Experimental and applied study on the removal of polyurethane adhesive from the archaeological textiles

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Abstract

The objective of this work is to evaluate the efficacy of the gel and nanostructured fluids in the removal of polyurethane adhesive stuck to an archeological textile fragment that suffers from many deterioration forms. The study is divided into two sections; (a) in-vitro experiments, which were conducted on modern sheep woolen textile mock-ups after brushing with fresh polyurethane adhesive and accelerated aging. Three techniques were used in the removal of polyurethane from these mock-ups. Colorimeter, Fourier transform infrared spectroscopy, stereo microscope, and weight measurements were used to assess the selected experiments. The obtained results revealed that Nano restore Cleaning ®Polar fluid confined in Nano restore Gel ®Peggy is the most effective and suitable technique among the examined ones. (b) The applied section, which was assigned to using Nano restore Cleaning ®Polar fluid confined in Nano restore Gel ®Peggy in the removal of polyurethane adhesive from the case-study fragment, after identifying its fibers and dyes using a Fourier transform infrared spectroscopy and a high-performance liquid chromatography-diode array detector-mass spectrometry. The obtained results revealed using blank linen and sheep wool dyed with weld dye (beige color) and indigo natural dye (brown color). Beige and brown yarns were used in weaving the fragment background using the tapestry structure, and the beige wefts were used in the additional embroidery stitches. The used gel-confined fluid Nano restore Cleaning ®Polar fluid confined in Nano restore Gel ®Peggy was capable of the safe removal of the adhesive form the fragment, which was then washed and supported by a new linen fabric using thin needles and dyed silk threads. The fragment was finally re-exhibited in a standard museum display.

Keywords:

Polyurethane adhesive, Coptic textiles, Nano restore, Gel cleaning, Archaeological conservation.

INTRODUCTION

Adhesives are nonmetallic substances capable of joining materials by surface bonding (adhesion). It is a generic term that covers other common terms, such as gums, glue, paste, bonding agent, etc. Adhesion is one of the oldest technologies through history. In ancient Egypt, animal glues were well-known in wood furniture and other life works. In ancient Rome, flour and casein-based adhesives were used. Wood rosin was well-known in China, as was the natural Arabic rubber and gum used in South America and Asia. With the developments in chemistry in the early1900s, the technology of variant adhesives such as phenolic, epoxy, urea, melamine, and cyanoacrylates resins began to gradually supersede the old natural adhesives[1, 2].

Synthetic resins were not only used in the adhesion of ancient materials, but also were used in creating and crafting the heritage collections in the 20th century. They have become an integral parts of the museum collections everywhere. Moreover, synthetic resins are used in a wide

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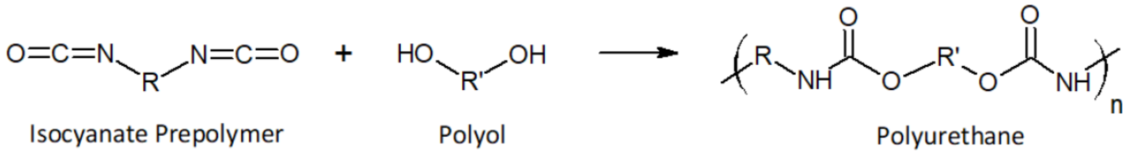
variety of forms in heritage collections, especially as packing and storage materials. Cellulose nitrate, cellulose acetate, nylon, polystyrene, rubber, polypropylene, polyethylene, polyvinyl chloride, and polyurethane are the most common types of polymers identified in many heritage collections [3-5]. Polyurethanes (PU) are synthesized resins composed of polymerized urethane, the products of a chemical reaction between an isocyanate (pre polymer) and a hydroxyl group (polyol), as shown in the following equations [6, 7]. They have become very valuable to the industry of adhesives through recent decades. They are commonly used in a wide range of applications, such as fibers, adhesives, coatings, elastomers, flexible, and rigid foams [1].



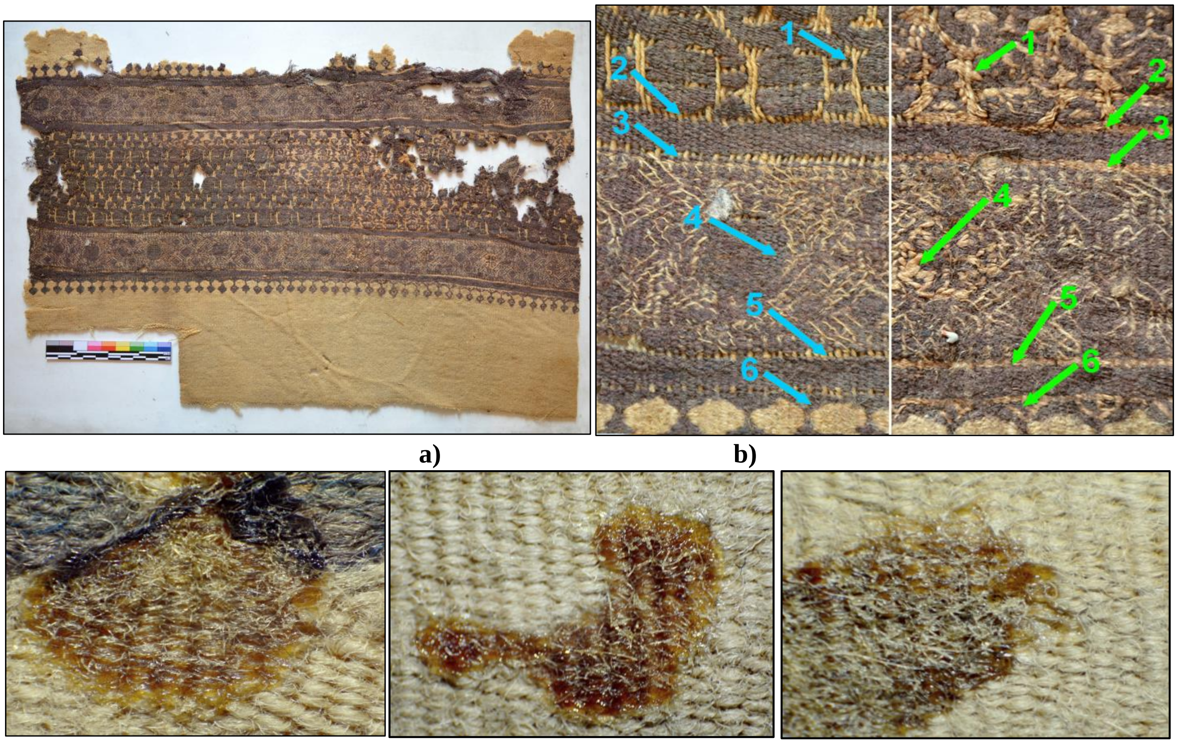
In addition to its using in crafting heritage collections in the 20th century [5], PU was used in different applications of heritage collections restoration. It was used as a coating for the outdoor painted sculptures [8] and a protecting material of stone surfaces [9]. It was also used as lining adhesive for oil paintings on both cotton and linen fabrics, it proved a significant ability to resist deterioration factors, thanks to its penetration into the textile fibers [10]. Moreover, the make-up sponges made of PU are the most efficient and safe materials used in the cleaning of different painted surfaces [11]. PU resin is the most widely used material as an adhesive for joining components in different objects, thanks to its resistant to water, petrol, oils, and grease, and to its flexibility, high strength, versatile properties, and suitable behavior at different temperature degree [12, 13].

The problem of the research is corresponding to the case-study object which was previously adhered by PU adhesive. During the conservation of the case-study, the PU adhesive was appeared as a difficult drawback to come over, due to its durability and resistance to most traditional cleaning agents. It was not so easy to be removed, especially in this case it was applied to textile, as a flexible material. This case needs a special methodology and experience to safely remove the PU adhesive. Literature has no focus on this attractive area of research. Many articles focused on new technologies for the removal of many kinds of soiling matters from the surfaces of both mural and oil paintings [14-18], but, up to the author's knowledge, only an article focused on the removal of PU old varnish from the surface of historic oil painting [19]. That's why the present study introduces a pioneer experimental and applied work in the removal of PU from the archaeological textiles, especially the woolen ones. It will point out the most efficient and suitable technique used in the removal of PU and preserving the textile and dye at the same time.

Organic solvents were the most common agents in the removal of varnishes, adhesives, grime, stains, dirt, and other soiling matters during the 19th and 20th centuries. But these solvents usually cause damage to the cleaned objects if they diffused into the objects [20, 21], that's why a new methodology of using solvents in a form of gel was introduced by wolbers in 1990 to reduce the diffusion of solvents into the cleaned objects[22]. Later, the technological developments introduced the Nano gel materials, to ensure more efficiency and less damage to the cleaned object. Many acidic and alkaline recipes were used to produce a gel matrix for the removal of aged resins upon the painted surfaces. Other articles successfully applied some new formula of Nano gels and organic solvents [14-18], the methodology followed by the present study to remove the PU adhesive form woollen mock-ups, then, remove it from the archaeological case-study textile fragment according to the ideal results obtained from the in-vitro experiments.

The case-study object (Fig.1a) is a Coptic textile fragment, with a museum record no. 323/6 in the Agricultural Museum in Egypt. It measures 46×32 cm. According to its stylistic designs, ornaments, colors, and weaving technique, the fragment is dated to the 3rd-4th century. The fragment has three cross-sectional decorative strips; two upper and lower narrow strips, and intermediate wide one. The two upper and lower ones have a substrate of brown and beige wefts embroidered with beige yarns, depicting geometrical alternating designs. The intermediate wide strip has brown and beige wefts used in depicting modified (abstract) human-like ornaments. The beige wefts in the left side are almost missing, especially in the intermediate strip, while in the right side they are completely available (Fig.1b).

The main deterioration feature in the fragment, which represents the problem of the present study, is the previously PU adhesive stuck to the fragment from reverse to obverse. (Fig. 1c-h). This PU adhesive is spotting variant beige areas in the fragment, which is made of woolen wefts. That's why the study will be divided into two sections: (a) the experimental section includes using woolen mock-ups brushed with PU resin, then cleaned with different techniques after accelerated aging. (b) the applied section includes the removal of PU adhesive from the case-study fragment, using the most effective and suitable technique obtained from of the experimental results, after identifying the fragment materials, mainly fibers and dyes.



a) b)

c) d) e)

f) g) h)

Figure (1): a. the case-study fragment. b. missing wefts in the left side, and the similar wefts available in the right side. c., d., e. f. g. h. graphs and micro-graphs of PU stuck to the fragment

MATERIALS AND METHODS

PU resin

The study used PU resin (El-Nasr Pharmaceutical and Chemical Co., ADWIC, Egypt). The resin results from the reaction between methylene diphenyl diisocyanate and polyester. It was used as it is delivered without dilution.

Woolen fabric

A pure sheep woolen fabric (Wools Golden Tex Company, Egypt) was used in the experimental section of the present study. The color of the fabric was natural creamy, not dyed. The weave structure was plain 1/1. The number of yarns was 44/cm in both warps and wefts. The woolen fabric was immersed and stirred in a water bath contains distilled water and alkali soap for 30 minutes at 50°C., then it was repeatedly rinsed in fresh distilled water, then dried in an electric oven at 50°C (ASTM- D629, 1999). Each sample was cut to 3×3 cm strip, then brushed with 1 ml of PU adhesive, and kept till dryness at 20°C for 72 hours [23, 24].

Accelerated aging

The PU-brushed woolen samples were exposed to the accelerated natural aging outdoor at an angle of 45° to the horizon for 12 weeks from April to June in Damietta, Egypt. The temperature range was 16-32°C during the days and nights. The relative humidity range was 50-92% [25]. The aged PU-brushed woolen samples (here and after called APS) were kept for 72 hours at room temperature before treatment.

Chemicals and cleaning agents

- Sodium tetraborate dehydrate "Borax" (Sigma-Aldrich), polyvinyl alcohol PVAL (Sigma-Aldrich), ethanol (Merck), and distilled water. The dispersion was prepared by dissolving 0.4 wt% of borax in ethanol and distilled water (1:1). PVAL was added (2 wt%) and dissolved by stirring and heating the mixture at 90°C for 3 hours. The dispersion was kept at 20°C for 2 hours till gelling [26] (here and after called F1).
- Nano restore Cleaning ®Polar coating B (CSGI lab, Department of Chemistry, University of Florence, Italy), a nanostructured fluid containing an alcohol ethoxylate nonionic surfactant and a mixture of methyl ethyl ketone (MEK) and 2-butanol. It was confined in Nano restore Gel® Peggy 5 (CSGI lab, Department of Chemistry, University of Florence, Italy) (here and after called F2).
- Nano restore Cleaning ®Polar coating G (CSGI lab, Department of Chemistry, University of Florence, Italy), a nanostructured fluid containing an alcohol ethoxylate nonionic surfactant and a mixture of methyl ethyl ketone (MEK), 2-butanol, ethyl acetate, and propylene carbonate. It was confined in Nano restore Gel® Peggy 5 (here and after called F3) [27, 28].

Each technique (F1, F2, F3) was applied upon the APS (here and after called APS-F1, APS-F2, APS-F3) at room temperature for 20 minutes then removed. The fabric was then gently rinsed with ethanol [26, 29].

Stereo Microscope

The study used a stereo microscope SM (SMZ800, Nikon) coupled with a digital camera (Canon EOS 700D) to physically assay the efficiency of the examined techniques used in the removal of PU adhesive form woolen mock-ups (APS-F1, APS-F2, APS-F3). It will be also used to characterize the weave structure and the deterioration forms in the archaeological fragment.

Color Spectrophotometer

The study used a colorimeter (Optimatch 3100 Colour Spectrophotometer) using the CIE L*a*b* colour system to assess the effects of the three techniques (F1, F2, F3) on the samples' color to point out if any colour changes correspond to using the different techniques on mock-ups (APS-F1, APS-F2, and APS-F3). L* measures darkness/lightness axis, a* measures red/green axis, b* measures yellow/blue axis, $\Delta L^* = (L^*_1 - L^*_2)$, $\Delta a^* = (a^*_1 - a^*_2)$, and $\Delta b^* = (b^*_1 - b^*_2)$ express the difference between two measures in each axis, before and after PU removal. $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ [30, 31].

FTIR

To characterize the efficiency of the examined techniques in the removal of the PU resin, Fourier transform infrared spectroscopy (FTIR) (Nicolet 380, Thermo Fisher Scientific, Waltham, USA) was used. Four samples were analyzed: (APS, APS-F1, APS-F2, APS-F3). FTIR-ATR (Nicolet 8700, Thermo Fisher Scientific, Waltham, USA) equipped with an MCT detector was used to identify the fibers' type(s) in the case-study fragment. The spectra in both instruments were collected at room temperature in the spectral range from 4000 to 500 cm^{-1} with a 4 cm^{-1} resolution. The analysis was controlled by Omnic software (Thermo Fisher Scientific, Waltham, USA).

HPLC-DAD-MS

A high-performance liquid chromatography-diode array detection-mass spectrometry (HPLC-DAD-MS) was used to identify the beige and brown dyes. The study used an HPLC system (Agilent 1200 series system, Agilent Technologies, Germany), coupled with MS (Agilent Q-TOF MS 6538, Santa Clara, CA) operated in a negative mode. The analytics were monitored with DAD and MS online connected and characterized by retention times, UV-vis, and mass spectra. The extracts' components were separated on a column (ZORBAX SB--C18, 4.6×150 mm, 3.5µm, Agilent Technologies, USA). A gradient of methanol/acetonitrile and water was used to ensure optimal resolution for the different chemical compounds. Agilent MassHunter software (B.07.05) was used.

Before analysis, the dyes were extracted from 0.2 mg micro-fibers using an ultrasonic bath for 1 hour (4×15 min) at ≤ 40°C using 500 µL of a solution containing 0.4 M hydrofluoric acid /methanol /acetonitrile/ DMSO (2:1:1:1, v/v/v/v). after that it was centrifuged at 9000 rpm for 5 minutes, and the supernatants evaporated almost to dryness under a stream of nitrogen at room temperature. The residues were dissolved in 300 µL of ACN/MeOH/DMSO (1:1:1, v/v/v), out of which 20 µL was injected into the HPLC column [32, 33]. The mobile phase comprised: (A) 0.1% formic acid in water, (B) 0.1% formic acid in ACN/MeOH (1:1; v/v), isocratic gradient of 90A + 10B for 0-3 min, 0A + 100B for 20-30 min. The elution was performed at 0.5 mL/min flow rate and 20 µL injection volume. For the MS; drying gas flow (12 L min^{-1}), drying gas temperature (300C°), nebulizer pressure (50 psi), ionization voltage (4 kv), acquisition in production scan (mass range 50-650 m/z, CE 25 eV).

RESULTS

Macroscopic and microscopic results

The obtained graphs and micro-graphs (Fig. 2) show the woolen mock-ups before and after the removal of PU using the three examined techniques. The results revealed that F3 is the most effective technique in the removal of PU resin. The APS-F3 cleaned sample returned clean as no PU resin occurred. F2 also revealed good results with a very little amount of remaining PU. F1 is not so bad, but not acceptable in comparison with F2 and F3.

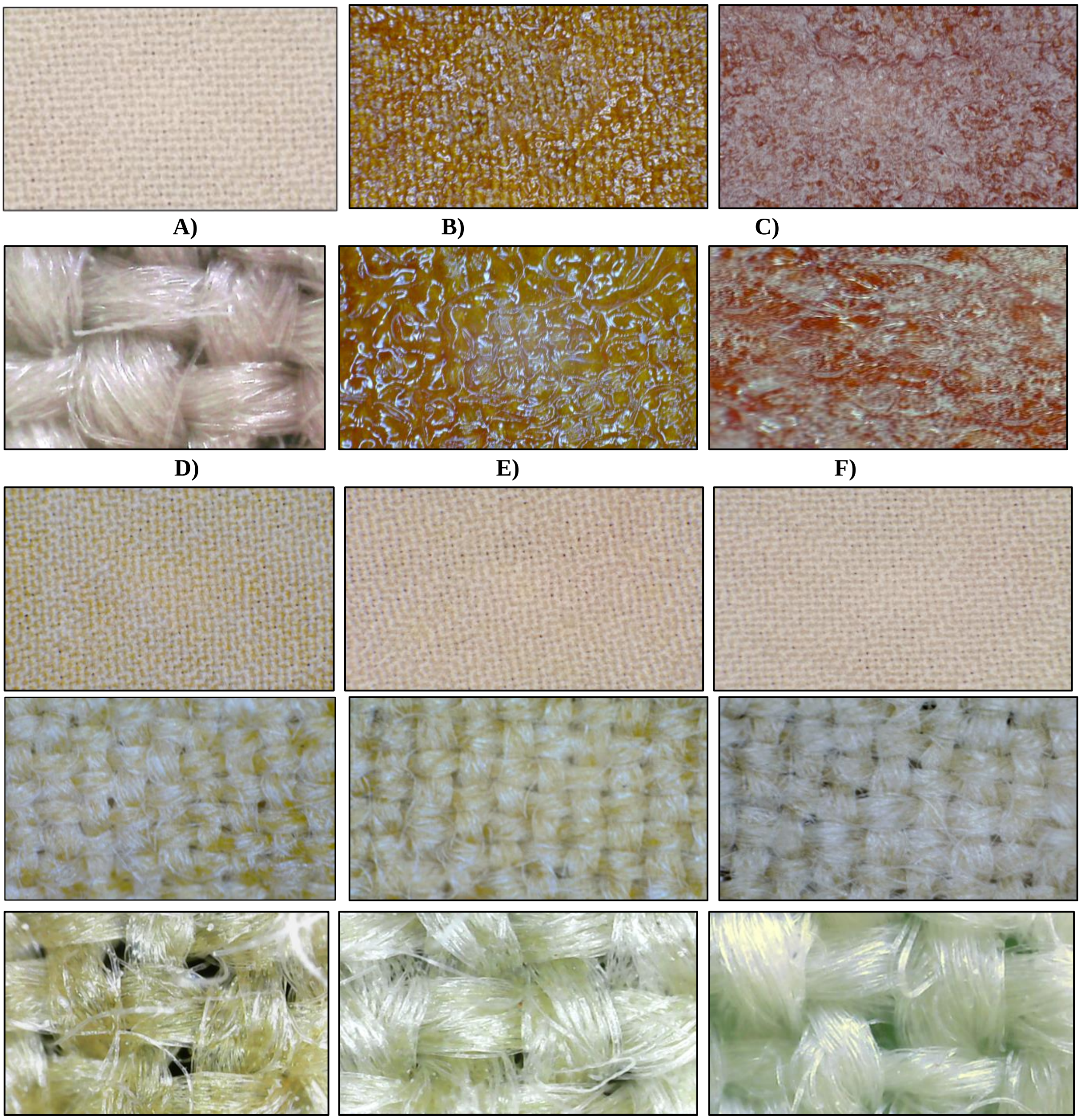


Figure (2): graphs and SM micro-graphs of the samples before and after PU removal, a. the pure wool, b. the PU-brushed samples, c. the PU-brushed samples after aging (APS), d. graph and 2 SM micro-graphs of APS-F1, e. graph and 2 SM micro-graphs of APS-F2, f., graph and 2 SM micrographs of APS-F3.

Colorimetric and weight measurements

The colorimetric results (Table 1, Fig. 3a) of the cleaned samples, compared to the reference one (aged PU-brushed woollen sample, APS) revealed that the maximum ΔE changes were in APS-F3. This change is attributed to lightness increase (ΔL=+26.6), and redness decrease (Δa=-4.28). The minimum ΔE changes were in APS-F1. This change is attributed to the little increase in lightness (ΔL=+17.24), and yellowness increase (Δb=+11.65) [31, 34]. Variant changes in the mock-ups weight occurred (Table 1, Fig. 3b) thanks to the variant efficacy of the F1, F2, and F3 in the removal of PU. F3 showed the best results. The weight of the cleaned samples (APS-F3) is almost similar to the weight of the pure woollen samples, i.e. no PU residues in the fibres. F1 and F2 weren't able to completely remove the PU like F1 results.

Table (1): The colorimetric measurements and weight changes of the samples before and after cleaning

	Colorimetric measurements				**Weight (gm)**		
	ΔL	**Δa**	**Δb**	**ΔE**	**Pure wool**	**APS Before cleaning**	**APS After cleaning**
APS-	17.24	-1.12	11.65	20.84	2.56	4.28	3.04
APS-	23.2	-1.86	4.23	23.66	2.49	4.45	2.73
APS-	26.61	-4.28	1.71	27.01	2.55	4.32	2.61

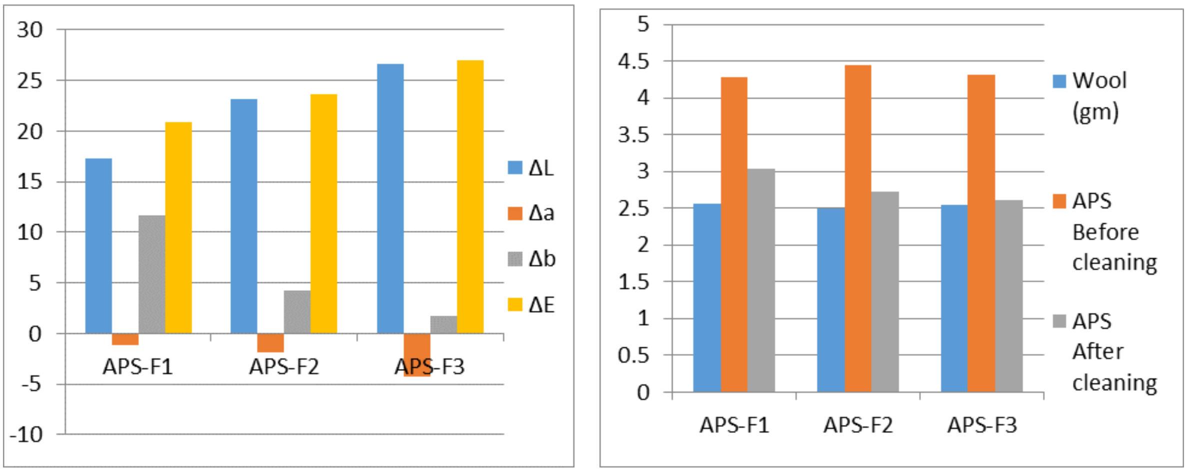


Figure (3): a. Colorimetric measurements. b. weight changes of the samples before and after cleaning

Chemical changes

The FTIR obtained spectra (Fig. 4) revealed that APS is almost a pure PU resin. A strong secondary urethane N=H stretch/NH bonded/N–H stretching vibration band at 3330 cm^{-1} appears only in APS and almost disappeared in the cleaned samples which have broad streching bands of amino-NH and phenolic –OH groups at 3275 cm−1. Absorption at 2930 and 2860 cm−1was corresponding to the νa C-H and νs C-H of aliphatic carbon compounds, both bands were stronger in APS than other cleaned samples. A very strong free C=O stretch at 1725 cm^{-1} is appeared only in APS and turned into a small shoulder in APS-F1, and to a very small shoulder in APS-F2, and almost disappeared in APS-F3, referring to the much amount of PU in

APS, and the small amount in APS-F1 and APS-F1, and almost no PU in APS-F3. The absorption in the three samples (APS-F1, APS-F2, APS-F3) at ~1630, 1515, 1230 cm−1 are corresponding to amide I, amide II, and amide III respectively, referring to the main group in woolen fibers, where these groups disappeared in ASP, but very strong absorption of (O=)C–O–C stretch/Urethane C–O stretch at 1250 cm-1 in the APS appeared [8, 35, 36].

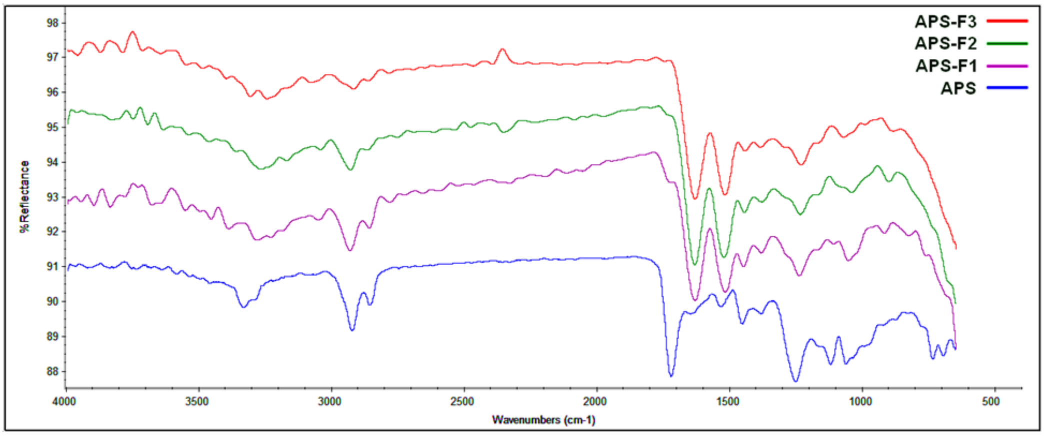


Figure (4): The FTIR spectra of the mock-ups before (APS) and after PU removal (APS-F1, APS-F2, APS-F3)

APPLIED SECTION

Description of the fragment

The captured graphs and micrographs of the handy camera and SM revealed that the details of weave structure are as follows: the technique is a plain tapestry structure (1/1), with embroidery stitching, the number of yarns is 8 warps/cm, and 30 wefts/cm, yarns of warps and wefts are twisted in "S" direction (Fig. 5). Many deterioration forms are affecting the fragment such as dust, stains, tears, missing parts, fragility, and color changes. The main problem of the present study was the adhesive material stuck to the fragment, which represents diffecult drawback to come over (Fig. 1c-h). FTIR spectroscopy was used to identify that adhesive. The obtained results (Fig. 6) revealed that the adhesive material is a PU resin. The urethane N=H stretch/NH bonded/N–H stretching vibration band is identified at 3350 cm^{-1}. The bands va C-H and vs C-H of aliphatic carbon compounds and the free C=O stretch were strong bands at 2930, 2860, 1725 cm−1 respectively. Moreover, a very strong absorption of (O=)C–O–C stretch/Urethane C–O stretch at 1250 cm-1 was identified [8, 35].

A) **B)** **C)**

D) E) F)

Figure (5): Description of the fragment. a. beige and brown woolen wefts. b. beige woolen wefts on a brown substrate. c. blank linen wefts. d., e. plain 1/1 tapestry weave structure in beige and brown wefts. f. the "S" twist direction of yarns.

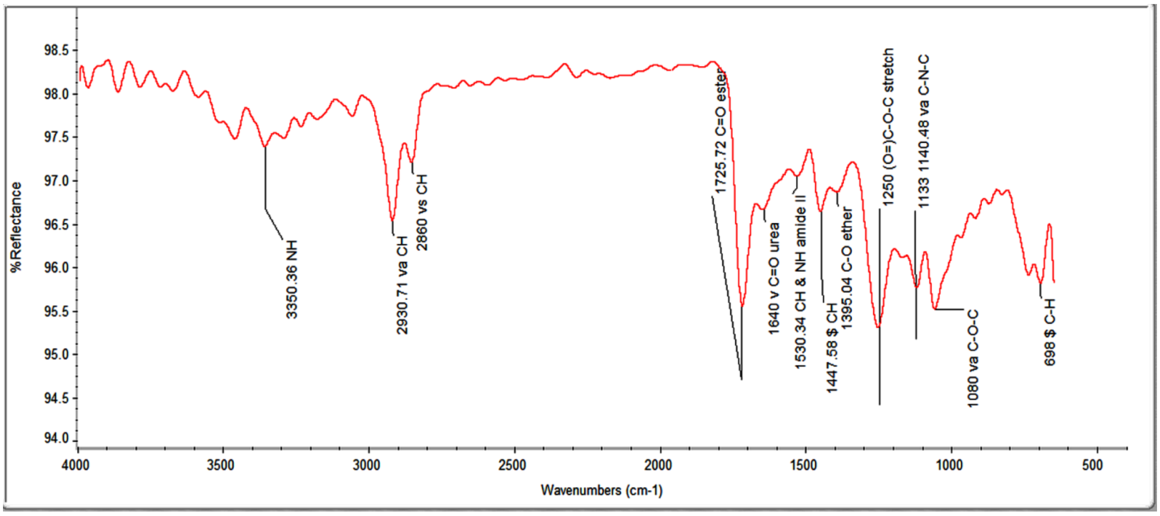


Figure (6): The FTIR spectra of the polyurethane adhesive stuck to the fragment

Identification of fibers and dyes

The obtained FTIR-ATR spectra of the examined fibers (Fig. 7) revealed that the warps (Wp), the beige wefts (BW), and the brown wefts (RW) are from sheep woolen fibers. The peaks at ~1652 cm^{-1}, ~1544 cm^{-1}, ~1235 cm^{-1}, ~1122 cm^{-1}, and ~1070 cm^{-1} refer to -C=O stretching amide I, -NH bending amide II, -N-H & -N-OC mixed vibration amide III, -SO2-S-cysteine dioxide, and -SO-S- cysteine monoxide respectively [36, 37]. The obtained results of the FTIR-ATR spectra of the examined blank embroidery (BE) revealed that it is from linen origin. The bands at ~1315 cm^{-1}, ~1335 cm^{-1}, and ~1370 cm^{-1} are corresponding to the COH and HCC bending vibrations. The bands at ~1430 cm^{-1}, ~1370 cm^{-1}, ~1335 cm^{-1}, and ~1280 cm^{-1} are corresponding to the crystalline phase of cellulose, while the bands at ~900 cm^{-1} are corresponding the amorphous one [38, 39].

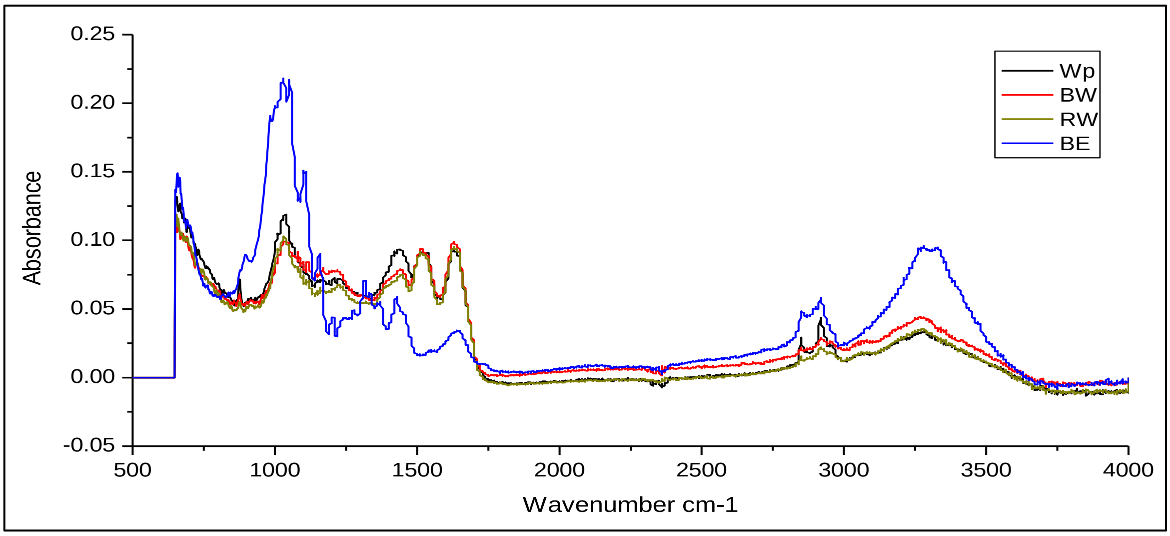


Figure (7): The FTIR spectra of the fragment fibers, revealing that all fibers are woolen except BE is linen

The HPLC-DAD-MS results obtained from examined extracts of both beige and brown woolen wefts (Table 2) revealed that weld dye was identified in the beige fibers, while natural indigo was identified in the brown fibers. Apigenin-C-diglucoside, luteolin-7-O-glucoside, chrysoeriol-O-glucoside, luteolin-4'-O-glucoside, luteolin, apigenin, and chrysoeriol were characterized at 593m/z, 447 m/z, 461 m/z, 447 m/z, 285 m/z, 269 m/z, and 299 m/z respectively at different retention times [40, 41]. Indigotin and indirubin were identified at 261 m/z in tR 19.6 and 20.5 min. respectively. Both indigotin and indirubin compounds are characteristic of indigo/woad dyes, but indigo is suggested [42].

Table (2): Results of the HPLC-DAD-MS for the beige and brown dyes' extracts

Sample	tR (min)	[M–H]−	Detected compounds	Chemical formula	Dye source
Beige	9.7	593	Apigenin C diglucoside	$C_{27}H_{30}O_{15}$	Weld (Reseda luteola)
	10.6	609	Luteolin 3,7' O diglucoside	$C_{27}H_{30}O_{16}$	
	12.3	461	Chrysoeriol O glucoside	$C_{22}H_{22}O_{11}$	
	12.9	447	Luteolin-4'-O-glucoside	$C_{21}H_{20}O_{11}$	
	14.3	285	Luteolin	$C_{15}H_{10}O_{6}$	
	15.4	269	Apigenin	$C_{15}H_{10}O_{5}$	
	15.6	299	Chrysoeriol	$C_{16}H_{12}O_{6}$	
Brown	19.6	261	Indigotin	$C_{16}H_{10}N_{2}O_{2}$	Indigo (Indigofera
	20.5	261	Indirubin	$C_{16}H_{10}N_{2}O_{2}$	

Cleaning the fragment

According to mentioned above deterioration forms, especially dust, different soiling matters, fragility, tears, and missing parts, conservation procedures for the fragment have to be planned. The conservation plan started with the mechanical removal of dust and different soiling matters using a soft handy brush and vacuum cleaner. A scalpel was used to gently attenuate the layer of PU resin as possible to facilitate the chemical removal of the residues [43]. Due to its best results in the experiments, F3 (Nano restore Cleaning ®Polar coating G confined in Nano restore Gel® Peggy 5 was applied upon the APS for 20 minutes then removed. The fabric was then gently rinsed with ethanol (Fig. 8a-c) [26, 29, 43].

After the removal of the PU resin, the fragment was prepared for the washing process. It was a very important step because of the much amount of dust and soiling matters in the fragment. The fragment was laminated with a tulle net and humidified with a water sprayer. A water bath of 1% neutral soap in distilled water was prepared. The fragment was soaked in the bath for 20 minutes, including a soft handy pressure using a sponge. The water in the bath was drained and replaced with a fresh one for re-washing as previously mentioned. The water of the bath was drained and replaced with afresh one for rinsing several times to ensure that no soap residues. The fragment was then dried in the room temperature after using towels to absorb the excess water to accelerate the dryness (Fig. 8d, e) [43, 44].

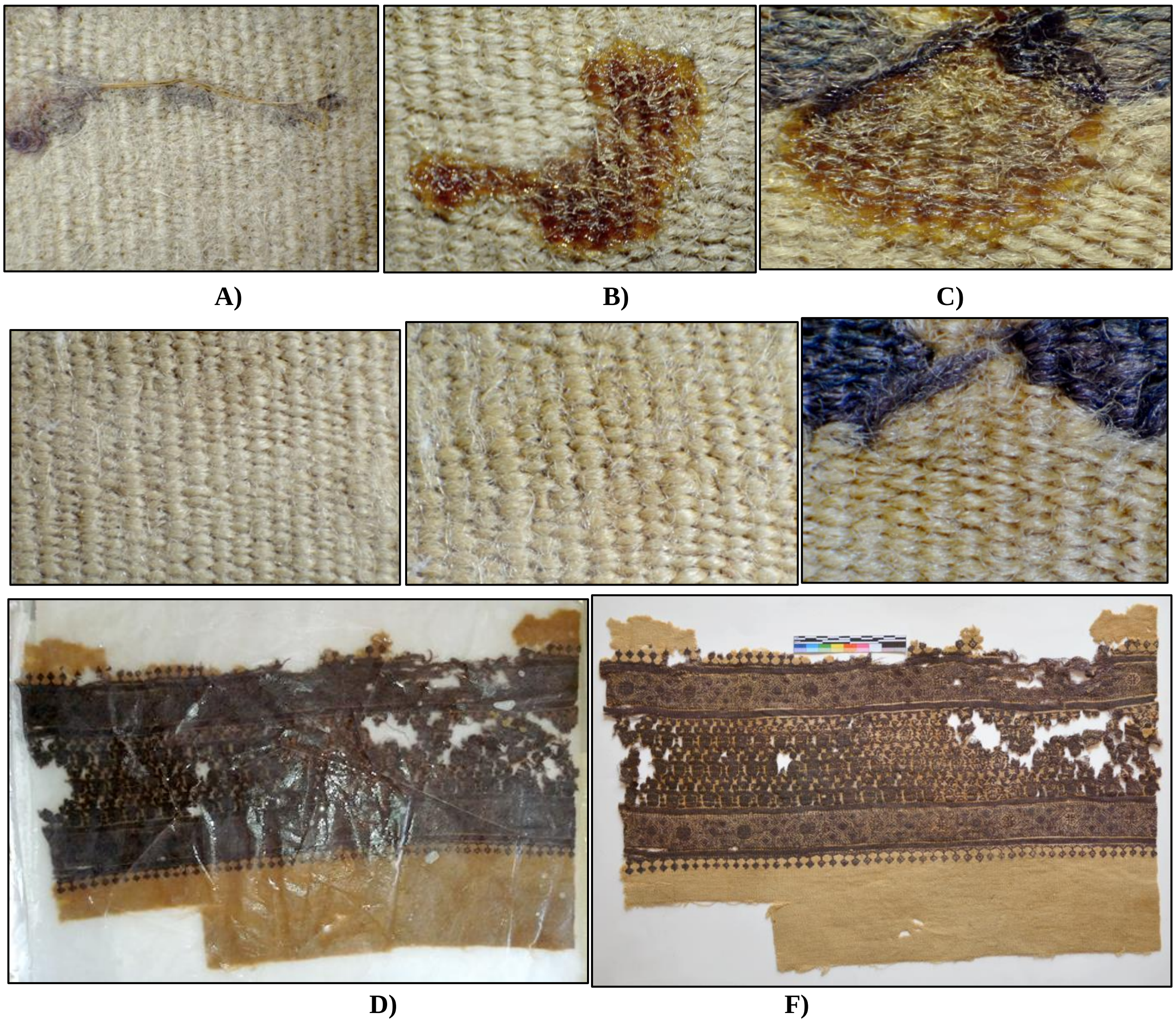
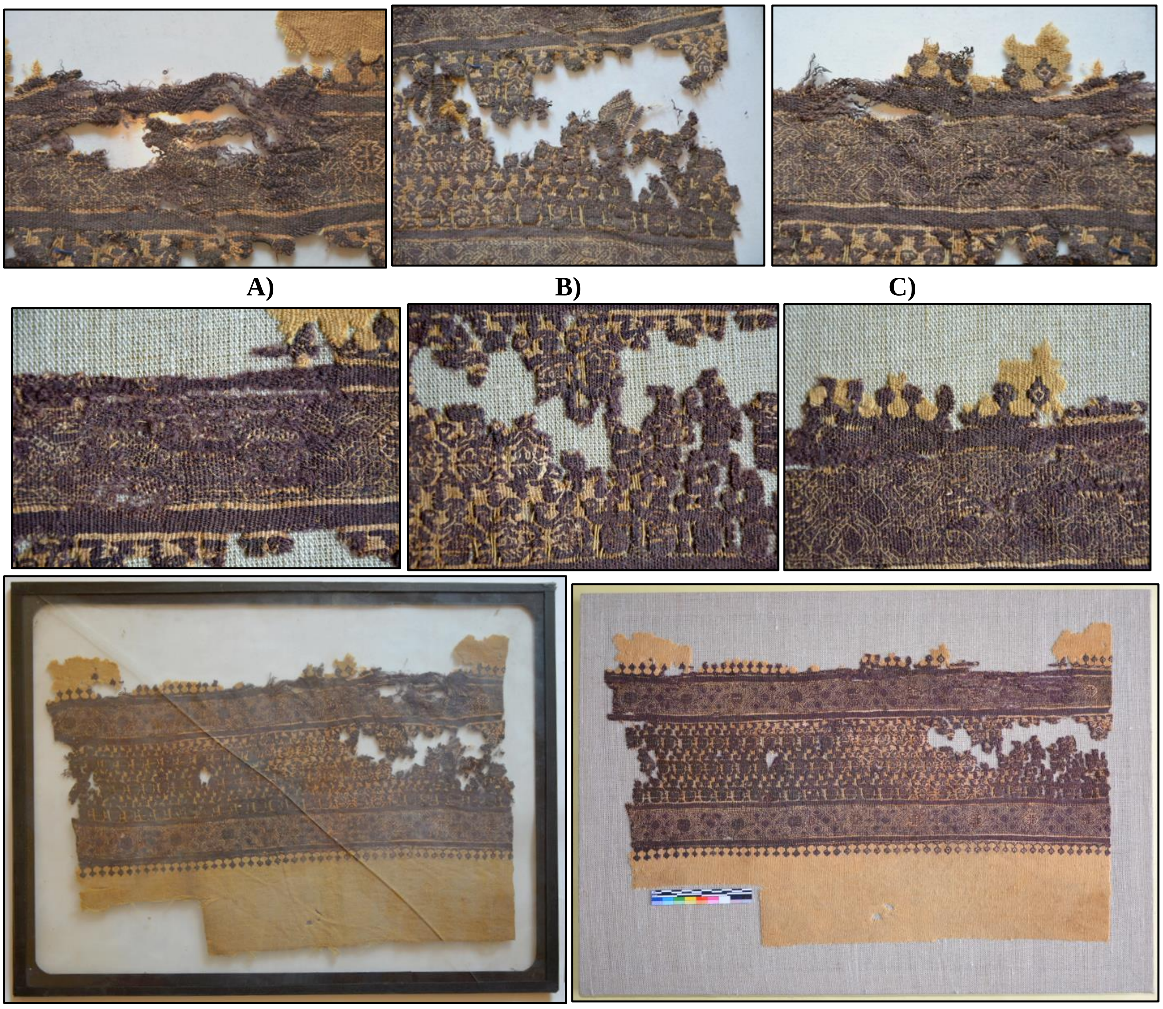


Figure (8): Cleaning the fragment. a., b., c. different spots of PU before and after removal by F3, d. washing the fragment, e. drying the fragment after washing.

Supporting the fragment

As mentioned above, the fragment is suffering from many tears, cuts, missing parts, brittleness, and fragility. That's why it was necessary to support the fragment by on a new fabric. Linen textile was selected, thanks to its suitability to this procedure. A 55x40 cm wooden frame was prepared and painted with a fresh PU varnish and left to dry. A 65x50 cm linen fabric was prepared by washing it in boiling water for 30 minutes, then dried, ironed, and stretched upon the wooden frame using pins. The fragment was then stitched on the new linen support using beige and brown silk threads and a soft needle. The stitching procedure started from inner to the outer parts in longitudinal and cross-sectional directions. The tears and missing parts were also stitched using the basting and herringbone stitches [43, 45]. Finally, the fragment was redisplayed in the showcase after finalizing the conservation plan (Fig. 9).



A) B) C)

D) F)

Figure (9): Supporting the fragment. a., b., c. some parts in the fragment before and after supporting, d., e. the fragment before and after treatment.

DISCUSSIONS

The case-study object is a Coptic textile fragment exhibited in the Agricultural Museum in Egypt. According to literature and stylistic features, it was dated to the3rd-4th century. The decorative elements are showed an ideal example of the Coptic style in the time of early Christianity. It appeared as a part of a Coptic textile tunic cut by a looter or even an amateur archaeologist in the past, due to the straight and sharp cut, which almost was intentionally done by a sharp tool [46, 47].

The worthy mentioning and confusing matter is the longitudinal asymmetric ornaments in the right and left sides. The beige wefts in the left side are almost missing, especially in the intermediate strip, while in the right side they are completely available. Through the deep focus and research in art and history of Coptic textiles, the author can confirm that these missing wefts aren't missing, but the fragment itself is uncompleted. The craftsman completed the main body of the human-like shapes using brown wefts in both right and left sides, after that he started weaving the details from the right side to the left one, but he stopped. The reason is unknown, but it could be attributed to the persecution and social circumstances the ancient Copts suffered from during the time of early Christianity [46, 48].

The main problem of the present study was the PU adhesive stuck to the fragment. It is probably a soiling adhesive from the construction and renovation works in the museum a few years ago, or, it might be an old treatment by an amateur conservator to adhere the fragment to a substrate. The second reason is more acceptable, especially the different spots of PU adhesives were identified in the fragment reverse, not obverse. Using the woolen fibers dyed with weld was so common in Coptic art, but using linen fibers as wefts and as embroidery threads interlacing the beige background wasn't so common [41, 42].

Indigotin and indirubin were indentified in the brown color fibers. Both compounds correspond to natural indigo and woad. The author attributes both to indigo, which was very common in ancient Egyptian textile art, on the contrary, woad wasn't [42, 49, 50]. Regarding the brown color, the microscopic examination showed it is a reddish-blue one, confirming using the blue natural indigo dye. This visible color change is attributted to the environmental deterioration factors, especially light and temperature. Other deterioration forms such as dust, stains, fragility, tears, missing parts, etc., are corresponding to these factors, in addition to other natural and human factors affecting the fragment before or after the exhibition in the museum [19, 51].

The results of the in-vitro experiments conducted on APS using F1, F2, and F3 revealed the best efficacy of F3 in the removal of PU resin. Each assessment confirmed this result. The APS-F3 showed cleaned fibers either in the handy cam photos or in the SM micrographs. The chemical assessment by FTIR revealed that the APS-F3 spectrum is almost as the same of the wool spectrum, i.e. no PU resin identified in comparison to the APS spectrum, which is almost as the same as PU spectrum. The weight of all samples before and after PU removal showing a significant decrease in APS-F3, i.e. all PU resin was almost removed, while a little decrease was noticed in APS-F1 weight, i.e. a significant amount of PU wasn't removed. These results were also confirmed through the ΔE measurements. According to these experimental results, APS-F3 was used to clean the PU resin from the case-study fragment.

CONCLUSION

- The case-study object is classified as a Coptic textile fragment dates to the 3rd-4th century. It is suggested as a part of tunic.
- The fragment is composed of beige woolen warps, beige woolen wefts, brown woolen wefts, and blank linen wefts, weaved in tapestry technique and embroidery stitches.
- The beige woolen warps and wefts are dyed with weld dye. The brown woolen wefts are dyed with natural indigo dye.
- The fragment suffers from many deterioration forms, such as color changes, dust, stains, soiling matters, brittleness, tears and missing parts, caused by light, temperature, humidity, air pollutants, human factors, etc. affected the fragment in the past, or during the display time in the museum.
- A polyurethane adhesive stuck to the fragment reverse is spotting variant areas in the fragment. It wasn't so easy to be removed.

- Nanorestore Cleaning®Polar coating G, a nanostructured fluid containing an alcohol ethoxylate nonionic surfactant and a mixture of methyl ethyl ketone (MEK), 2-butanol, ethyl acetate, and propylene carbonate, confined in Nanorestore Gel® Peggy 5 (F3) was proven as the most effective and suitable examined technique.
- The polyurethane adhesive was cleaned from the fragment using F3. Other essential conservation methodologies were applied to the fragment till the museum display in a standard.

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REFERENCES

1. Gierenz, G.; Karmann, W., Adhesives and adhesive tapes. John Wiley & Sons: 2008.
2. Bekhta, P.; Krystofiak, T.; Proszyk, S.; Lis, B., Adhesion strength of thermally compressed and varnished wood (TCW) substrate. Progress in Organic Coatings **2018,** 125, 331-338.
3. Yvonne, S., Conservation of Plastics: materials science, degradation and preservation. Butterworth-Heinemann, Slovenia: 2008.
4. Coughlin, M.; Seeger, A. M., You collected what?! The risks and rewards of acquiring cellulose nitrate. Proceedings of plastics-looking to the future and learning from the past **2007**, 119-124.
5. van Aubel, C.; de Groot, S.; van Keulen, H.; Snijders, E., Digging into the past of nature carpets. The evaluation of treatments on artworks by Piero Gilardi made from polyurethane ether foam. Journal of Cultural Heritage **2019,** 35, 271-278.
6. Altafim, R. A. C.; Murakami, C. R.; Claro Neto, S.; Araújo, L. C. R.; Chierice, G. O., The effects of fillers on polyurethane resin-based electrical insulators. Materials Research **2003,** 6 (2), 187-191.
7. Trovati, G.; Sanches, E. A.; Neto, S. C.; Mascarenhas, Y. P.; Chierice, G. O., Characterization of polyurethane resins by FTIR, TGA, and XRD. Journal of Applied Polymer Science **2010,** 115 (1), 263-268.
8. Defeyt, C.; Langenbacher, J.; Rivenc, R., Polyurethane coatings used in twentieth century outdoor painted sculptures. Part I: comparative study of various systems by means of ATR-FTIR spectroscopy. Heritage Science **2017,** 5 (1), 11.
9. Licchelli, M.; Marzolla, S. J.; Poggi, A.; Zanchi, C., Crosslinked fluorinated polyurethanes for the protection of stone surfaces from graffiti. Journal of Cultural Heritage **2011,** 12 (1), 34-43.
10. Mohie, M. A.; Ali, N. M.; Issa, A. A. A. B.; Alkareem, A. A., A NEW METHOD OF LINING OIL PAINTINGS USING POLYURETHANE. Mediterranean Archaeology and Archaeometry **2019,** 19 (2), 9-21.
11. Daudin-Schotte, M.; Bisschoff, M.; Joosten, I.; van Keulen, H. In Dry cleaning approaches for unvarnished paint surfaces, New Insights into the Cleaning of Paintings: Proceedings from the Cleaning 2010 International Conference, Universidad Politécnica de Valencia and Museum Conservation Institute, 2013; pp 209-220.

12. Cao, C. L.; Cheng, J.; Liu, X. D.; Wang, R.; Zhang, J. Y.; Qu, J.; Jaeger, U., Study of properties of one-component moisture-curable polyurethane and silane modified polyurethane adhesives. Journal of Adhesion Science and Technology **2012,** 26 (10-11), 1395-1405.
13. Szycher, M., Szycher's handbook of polyurethanes. CRC press: 1999.
14. Al-Emam, E.; Motawea, A. G.; Janssens, K.; Caen, J., Evaluation of polyvinyl alcohol–borax/agarose (PVA–B/AG) blend hydrogels for removal of deteriorated consolidants from ancient Egyptian wall paintings. Heritage Science **2019,** 7 (1), 22.
15. Kanth, A.; Pandey, S. C., Optimizing the rigidity of Gellan and Agar gels for cleaning sensitive acrylic emulsion painted surfaces. International Journal of Conservation Science **2018,** 9 (3).
16. Carretti, E.; Dei, L.; Weiss, R. G.; Baglioni, P., A new class of gels for the conservation of painted surfaces. Journal of cultural heritage **2008,** 9 (4), 386-393.
17. Bakalarou, A.; Theodorakopoulos, C., Cleaning of water-gilded surfaces using hydro-and solvent-gels. e-conservation magazine **2013,** 25, 89-105.
18. Baglioni, P.; Berti, D.; Bonini, M.; Carretti, E.; Dei, L.; Fratini, E.; Giorgi, R., Micelle, microemulsions, and gels for the conservation of cultural heritage. Advances in Colloid and Interface Science **2014,** 205, 361-371.
19. Elsayed, Y., Conservation Of A Historic Panel Oil-painting Coated By An Ancient Varnish Layer. Shedet **2019,** 6, 238-256.
20. Phenix, A., The swelling of artists' paints in organic solvents. Part 2, Comparative swelling powers of selected organic solvents and solvent mixtures. Journal of the American Institute for Conservation **2002,** 41 (1), 61-90.
21. Galatis, P.; Boyatzis, S.; Theodorakopoulos, C., Removal of a synthetic soiling mixture on mastic, shellac & Laropal® K80 coatings using two hydrogels. E-Preservation Sci **2012,** 9, 72-83.
22. Wolbers, R., Cleaning painted surfaces: aqueous methods. 2000.
23. Petrie, E. M., Handbook of adhesives and sealants. **2000**.
24. Yong-hua, R.; Bian-xia, L.; Xiao-ning, S., Research on the Aging of Natural Fiber Textiles. Advances in Biomedical Engineering **2012,** 9, 1.
25. Wu, Y. C.; Huang, C. M.; Li, Y.; Zhang, R.; Chen, H.; Mallon, P. E.; Zhang, J.; Sandreczki, T. C.; Zhu, D. M.; Jean, Y. C., Deterioration of a polyurethane coating studied by positron annihilation spectroscopy: Correlation with surface properties. Journal of Polymer Science Part B: Polymer Physics **2001,** 39 (19), 2290-2301.
26. Carretti, E.; Natali, I.; Matarrese, C.; Bracco, P.; Weiss, R. G.; Baglioni, P.; Salvini, A.; Dei, L., A new family of high viscosity polymeric dispersions for cleaning easel paintings. Journal of Cultural Heritage **2010,** 11 (4), 373-380.
27. Mastrangelo, R.; Montis, C.; Bonelli, N.; Tempesti, P.; Baglioni, P., Surface cleaning of artworks: structure and dynamics of nanostructured fluids confined in polymeric hydrogel networks. Physical Chemistry Chemical Physics **2017,** 19 (35), 23762-23772.
28. Baglioni, P.; Chelazzi, D.; Giorgi, R., Nanotechnologies in the Conservation of Cultural Heritage: A compendium of materials and techniques. Springer: 2014.
29. Bonelli, N.; Poggi, G.; Chelazzi, D.; Giorgi, R.; Baglioni, P., Poly (vinyl alcohol)/poly (vinyl pyrrolidone) hydrogels for the cleaning of art. Journal of colloid and interface science **2019,** 536, 339-348.

30. Atodiresei, G. V.; Sandu, I. G.; Tulbure, E. A.; Vasilache, V.; Butnaru, R., Chromatic characterization in CieLab system for natural dyed materials, prior activation in atmospheric plasma type DBD. Revista de Chimie **2013,** 64 (2), 165-169.

31. Schanda, J., Colorimetry: understanding the CIE system. John Wiley & Sons: 2007.

32. Witkowski, B.; Ganeczko, M.; Hryszko, H.; Stachurska, M.; Gierczak, T.; Biesaga, M., Identification of orcein and selected natural dyes in 14th and 15th century liturgical paraments with high-performance liquid chromatography coupled to the electrospray ionization tandem mass spectrometry (HPLC-ESI/MS/MS). Microchemical Journal **2017,** 133, 370-379.

33. Otłowska, O.; Ślebioda, M.; Kot-Wasik, A.; Karczewski, J.; Śliwka-Kaszyńska, M., Chromatographic and Spectroscopic Identification and Recognition of Natural Dyes, Uncommon Dyestuff Components, and Mordants: Case Study of a 16th Century Carpet with Chintamani Motifs. Molecules **2018,** 23 (2), 339.

34. Foster, D. H., Color appearance. The Senses: A Comprehensive Reference, Vol. 2, Vision II **2008**, 119-132.

35. Mitchell, G.; France, F.; Nordon, A.; Tang, P. L.; Gibson, L. T., Assessment of historical polymers using attenuated total reflectance-Fourier transform infra-red spectroscopy with principal component analysis. Heritage Science **2013,** 1 (1), 28.

36. Odlyha, M.; Theodorakopoulos, C.; Campana, R., Studies on woolen threads from historical tapestries. AUTEX Research Journal **2007,** 7 (1), 9-18.

37. Hofmann-de Keijzer, R.; van Bommel, M. R.; de Keijzer, M., Coptic textiles: Dyes, dyeing techniques and dyestuff analysis of two textile fragments of the MAK Vienna. In Methods of Dating Ancient Textiles of the 1st Millennium AD from Egypt and Neighbouring Countries, Lannoo Publishers: Antwerp, 2007; pp 214–228.

38. Proniewicz, L. M.; Paluszkiewicz, C.; Wesełucha-Birczyńska, A.; Majcherczyk, H.; Barański, A.; Konieczna, A., FT-IR and FT-Raman study of hydrothermally degradated cellulose. Journal of Molecular Structure **2001,** 596 (1-3), 163-169.

39. Garside, P.; Wyeth, P., Identification of cellulosic fibres by FTIR spectroscopy differentiation of flax and hemp by polarized ATR FTIR. Studies in conservation **2006,** 51 (3), 205-211.

40. Peggie, D. A.; Hulme, A. N.; McNab, H.; Quye, A., Towards the identification of characteristic minor components from textiles dyed with weld (Reseda luteola L.) and those dyed with Mexican cochineal (Dactylopius coccus Costa). Microchimica Acta **2008,** 162 (3-4), 371-380.

41. Marques, R.; Sousa, M. M.; Oliveira, M. C.; Melo, M. J., Characterization of weld (Reseda luteola L.) and spurge flax (Daphne gnidium L.) by high-performance liquid chromatography–diode array detection–mass spectrometry in Arraiolos historical textiles. Journal of chromatography A **2009,** 1216 (9), 1395-1402.

42. Ortega Saez, N.; Vanden Berghe, I.; Schalm, O.; De Munck, B.; Caen, J., Material analysis versus historical dye recipes: ingredients found in black dyed wool from five Belgian archives (1650-1850). Conservar Património **2019,** 31, 115-132.

43. Landi, S., The textile conservator's manual. Routledge: 1998.

44. Shashoua, Y. In Investigation into the effects of cleaning natural, woven textiles by aqueous immersion, 1990; pp 313-318.

45. Lennard, F., The art of tapestry conservation. In Tapestry Conservation: Principles and Practice, Routledge: 2006; pp 29-38.
46. Davis, S. J., Coptic Christology in practice: Incarnation and divine participation in Late Antique and Medieval Egypt. Oxford University Press: 2008.
47. Pritchard, F., Clothing culture: dress in Egypt in the first millennium AD: clothing from Egypt in the collection of the Whitworth Art Gallery, the University of Manchester. 2006.
48. Thomas, T. K., Coptic and Byzantine textiles found in Egypt: Corpora, collections, and scholarly perspectives. na: 2007.
49. Mouri, C.; Aali, A.; Zhang, X.; Laursen, R., Analysis of dyes in textiles from the Chehrabad salt mine in Iran. Heritage Science **2014,** 2 (1), 20.
50. Cooksey, C. J., Indigo: an annotated bibliography. Biotechnic & Histochemistry **2007,** 82 (2), 105-125.
51. Elsayed, Y., Conservation of The Flowers Canvas Painting (1) at The Egyptian Agricultural Museum. Egyptian Journal of Archaeological and Restoration Studies **2019,** 9 (1), 39-51.