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INVESTIGATION AND CONSERVATION OF A PRIVATE PHOTOGRAPHIC COLLECTION OF ALBUMEN PRINTS, EGYPT

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Abstract:

Albumen prints are the most important photographic prints of the late 19th century. It is basically composed of two layers: the first layer is the paper support (i.e. cellulose), and the second layer is the image layer (i.e. image silver particles embedded in an albumen binder layer). There are several factors threatening the permanence of albumen prints (e.g., fluctuating temperatures and relative humidity, frequent handling, air pollution, light, and improper storage and display). Unlike other paper objects, photographs have special conservation requirements due to their complex and unique nature. A private collection was selected for this study. The collection consists of three albumen prints from Francis Amen's photo collection, which originally belonged to the Elhagar family. Francis Amin is a well-known photo collector in Egypt. The prints date back to 1890. The photographs were characterised and studied by visual inspection, digital microscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). Microbiological studies were carried out in the microbiology laboratory at the Faculty of Archaeology at Cairo University. Results revealed that the albumen layer suffers from cracks and chemical degradation, and the secondary supports suffer from both oxidation and hydrolysis. Based on the obtained results, the following conservation procedures were selected and carried out: disinfection, dry cleaning, tear mending and compensating for losses, remounting, retouching, and rehousing.

1. Introduction

Albumen prints are photographs on paper where the emulsion holding the light-sensitive silver salts is made with egg whites (i.e., albumen) coated on very thin paper. Albumen prints are mounted on very thick cardboard to prevent the curling of the prints [1]. The most common form of integral secondary support is original mounts. A mount for a print involves both an adhesive and the mount itself. Starch, gelatin, and sulfur-containing adhesives such as rubber cement were used as adhesives [2]. This study is dedicated to albumen prints. The albumen process was the main photographic process of the nineteenth century. It was invented by Louis-Désiré Blanquart-Evrard, a French cloth merchant from Lille who became a student of photography in the 1840_s. In 1850, Blanquart-Evrard presented his process to the French Academy of Sciences [3]. The collection consists of three albumen prints of photographs which belong

to the El-Hagar family and date back to 1890. All three photographs consist of a black and white paper based image fixed to an integral secondary support, which is comprised of two layers, with the bottom layer made of very poor-quality wood pulp. Each secondary support carries unique decoration and inscriptions. Albumen prints are prone to deterioration and/or degradation by numerous agents, such as natural decay, poor processing [4], improper or fluctuating temperature and relative humidity levels [5,6], light [7], biological threats [8], inappropriate handling and misuse, atmospheric pollutants, and inappropriate display and storage materials [9]. There are common forms of damage found in albumen prints, such as highlight yellowing, highlight detail loss, image fading, and image discoloration. The primary factors controlling the rate of this form of damage are relative humidity and temperature. Millard reaction, or protein-sugar reaction, produces highlight yellowing, which is characteristic of albumen print [10], On the other hand, highlight detail loss, overall image fading, and image discoloration are all related to chemical and micro structural changes in the silver and gold image. Albumen prints are sensitive to air pollution. Pollutant gases are known to be very damaging to the image silver, the albumen binder, and the paper support [11]. Gaseous pollutants which are harmful to albumen prints include oxidants, sulphur gases, and acidic gases [12]. Most pollutants are oxidising agents in various forms, and these include peroxide, nitrogen oxides, ozone, sulphur dioxide, and hydrogen sulphide [13]. Acidic gases that are often present in the air cause paper supports to discolour and become brittle, and albumen to degrade. Albumen prints with their rich organic and hygroscopic components (i.e., proteins and cellulose) encourage the growth of fungi. The effect of fungi on photographic material can appear as spots or blemishes, and their hyphae can exert mechanical pressure on the support, causing weakness [14]. They can have colours like white, black, brown yellow, or others [15]. Fungi feed on organic materials, extracting carbon and nitrogen through an enzyme hydrolysis reaction. Hydrolytic enzymes such as cellulase, xylanase, and pectinase can cause mechanical, chemical, and aesthetic damage to valuable documents [16,17]. Microorganisms can disturb the visualisation of photographic images simply by their growth and by producing pigmented metabolites. They can cause damage through the breakdown of the surface material and through the production of enzymes and organic acids. In the case of the albumen binder layer, enzymes and acids can cause the solubilisation and disintegration of images [15]. Insects are also a potential threat to photographic collections [18]. Insects are attracted to photographic collections by paper, proteinous binder, size, glues, pastes, and starches [19]. Insects consume organic materials, leaving them damaged and weak [20]. Silverfish feed on starch and the sizing in paper and on glue. Firebrats, moths, German cockroaches, furniture beetles, and termites are common species that damage photographs. Insects cause discoloration, fading, or bleaching of the image in localised areas. Albumen prints are also highly susceptible to physical damage from improper handling. The most common physical forms of damage caused by poor handling include scratches, tears, creases, cracked corners, rips in paper support, or even a piece missing from a print. Besides physical damage, other deterioration forms can arise. Fingerprints contribute to long-term chemical deterioration as oils, acids, and salts from the skin may cause future irrevocable damage to the image [21]. The protection of photographic prints is accomplished by means of physical barriers such as contact materials. However, improper selection or usage of contact materials will lead to deleterious effects. Contact materials include mounts, enclosures, and boxes [18]. Mounts are often made of poor-quality board covered with a thin layer of good- quality paper. This board can eventually lead to the acidification of the entire photograph and can further cause mechanical damage [22]. The selected col-

lection suffered from image discoloration, cracking of the binder, tears, missing parts, and fungal infection. The aim of this work was to study the structure of the three selected historical albumen prints and their deterioration level by means of visual inspection, digital microscope, scanning electron microscope (SEM) with EDX unit, and Fourier transform infrared (FTIR). It is also aimed at applying different preventive conservation treatments which will improve the physical appearance of the photographs and allow for safer handling and viewing as well.

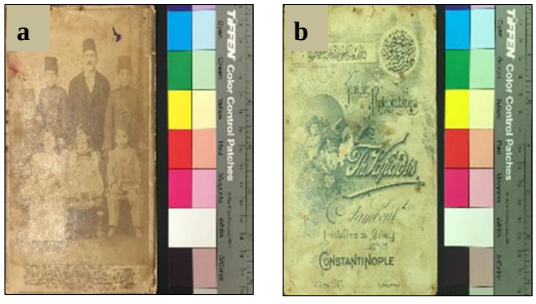
2. Materials and Methods

2.1. *El-Hagar family photographic collection*

The collection consists of three black and white photographic prints. It originally belonged to the El-Hagar family and dates back to 1890. It is now owned by Dr. Francis Amen, a well-known photo collector based in Luxor, Egypt. All three photographs consist of a black and white image on a paper support that is fixed to an integral secondary support comprised of two layers, with the bottom layer made of very poor quality wood pulp. Each secondary support carries unique decoration and inscriptions. The photographic prints were identified as albumen prints due to the presence of a thin primary support, fig. (1) the yellowing of the image layer, and the brownish tone of the prints. Table (1) shows the surface characteristics of each photographic print in terms of surface texture and sheen.

Table (1) Surface characteristics of the photographs

	Object No. 1	Object No. 2	Object No. 3
Texture	Fine grain	Fine grain	Fine grain
Sheen	Semi glossy	glossy	Semi glossy



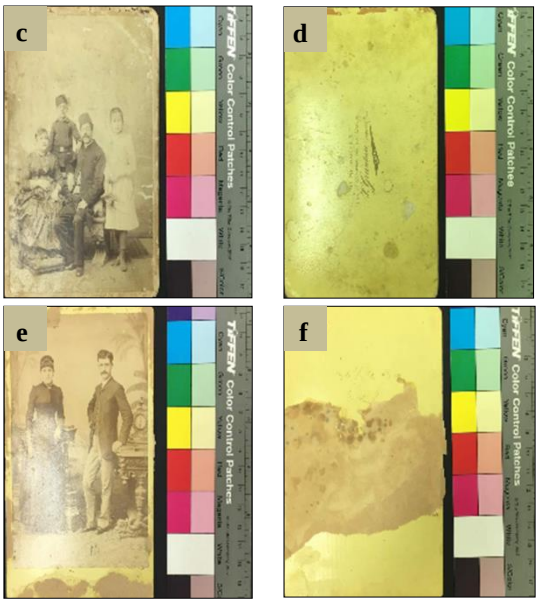


Figure (1) Shows photos before treatment **a.** photo 1 recto, **b.** photo 1 verso, **c.** photo 2 recto, **d.** photo 2 verso, **e.** photo 3 recto, **f.** photo 3 verso.

2.2. *Examination and analysis methods for condition assessment of the collection*

2.2.1. Digital microscope

A Supereyes PZ01 500X USB digital microscope was utilized to document the surface characteristics of the image side of the photographs and the deterioration aspects that cannot be seen with the naked eye, such as the inscriptions behind the paper adhesive and the stains.

2.2.2. Isolation and identification of fungi

Microbiological studies of all three photographic prints were conducted at the Microbiology Laboratory of the Faculty of Archeology at Cairo University, Egypt, to isolate the fungi responsible for the degradation of the photographs. There are different ways to obtain samples; however, due to the value of the photographs, the conventional methods of swabbing and streaking were used [23]. Sterile cotton swabs were used to gently wipe the infected areas of the image layer and secondary support of each photograph. The swabs were then transferred to the lab in sterile tubes to be used for fungal culturing and identification [24]. The agar medium chosen for this study was a potato dextrose agar (PDA) containing potato starch (200 g),

dextrose (20 g), agar (15 g), distilled water (1 L) [25]. Potato dextrose agar (PDA) is one of the most commonly used media for the isolation and cultivation of fungi, with morphological features and pigmentation in culture often being important for identification of cultures [26]. Fungi were isolated by wiping swabs on culture medium, and then the Petri dishes were closed and sealed with Para film. After inoculation, the plates used were incubated at 28 °C for 14 days. After one week, small circles of mould growth began to form in the Petri dishes. This fungus was then purified in the same cultural media to get pure cultural media from each fungus for easy identification. The identification was performed morphologically with a light microscope by using taxonomic keys [27,28].

2.2.3. Scanning electron microscope with energy dispersive X-ray analysis (SEM-EDX)

This analysis was carried out using a SEM-JEOL.QUANTA FEG 250. All the examined samples have been prepared according to standard procedures. Samples were first coated in gold using an EMI TECH K450X sputter coater. Sputtering was performed for 30 sec. with an Argon gas flow at a working distance of 50 mm at 0.05 mbar and a current of 40 m, followed by observation with a scanning electron microscope at an accelerated voltage of 5-15 kV. The SEM-X-ray microanalysis was performed at the SEM Laboratory, NRC in Cairo, Egypt.

2.2.3. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

Spectra were obtained by using a Nicolet 380 FTIR Spectrometer in the frequency range of 4000-400cm^{-1}. The ATR accessory was a Thermo Scientific TM Performer Plate Zn Se Crystal with an angle of incidence of 45°. The diamond has an active area of 1 mm in diameter, and the depth of each scan was approximately 2 microns below the surface. No preparation of the samples was necessary. The analysis was performed at the Infrared Spectroscopy Laboratory, National Research Center (NRC) in Cairo, Egypt.

3. Results

4.1. *Condition assessment*

4.1.1. Digital microscope

A portable digital microscope was used in order to reveal details that could not be seen through visual examination. Images revealed the surface characteristics of the image, the presence of cracks in the image layer, and the presence of gilding. Spots on the recto and verso of the photos were documented, as well as losses in the image layer, fig. (2).

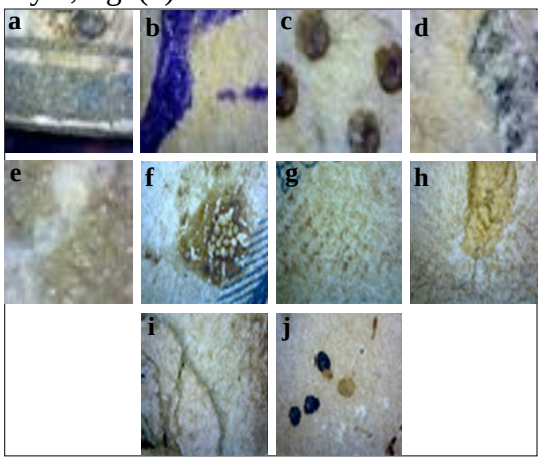
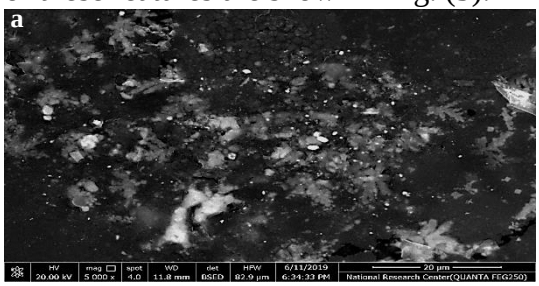


Figure (2) Shows different damage forms affected the selected photographs; *the recto*, **a.** insect dropping, gilding, **b.** colour spots, **c.** foxing spots, **d.** mildew, **e.** loss in emulsion, cracks, *the verso*, **f.** foxing spots, **g.** fingerprints, **h.** sticky, **i.** embrittlement of paper, **j.** brown spots.

4.1.2. Scanning electron microscope with energy dispersive X-ray analysis (SEM-EDX)

The results proved that they have different deterioration forms, such as the cracks in the albumen layer, micro racks and paper fiber. Furthermore, the results have identified the source of cellulose used in both of the primary and secondary supports. In addition to the effect of microbiological attack affected the study photographs, all of these features are shown in fig. (3).



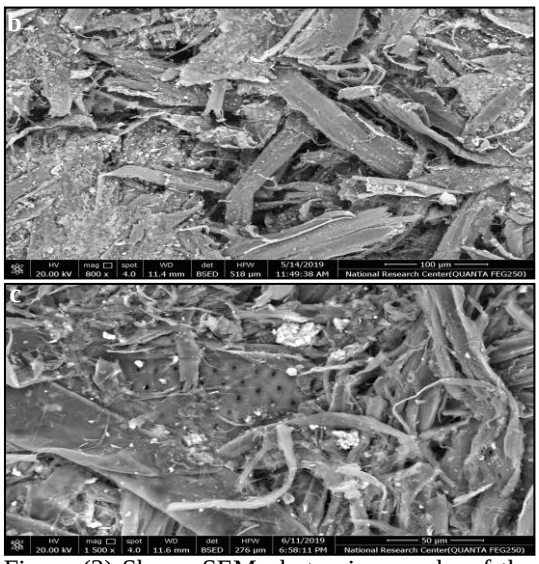


Figure (3) Shows SEM photomicrographs of the investigated samples; **a.** the surface of the sample, **b.** the fiber of the paper of the major support, **c.** the effect of fungus attack on the secondary support

EDX results of the investigated image materials, tab. (2) showed the presence of Ag in a large proportion which is logic since the final image material that makes up albumen prints is metallic silver [11]. The presence of both chlorine and sodium is most likely due to the use of sodium chloride in preparing the image itself, fig. (4-a), and the presence of cadmium may be due to the gilding process, the presence of carbon and oxygen in the major support this indicates that this support was made of cellulose, fig. (4-b). The presence of sodium, aluminum, magnesium, and carbon is an indication of the presence of paper filler [29], fig. (4-b). The presence of calcium, fig. (4-c) may be due to the use of calcium carbonate as a filler to improve the properties of paper

Table (2) EDX elemental data of analyzed samples

Elements	Weight %		
	S 1	S 2	S 3
C K	-	47.12	44.09
N K	-	-	-
O K	57.7	52.83	46.79
Na K	4.37	-	0.58
Mg K	2.9	-	2.2
Al K	2.8	-	0.49
Si K	2.29	-	2.66
S K	13.3	-	1.17
Cl K	4.79	-	0.34
Ag L	6.16	-	-
Cd L	0.89	-	-
Ca K	1.88	-	1.04
CuK	-	-	0.64

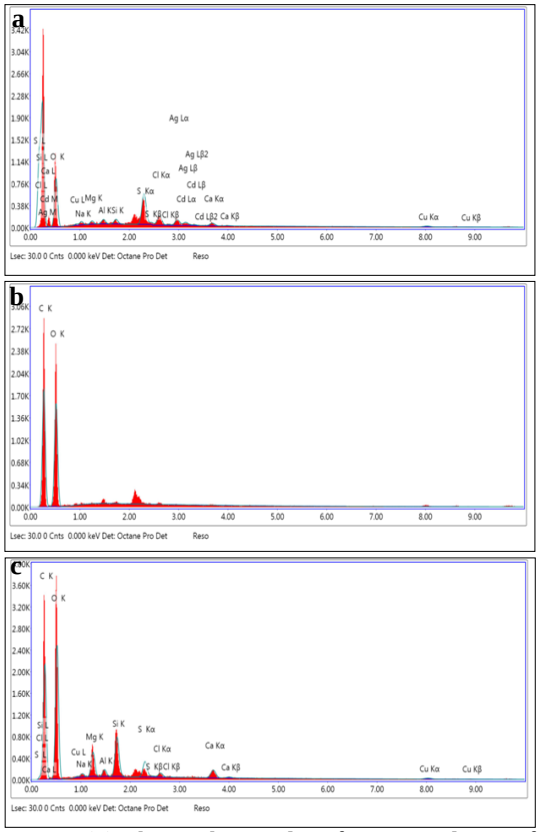


Figure (4) Shows the results of EDX analyses of as a representative case photograph (1); **a.** the surface, **b.** the major support, **c.** the secondary support

4.1.3. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

Spectra for all three photographs show the two main bands characteristic of protein, amide I and amide II. The amide I band is mainly related to C=O stretching with very minor contributions from the C-N groups, and it occurs in the range of 1600-1700 cm^{-1} [30], while the amide II band relates to the N-H bending vibration along with both the C-N stretching vibrations and the C-C stretching vibrations, and it occurs in the range of 1500-1600 cm^{-1}. As for the primary and secondary support, characteristic signals from cellulose fibres were clearly observed in all photographs, with absorption bands at around 3600-3100 cm^{-1}, corresponding to OH stretching vibrations [31]. 2894 cm^{-1} = symmetrical CH_2 stretching; 1642 cm-1 = H_2O; 1427 cm^{-1} = CH_2 deformation stretching; 1369 cm^{-1} =

CH deformation stretching; 1315 cm^{-1} = OH deformation stretching; 1160-898 cm^{-1} = COH/C-O-C C-O stretching Hydrolysis of albumen appears as an increase in the OH stretching or bending frequencies found at 3400 and 1650 cm^{-1}, respectively. Since the amide I band also occurs near 1650 cm^{-1}, an increase in the OH band at 1650 cm^{-1} would result in an increase in the absorption intensity or height of the amide I band. This can be seen by comparing the relative absorption intensities of the amide I band to that of the amide II [32]. On the other hand, oxidation results in the forma-tion of carbonyl compounds, which would be absorbed in the 1700-1750 cm^{-1} wave number region. This can be seen as a slight shoulder on the amide I carbonyl band and may result in an increase in the area of the amide I band [33]. The effect of fungi on the albumen prints occurs in the wave number range of 1736-960 cm^{-1} [34]. Fungi enzymes hydrolyze the amorphous regions of cellulose [35], producing lactones. Lac-tones were converted to cello bionic acid by fungi enzymes, which then released final glucose and glycolic acid products [36]. The oxidation of cellulose involves the primary and secondary hydroxyl groups of the pyranose ring, which results in the creation of carbonyl (C=O) and carboxyl groups (-COOH). The groups are chromospheres, and their creation is one of the reasons paper yellows as it ages. The formation of carboxyl groups increases acidity and induces de-polymerization of the cellulose. As a result, the physical and mechanical strength of the material decreases. Based on the obtained FTIR data, all photographic prints under study are albumen prints showing amide I and amide II bands, characteristics of albumen at 1631 and 1530 cm^{-1} for photograph 1, fig. (4-a); 1631 and 1514 cm^{-1} for photograph 2, fig. (4-b); and 1634 and 1518 cm^{-1} for photograph 3, fig. (4-c), respectively. With respect to the albumen binder of photographs 1, 2, and 3, no signs of deterioration were observed. The shift of amide II to lower wave numbers of 1514 and 1518 cm^{-1} in photographs 2 and 3 indicates the presence of an intermolecular hydrogen bond. Amide I appeared in all the studied photographs between1631-1634 cm^{-1}, reflecting the presence of a B-sheet structure, fig. (4-b, c). [37,38].

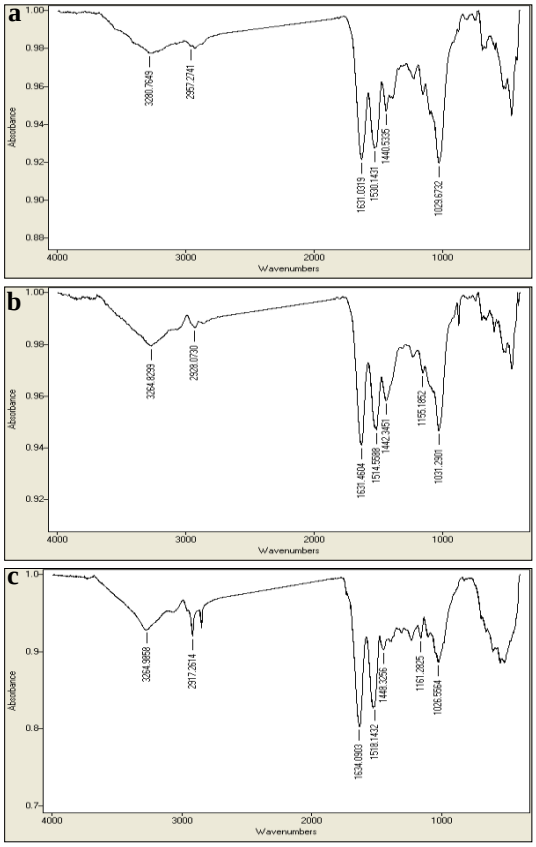


Figure (5) Shows ATR-FTIR the surface of; **a.** photograph (1), **b.** photograph (2), **c.** photograph (3)

4.1.4. Identification of fungi

The isolated fungi were morphologically identified with a digital microscope. The color, size, and morphology of the vegetative and reproductive structures were examined. The identification was performed morphologically with a light microscope by using taxonomic keys [27,28]. The isolated species represent ten fungi in all the collected samples. The fungal species which were isolated from the surface of the photographs (i.e., the recto) and the fungal species which were isolated from the paper support (i.e., the verso) are represented in tab. (3), and morphology captured under a digital microscope, fig. (5).

Table (3) Fungal species isolated from the photographs (i.e. recto and verso).

Fungi isolated from the photographs	
Recto	***Surface***
A. sydowii	*A. flavus*
P.chrosogenum	*A. niger*
T.atrouses	*A.vericolor*
Alternaria alternate	*A. tamari*
P. carenum	
Aurobasidiumpullulans	

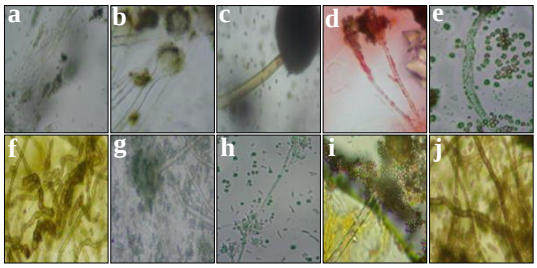


Figure (5) Shows the morphological features of isolated fungus under digital microscope; **a.** *P. carenum*, **b.** *A. flavus*, **c.** *A. niger*, **d.** *T. atrouses*, **e.** *A. vericolor*, **f.** *Alternaria alternate*, **g.** *A. sydowii*, **h.** *P. chrosogenum*, **i.** *A. tamarii*, **j.** *Aurobasidium pullulans*

4. Discussion

The selected albumen prints are of historical value, as they date back to the nineteenth century; accordingly, it was a necessity to protect them from the surrounding factors of deterioration in order to prolong their lifespan. Different examination and analytical techniques were used in order to assess their condition and consequently select proper treatments. Some images of the albumen do not show cracks, implying that a layer of varnish was placed on it, as could be seen in fig. (3-a), and the shape of the fibers of the primary support, which was made from linen fibers, and the secondary support, which was made from wood pulp, where All paper up until the 19th century was hand-made, primarily from cotton and linen rags and hemp, which produced papers of great strength and permanence. As the need for paper increased, ground wood was introduced as a paper-making fiber. This resulted in the mass-production of papers that were weaker and less permanent due to the higher presence of lignin [39,40] and the effect of the fungus on the fiber of the paper support since the high cellulosic component of paper increases fungal attack and thus decomposes the paper fibers [41, 42]. EDX analysis results revealed the presence of silver (i.e., the final image material) in a large amount. It also showed the presence of carbon and oxygen, which is logic since the sample contains paper, which is made of pure cellulose. Elements related to paper manufacture, such as Ca, C, Al, Si, and Mg, were also detected [43]. ATR-FTIR showed two main characteristic bands of protein: amide I and amide II. The amide I band is mainly related to C=O stretching with very minor contributions from the C-N groups, and it occurs in the range of 1600-1700 cm^{-1} [30], while the amide II band originates from the in-plane N-H bending, along with both the C-N stretching vibrations and the C-C stretching vibrations, and it occurs in the range of 1500-1600 cm^{-1}. Protein degradation is responsible for the amide II shifts [44]. Both *Penicillium* and *Asperagillius* were isolated from the studied collection, and this is in accordance with previous studies that isolated *P. chrosogenum* from albumen print [8] and studied the effect of *A. flavus*, and *p. chrosogenum* on gelatin emulsion [15]. Microorganisms most often recorded in photographs include *Penicillium, Asperagillius, Cladosporium, and Alternaria* [45]. The collection was cleaned using soft brushes for the image side of the prints, while the supports were cleaned using an eraser. Wet treatments were avoided due to their damaging effect on albumen prints [46]. For the consolidation of embrittled parts, Klucel G, a non-ionic cellulose ether, was used. Enclosures for the collections were made from paper containing a high amount of alpha-cellulose and free of lignin [4].

5. Preventive conservation

Based on the condition of the collection, it was decided to perform the following procedures: disinfection, mechanical cleaning, consolidation of fragile parts, and compensating for losses**.** Retouching, rehousing**.**

5.1. *Disinfection*

The use of essential oils to control microbiological growth in cultural heritage is a safe alternative to the conventionally used chemical methods [47]. Based on the results of the experimental study on the effect of (thyme oil, clove oil, lemon grass oil) with different concentrations (6.0 ppm, 1.25 ppm, 250 ppm, 500 ppm, 1000 ppm) of essential oils on fungal species isolated from El-Hagar's photo collection, lemongrass oil was selected for this disinfection step since it proved to be efficient in inhibiting the growth of the isolated fungal species. The essential oil was applied in the vapor phase in desiccators. The sterilization process was carried out using lemongrass oil at a concentration of 250 ppm. The oil was placed in a sterile Petri dish, and filter paper was placed under the disc. The photographs were then placed in the dissector for ten days, fig. (6).

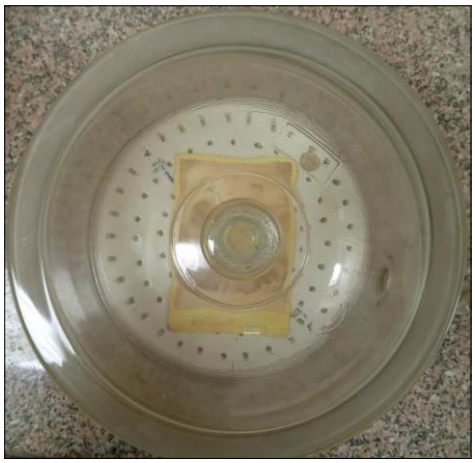


Figure (6) Shows the disinfectant methods to the collection

5.2. *Mechanical cleaning*

The front and back of the secondary supports were cleaned using soft brushes and a fiber castle eraser to remove surface dirt [48]. This step is very important prior to mount removal in order to avoid the penetration of dirt inside the paper fibers [49]. The supports were then thoroughly brushed to remove the residue, which might cause future problems due to the sulphur content of the eraser. A very fine brush was used to gently clean the image side of the photographs to avoid producing scratches. All the photographs were cleaned in the same manner, fig. (7).

Figure (7) Shows the different tools used for mechanical cleaning, of the studied photographs

5.3. *Consolidation of fragile parts and compensating for losses*

The collection suffers from many tears and missing parts. Tears were recommended using Klucel G (i.e., hydroxy propyl cellulose) at a concentration of 5% [50]. Losses were restored using cotton paper of the same thickness as the photograph. The fill paper was dyed in a color similar to the tone of the photograph, and it was glued using Klucel G and Japanese paper, fig. (8).

Figure (8) Show the photographs during the consolidation

5.4. *Retouching*

Retouching was performed on photos 1, 2, and 3. The retouching was done using a Faber-Castle Art and Graphic Polychromos set, fig. (9) [10]. Color pencils are used to apply a series of minuscule dots of the required color. In this process, nothing appears to be happening at first, as the density is gradually built up in the area to be retouched. One must continue slowly dotting the area until the flaw gradually disappears. There are some ethical issues

involved in retouching photographs since they modify the original in such a way that its integrity could be compromised. However, a moderate solution is to retouch to the point where abrasions blend into their surroundings. Because all treatments must be reversible, an isolating layer of albumen was placed between the photographic paper and the retouching medium. The pencil is the simplest retouching tool. Yet, despite its simplicity, it can accomplish a lot of work.

Figure (9) Shows the color of three photograph after retouching.

5.5. *Rehousing*

It is necessary to preserve the photographs in proper folders in order to protect them from improper handling, pollutants, etc., fig. (10) [51]. It was necessary to choose materials that did not harm the photographs. Portfolios were made of cotton paper, which is characterized by containing a high amount of alpha cellulose and being free of lignin. A harmless archival tape was used. Polyethylene was used to cover the image from the front and back, as indicated in the pictures.

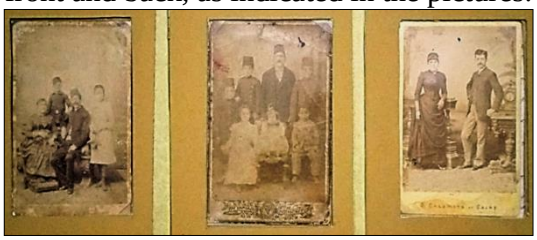


Figure (10) Showing the portfolios of a set of photographs

6. Conclusion

The El-Hagar family collection was identified as albumen prints through visual inspection, SEM-EDX, and ATR-FTIR. Albumen prints have the following characteristics: ****)*** *The final image material is metallic silver.* ****)*** *Two -layer structure (i.e., albumen binder and primary support).* ****)*** *Visible paper fibers.* ****)*** *Neutral black and white tones. Several deterioration aspects were identified through visual inspection, such as cracks in the binder layer, losses in the albumen binder layer, embrittlement of the secondary support, and losses in the paper support. SEM-EDX analysis revealed a two-layer structure of the images consisting of an image layer and a paper support. The final image material was identified as metallic silver (AgO). The SEM investigation also proved that the primary supports were made from cotton fiber, while the secondary supports were made from wood pulp. The secondary supports were found to suffer from severe embrittlement, and several cracks were also apparent in the binder layer. Results of SEM confirmed that fungi play an important role in the deterioration of secondary support and cause damage to the fibres (i.e., holes in the paper fiber). FTIR analysis showed insignificant changes, particularly with Amide I. The shift observed in the position of Amide II indicates that a very minor change has occurred, causing the albumen to convert from the triple helices to random coils. The fungi isolated from the collection were identified using a digital microscope with a digital camera as A. sydowii, P. chrosogenum, T. atrouses, Alternaria alternate, P. carenum, and Aurobasidiumpullulans, which were isolated from the surface of the photographs, and A. flavus, A. niger, A. vericolor, and A. tamari, which were isolated from the secondary support. The conservation of the photographic collection was effectively carried out following several interventive treatments. Disinfection was carried out using lemongrass oil with a concentration of 250 ppm. Dry cleaning was carried out using a fine brush and a vinyl eraser. Tear mending and compensating for losses were done to consolidate the structure of the photograph. Only minor pencil retouching was carried out to enhance the appearance of the photographic prints. The photographs were finally housed in paper folders. All treatments fulfilled the aim of reinforcing the structure of the photographs, enhancing their appearance, and stabilizing their condition to prevent further deterioration and mechanical damage.*

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