonly used for the removal of the discolored dammar varnish from the artificially thermally aged oil-painted mock-ups. The research mainly focuses on the investigation of the sensitivity of two different oil-painted formulas toward dimethyl carbonate and dimethyl glutarate as green solvents during the cleaning procedure. The microscopic and analytical protocols were established for the varnished, unvarnished, and cleaned mock-ups to evaluate the effectiveness of the cleaning test. Complementary investigation of different microscopy techniques at a multi-scale started with Stereo Microscope (SM), Atomic Force Microscope (AFM) and followed by Scanning Electron Microscope (SEM). The colorimetric measurements were carried out to compare the cleaned mock-ups with their varnished and unvarnished reference equivalents. The analytical protocol of cleaning assessment involved Gas Chromatography-Mass Spectrometry (GC/MS), Attenuated Total Reflection- Fourier Transform Infrared Spectroscopy (ATR-FTIR), and Thermo-gravimetric analysis (TGA) to respectively study leaching phenomena, the possibility of carboxylates formation and retention time of solvent inside the oil painted layer. Although the results varied, dimethyl carbonate exhibited promising results with respect to removal of the discolored aged dammar varnish with reducing the risk of paint removal and retentive time of the solvent inside the painted layer compared to dimethyl glutarate.

Keywords; *cleaning, swelling, leaching, retention, green solvents, dimethyl carbonate, dimethyl glutarate*

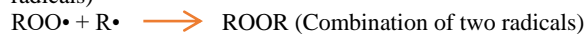
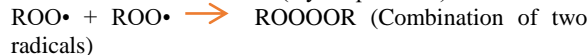
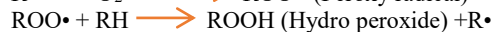
### 1. Introduction

The historic oil paintings are commonly composed of four successive layers; support, ground layer, oil painted layer, and the final protective varnish. The oil-painted layer composes of pigment particles suspended in a drying oil 'typically linseed oil'. The drying oil mainly depends on the polyunsaturated fatty acids to be solidified. The initiation reaction of drying oil oxidation involves spontaneous hydrogen abstraction from an active methylene group between two double bonds in the polyunsaturated fatty acid chain producing an initiator free radical [1]. As soon as the free radical meets the oxygen molecules from the air, they immediately react to generate the peroxy radicals which attack another unsaturated fatty acid molecule to form a new free radical [2]. The free radical reactions are influenced by the existence of metallic ions in pigments working as oxidants to fasten the reaction or antioxidants to retard the reaction [3]. The free radicals propagate forming the primary oxidative products of peroxide and hydro-peroxide which are not stable and can be

readily broken forming radicals. The chain reaction is terminated by reactions that remove the free radicals by the combination of two radicals to form non-radical "more stable" products. During this reaction, the metal ions of some pigments play an important role in the recombination of two peroxy radicals to give intermediate tetra peroxide [4]. The oxidative polymerization mechanism of the drying oil is summarized as follows [5] [6];



(Initiator free radical)+(Methylene group)  $\longrightarrow$  (Free radical tend to react)



Due to the high reactivity of the oil medium, transparent di/tri-terpenoid resins have been applied to the surface of the historic oil paintings to provide a protective layer from the environmental conditions. Natural aging of these varnishes leads to oxidized yellow products which can obscure the whole painted

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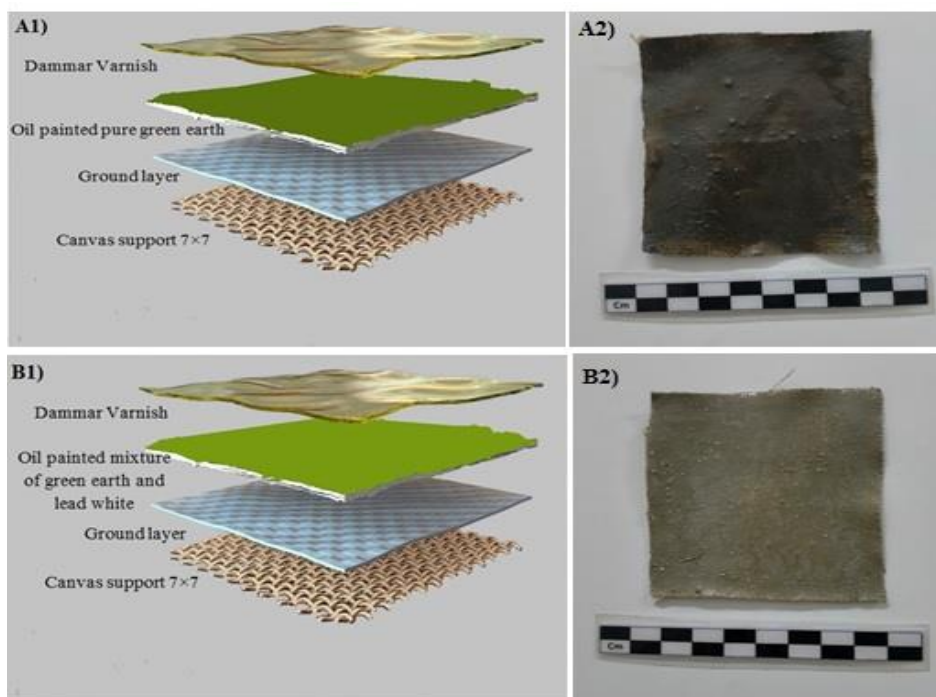
layer with an urgent need to be replaced [7]. The term oil painting cleaning involves the total or partial removal of any extraneous material deposited over the oil painted surface since it was painted as degraded varnishes or successive deposits either from the ambient environment or from conservation interventions [8]. Varnish removal is considered to be one of the major problems encountered due to the potential concerns that could affect the underlying painted layers [9]. Organic solvents are the most widely used materials for cleaning the degraded varnishes from the oil paintings however; they have potential risks to the paint formulations, especially the oil medium. The literature demonstrated the potential unwanted side effects of using solvents as a cleaning agent. Various degrees of swelling, leaching, solvent evaporation and retention inside the painted layer were practically confirmed [10]. These phenomena principally depend on the oil painted film age, pigment formula, nature, and time of solvent exposure [11]. Swelling is an immediate and tangible phenomenon in which the organic binder is softened due to solvent sorption and reducing the binding power of the paint medium. Thus, then the paint is vulnerable to being removed. Aged painted films showed low magnitudes of swelling in solvents compared to their young counterparts this is because of increased cohesiveness conferred by internal electrostatic bonding. Swelling can be determined by measuring the dimension change in the film plane or the perpendicular direction [8]. Leaching is a term describing the extractable soluble components of the oil binder. The soluble components have plasticizing properties in the film. The risk of leaching includes the brittleness of the film with the matt increase of the paint surface. The analyses of the extractable components contained saturated acids of palmitic and stearic, un-polymerized triglycerides, the less reactive mono-saturated oleic acid in combination with low molecular weight oxidative products as dicarboxylic acids, aldehydes, and hydro-peroxide [12]. Solvent retention refers to the concentration of the solvent in the painted film. It is administered by the speed of solvent to diffuse outwards [9]. De-swelling is slower than swelling due to the affinity of the paint film binder for solvent. The initial stage is controlled by solvent evaporation and a later stage is loss of the absorbed from the paint [8]. Recently, high demands are directed toward the conservators' health and the environmental considerations regarding the petroleum solvents' use. In this concept, conservators are looking for greener alternatives to reduce healthiness, environmental, and artifact impacts. In the last few years, green chemistry has gained a strong foothold in the field of cultural heritage cleaning by using gels, micro-emulsions, and ionic

liquids [13][14][15] that have served in toxicity minimization with continuous development to achieve more desirable results for the safety of the artifact itself [16]. In this study, Dimethyl carbonate (DMC) and Dimethyl glutarate (DMG) were evaluated as green solvents for the cleaning of the discolored dammar varnish from the two various thermally aged laboratory prepared oil painted systems; the first painted layer represents the pure green earth in cold-pressed linseed oil, and the second is composed of a mixture of lead white and green earth in cold-pressed linseed oil. The main aim of these systems is to study how the different types of oil paint contents either having a catalytic effect 'lead white' on the drying and cross-linking processes of the oil binder or not could affect the sensitivity of the painted toward the solvent during the cleaning procedure of the painting.

## 2. Materials and Methods

### 3. 2.1 Samples

The oil-painted mock-ups were prepared according to the same structure, painting materials and age as a 19<sup>th</sup> painting dedicated to the Military Museum, Saladin Citadel, Cairo. Each sample is 7 × 7 cm of canvas followed by a single ground layer. The ground layer consists of a mixture of barium sulfate, calcium carbonate, basic lead carbonate, zinc oxide, and glue. The ground layer is followed by the paint layer mainly composed of 1g of powder pigment to 1 ml of cold-pressed linseed oil. Two mock-up groups were prepared: the first group includes 3 mock-ups painted with green earth. The second group includes 3 mock-ups painted with a mixture of green earth and lead white (1:1) 0.5g from each powder pigment. The prepared painted mock-ups were left in laboratory conditions for 15 days before varnish application. The painted layer is brushed by a single stroke of dammar turpentine fig.2. (1ml to each mock-up). Two separate mock-ups from each group were prepared with no application of the varnish layer to be compared with the tested cleaned mock-ups. The laboratory prepared samples have been artificially aged according to standard ISO 5630-1 with accelerated thermal aging (dry- heat) carried out at 105° C. Aging times were 0, 0.6, 1.2, 3, 6, and 12 days, which corresponds approximately to 0, 5, 10, 25, 50, and 100 years of natural aging [17]. The samples were aged by thermally accelerated aging at 105° C for 15 days (360 hours) which is assessed to correspond to 125 years. Dry heat artificial aging was selected to this study to track the effect of solvent on the oil medium. Artificial moisture cycles were not option for this study due to its possible effect on the hydrolysis of the oil medium.

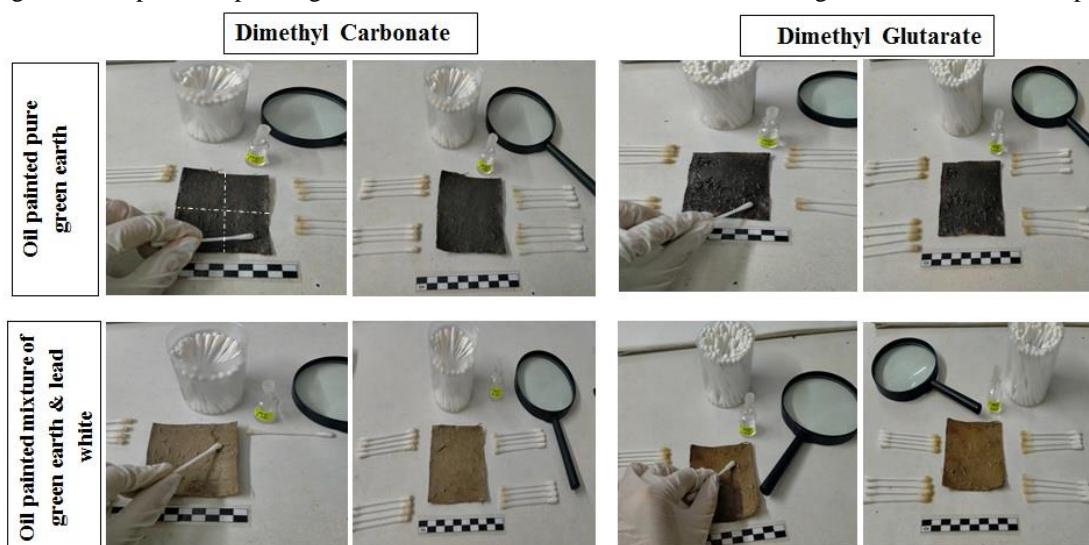


**Fig. 1.** Stratigraphic structure of the laboratory prepared samples A1, A2 of the pure green earth oil painted layer & B1, B2 the mixture of green earth and lead white oil painted layer.

## 2.2 Materials

The painting materials used for mock-ups preparation were purchased from Kremer pigment, GmbH & Co.KG, Germany; Dammar varnish (79321), calcium carbonate (58000), barium sulfate (46100), zinc oxide (46300), lead white ((46000), green earth (40821), cold-pressed linseed oil (1515). All information on the purchased materials; chemical compositions, manufacturing process, and handling can be found on the Kremer website (Kremer pigmente. com) by looking for the specified painting material with its

code. Dimethyl carbonate solvent is a carbonate ester with the formula of  $C_3H_6O_3$ . It possesses the properties of nontoxicity and biodegradability. It is an aprotic solvent classified in the greenest bracket according to solvent selection guide. DMC was purchased from Loba Chemie PVT.LTD with 99% purity. Dimethyl glutarate is a natural product and is also known as glutaric acid dimethyl ester with the molecular formula  $C_7H_{12}O_4$ . DMG was purchased from ACROS Organics with 98% purities.



**Fig. 2.** The cleaning tests of the oil painted pure and mixed mock-ups with dimethyl carbonate and dimethyl glutarate

## 2.3 Methods

### 2.3.1 Cleaning test protocol

The two groups of thermally aged oil painted laboratory prepared samples were cleaned with the selected green solvents. Swabbing by rolling was used for cleaning the samples. Each sample was divided into four quarters. The number of swabs, the number of rolls, and the cleaning time for each quarter were unified at a room temperature of 25° C. For each quarter of the sample; 4 swabs were rolled 7 times of each swab for 7.5 minutes. The amount of each solvent was unified. Five millimeters of each solvent were used to clean both pure and mixed mockups.

### 2.3.2 Microscopy

Microscopic examinations were performed for the varnished, unvarnished, and cleaned laboratory prepared mockups using Carl Zeiss c-2000 stereomicroscope (Germany) and Zeiss sigma scanning electron microscope coupled with dispersive x-ray spectrophotometer (SEM-EDS) to achieve elemental analysis with in-class geometry of Zeiss sigma 500. Zeiss Gemini in-lens detects Secondary (SE) mode with EHT 3.00 kV and vacuum pressure of 1.01e-09 mbar. The atomic force microscope was used to study the topography of the mockups. The micro- images of each sample were investigated with a high-resolution non-contact mode using an atomic force microscope SPM 9600 (Shimazu, Japan). All the measurements were performed with a scan size of 5 × 5 μm in 2D and 3 D images. The software was employed for image analysis providing the measurement of average roughness and the average maximum tops of each sample.

### 2.3.3 Colorimetric measurements

Colorimetric measurements were performed by the Commission "Internationale de l'Eclairage" (CIE) Lab color system (1976) using Spectro densitometer (Exact X-Rite, Switzerland) to measure color changes on the L\* scale (Luminosity, 100 = white, 0 = black)), b\* scale (yellow/blue color, positive sign = yellow, negative sign = blue) and a\* scale (red/green color, positive sign = red, negative sign = green). Three to five measurements were averaged to obtain one data point. Total color differences ΔE was calculated by the equation;  $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$  [18][19].

### 2.3.4 Attenuated Total Reflection- Fourier Transform Infrared Spectroscopy (ATR- FTIR)

For identification of the changes that occurred to the medium upon using solvents for the cleaning test, FTIR spectra were collected from FTIR- VERTEX 80/80 V Bruker. Nondestructive analyses were carried out with a platinum single reflection diamond

ATR module with a resolution of 4 cm<sup>-1</sup> in the range of 4000-400 cm<sup>-1</sup>.

### 2.4.5 Gas Chromatography-Mass Spectroscopy (GC/MS)

For studying the leaching of the cleaned mock-ups, each mock-up's weight was unified to be 0.2 g. Each weight was then dissolved in petroleum ether 40-60 % and filtered. The filtrate became ready for the methylation process using sodium methoxide to derivative the fatty acids from the sample. 0.1 micro-litre of the derivative was directly injected into GC. The low-weight molecular extractable materials were measured by using Agilent 8890 GC system. For GC/MS detection, an electron ionization system with ionization energy of 70 eV was used, Helium gas was used as the carrier gas at a constant flow rate of 1mL/min. The injector and MS transfer line temperature were set at 280 °C. The oven temperature was programmed at an initial temperature of 50 °C (hold 2 min) to 150 °C at an increasing rate of 7 °C /min. then to 270 °C at an increasing rate of 5 °C /min (hold 2min) then to 310 °C as a final temperature at an increasing rate of 3.5 °C /min (hold 10 min). The quantification of all the identified components was investigated using a percent relative peak area. Tentative identification of the compounds was performed based on the comparison of their relative retention time and mass spectra with those of the NIST, WILLY library data of the GC/MS system.

### 2.4.6 Thermo-gravimetric analysis

The capacity of two painted system groups to retain the solvent was evaluated by thermo-gravimetric analysis. PerkinElmer simultaneous thermal analyzer model STA 6000 was used. Analysis of samples (about 10 mg) and solvents (20 micropipettes) was performed at 40 °C for 90 minutes [8]. This condition was selected as the most similar to the exposition condition for the conservator during the cleaning practice.

## 3. Results

### 3.1 Cleaning test evaluation

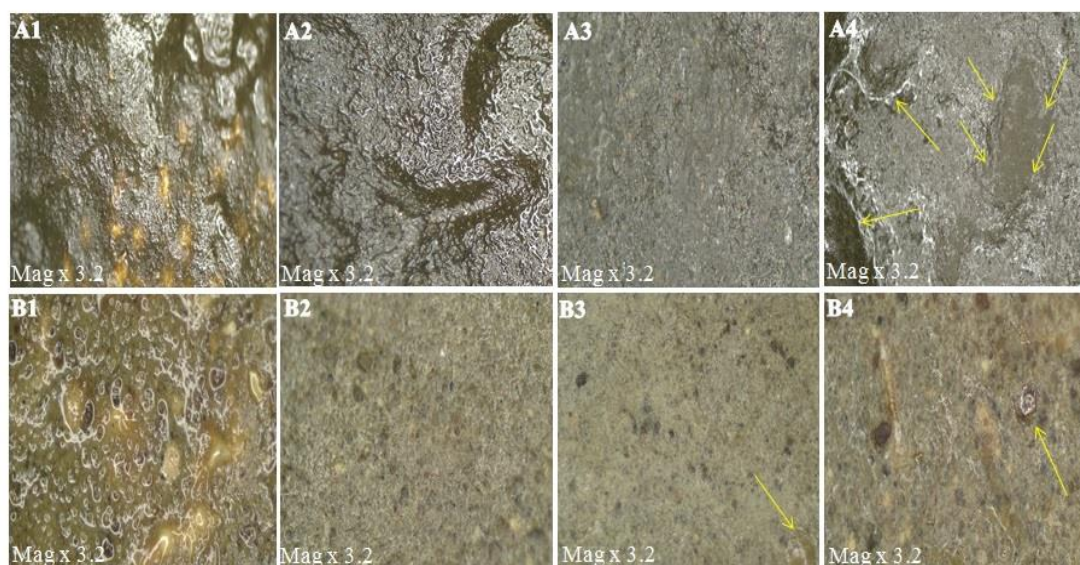
The visual investigation of both cleaned oil-painted systems with dimethyl carbonate and dimethyl glutarate yielded good results for dammar varnish removal. This was observed from the color change of the swabs to yellow from the first swab roll. While the cleaning by dimethyl carbonate yielded good results with the pure green earth painted mock-up, it gave slower results with the mixed oil painted mock-up than that for the oil pure painted mock-up. While

dimethyl glutarate showed faster results in varnish removal, the tangible phenomenon of swelling was observed with the cleaning of the oil-painted pure mock-up. The swelling phenomenon was enhanced during the mechanical action of swabbing especially at the cupping area causing a partial removal of the painted layer fig 2. Cleaning test control was achieved by unifying the time exposure to the solvent, swabs, and rolls number with the amount of solvent used for cleaning each of the oil-painted systems.

### 3.2 Microscopy

Stereomicroscope images of the oil painted pure green earth mockup cleaned with dimethyl glutarate showed a matt surface in some areas than the others with swelling of the painted layer (fig 3.A4). While dimethyl glutarate showed faster results than dimethyl carbonate in varnish removal during the cleaning tests, stereo microscope images characterized remnants of varnish on both of the cleaned oil painted mixed mockups. This could refer to the longer time needed for swabbing to completely remove the all varnished layer.

Atomic Force Microscope (Fig 4 &5) was directly used after the cleaning test in a trial to study the swelling effect and the cleaning effectiveness of the used green solvents by comparing the roughness average, highest, lowest average tops measured on the topographical surface of unvarnished and varnished references with each cleaned mock-up. The main interpretation of data mainly depends on the comparison of cleaned samples with unvarnished references. Increasing the average of maximum tops could refer to swelling. The closer is the average roughness of the cleaned samples to the sample before varnishing, the more successful does it refer to the cleaning effectiveness (Table 1). By comparing the roughness average of the varnished and unvarnished references, the varnished references of pure and mixed painted samples showed lower roughness than the unvarnished references. This could be easily interpreted as the varnish smoothing the surface, changing the refractive index, and increasing the specular reflection [20]. By comparing the roughness average of the unvarnished oil painted pure and mixed mock-ups with the cleaned ones, they showed convergence in values referring to the cleaning effectiveness.



**Fig. 3.** Stereomicroscope images of oil painted pure green earth mock-ups A1 varnished reference, A2 unvarnished reference, A3 mock-up cleaned with DMC, A4 mock-up cleaned with DMG & oil painted mixed mock-ups of B1 varnished reference, B2 unvarnished reference, B3 Mock-up cleaned with DMC, B4 mock-up cleaned with DMG

While the average of maximum tops of both oil painted pure and mixed cleaned mock-ups with DMC did not show increasing by comparing their unvarnished equivalents, the average of maximum tops of oil painted pure and mixed mock-ups cleaned with DMG showed increasing. The maximum top average of the cleaned oil painted pure mockup was higher than that of the cleaned oil painted mixed mockup. This could refer to the higher swelling of the

cleaned pure mockup than the cleaned mixed mock-up. This could be interpreted from the cohesiveness increase of the oil painted mixed mockup due to the catalytic effect of lead ions 'in lead white' in the drying and cross-linking process. Secondary electron images of SEM of the artificially thermally aged unvarnished oil painted pure and mixed references showed the smoothness of the painted surface. This could be due to the coating of the pigment particles

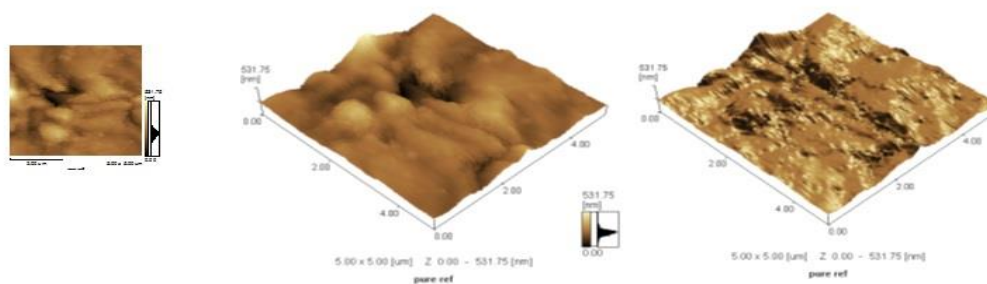
with the oil medium. No evidence provided the existence of cracks, voids, or lacunae via artificial aging. The smoothness of the thermally aged varnished pure and mixed references was greater than the unvarnished references with the existence of superficial micro-cracks on the varnished mixed reference. No evidence of the existence of the cracks on the varnished pure reference was characterized.

The existence of micro-cracks on the varnished oil painted mixed reference could be due to the multiplicity of the layers with the duplication of the aging effect via the catalytic lead ions in the painted layer and the thermal aging.

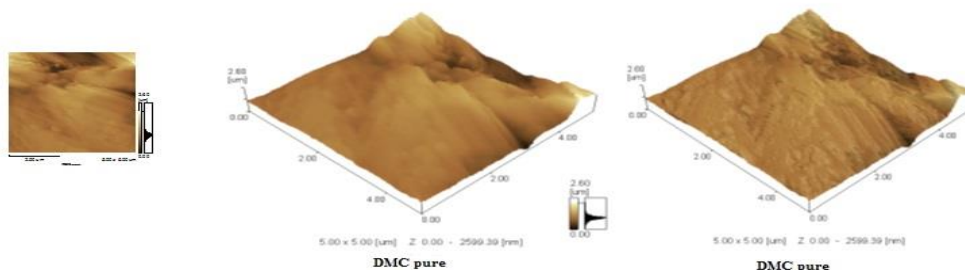
**Table 1.** AFM measurements of roughness average, average of the maximum and minimum tops of the oil painted pure and mixed ' varnished, unvarnished & cleaned' mock-ups

Sample Code	Roughness average	Average of maximum tops	Average of minimum tops	Sample Code	Roughness average	Average of maximum tops	Average of minimum tops
Pure ref.	1.422	3.99	0.601	Pure Mix.	1.50	3.30	0.601
Varnished pure	1.40	3.15	0.601	Varnished Mix	1.32	2.90	0.601
DMC pure	1.44	3.57	0.601	DMC Mix	1.45	3.20	0.601
DMG pure	1.41	4.717	0.601	DMG Mix	1.51	3.961	0.601

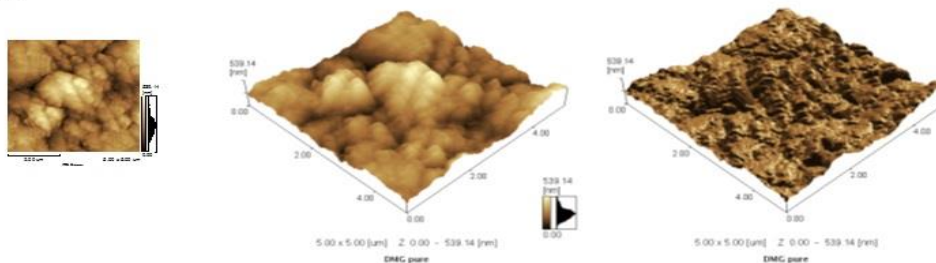
### A1



### A2



### A3



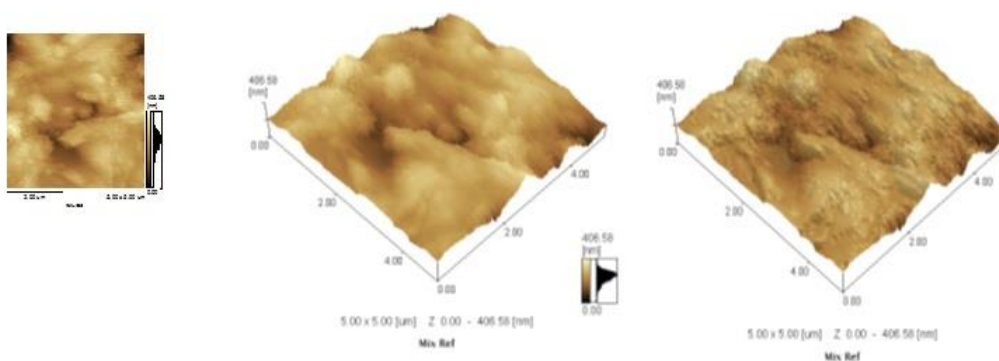
By comparing the SEM images of unvarnished oil painted pure green earth reference with the oil painted pure green earth mock-ups cleaned with dimethyl carbonate and dimethyl glutarate

respectively, the mock-up cleaned with dimethyl carbonate did not show a difference on the painted layer after cleaning. The rough texture of the cleaned mock-up is due to the varnish removal. The oil

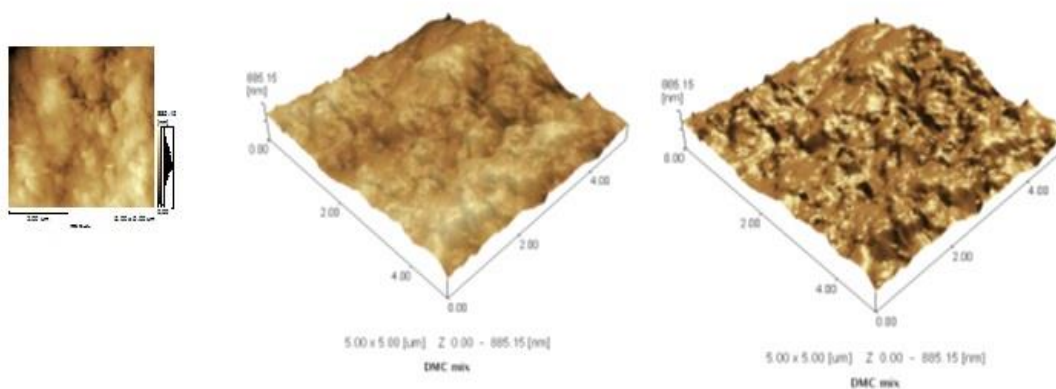
painted pure green earth mock-up cleaned with dimethyl glutarate showed the existence of voids on the painted surface (Fig. 6- A4). The comparison between the cleaned oil painted mixed mock-ups with

the unvarnished oil painted mixed reference did not show change occurrence on the painted layer in both cases of dimethyl carbonate and dimethyl glutarate.

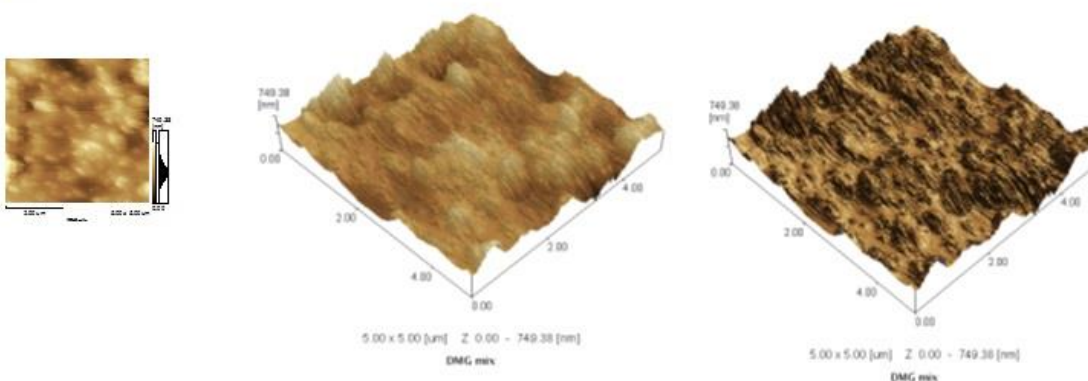
### B1



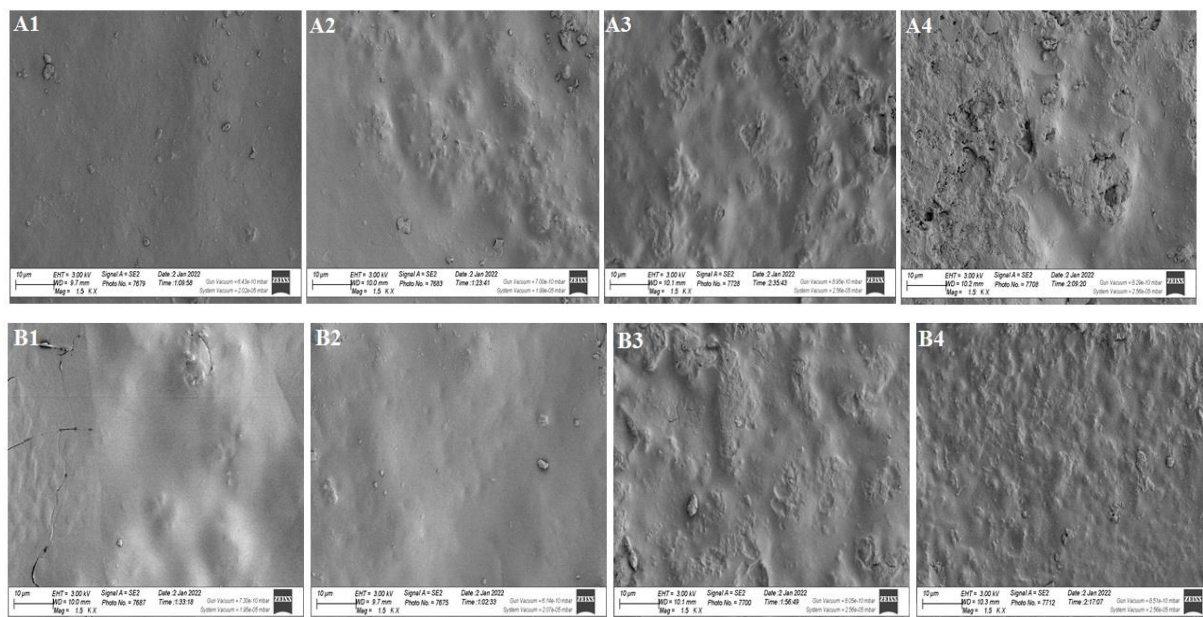
### B2



### B3



**Fig. 5.** 2D & 3D AFM images 5X5 micron B1) the unvarnished oil painted mixed reference, B2) the oil painted mixed mock-up cleaned with DMC, and B3) the oil painted mixed mock-up cleaned with DMG



**Fig. 6.** Secondary electron images of SEM mag X1.5K (A) oil painted pure green earth mock-ups, A1 varnished reference, A2 unvarnished reference, A3 cleaned with DMC, A4 cleaned with DMG & (B) oil painted mixture of green earth and lead white mock-ups, B1 varnished reference, B2 unvarnished reference, B3 cleaned with DMC, B4 cleaned with DMG

### 3.3 Colorimetric measurements

The total color difference  $\Delta E^*$  below (3) refers to an insignificant color change to the naked eye. In case, it records a value greater than (3), the color change is considered to be visually detectable. The value above (6) reflects the large chromatic change for the naked eye [19]. In the colorimetric measurements data obtained from  $\Delta E^*$  for pure and mixed mock-ups, the total color difference in mixed mock-ups was more visually detectable than the pure mock-ups due to the lighter tonality. Two total color differences  $\Delta E_v$  and  $\Delta E_{Un-v}$  were obtained.  $\Delta E_v$  represents the comparison of the cleaned mock-ups with the varnished references while  $\Delta E_{Un-v}$  refers to the comparison of the cleaned samples with the unvarnished references. While the insignificant total color change  $\Delta E_{Un-v}$  refers to the convergence of color coordinates between the unvarnished references and cleaned mock-ups, the greater value of  $\Delta E_v$  represents the visual detection of color difference and the effectiveness of the cleaning procedure.  $\Delta E_v$  of the oil painted pure mock-up cleaned with dimethyl carbonate exhibited the value of 1.42 with a noticeable increase in  $L^*$  value and somewhat decrease in  $b^*$  value by comparing with the varnished sample.  $\Delta E_{Un-v}$  of the oil painted pure mock-up cleaned with dimethyl carbonate showed a neglected value of 0.34 which represents the convergence of color coordinates between the unvarnished pure reference and the pure cleaned mock-up.  $\Delta E_v$  of the oil painted mixed mock-up cleaned with dimethyl carbonate visually detected the value of 4.31 and

non-visual detection of 1.12 for  $\Delta E_{Un-v}$ . The comparison between the colorimetric measurements of the unvarnished, varnished and cleaned mockups with dimethyl glutarate showed retrieving of  $L^*$ ,  $a^*$ , and  $b^*$  values of the pure and mixed cleaned mock-ups to some extent.  $\Delta E_v$  of the pure cleaned mock-up with dimethyl glutarate exhibited the value of 1.47 with a relative increase in  $L^*$  value and decrease in  $b^*$  value by comparing with the varnished reference.  $\Delta E_{Un-v}$  of the pure sample cleaned with dimethyl glutarate showed a neglected value of 0.43 which represents the convergence of color coordinates between the unvarnished pure reference and the pure cleaned sample.  $\Delta E_v$  of mixed sample cleaned with dimethyl glutarate exhibited the value of 4.36 and non-visual detection of 1.22 for  $\Delta E_{Un-v}$ .

### 3.3 Attenuated Total Reflection- Fourier Transform Infrared Spectroscopy (ATR-FTIR)

The exposure of the paint layer to the solvent during the degraded varnish removal leads to the penetration and retention of the solvent inside the paint layer causing the paint swelling and the extraction of the soluble organic materials from the binding medium. The prolonged periods of solvent retention inside the paint layer could result in a chemical reaction through the migration of soluble components of the organic medium enhancing the rate of degradation inside the oil paint. The most studied chemical reactions in oil paint that could be affected by the use of solvents are the hydrolysis of the triglycerides of the oil binder and metal soaps formation which are complicated

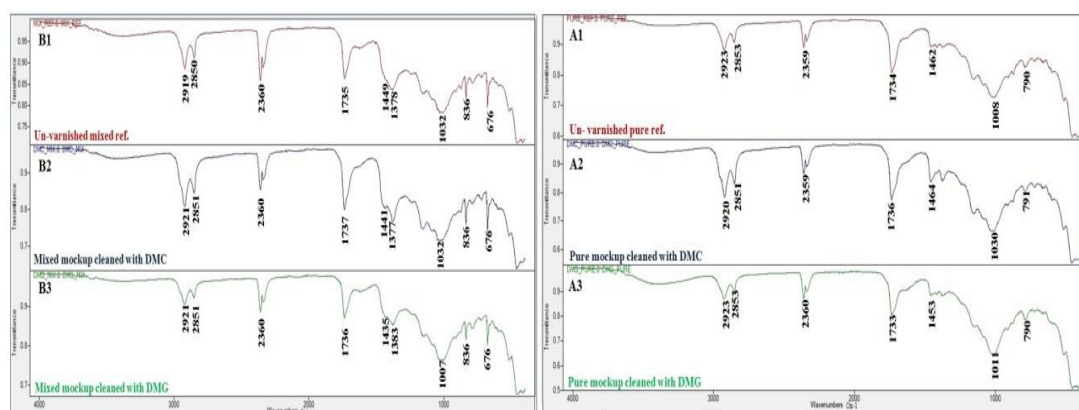


reactions of the metal ions ( $\text{Pb}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Al}^{+++}$ , etc) from the pigments and the ground layer with long-chain saturated fatty acids of the oil medium forming metal carboxylates [9]. Fourier transform infrared spectroscopy is a powerful analytical technique that identifies metal carboxylates via the position of the asymmetric stretch band of carboxylates group  $\text{COO}^-$  [22]. Well-characterized metal carboxylates give sharp characteristic peaks

between  $1500\text{--}1600\text{ cm}^{-1}$  depending on the specific metal cation and fatty acid [23]. The comparison between the characteristic bands of the unvarnished references with the cleaned mock-ups showed that there is no signal referring to the formation of carboxylates after cleaning the pure and mixed mock-ups with dimethyl carbonate and dimethyl glutarate (fig.7.).

**Table 2.**  $L^*$ ,  $a^*$ ,  $b^*$  and total color difference  $\Delta E$  values of the experimental mock-ups

Sample name	$L^*$	$a^*$	$b^*$	$\Delta E_v$	$\Delta E_{Un-v}$	$L^*$	$a^*$	$b^*$	$\Delta E_v$	$\Delta E_{Un-v}$
	Dimethyl carbonate					Dimethyl glutarate				
Varnished pure ref.	25.64	2.4	7.13	-----	-----	25.64	2.4	7.13	-----	-----
Unvarnished pure ref.	27.14	2.6	6.64	-----	-----	27.14	2.6	6.64	-----	-----
Oil painted pure mockup.	27.00	2.29	6.72	1.42	0.34	26.98	2.21	6.55	1.47	0.43
Varnished mixed ref.	38.68	4.2	19.62	-----	-----	38.68	4.2	19.62	-----	-----
Unvarnished mixed ref.	43.50	4.79	19.4	-----	-----	43.50	4.79	19.4	-----	-----
Oil painted mixed mockup	42.87	4.31	18.59	4.31	1.12	42.86	4.50	18.39	4.36	1.22



**Fig.7.** FTIR spectra of A1 unvarnished pure ref., A2 pure mock-up cleaned with DMC, A3 pure mock-up cleaned with DMG & B1 unvarnished mixed ref., B2 mixed mock-up cleaned with DMC, B3 mixed mock-up cleaned with DMG

**Table 3.** Comparison between the un-varnished pure and mixed references ATR-FTIR bands and cleaned mockups

Band Diagnosis	Comparison of band Wavenumbers $\text{cm}^{-1}$			Observations	Band Diagnosis	Comparison of band Wavenumbers $\text{cm}^{-1}$			Observations
	Pure Ref.	Cleaned pure DMC	Cleaned Pure DMG			Mix Ref.	Cleaned Mix DMC	Cleaned Mix DMG	
Asymmetric C-H stretching	2923	2920	2923	No signal of Carboxylates formation	Asymmetric C-H stretching	2919	2921	2921	No signal of Carboxylates formation
Symmetric C-H Stretching	2853	2851	2853		Symmetric C-H stretching	2850	2851	2851	
C=O of oil	1734	1736	1733		C=O of oil	1735	1737	1736	
C-H bending	1462	1464	1453	C-H bending/ $\text{CO}_3^{2-}$	1449	1441	1435		
C-O	1008	1030	1011	C-H bending	1378	1377	1383		
C-H Torsion	790	791	790	Si-O stretching	836	836	836		

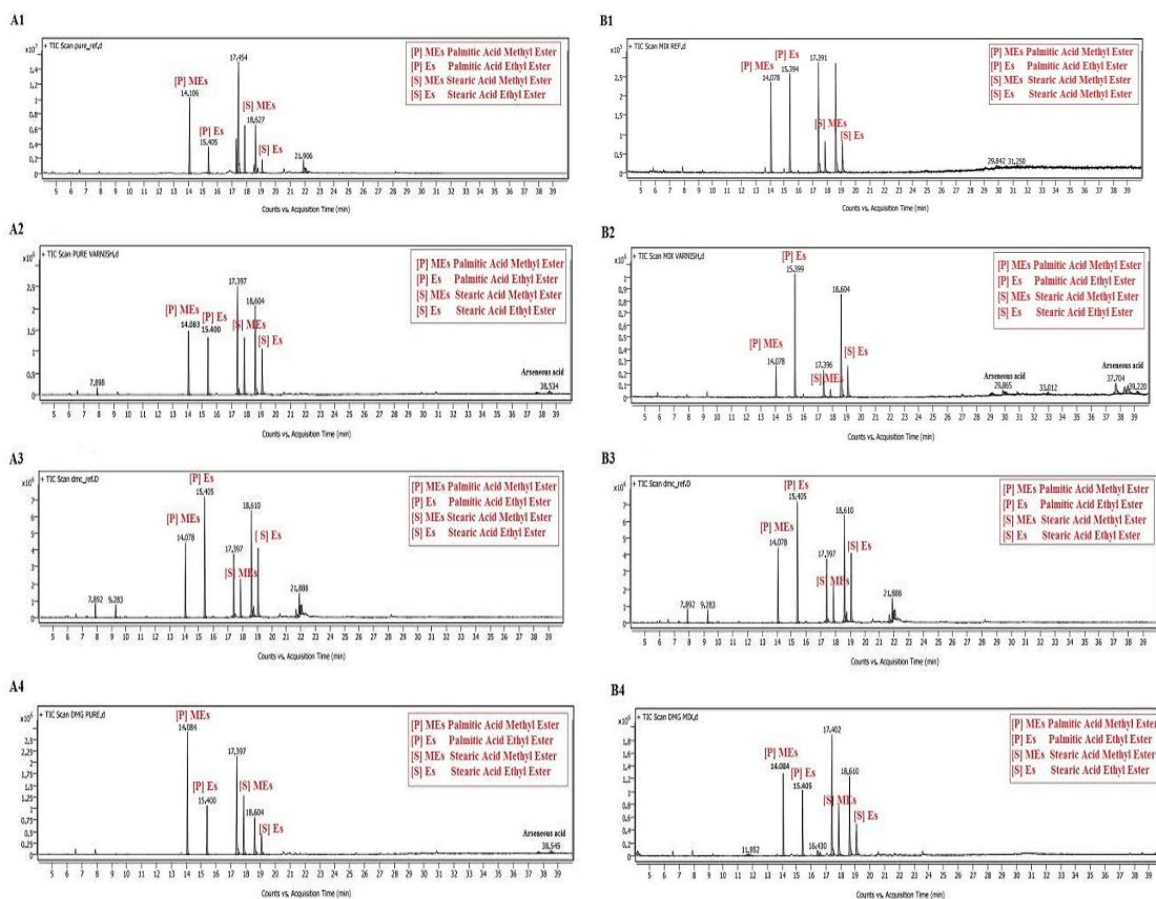
### 3.5 Gas Chromatography-Mass Spectroscopy (GC/MS)

The response of the oil medium to the two used green solvents was determined by using GC/MS. The quantities of the saturated acids of palmitic and stearic were investigated from the unifying of samples' weight before varnishing, after varnishing, and after the cleaning procedure. Comparisons of the levels of the fatty acids in the various groups of samples provided estimations of the saturated fatty

acids variability quantities that are not involved in oxidation reactions and therefore the quantities of leached acids. The quantities of palmitic and stearic acids were achieved by calculating the amounts of ethyl and methyl ester of each acid (fig. 8). Controlling the cleaning test was achieved by unifying the time exposure to the solvent, swabs, and rolls number with the amount of solvent used for cleaning each of the oil-painted systems.

**Table 4.** Changes in palmitic and stearic acid levels in pure and mixed mock-ups before, after varnishing and

Palmitic concentration	DMC Pure	DMG Pure	DMC Mix	DMG Mix	Stearic concentration	DMC Pure	DMG Pure	DMC Mix	DMG Mix
[P] ref.	38.4	38.4	38.64	38.64	[S] ref.	21.68	21.68	19.51	19.51
[P] varnished ref	37.28	37.28	37.1	37.1	[S] varnished ref	20.54	20.54	18.4	18.4
[p] Mock-up after cleaning	37.25	37.06	37.03	36.9	[S] Mock-up after cleaning	20.59	20.21	18.24	18.15



**Fig. 8.** GC/MS chromatograms of A1 unvarnished pure reference, A2 varnished pure reference, A3 pure mock-up cleaned with DMC, A4 pure mock-up cleaned with DMG & B1 unvarnished mixed reference, B2 varnished mixed reference, B3 mixed mock-up cleaned with DMC, B4 mixed mock-up cleaned with DMG after cleaning treatments

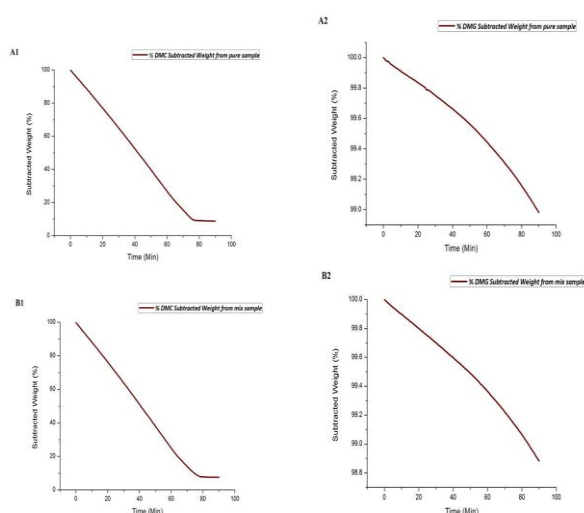
Reductions in palmitic and stearic acids were observed after varnishing. The neglected reduction was observed in palmitic and stearic acid

concentrations after cleaning. The reduction percentages are not exceeded 0.3 for dimethyl glutarate. Dimethyl carbonate showed better results as the reduction of acid concentrations are not

exceeded 0.2 taking into consideration the mistake rate of the device from 0.05 to 0.1 (Table 4). While a neglected percentage of resinous acid was detected in the pure mock-up cleaned with dimethyl glutarate, the mixed mock-up cleaned with dimethyl carbonate showed the existence of a neglected percentage of resinous acid from the remnants of dammar varnish on the painted surface. The ratios of palmitic to stearic after cleaning were ranging from 1.80 to 2.03 for pure and mixed cleaned mock-ups which are typical of linseed [24]

### 3.6 Thermo-gravimetric analysis

The retention capability of the tested solvents from the two different oil painted formulas was measured by thermo-gravimetric analysis by comparing the weight loss percentage during the isothermal run at 40 °C for 90 minutes with a slight difference between the pure and mixed mock-ups due to the slight difference in the starting solid mock-up weight. The results of the gravimetric analysis showed a high evaporation rate of dimethyl carbonate from the two different oil painted formulas with a slight difference between the weight loss percentage of dimethyl carbonate in oil painted pure mock-up and the oil painted mixed mock-up. The percentages of weight loss of the dimethyl carbonate from the pure and mixed mock-ups were 91.2% and 92.45% respectively in the 78<sup>th</sup> minute with continuous weight stability until the 90<sup>th</sup> minute. Dimethyl glutarate showed the highest retention inside the various painted surfaces. The percentage of weight loss did not exceed 1.12 %. While the percentage of weight was 98.98% for the pure sample, it became 98.88% for the mixed mock-up in the 90<sup>th</sup> minute



**Fig. 9.** TGA analyses isothermal run at 40°C. of weight loss percentage of dimethyl carbonate in pure mock-up A1, mixed mock-up A2 & weight loss percentage of dimethyl glutarate in pure mock-up B1, Mixed mock-up B2

### 4. Discussion

While the visual and preliminary microscopic investigations from the controlled cleaning test yielded better and faster results in the case of using dimethyl glutarate for the removal of aged dammar varnish from the two different oil painted formulas than those cleaned with dimethyl carbonate, the oil painted pure mock-up cleaned with dimethyl glutarate showed a partial removal of the cupping area during the cleaning test. The used microscopic protocol to evaluate the cleaning procedure showed that dimethyl glutarate caused higher swelling of the oil painted pure cleaned mock-up than that occurred in the oil painted mixed cleaned mock-up. This could be interpreted from the nature of the pigment used in the oil-painted layer. While the oil-painted pure layer is composed of pure green earth pigment that does not have a catalytic effect in the drying reactions of the oil medium, the lead ions from the oil-painted mixed layer have a catalytic effect in the drying process increasing the compactness of the oil painted layer. This is highly compatible with the literature that tested the action of the conventional solvents on the oil-painted layer [9][12]. Swelling phenomena could be enhanced the risk to the painted layer in a longer period of swabbing. The comparison between the roughness averages and the colorimetric measurements of the cleaned mock-ups with their reference equivalents confirmed the cleaning effectiveness of dimethyl carbonate and dimethyl glutarate for cleaning the aged dammar varnish layer from the oil-painted surface. The atomic force microscope showed the proximity of the roughness average of the cleaned mock-ups with their unvarnished reference equivalents. The colorimetric measurements also confirmed the effectiveness of the cleaning procedure. The neglected change in palmitic and stearic quantities in the cleaned mock-ups did not cause variation in the typical ratio of palmitic to stearic acid of linseed oil. The retention time of dimethyl glutarate inside the painted layer is too high and the risk of this lies in the possibility to re-soluble the low molecular weight component from the oil medium enhancing the complicated reactions between the metal ions from the ground and painted layers [25]. Although ATR-FTIR analysis did not characterize metal carboxylates inside the painted layer, some researchers proved the possibility of the existence of solvent traces inside the paint layer to 120 days [10] which could affect the reactions in long term. While dimethyl carbonate showed slower results in the cleaning test, the advantage of its high evaporation of the sensitive oil painted system is vital to the cleaning procedure preventing further actions of the solvent in case of needing a longer time of cleaning procedure. This is aligned with its good profile for conservators' health and the environment.

## 5. Conclusion

Dimethyl carbonate is a non-hazardous solvent for the environment, and the conservators' health, and proved its safeness to the oil painted layer. The microscopic, colorimetric and analytical studies confirmed that it is safely used for cleaning the aged dammar varnish from both the oil painted formulas.

Being characterized by a high evaporation rate, give the solvent the ability to perfectly clean the painted surface without characterization of swelling phenomena. No chemical changes occurred to the oil medium of the painted film as proven in ATR-FTIR and GC/MS results. The problem of dimethyl glutarate was observed with the oil painted pure cleaned mockup than that painted with a mixture of green earth and lead white. Higher swelling and retentive time could enhance the risk to the painted layer. Further experiments with dimethyl glutarate are recommended to minimize the diffusion of the solvent inside the painted layer.

## 6. Conflicts of interest

There are no conflicts to be declared

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## 8. References

- Mallécol, J., Lemaire, J., Gardette, J.L., Drier influence on the curing linseed oil, *Progress in organic coating*, (39), pp 107-113 (2000).
- Van den Berg, J. D. J., Analytical chemical studies on traditional linseed paints, Ph.D. thesis, University of Amsterdam, MolArt (2002).
- Izzo, F.C., 20<sup>th</sup>-century artists' oil paints; chemical-physical survey, Ph.D. thesis, Ca' Foscari University of Venice (2009).
- Soltan, M.A., The drying of linseed oil, *Chemistry for fine art conservators*, Master thesis, North Umbria University, school of art and social science (2008).
- Schwarcman, A., Some known reactions of drying oil films and polymerization, *Journal of the American oil chemists society*, Vol 21 (7), pp 204-206 (2001)
- Scrimgeour, Ch., *Chemistry of fatty acids*, Bailey's industrial oil and fat products, 6<sup>th</sup> edition, P 16 (2005)
- Cortina, L.O. & Carbo, M.T.D., Study on the effect of chemical cleaning on Pinaceae resin-based varnishes from panel and canvas paintings using pyrolysis-gas chromatography/ mass spectroscopy, *Journal of analytical and applied pyrolysis*, 76, pp144-153 (2006).
- Volpi, F., Green strategies for the cleaning of works of art setting up of an analytical protocol for the evaluation of cleaning, Ph.D. thesis, University of Bologna (2017).
- Baij, L., Hermans, J., Ormsby, B., Noble, P., Iedema, P., Keune, K., A review of solvent action on oil paint, *Heritage Science*, pp1-23 (2020).
- Phenix, A. & Sutherland, K., The cleaning of paintings; effects of organic solvents on oil paint films, *Studies in Conservation* 46(2), pp 47-60 (2001).
- Tsang, J.S. & Erhardt, D., Current research on the effect of solvents and gelled and aqueous cleaning systems on oil paint films, *JAIC*, 31, pp87-94 (1992).
- Sutherland, K.R., Solvent extractable components of oil paint films, Ph.D. thesis, University of Amsterdam (2001).
- Baglioni, P.; Bonelli, N.; Chelazzi, D.; Chevalier, A.; Dei, L.; Domingues, J.; Fratini, E.; Giorgi, R.; Martin, M., Organogel formulations for the cleaning of easel paintings, *Applied Physics A*, 121, PP 857–868, DOI [10.1007/s00339-015-9364-0](https://doi.org/10.1007/s00339-015-9364-0) (2015).
- Prati, S., Sciutto, G., Volpi, F., Rehorn, C., Vurro, R., Blümich, B., Mazzocchetti, L., Giorgini, L., Samorì, C., Galletti, P., Cleaning oil paintings: NMR relaxometry and SPME to evaluate the effects of green solvents and innovative green gels. *New journal of chemistry*, 43, 8229–8238 (2019).
- Pacheco, M.F., Pereira, A.I., Branco, L.C., Parola, J.A., Varnish removal from painting using ionic liquids, *Journal of materials chemistry A*, 1(24), PP 7016-7018 (2013).
- Jia, Y.; Sciutto, G.; Mazzeo, R.; Samorì, C.; Focarete, M.L.; Prati, S.; Gualandi, C., Organogel Coupled with Microstructured Electrospun Polymeric Nonwovens for the Effective Cleaning of Sensitive Surfaces. *ACS Applied Materials Interfaces*, 12, 39620–39629 (2020).
- Vizarova, K., Rehakova, M., Kirschnerova, S., Peller, A Stability studies of materials applied in the restoration of Baroque paintings, *Journal of Cultural Heritage*, (12), pp190-195 (2011).
- Booth J., *Principles of textile testing*. Butterworth- Heinemann, USA, pp 118–169. (1984).
- Wyszecki G, Stiles W., *Color science concepts and methods*, 2<sup>nd</sup> edition. Quantitative data and formulae, New York, (2000).

- 20- Pereira, C.L.C, Application of ionic liquids and enzymes for the removal of proteinaceous layers from polychrome of works of art and evaluation of cleaning effectiveness, Master thesis, Faculty of science and technology, University of Nova de Lisboa, Portugal (2012).
- 21- Ibrahim, M.M., Mohamed, W.S., Mohamed, H.M., Comparative and experimental studies for evaluation of paraloid B-72 in traditional and nanoforms for joining pottery samples, *Journal of Nano Research*, Vol 61, pp 61-71 (2020).
- 22- Hermens, J.J., Keune, K., Van Loon, A., Ledema, P.D., An infrared spectroscopic study of the nature of zinc carboxylates in oil paintings, *Journal of Analytical Atomic spectrometry*, (30), pp 1600-1608 (2015).
- 23- Henderson, E.J., Helwig, K., Read, S., Rosendahl, S.M., Infrared chemical mapping of degradation products in cross-sections from paintings and painted objects, *Heritage Science*, 71(7), pp 1-15 (2019).
- 24- Manzano, E., Rodriguez-Simon.L.R., Navas, N.,Checa-Moreno,R., Romero\_Gamez, M., Capitan-Vallvey, L.F., Study of the GC-MS determination of the Palmitic-Stearic acid ratio for characterization of drying oil in painting; La Encarnacion by Alonso Cano as a case study, *Talanta*, 84, pp1148-1154 (2011)
- 25- Baij, L., Astefanei, A., Hermans, J., Brinkhuis, F., Groenewgen, H., Chassouant, L., Johansson, S., Corthals, G., Tokarski, C., Ledema, P., Keuene, K., Solvent mediated extraction of fatty acids in bilayer oil paint models; a comparative analysis of solvent application methods, *Heritage Science*, Vol 31(1), pp 1-8 (2019).