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INVESTIGATION AND CONSERVATION OF EL-SHENAWY PALACE PHOTOGRAPHIC COLLECTION IN MANSOURA, EGYPT

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ABSTRACT

Paper-based photographic collections are an essential part of the Egyptian cultural heritage both for their artistic and documentary value and as a record of the history of photography, as a technique as well as a form of artistic expression. Due to their significance, the interest in photographs is growing worldwide and institutions are making great efforts to increase access to photographic collection, as well as preserve originals for future generations. The threats to photographs are many. They are very sensitive to 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 five black and white photographic prints documenting one of the most valuable structures of architectural heritage in the city of El-Mansoura. This paper describes the signs of deterioration present in the collection through documenting the preservation status of El-Shenawy palace photographic collection. It also describes the conservation treatments carried out to prolong their lifespan. Prior to treatment, the photographs were characterized and studied by visual inspection, digital camera, Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). Scanning electron microscope (SEM) provided with an energy dispersive X-ray spectroscopy unit was used to identify the components of the photographs, assess their preservation status, as well as study the morphology of the paper fibres in both the primary and secondary supports. Microbiological studies and pH measurements were also carried out. The results of the investigations revealed that image silver in most cases suffered from sulfiding, the secondary supports suffered from both oxidation and hydrolysis, and the gelatin binder also showed signs of degradation. Based on the results of previous studies, the following interventive conservation procedures were selected and carried out: disinfection, cleaning, dismantlement of the secondary support, deacidification, tear mending and compensating for losses, remounting, retouching, and rehousing.

KEYWORDS: Photographic records, threats, FTIR, SEM, XPS, interventive conservation.

1. INTRODUCTION

The collection documents one of the most valuable structures of architectural heritage in the city of El-Mansoura, El-Shenawy palace. The palace was built in 1928 for Mohamed Bek El-Shenawy, one of the aristocratic families in El-Mansoura city and member of Al-Wafd party, a nationalist liberal political party in Egypt and it was said to be Egypt's most popular and influential political party for a period from the end of World War I through the 1930s . The collection consists of five silver gelatin photographs showing the sophisticated Italian style of the palace as well as its huge beautiful gardens. Mohamed El-Shenawy Pasha appears in one of the images along with two public figures. Black and white photographic process dominated photography for a very long time; however, the silver gelatin process is by far the most common process. A silver gelatin print is mainly composed of three components: the primary support material, paper; the binder, gelatin; and the image-forming substance, silver grains (Roosa, 2004). A fourth component which may be included is an interlayer between the support and the image layer known as the baryta coating (Hendricks and Ross, 1998). Baryta layer consists of finely ground white barium sulfate in gelatin (Hendriks, 1984). An integral secondary support may be present. The most common form of integral secondary supports for prints 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 (Reilly, 2005). Silver gelatin prints are prone to deterioration and/or degradation by numerous agents such as i) natural decay, ii) poor processing, iii) improper or fluctuating temperature and relative humidity levels, iv) light, v) biological threats, vi) inappropriate handling and misuse, vii) atmospheric pollutants, and viii) inappropriate display and storage materials (Wilhelm and Brower, 1993). Deteriorated silver gelatin prints present a very challenging problem in the conservation field due to their fragile and complex nature. In Egypt, particularly in Cairo, a city known for its high pollution rates, silver gelatin prints exhibit severe chemical decay in the form of silver mirroring, discoloration, staining, etc. Other decay forms arise from the lake of knowledge about the nature of silver gelatin prints and the most appropriate methods for their care; and also from the lake of trained professionals in this field.

Silver gelatin prints are sensitive to air pollution. Pollutant gases are known to be very damaging to the image silver, the gelatin binder, and the paper support (Porck and Teygeler, 2000). Gaseous pollutants which are harmful to silver gelatin prints include oxidant, sulfur gasses, and acidic gases (Donaldson, 2000). Most pollutants are oxidizing agents in various forms; and these include peroxide, nitrogen oxides, ozone, sulfur dioxide and hydrogen sulfide (Clark and Frey, 2003). A combination of high temperature, high relative humidity, and contaminants in the atmosphere causes oxidation to occur. Oxidation is the basis of the chemical degradation of silver gelatin prints since nearly all image decay begins with the oxidation of the image silver (Nishimura, 1993). Symptoms of silver oxidation include fading, silver mirroring, and discoloration (Weaver, 2008). Moreover, acidic gases that are often present in the air cause paper supports to discolor and become brittle, and gelatin to degrade.

Mold is a common cause of damage to photographs. Gelatin binders, with their high-protein content, and paper with their high-cellulose content provide the culture medium required for mold growth. When proper combination of nutrients and environmental condition is present, spores absorb water and grow. They grow rapidly and branch repeatedly forming a mold colony. Mold feeds on gelatin and paper extracting carbon and nitrogen through an enzyme hydrolysis reaction. This reaction results in fragility and disfiguration of photographic materials and can destroy the image layer entirely (Adcock et al., 1998). Mold also produces colored materials which stain the paper (Egunnike, 2003). Growth of mold can also lead to pitting of gelatin binder (Donaldson, 2000). In the case of mounted photographs, hygroscopic pastes and gums accelerate possible fungus attack because of the moisture absorbed by the adhesive. The damage can spread until the image, binder, and base are totally destroyed (Lavédrine, 2003). Insects may be attracted to fungus growths, and they or their excrement may do additional damage (Eastman Kodak Company, 1985).

Insects are also a potential threat to photographic collections (Lavédrine, 2003). Insects are attracted to photographic collections by paper, gelatin, size, glues, pastes, and starches (Teygeler, 2001). Insects consume organic materials, leaving them damaged and weak (Roosa, 2004). Insect damage does not come solely from eating habits; photographic collections are also damaged by bodily secretions (Teygeler, 2001). Certain chemicals present in insect excretion can discolor, fade or bleach the image in localized areas (Eastman Kodak Company, 1985). Silverfish, firebrats, psocids, German cockroaches, furniture beetles and termites are common species that damage photographs (Lavédrine, 2003).

Silver gelatin prints are also highly susceptible to physical damage from improper handling. The most common physically forms of damage caused by poor handling include scratches, tears, creases, cracked

corners and rips in paper supports, gelatin abrasion, or even a piece missing from a print. Beside physical damage, other forms of deterioration 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 (Wilhelm and Brower, 1993). If silver gelatin prints are poorly processed, handled with dirty hands, or stored in humid and hot conditions, they sometimes take on a silvery sheen, a form known as silver mirroring, in the darkest areas of the prints (Morris, 2003). The protection of photographic prints is accomplished by means of physical barriers such as contact materials. However, improper selection or usage will lead to deleterious effects. Contact materials include mounts, enclosures, and boxes (Lavédrine, 2003). 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(Durant, 2005). In very severe acid attacks, the paper base and the gelatin will also be brittle, and probably discolored (Ryhl-Svendsen, 1999). Adhesives used in the past for mounting photographic prints often become brittle and brown, causing further discoloration (Clark and Frey, 2003).

There are different methods used to study silver gelatin prints prior to treatment. These help to identify the type of photographic process and materials involved. Moreover, they assist in the evaluation of the damage or deterioration which has occurred. Accurate diagnosis of the problem leads to making correct treatment and conservation choices. The most common examination method is visual inspection, which is one of the most effective means of examining photographic materials (Hendricks et al., 1991). Light also plays an important role when viewing photographs. Proper lighting will reveal aspects of a print that cannot otherwise be seen. . An object's morphology (size, shape, texture) or optical properties (color, gloss, etc.) can be revealed through visual examination using different wavelengths of light (Weaver, 2008). By utilizing electrons instead of conventional light, the SEM achieves a much higher resolution. The SEM can also be used to help determine the elements present in the material and their location in the sample. In order to do this, an energy dispersive X-ray (EDX) analyzer is attached. Using EDX in conjunction with the ESEM, yield information on the structure of the photographic material, its chemical make up, as well as, information about the distribution of the elements in the sample. Understanding the chemical structure of the material is vital to the interpretation of analytical results obtained from various types of analyses. Another important analytical tool is Fourier transform infrared spectroscopy (FTIR). The technique produces a spectrum that provides intrinsic details about bonding features between atoms or characteristic functional groups in a molecule. It also provides information regarding chemical changes due to chemical treatment or aging, based on appearance of a new band, band shift, or intensity change of individual bands. One of the important advantages of using this technique is the ability to perform non-destructive analysis on historical objects (The Getty Conservation Institute, 2013). X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that gives the kinetic energy spectra of the electrons emitted as a result of the material bombardment with X-ray photons. This analytical technique is new to the field of photograph conservation.

The selected collection suffered from image discoloration, flaking of the binder, tears, missing parts, scratches, and fungal infection. The aim of this work was to study the structure of the five selected historical silver gelatin prints and their deterioration level by means of visual inspection, digital camera, scanning electron microscope (SEM), fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS). It also aimed at applying different interventive 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-Shenawy palace black and white photographic collection

A private collection of five black and white photographic prints was selected for this study. The photographs show the sophisticated Italian style of the palace as well as its huge beautiful gardens. Mohamed El-Shenawy Pasha appears in one of the images along with two public figures. In terms of their structure, all five 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 an aluminum label with the photographer's name and location (Photographer Shoukry/ Mansourah). Due to the appearance of silver mirroring in the images and the likelihood of a gelatin binder layer, the researcher concluded that these images are most likely silver gelatin prints (Fig. 1). They appear to have been created using a developed-out process (DOP), where paper is exposed by projecting the image through an enlarger and printed using a developing solution. Table I shows the surface characteristics of each photographic print in terms of surface texture and sheen.

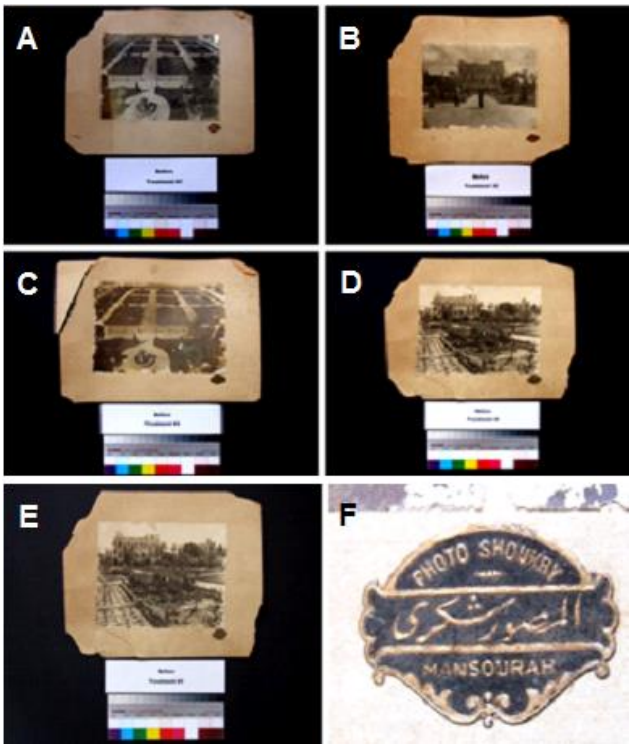

Figure 1. Photograph 1 (A), photograph 2 (B), photograph 3 (C), photograph 4 (D), and photograph 5 (E) before treatment. The photographer's label (F)

Table I. Surface Characteristics of the photographs

	Object No. 1	Object No. 2	Object No. 3	Object No. 4	Object No. 5
Texture	Fine grain	Fine grain	Fine grain	Fine grain	Fine Grain
Sheen	Glossy	Glossy	Glossy	Matt	Glossy

2.2 Condition assessment of the collection by digital camera

A photographic survey was carried out before, during and after treatment in ambient light using a Fujifilm's FinePix S9500 with the following features:

- 1/1.6" Type CCD with million effective pixels.
- Lens: 28 mm – 300 mm.
- 21.4x total zoom (10.7X optical, 2.0X digital).
- Macro mode starting from 1 cm.
- Sensitivity: ISO equivalent to ISO 80/100/200/400/800/1600.
- Shutter speed: 30 sec. to 1/4000 second.
- The LCD screen can be tilted up to an angle of 45° and 90° and down to 45°.

2.3 Scanning electron microscopic analysis

Scanning electron Microscopic analysis (SEM-EDX) of the samples was carried out using a Zeiss LEO Supra 55VP Field Emission with EDX Oxford Instrument X-act PentaFET precision model 51-ADD001. All the samples examined have been prepared according to the standard procedures. Samples were first coated in gold using EMITECH K450X sputter coater. Sputtering was performed under an Argon gas flow at a working distance of 50 mm at 0.05 mbar and a current of 40mA for 30 second and then observed the scanning electron microscope operated at an accelerated voltage of 5 - 15 kV. The SEM–X-ray microanalysis was performed at the SEM Laboratory, Department of Chemical Sciences, the University of Catania.

2.4 Fourier Transform Infrared Spectroscopy

FTIR analysis was used to identify the type of photograph, the binder, and the presence of degradation. The FTIR instrument used for this analysis is JASCO FT/IR-6100 FT-IR Spectrometer, in the range of 4000 – 400 cm $^{-1}$, in transmission mode. The analysis was performed at the Infrared Spectroscopy Laboratory, National Research Center (NRC) in Cairo, Egypt.

2.5 X-ray photoelectron spectroscopy

The surface characterization and study of silver mirroring phenomenon was obtained by X-ray photoelectron spectroscopy (XPS). The analysis was performed on specimens singled out on the basis of their degradation.XPS measurements were carried out using a PE-PHI ESCA/SAM 5600 monochromator system spectrometer with an analysis chamber base pressure of 5×10^{-10} Torr. X-ray photoemission measurements were performed using a monochromatic AlKα (hv =1486.6 eV) source. Analyses were carried out with a photoelectron angle of 45° (relative to the sample surface) with an acceptance angle of 7°. The energy scale of the spectrometer was calibrated with reference to the Ag3d3/2 = 368.3 eV photoelectron line. Binding energies were calculated with respect to the C1s ionization at 285.00 eV from adventitious carbon that is generally accepted to be independent of the chemical state of the sample under investigation. The analysis was performed at the X-ray Analysis Laboratory, Department of Chemical Sciences, University of Catania, Italy.

2.6 Isolation and identification of fungi

Microbiological studies of all five photographic prints were conducted at the Microbiology Laboratory of the National Archives in Cairo, Egypt. To isolate the fungi responsible for the degradation of the photographs, a protocol was developed. There are different ways to obtain samples; however, due to the value of the photographs, the swab sampling technique was used to minimize damage since it is considered a non-invasive sample prelevation method (Baldasici and Barbu-Tudoran, 2012). Sterile cotton swabs were used to gently wipe the infected areas of the image layer and secondary support of each photograph then transferred to the lab in sterile tubes to be used for fungal culturing and identifica-

tion (Montanari et al., 2012). Samples were kept frozen until isolations were made in the laboratory (Held et al., 2012). 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) (da Silva et al., 2013). 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 (Griffith et al., 2007). Fungi were isolated by wiping swabs on culture medium, and then the Petri dishes were closed and sealed with Parafilm. After inoculation, the plates used were incubated at 28°C for 14 days. After one week small circles of mold growth began to form in the Petri dishes. Within two weeks these circles have spread and formed distinguishable patterns.

2.7 pH measurements

The state of preservation of all five integral secondary supports (i.e. brittle and yellowed) indicates that they are acidic. The pH of the paper supports was evaluated using pH paper strips.

3. INTERVENTIVE CONSERVATION

3.1 Aims of conservation treatments

The priority of the owner of this private collection was to reinforce the structure of the photographs, enhance their appearance, and stabilize their condition to prevent them from further deterioration and mechanical damages.

3.2 Issues taken into consideration

Given the advanced state of the degradation of the photographic prints, any intervention proposed had to contribute positively to their preservation. Several preservation issues were of great concern andtherefore, the restoration work was done with much consideration. A major decision was made concerning conservation that is to limit the treatment to only that which is necessary. Other important preservation issues that this collection has are ascribable to the complex nature of the photographs, the high sensitivity of the binder to water, and the severe degradation of the secondary supports. Deciding on whether to maintain or remove the "original" secondary support, as it reflects technical knowledge, and therefore has historical value, was controversial. Indeed, treatments should respecthe aesthetic, historic, and the physical integrity of the photographs. Thus if maintaining the historical value of the secondary supports is a priority, they cannot be removed.

3.3 Conservation technique used

Given these consideration, it was decided that the conservation treatments would involve disinfection treatment, mechanical (dry) cleaning, minor solvent cleaning, dismantlement of secondary supports, deacidification, consolidation of paper supports, remounting, minor retouching, and finally housing.

4. RESULTS AND DISCUSSION

4.1 Condition assessment by digital camera

The secondary supports of all photographs appeared to be acidic, yellowed and embrittled, with structural damage such as cracking, tears and losses. These forms are typical degradation of cellulose (Fig. 2).

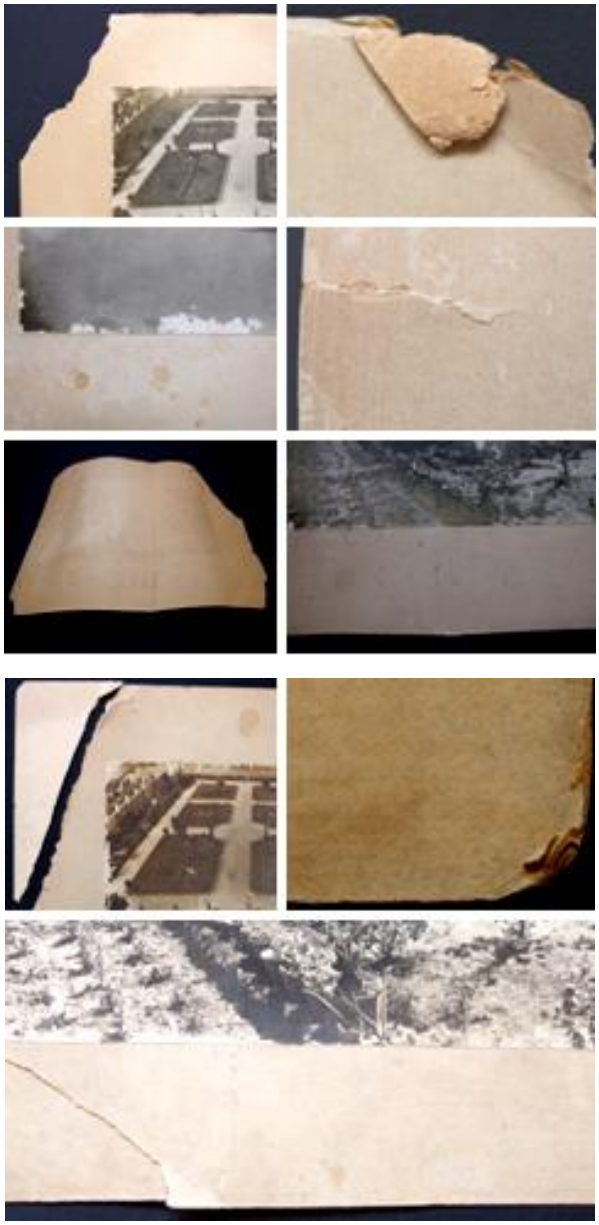

Figure 2. All secondary supports suffer from loss of mechanical strength and damage forms such as losses, tears, and fragility.

Overtime, paper undergoes unavoidable aging processes that cause cellulose degradation. These phenomena can involve acid substances and the moisture present in the print (acid hydrolysis), oxidative agents and the atmospheric O_2 (oxidation), microorganisms (biodeterioration), and the light (photodegradation) (Princi et al., 2008). All these previous factors act cooperatively and lead to both the progressive shortening of the polymeric chains and the variation of the crystalline content of cellulose (Giorgi et al., 2002). Table II lists the different damage forms found in the secondary support of each photograph.

Photograph 1 (row 1), photograph 2 (row 2), photograph 3 (row 3), photograph 4 (row 4), photograph 5 (row5).

Table II. Forms of damage found in secondary supports.

	Losses	Tears	Warping	Cracking	Yellowing/ Embrittlement
1	√	√	√	√	√
2	√	√	√	√	√
3	√	√	√	√	√
4	√		√	√	√
5	√	√	√	√	√

The binder layer (gelatin) was in a very bad condition. Due to the extreme reactivity of the gelatin binder layer, there was severe flaking and cracking in all photographic prints. In addition, minor scratches are visible, possibly caused by improper handling of the photographs and the absence of appropriate enclosures (Fig. 3), (Fig. 4), (Fig. 5), (Fig. 6), and (Fig. 7). Despite the presence of silver salts and other potentially toxic compounds in the gelatin layer of black and white images, the concentrations are apparently not high enough to inhibit fungal and microbial growth as visual examination revealed the presence of biodeterioration. The biodegradation of gelatin involves the proteolytic hydrolysis of its peptide bonds (Vivar et al., 2013).

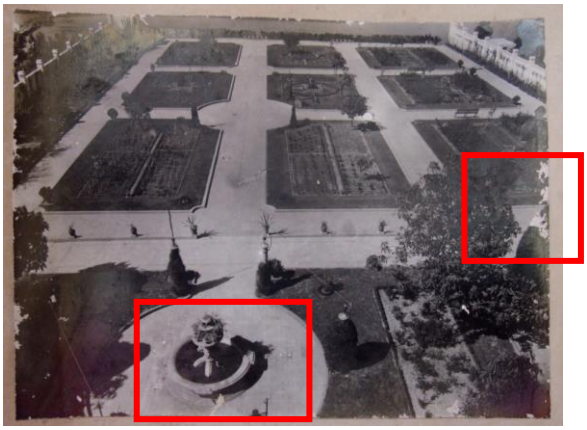

Figure 3. Photograph 1. Images show flaking of the image layer in different locations.

Figure 4. Photograph 2. The gelatin binder shows signs of staining and losses, particularly around the edges.

Figure 5. Photograph 3. The main problem with this case is the split across the center of the photograph which has resulted due to the embrittlement of the secondary support. Loss in the image layer is also apparent in different areas of the photograph.

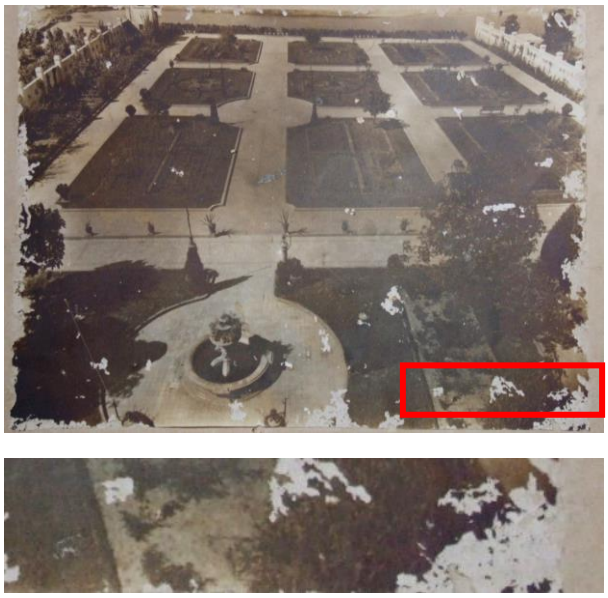

Figure 6. Photograph 4. This print is extremely deteriorated, showing loss and yellowing of the gelatin binder. Attempts of retouching have been improperly carried out.

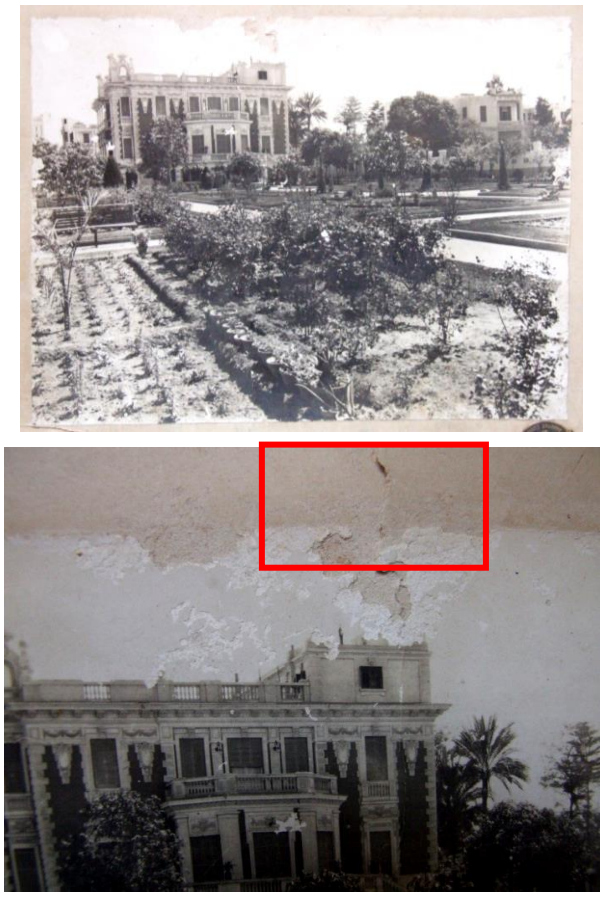

Figure 7. Photograph 5. Visual examination has revealed that the gelatin binder suffers from insect attack. The binder also displays losses.

Table III summarizes the different damage forms found in the gelatin binder of each photographic print.

Table III. Binder decay

	dirt	losses	Cracks	Insect attack	stains	Yellowing
1	√	√		√		√
2	√	√		√	√	√
3	√	√	√	√	√	√
4	√	√		√	√	√
5	√	√	√	√		√

There are many toxins which will chemically attack the image producing dramatic changes in the color and density of the final image material which in this case is metallic silver, altering its original appearance (Donaldson, 2000; Clark and Frey, 2003). Symptoms of image silver decay include loss in highlight detail, fading, discoloration, and silver mirroring (Weaver, 2008). Nearly all silver gelatin prints are affected by the later symptom (Cycleback, 2010). All photographic prints suffered from overall silver mirroring giving high density areas a bluish metallic sheen (Fig. 8), (Fig. 9), (Fig. 10), and (Fig. 11). Overall mirroring has mainly occurred due to the attack of the toxins such as lignins, sulfurous gases, and peroxides released from the poor quality secondary support. These toxins have also caused fading and yellow/brown discoloration of the silver image (Fig. 12). Yellow/brown discoloration and fading is the classic form of silver gelatin print deterioration (Weaver, 2008). Table IV summarizes the image silver decay of each photographic print. Figure 13 documents the photographer's label.

Table IV. Image silver decay

	Silver mirroring	Fading	Yellow/brown discoloration	Localized and irregular patterns
1	√	√	√	
2	√	√	√	
3	√	√	√	
4	√	√	√	√
5	√	√	√	

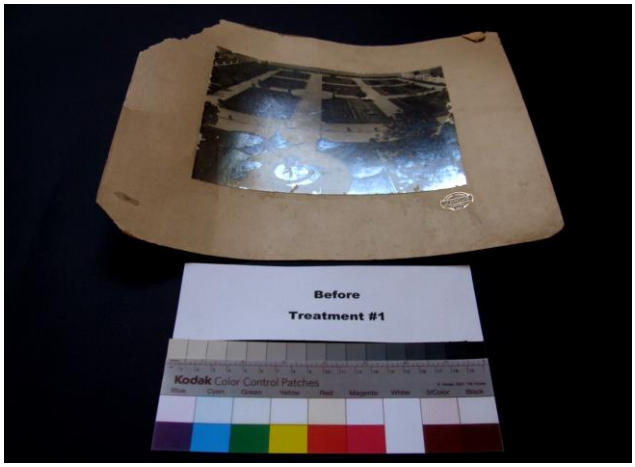

Figure 8. Photograph 1 before treatment, photographed at an angle displaying silver mirroring decay (top). Shadow areas show a severe case of overall silver mirroring (bottom). The image also suffers from yellow/brown discoloration.

Figure 9. Photograph 2 displays silver mirroring in shadow areas and is visually observed at best when photographed at an angle (bottom left). The same previous shot photographed at 90° (bottom right). The image also suffers from yellow/brown discoloration.

Figure 10. Photograph 3, photographed at an angle displaying silver mirroring decay. When silver mirroring is very severe it appears green or bronze in color. Yellow/brown discoloration is also apparent in the highlights and midtones.

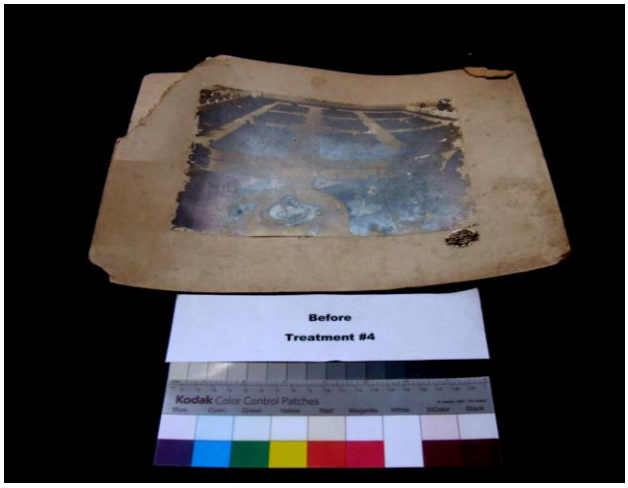

Figure 11. Photograph 4, photographed at an angle displaying severe image silver decay in the form of silver mirroring (top), irregular decay patterns and yellow/brown discoloration and fading (bottom).

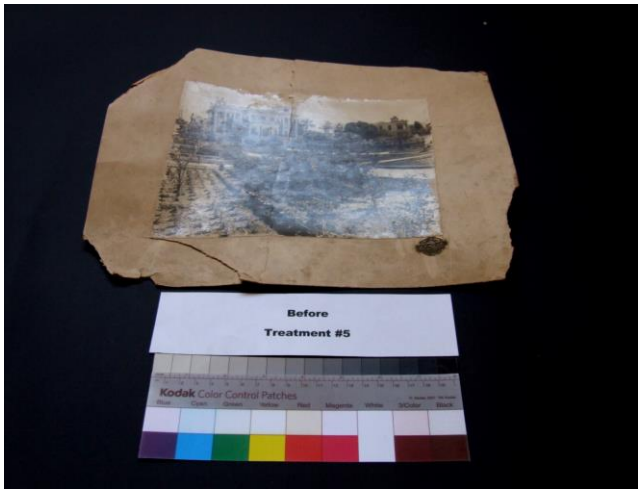

Figure 12. Photograph 5 before treatment, photographed at an angle displaying image silver decay in the form of silver mirroring, yellow/brown discoloration and fading.

Figure 13. Photographer's labels displaying his name and location. Photograph one to five from left to right.

4.2 SEM-EDX analysis

Scanning electron microscopic analysis (SEM-EDX) of the samples was carried out using a Zeiss LEO Supra 55VP Field Emission with EDX Oxford Instrument X-act PentaFET precision model 51-ADD001. All the samples examined have been prepared according to the standard procedures. Samples were first coated in gold using EMITECH K450X sputter coater. Sputtering was performed under an Argon gas flow at a working distance of 50 mm at 0.05 mbar and a current of 40mA for 30 second and then observed the scanning electron microscope operated at an accelerated voltage of 5 - 15 kV. The SEM–X-ray microanalysis was performed at the SEM Laboratory, Department of Chemical Sciences, the University of Catania.

Fig. 14 shows the location of samples collected from photograph 1, where sample (1) represents the layer structure of the photograph, sample (2) refers to the top sheet of the secondary support and sample (3) refers to the poor–quality bottom sheet.

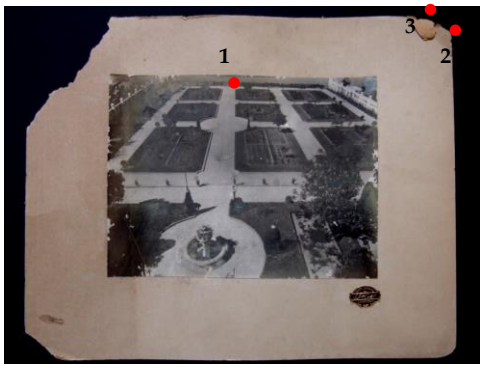

Figure 14. Locations of the samples collected from photograph 1 before treatment.

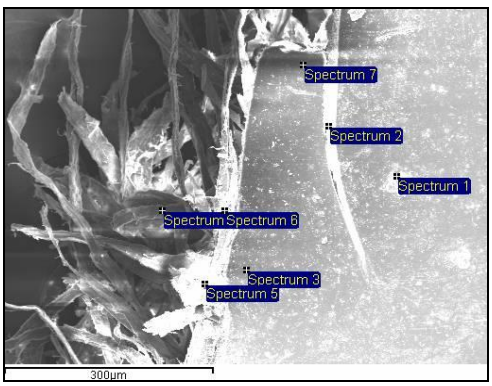

Figure 15. SEM micrographs of the three layer structure of photograph and the locations of the EDX analysis.

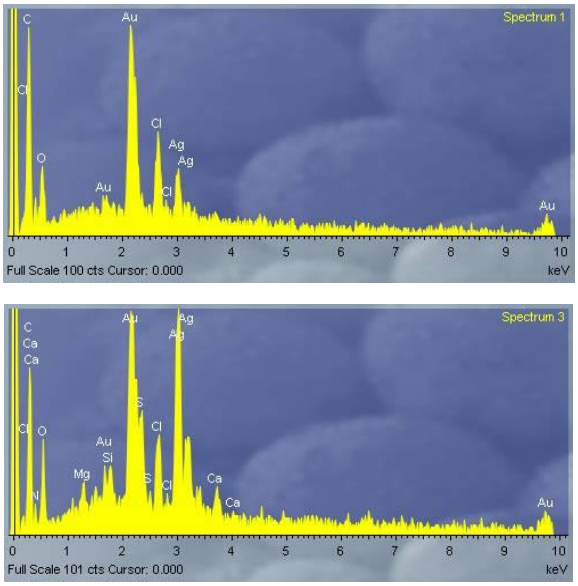

Figure 16. X-ray spectrum 1 reveals the presence of silver in small quantity in the midtones (top) compared to the shadow areas (bottom).

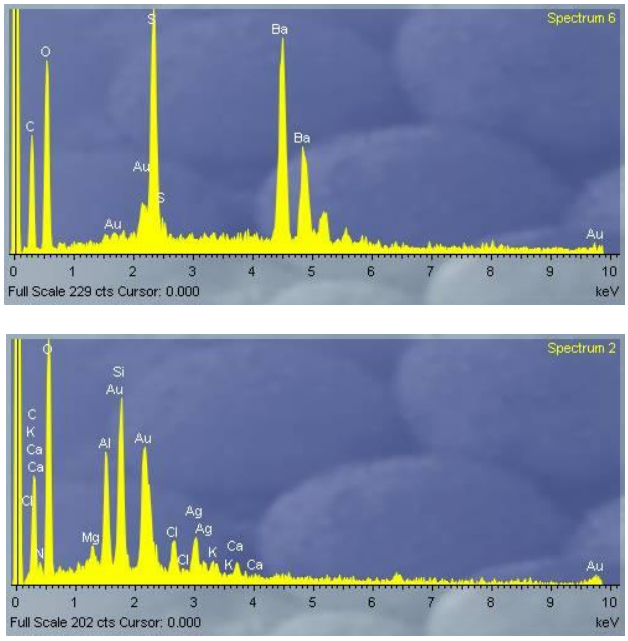

Figure 17. X-ray spectrum 6 shows barium and sulfur indicating the presence of the baryta coating (top). X-ray spectrum 2 reveals the presence of carbon, calcium, silicon, magnesium, and aluminum, which are elements related to paper making (bottom).

Examination also allowed for definition of the plant origin of the cellulosic materials of the primary support as being cotton because of the distinctive morphology of the fibres. SEM observations of the secondary support showed a high deterioration degree on the secondary support paper with the cellulose fibres broken. The source of the cellulose fibres of the bottom layer of the secondary support has been identified as wood pulp (Fig. 18), while the top layer is made of linen fibres.

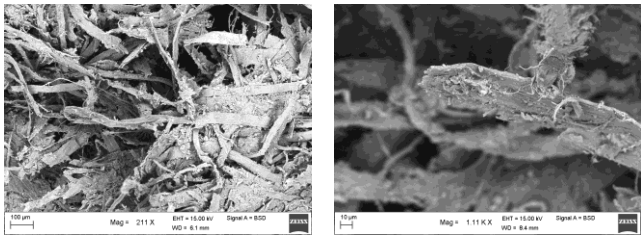

Figure 28. SEM micrographs of the cellulose fibres of the bottom layer of the secondary support showing severe damage.

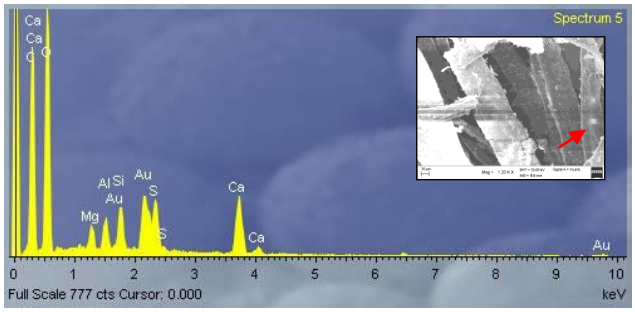

Figure 19. SEM micrographs of the cellulose fibres of the top layer of the secondary support showing the presence of white particles and elemental analysis of the particles showed that it is composed of elements used as paper fillers.

As shown in (Fig. 19), few small particles bound to the cellulose fibres are evidenced in the top layer of the secondary support. EDX analysis of these particles detected the presence of carbon, calcium, silicon, sulfur, and magnesium that forms the fillers of paper.

SEM examination of photograph two also revealed the common basic three layer structure of photographs: image layer (silver particles embedded in a gelatin binder), baryta layer, and the primary support (Fig. 20). EDX analysis revealed silver as the image forming substance and detected the presence of a baryta coating. The silver is present in high quantity since the sample was collected from the shadow areas. EDX analysis of the midtone sample showed a decrease in the amount of silver present (Fig. 21).

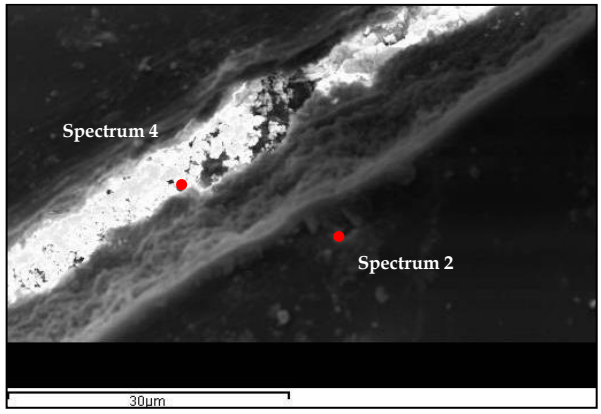

Figure 20. SEM micrographs of sample 1 representing the layer structure of the photograph 2. The sample was taken from the shadow areas of the photographs.

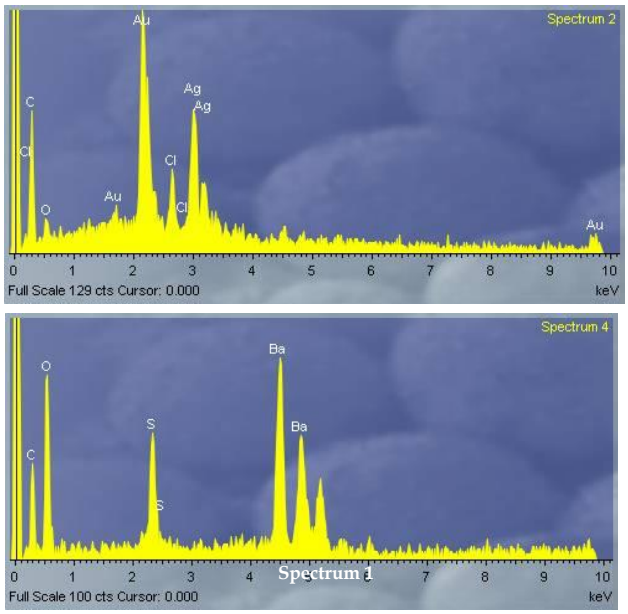

Figure 21. X-ray spectrum 2 showing the presence of silver as the final image material (top) and baryta coating is identified by the presence of barium and sulfur in spectrum 4 (bottom)

The bottom layer of the secondary support is in very bad condition displaying weak, embrittled fibres. The morphology of the fibres identifies the cellulose fibres as wood pulp. On the other hand, the top layer seems to be in a better state of preservation and is made of linen fibres (Fig. 22).

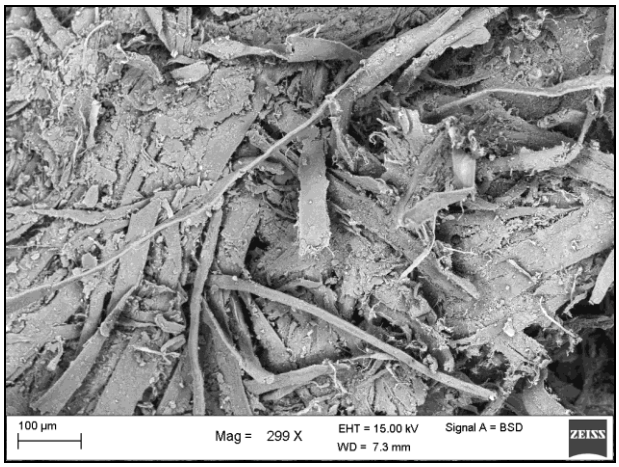

Figure 22. SEM micrographs showing the bottom layer of the secondary support displaying severe degradation (left).

SEM examination revealed the presence of a small quantity of minute white particles distributed on the surface of the top layer fibres. EDX analysis showed the presence of carbon, calcium, aluminum and silicon suggesting that calcium carbonate or silicates were used in the paper making process (Fig. 23).

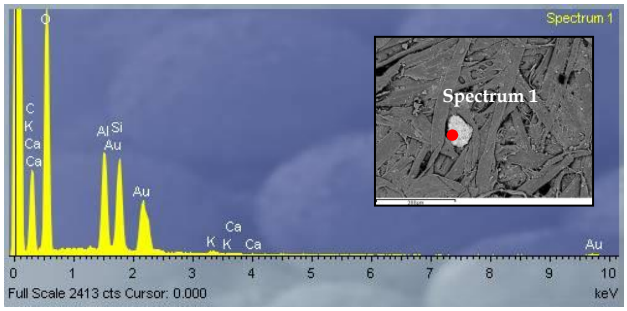

Figure 23. SEM micrograph of the top layer of the secondary support showing the presence of white particles. X-ray spectrum 1 showing the elemental composition of paper filler added during the making of the paper.

SEM observation of photograph 3 also revealed information about the structure of the photograph showing the presence of the image layer, the baryta layer, and the primary support. The samples also showed signs of physical damage in the form of cracks and scratches through the image layer. Further examination of the fibres allowed the definition of the plant origin as being cotton (Fig. 24).

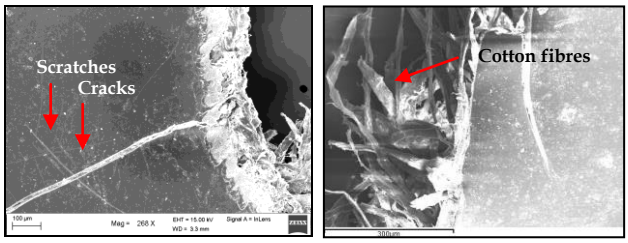

Figure 24. SEM micrograph of sample 1 representing the layer structure of photograph 3. The image layer suffers from cracking and few scratches are present (left). SEM image of cotton fibres used to make the photographic paper (right)

Like previous EDX analysis, results revealed the presence of a high amount of silver which was expected since the sample was taken from the shadow area. The analysis also detected the presence of the baryta coating. Fibres of the secondary support are severely damaged. The fibres have been broken to shorter fibres properly due to the attack of acids through an acid catalyzed hydrolysis process.

SEM examination showed the cracking of the image layer and the presence of the baryta coating. It also identified the fibres of the top layer of the secondary support as linen. On the other hand, the bottom layer of the support was made of wood pulp and is severely deteriorated. Broken fibres explain the extreme embrittlement of the secondary support (Fig. 25).

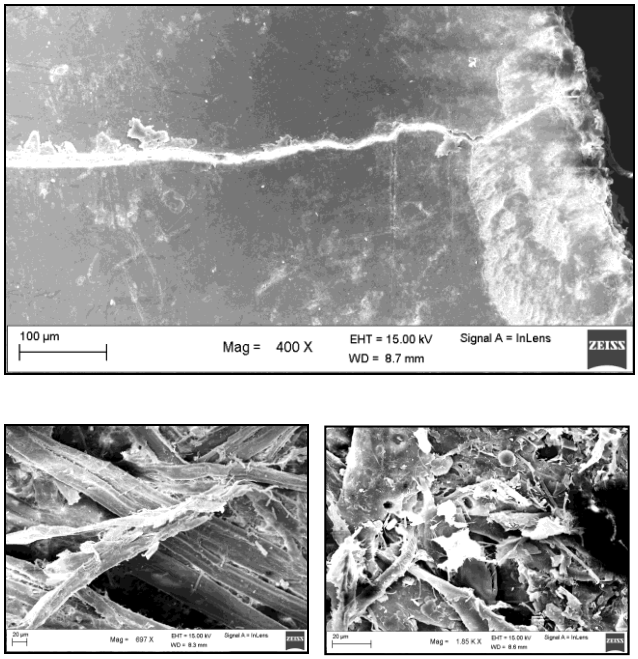

Figure 25. SEM micrograph of photographic 4 showing the image layer with signs of cracking (top), SEM micrograph representing the fibres of the top layer of the secondary support (bottom, right), and SEM micrograph representing the bottom layer of the secondary support. The cellulose fibres are obviously broken and weak.

EDX analysis results were similar to previous cases, where silver was identified and it refers to the final image material. Analysis also showed the presence of both barium and sulfur indicating the presence of a baryta layer. Elements related to paper manufacture such as calcium, carbon, aluminum, silicon, and magnesium were also detected.

SEM/EDX examination and analysis revealed similar results for photograph 5. It is composed of three layers the image layer, the baryta coating and the primary support. Silver is present in SEM analysis of the image layer sample indicating that the photographic process used is a silver-based one. EDX analysis also revealed the presence of elements such as calcium, silicon, carbon, and aluminum suggesting the use of fillers.

SEM-EDX analysis indicates that all photographs have a three-layer structure consisting of the image layer, baryta coating, and primary support. In all cases, silver was found to be the final image material indicating that the photographic process used in a silver-based one.

Paper is but one aspect of the complex and multilayer fibre-based silver gelatin photographic prints; however, it greatly takes part in the deterioration cycle, particularly if the photograph is mounted. In general, the main constituents of paper are cellulose, hemicelluloses, and lignin. Paper is a relatively stable material but it can deteriorate as a result of the presence of acid substances, exposure to moisture, sudden changes in temperature, and the action of oxidizing agents and UV-visible light (Jablonský et al., 2013). Cellulose is a natural polymer of β-(1 → 4)-linked D-glucopyranose monomer units. SEM investigation of the primary supports reveal cotton as the raw material for paper making and examined samples are seen to retain the original fibrous structure. However, the secondary supports show a completely different picture. The fibres are broken into smaller fragments this could be clearly explained by the mechanisms of paper degradation.

Cellulose degradation should be regarded in terms of mixed oxidative and hydrolytic mechanisms (Giorgi et al., 2002; Qian Xiang, 2003; Łojewska et al., 2005; Lattuati-Derieux et al., 2006), and (Batterham and Rai, 2008). Acid hydrolysis of cellulose and/or other constitutive polymers is known to be the predominant reaction during the aging of paper (Lattuati-Derieux et al., 2006). According to the standard reaction-kinetic models, the rate of the hydrolytic process depends on the temperature, the acidity and the amount of moisture present in the paper, which is dependent on the relative humidity of the environment. In the middle of the 19th century, paper making from rag was replaced by the use of wood pulp (Giorgi et al., 2002). It has appeared that the addition of aluminum sulfate into wood pulp during the manufacture process acts as a catalyst of hydrolysis (Łojewska et al., 2005). Furthermore, as a consequence, lignin, hemicellulose, and hydrolyzed cellulose oxidize and produce substantial amounts of acidic degradation byproducts and therefore this process is termed "autocatalytic". The overall effect of this degradation process is the shortening of the average chain length of the cellulosic component, which leads to loss of paper strength (Giorgi et al., 2002).

Secondary supports in the present study appear to have been made from wood pulp, which is more chemically reactive compared to rag (Giorgi et al., 2002), and this explains why they have changed into smaller fragments (Fig. 25).

4.3 FTIR spectroscopy

Results of this section were explained and discussed in accordance with several studies. Samples were collected from the surface layer of the photographs (the image layer and primary paper support), and the components of the secondary support.

In general, protein gives rise to nine characteristic IR absorption bands, namely, amide A, B, and I-VII. Of these, the amide I and II bands are the two most prominent vibrational bands of the protein backbone (Adochitei and Drochioiu, 2011). FTIR analysis of silver gelatin photographs is usually a quick and

highly reliable way to identify the binder since it can differentiate between gelatin and albumen photographs. FTIR spectra of both photographs are almost identical. Both show Amide I and Amide II spectral peaks that indicate the presence of proteins as previously mentioned (Stulik and Kaplan, 2013). Amide I band is mainly related with the C=O stretching vibration and it occurs in the range of 1660 – 1600 cm^{-1}, while amide II band is relates with the N-H bending and C-H stretching vibration and it occurs in the range of 1565 – 1500 cm^{-1} (Derrick et al., 1999). The FTIR spectrum of gelatin-based photographs shows three peaks at about 1450, 1393, and 1312 cm^{-1}. The peaks at 1450 and 1393 cm^{-1} are not the same intensity, with the peak at 1450 cm^{-1} usually being much more intense than the peak at 1393 cm^{-1} (Stulik and Kaplan, 2013). Amide III occurs in the range of 1220 – 1300 cm^{-1}, and it results from in phase combination of C-N stretching and C=O bending vibrations (Vasconcelos et al., 2008).

Hydrolysis of gelatin 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 in by comparing the relative absorption intensities of the amide I band to that of the amide II. On the other hand oxidation results in the formation of carbonyl compounds which would absorb in the 1700 -1750 cm^{-1} wavenumber region. This can be seen as a slight shoulder on the amide I carbonyl band and may result in the increase in area of the amide I band (Derrick, 1991). In addition, the position of the Amide I, II, and III bands indicate the conformations of the gelatin: 1650 cm^{-1} (random coil) and 1630 cm^{-1} (β-sheet) for amide I, 1540 cm^{-1} (random coil) and 1520 cm^{-1} (β-sheet) for amide II, and 1230 cm^{-1} (random coil) and 1270 cm^{-1} (β-sheet) for amide III (Vasconcelos et al., 2008). The ratio between the amide III band and amide I can be used to observe the loss of the secondary structure of gelatin and formation random coil structure. An increase in amide I band intensity is related to an increase in random coil at the expense of the ordered secondary structure (Al-Saidi et al., 2012).

With respect to the primary support 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; 2894 cm^{-1} corresponding to CH_2 stretching symmetrical; 1642 cm^{-1} corresponding to H_2O; 1427 cm^{-1} corresponding to CH_2 deformation stretching; 1369 cm^{-1} corresponding to CH deformation stretching; 1315 cm^{-1} corresponding to OH deformation stretching; 1160 – 898 cm^{-1} corresponding to C-O stretching of COH/C-O-C.

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 chromophores and their creation is one of the reasons paper yellows as it ages. The formation of carboxyl groups, increases acidity and induces depolymerization of the cellulose, as a result the physical and mechanical strength of the material decreases. Cellulose is highly hygroscopic, the degree of which depends upon the number of hydroxyl groups (-OH) in the molecule. The greater the number of hydroxyl groups, the greater the chance of forming hydrogen bonding with water molecules. If the cellulose is oxidized, its hydration capacity decreases as there will be fewer hydroxyl groups to form hydrogen bonds. Hydroxyl groups vibrate in the region around 3300 cm-1 and consequently a smaller peak indicates that a portion of the cellulose has degraded (Batterham and Rai, 2008). In addition, if the FTIR absorption band at 1427 cm^{-1}, assigned to the CH_2 band, which is known as the "crystallinity band", decreaces in its intensity, this reflects reduction in the degree of crystallinity of cellulose. The FTIR absorption band at 898 cm-1, assigned to C-O-C stretching at β-(1→4)-glycosidic linkage, is designed as an amorphous absorbtion band (Ciolacu et al., 2011). The FTIR bands characteristics of lignin are located at 1598, 1509, 1460, and 1267 cm^{-1} (Ferrer and Sistach, 2007).

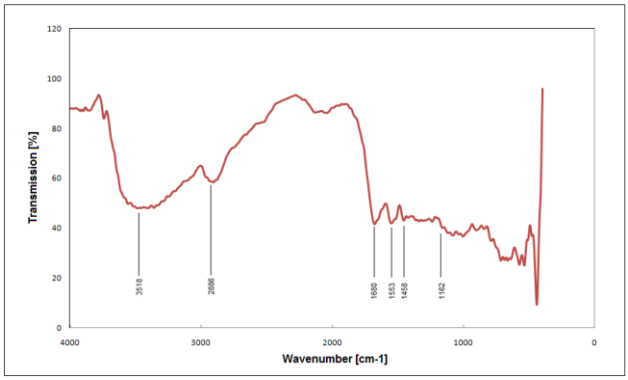

Figure 26. FTIR spectrum of a silver gelatin photograph from the collection.

Based on the obtained FTIR data in accordance with the previous studies, all photographic prints under study are gelatin-based showing amide I and amide II bands, characteristics of gelatin at 1680 and 1553 cm^{-1} for photograph 1; 1680 and 1558 cm^{-1} for photograph 2; 1693 and 1541 cm^{-1} for photograph 3; 1646 and 1539 cm^{-1} for photograph 4, and 1687 and 1561 cm^{-1} for photograph 5, respectively. The peaks at 1450 and 1393 cm^{-1} are not the same intensity, with the peak at 1450 cm^{-1} being much more intense

than that at 1393 cm^{-1} indicating that the binder is gelatin and not albumen (Fig. 26)

With respect to the gelatin binder of photograph 1, no signs of deterioration can be observed, with the Amide I and Amide II bands of the same intensity. The shift observed in the position of Amide III indicates that a very minor change has occurred causing the gelatin to convert from the triple helices to random coils. The paper support is also in good state of preservation, showing no signs of oxidation or hydrolysis.

Comparing the relative absorption intensities of the amide I band to that of the amide II in photograph 2, 3, and 4 reveals a difference in size, this can be assigned to the hydrolysis of the gelatin, (Fig. 46). Oxidation of the gelatin in photograph 3 gave rise to an intense growth of carbonyl vibrations at around 1695 cm^{-1} which resulted in the increase of the amide I band. The carbonyl group was assumed to be due to the oxidation of gelatin and not the paper support since visual inspection of all primary supports showed no signs of yellowing, a damage aspect which occurs as a result of oxidation. The increase in the area of the OH stretching band in photograph 5 indicates more hydrogen bonding which may be due to the hydrolysis of the gelatin (Fig. 26).

Most of the mounts used with photographic prints are composed of a good quality top (facing paper) and a bottom sheet of grounded or highly lignified fibres (backing board). This is the case with all five photographs. Samples were collected of each paper type from each photographic print (Fig. 27).

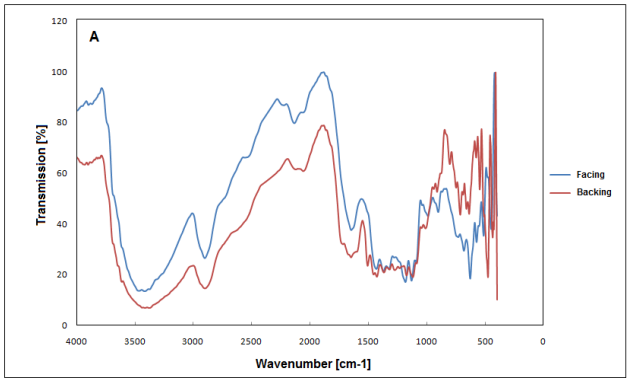

Figure 27. FTIR spectrum of the secondary support of a silver gelatin print from the collection, before treatment.

FTIR spectrum of secondary support used with photograph 1 revealed that the cellulose of the facing paper has been slightly hydrolyzed, showing an increase in the OH stretching band region at around 3415 cm^{-1}, the presence of the C-O stretching band, and the presence of the H_2O band at 1648 cm^{-1}. The spectrum of the backing board had a peak at around 1650 cm^{-1} which indicates the presence of carbonyl groups (C=O) which are a product of cellulose oxidation. Oxidation of cellulose also gave rise to carboxyl groups (-COOH) at around 3414 cm^{-1}. The presence of these groups explains the yellowing of the support. Carboxyl groups increases acidity and induces depolymerization of the cellulose which results in loss of the mechanical strength of the support. The increase in the OH stretching band is assigned to the hydrolysis of the cellulose and formation of hydroxyl groups. In addition, the very broad OH stretching band indicates more hydrogen bonding (Fig. 27).

FTIR spectrum of facing paper for photograph 2 reveals the presence of the carbonyl groups at around 1650 cm-1 indicating the occurrence of slight oxidation. The presence of the C=C stretching of the aromatic ring at around 1516 cm^{-1} indicates the presence of lignin. With respect to the backing board, it appears to suffer from severe degradation in the form of embrittlement and yellowing. Oxidation of the cellulose gave rise to a slight growth of carbonyl vibrations at around 1644 cm^{-1} and carboxyl vibrations at around 3466 cm^{-1}.

The secondary support of photograph 3 shows no signs of deterioration in terms of its facing paper; however, the backing board is in poor condition. The presence of the carbonyl groups (C=O) at around 1644 -1658 cm^{-1} and the carboxyl groups at 3413 cm^{-1} indicate that the cellulose has been oxidized (Fig. 28). With respect to secondary support of photograph 4, the facing paper shows no signs of deterioration. The presence of the C=C stretching of the aromatic ring at around 1514 cm^{-1} indicates the presence of lignin. The photograph is assumed to have been stored in a high temperature environment which has caused the breakage of some bonded OH bonds, giving rise to free OH bonds at 3618-3650 cm^{-1}. The spectrum also had a peak at 3464 cm^{-1} and a peak at 1646 -1676 cm^{-1} indicating the presence of carboxyl groups and carbonyl groups, respectively.

Similar state of preservation was observed in the secondary support of photograph 5. The facing paper is in good condition. FTIR spectrum shows a lignin peak at around 1514 cm^{-1}. The vibrations at 3436 cm^{-1} and 1647 cm^{-1} most evidently originating from the carboxyl and carbonyl groups, respectively, indicating that the cellulose has been oxidized.

All five backing boards had lignin vibrations for C=C stretching of the aromatic ring at around 1508, 1513, 1508, 1508-1599, and 1510 cm^{-1}, respectively (Lionetto et al., 2012). Upon natural aging and/or deterioration, the presence of lignin promotes the formation of free radicals such as keto, aldehyde and carboxylic groups, which cause the paper to discolor and become brittle on exposure to heat and light (Havermans and Dufour, 1997).

4.4 XPS analysis

Four samples were collected from different areas of photograph 2 and 4 (Fig. 28). Wide XPS spectra of the samples (SM2, SM4, Y4, and W4) are shown in figure 29.

Figure 28. XPS sample locations from photograph 2 (top) and photograph 3 (bottom).

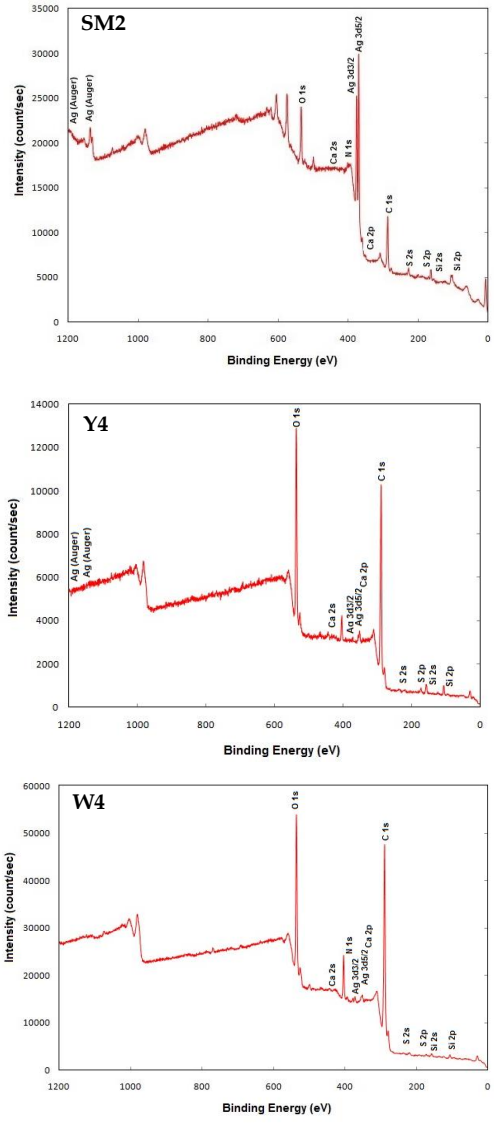

Figure 29. XPS wide spectra of mirrored samples collected from photograph 2 (SM2). XPS wide spectra of a yellowed sample (Y4) and a white sample (W4) collected from a midtone and highlight regions of photograph 4, respectively.

These spectra can only provide information about elemental composition of the photograph surfaces. In particular in the case of sample W that corresponds to a white area that doesn't show any mirroring degradation, the signals corresponding to C 1s, O 1s, Ag 3d, Ca 2p, Ca 2s, Si 2p, Si 2s, N 1s, S 2p and S 2s are detected (Fig. 29).

Most of these elements, such as silver, carbon, nitrogen and oxygen are expected for a photographic surface. The low intensity of the silver peak depends on the whitish region sorted out for the investigation. Calcium, silicon and sulphur clearly come from contamination of the surface. More information can be drawn by the expanded regions of the relevant ionizations. Looking at the C1 1s ionisation, it is possible to have two kinds of information: the first is that in the spectrum there is an electrostatic shift of 0.35 eV. The second is that some carbon atoms are partially oxidized being the band strongly asymmetric toward high binding energies. This observation is in line with the gelatine composition in which C-O-N, O-C-O and C=O groups are present (McArther et al., 2014). The silver 3d $_{5/2,3/2}$ ionizations are shifted to lower BE , being the value observed for the 5/2 component at 367.80 eV: this is an indication of the oxidation of the metal at the photograph surface. The band of nitrogen 1s is quite symmetric (figure. 30) and its binding energy (BE) is centred at 400.0 eV, it correspond exactly to the observed value for nitrogen in proteins (Vanea and Simon, 2011). No evidences of oxidized N=O groups have been observed.

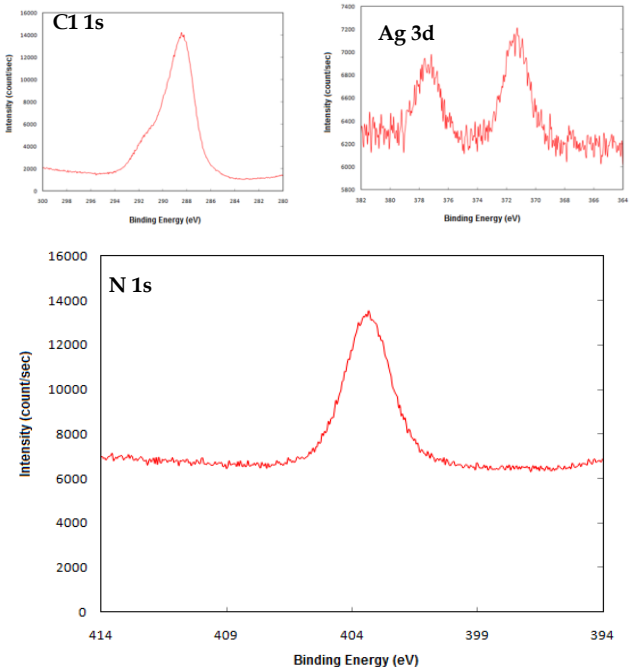

Figure 30. C1 1s, Ag 3d and N 1s expanded regions for the highlight sample (white).

Finally, calcium and sulphur ionizations strongly suggest the presence of calcium sulphate inside the image layer. The position of the S 2p band, centred at 168.80 eV, indicates the presence of the ion $SO_4^=$; on the contrary no $S^=$ has been detected. The presence of

calcium sulphate can be imputed to the use of the fixing solution obtained in normal freshwater (not deionised water) that actually shows moderately high content of calcium ions.

Mirroring degradation has been investigated in two different samples: SM2 and SM4. XPS spectra where obtained by analysing dark areas showing a clear mirroring effect. Both wide spectra are similar and show very high peaks due to the silver 3d ionizations being the spectra obtained from shadow area of the photographs (Fig. 30). Even if the qualitative description of the wide spectra could seem similar to the W ones, a deeper study of the expanded areas of the SM2 and SM4 spectra shows very interesting differences. Firstly the sulphur band is now a doublet of two components centred at 169.10 eV and 161.35 eV respectively. The new band at lower binding energies is related to the $S^{=}$ ion that is due to the presence of sulphide species.

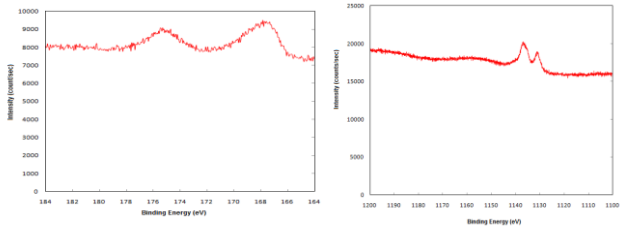

Figure 31. S 2p expanded regions (left) and AgMVV expanded regions (right) for the mirrored samples SM2.

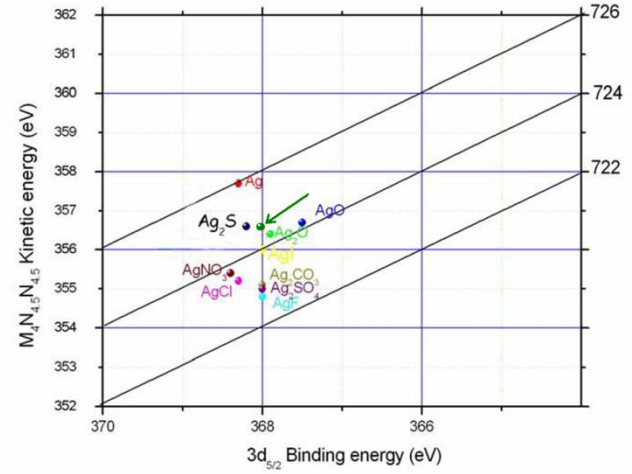

Figure 32. A 2D plot of silver auger parameters: the arrow indicates the position corresponding to peaks measure on the mirrored surface.

Moreover, in order to better investigate the spectroscopic properties of silver, the regions of the Auger lines MVV has been studied (Fig. 31). For the transition M_5VV a kinetic energy of 351.2 eV, corrected by the 1.2 eV electrostatic shift measured on C1s band, has been calculated. By considering the silver $3d_{5/2}$ ionization at 368.0 eV it is possible to calculate the Auger parameter (Altavilla and Ciliberto, 2012). The corresponding value has been reported in the plot of figure 32. The position of the Auger parameter appears to be quite close to the corresponding value of Ag_2S. Moreover by calculating the surface atomic concentrations of the two elements we obtain a ratio Ag:S of 2.2:1 instead of 2:1. This value indicates that the 90% of the silver is in form of Ag_2S on the surface.

4.5 Taxa identification

Table V shows the sources of the isolates collected from the photographs.

Table V. Isolate number and location

	1	2	3	4	5
Image layer	PE1	PE2	PE3	PE4	PE5
Secondary Support	PS1	PS2	PS3	PS4	PS5

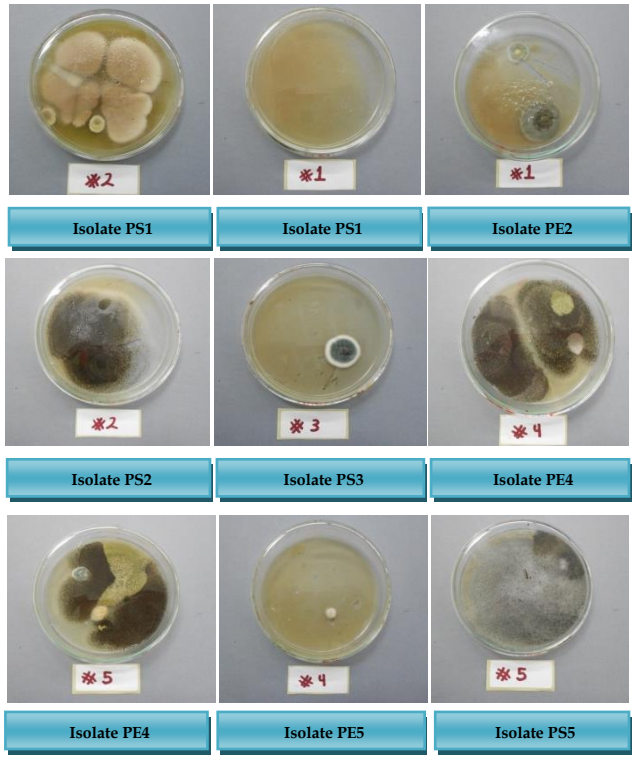

Figure 33. Inoculated plates showing fungal growth after two weeks of incubation at 28°C.

Table VI. Microscopic examination of mold growth (Fig. 33)

Isolate Number	Observation after 2 weeks of growth
PE1	1. No visible growth
PS1	1. Gray green circle with a fluffy appearance. 2. Fluffy white circle with an olive green center.
PE2	1. Beige with a white edge, fluffy, somewhat symmetrical circles that have grown into each other. 2. Yellow beige fluffy growth.
PS2	1. Black and does not have a fluffy appearance.
PE3	1. No visible growth.

PS3	1. Fluffy white circle with a dark green center.
PE4	1. Black and does not have a fluffy appearance. 2. Yellow green fluffy circle, somewhat symmetrical. 3. White flat growth.
PS4	1. Symmetrical circular fluffy white growth.
PE5	1. Grayish white fluffy circle. 2. White fluffy growth. 3. Olive green fluffy appearance.
PS5	1. Black and does not have a fluffy appearance. 2. Creamy white. 3. Light olive green fluffy growth. 4. Fluffy symmetrical white circle with a dark green center.

For characterization and identification, the isolates were studied under the light microscope (Table VI) and identified according to the morphological characteristics of the fungal colonies. Different species were isolated from the photographic prints and the results are listed in Table VII and Table VIII.

Table VII. Fungal species found on the image layer

Isolate Number	Fungal Species according to morphological identification
PE1	No growth
PE2	Aspergillus tamari Aspergillus sp.
PE3	Penicilium sp.
PE4	Aspergillus niger Aspergillus paraziticus Alternaria sp.
PE5	Alternaria sp. Nigrospora spaerita

Table VIII. Fungal species found on the secondary support

Isolate Number	Fungal Species according to morphological identification
PS1	*Alternaria sp.* *Penicilium sp.*
PS2	*Aspergillus niger*
PS3	No growth
PE4	*Aspergillus sp.*
PE5	*Aspergillus niger* *Aspergillus paraziticus* *Aspergillus ochrichus* *Penicilium sp.*

Fungal genera isolated from the photographic prints are frequently mentioned as being typical of photographic materials. Results reveal that *Aspergillus sp.* and *Penicilium sp.* are the most predominant species detected on both the image layer and the secondary paper support (Lavédrine, B., 2003; Vivar, I., et al., 2013).

5. INTERVENTIVE CONSERVATION

5.1 Disinfection

Natural products obtained from plants with biocidal activity represent an alternative and useful source in the control of biodeterioration of documentary heritage, without negative environmental and human impacts. Therefore, clove oil was used with all five photographs since it has antimicrobial antiseptic, and disinfecting action, given by its content in terpenes, aromatic aldehydes, terpenic aldehydes and phenolic compounds, among other components (Borrego et al., 2012).

5.2 Mechanical cleaning

Dry cleaning was performed on the back and front of all secondary supports using soft brushes and a Staedtler vinyl eraser to remove surface dirt. This step is very important prior to mount removal in order to avoid the penetration of dirt inside the paper fibres. The supports were then thoroughly brushed to remove the residue which might cause future problems due to its sulfur content. A very fine brush was used to gently clean the image side of the photographs without producing scratches. Silver mirroring was reduced using a Staedtler Rasoplast eraser. All photographs were cleaned in the same manner (Fig. 34).

Figure 34. Surface cleaning of the photograph 2 using a fine brush and a Rasoplast block eraser.

5.3 Dismantlement of the secondary support

Due to the poor condition of the secondary support and its contribution to the degradation of the photographic print, the researcher decided to remove the secondary support, which was not historically significant and did not contain any information. Later steps will involve deacidifying the top layer of the secondary support, which carries the photographer's label and fixing it to a proper backing. Dry removal of the secondary support was carried out using a microspatula. All photographs were demounted using the same technique. The wet removal method involved immersing the mount in a warm water and ethanol bath 3:1 for a period of 5 minutes. The wet paper facing was removed from the water, supported on a reemay support to avoid tearing it. In cases where the facing paper was not removed by complete immersion procedure, another step was carried out to mechanically remove the mount board using a microspatula (Fig. 35).

Figure 35. Dismantlement of the secondary support by immersion in water and ethanol bath 3:1, followed by removal of the backing board using a microspatula.

5.4 Deacidification

In this procedure, the facing papers of all five photographs were immersed in an alkaline solution (calcium hydroxide) until the acidity has been neutralized and the pH has been raised to 7.5. During the deacidification treatment, the facing papers were immersed in subsequent baths of 0.2% solution of calcium hydroxide and washed thoroughly with water. They were then removed from the water bath on a support and dried between blotters under light pressure for several days.

5.5. Solvent cleaning

Several spot tests were carried out on discrete areas of the prints to determine the effect of acetone, ethanol, and a mixture of toluene and ethanol on the image and stains. All tested solvents had no apparent effect on the image visually speaking; however, ethanol proved to be the most efficient. Solvents were applied to the image surface after dipping a cotton ball wrapped around a spatula lightly in a suitable solvent according to each case. The cotton was checked and changed continuously until the cotton no longer picked up dirt (Fig. 36).

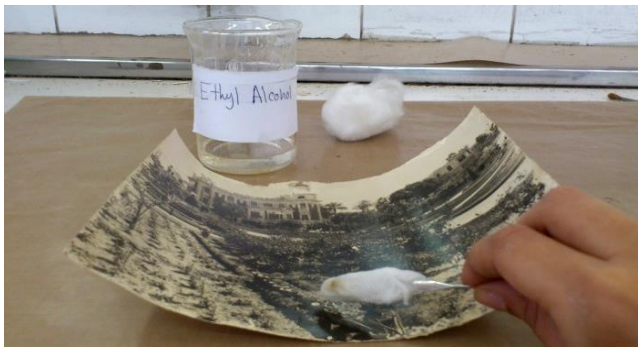

Figure 36. Solvent cleaning of photograph 2 using a mixture of ethanol and toluene 1:1 (top and center). Pure ethanol was used to clean photograph 5 (bottom).

5.6 Tear mending and compensating for losses

Structural repair of the facing papers was necessary to in order to limit further damage. For tear mending, a small strip of Japanese paper and polyethylene with the polyethylene side down was placed on the tears found on the verso of the facing papers, and using a cauter, the repaired areas were well pressed to secure the repair paper in place. This step is very important prior to leaf casting to consolidate weak areas in the paper. The leaf casting technique was employed to further repair the facing paper. The purpose of leaf casting is to mechanically stabilize paper that is weakened due to holes, ragged borders, or other such reasons (Fig. 37).

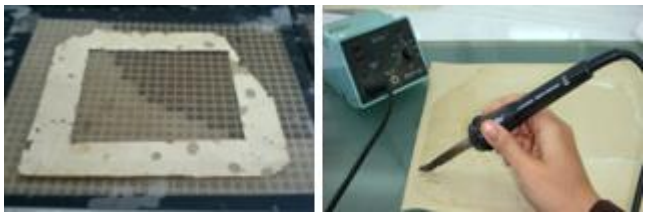

Figure 37. The leaf casting machine (left). Securing repaired parts using a cauter (right).

5.7 Remounting

Each repaired facing papers was fixed to an acid-free board using carboxy methyl cellulose (CMC). This was followed by securing the photographic images in place using the same adhesive. Finally, mounted prints were dried between two sheets of polyester webbing, followed by sheets of blotting paper under light pressure for several days (Fig. 38).

Figure 38. Photograph 3 after remounting using carboxy methyl cellulose and during drying under weights.

5.8 Retouching

There are some ethical issues involved in retouching photographs, since it modifies 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 surrounds. Because all conservation treatments must be reversible, an isolating layer of gelatin was place between the photographic paper and the retouching medium. The pencil is the simplest retouching tool. Yet, despite its simplicity it can accomplish much work. The work was done using a Faber-Castell Art and Graphic Polychromos set. Color pencils are used to apply a serious 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 (Fig. 39).

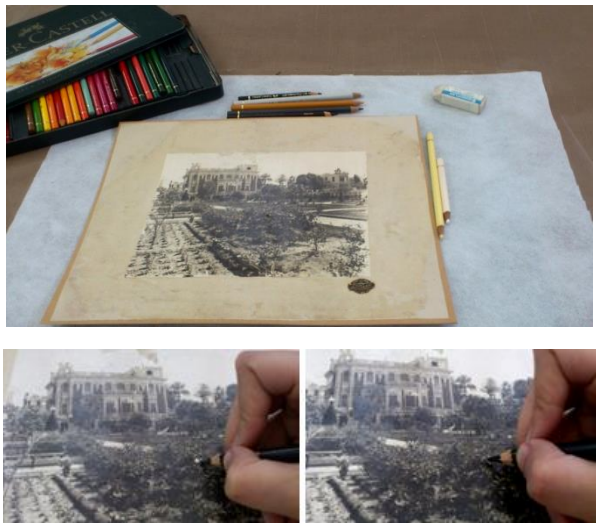

Figure 39. Retouching using Faber-Castell Art and Graphic Polychromos set. Photograph 5 before and after retouching.

5.9 Rehousing

The photographs were then housed in a custom made Mylar folders sealed on three sides and placed inside a custom made archival box.

6. CONCLUSION

El-Shenawy palace photographic collection was identified as developed–out silver gelatin images (DOP) through visual inspection, and SEM-EDX, FTIR and XPS analysis. Silver gelatin developed-out images have the following characteristics

- The final image material is metallic silver.
- Three layer structure (gelatin binder, baryta layer, and primary support).
- Paper fibres invisible.
- Silver mirroring common in dark areas.
- Neutral black and white tones.

Several deterioration forms were identified through visual inspection such as image discoloration in the form of fading, yellow/brown discoloration and mirroring; cracking and losses in the gelatin binder layer; embrittlement of the secondary support and other forms related to paper deterioration (i.e. tears, losses, and yellowing).

Results of SEM-EDX analysis revealed a three layer structure of the images consisting of an image layer, a baryta layer, and a paper support. The final image material was identified as metallic silver (Ag^0). SEM investigation also proved that primary supports were made from rag pulp, while 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.

FTIR analysis showed that only minor degradation has occurred in the gelatin binder in most cases. Hydrolysis of gelatin was observed in photographs 2, 3, 4, and 5. FTIR spectrum of photograph 3 shows an intense growth of carbonyl vibrations at around 1695 cm^{-1}, indicating the occurrence of oxidation. The secondary supports had a strong carbonyl vibration indicating that the cellulose has been oxidized. Lignin was detected by FTIR analysis in most secondary supports. The presence of lignin promotes discoloration and embrittlement of paper.

XPS analysis results allows us to conclude that silver mirroring is mainly formed of a surface layer of silver sulfide (Ag_2S), a result of the reaction between silver ions and an environmental sulfur-based compound.

Based on microbiological studied, the dominant fungi isolated from the photographs were identified as *Aspergillus tamari, Aspergillus sp., Aspergillus niger, Aspergillus paraziticus, Aspergillus ochrichus, Penicilium sp., Alternaria sp.,* and *Nigrospora spaerita.*

The conservation of the photographic collection was effectively performed following several interventive treatments. Dry cleaning was carried out using a fine brush and a vinyl eraser. Chemical cleaning using ethyl alcohol and in some cases a mixture of ethyl alcohol and toluene gave good results, visually speaking. Deacidification treatment using calcium carbonate was a necessary step to neutralize the high acidity of the secondary support since we decided to keep the facing paper of the supports for their historical value. Tear mending and compensating for losses were performed 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 Mylar folders. All treatments fulfilled the aim of reinforcing the structure of the photographs, enhancing their appearance, and stabilizing their condition to prevent them from further deterioration and mechanical damages.

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REFERENCES

Adcock, E., Varlamoff, M., Kremp, V. (1998) *IFLA principles for the Care and Handling of Library Materials*. International Preservation Issues, No.1, International Federation of Library Associations and Institutions Core Programme on Preservation and Conservation and Council on Library and Information Resources. Retrieved from http://www.ifla.org/files/assets/pac/ipi/pchlm.pdf

Adochitei, A., Drochioiu, G. (2011) Rapid Characterization of Peptide Secondary Structure by FT-IR Spectroscopy, *Rev. Roum. Chim.,Vol. 56, Issue 8*.

Al-Saidi, G.,Al-Alawi, A., Rahman, M., Guizani, N. (2012) Fourier Transform Infrared (FTIR) Spectroscopic Study of Extracted Gelatin from Shaari (*Lithrinus microdon*) skin: effects of Extraction Conditions, *International Food Research Journal*, Vol. 19, Issue 3.

Altavilla, C., Ciliberto, E. (2012) *Cultural Heritage Materials: An XPS Approach*. Nova Science Publishers, Inc. New York.

Baldasici, O., Barbu-Tudoran, L. (2012) Structural and Elemental Analysis of Biodegraded Artifacts., *Annals of RSCB*, Vol. XVII, Issue 2.

Batterham, I., Rai, R. (2008) A Comparison of Artificial Ageing with 27 Years of Natural Aging. *AICCM Book, Paper and Photographic Materials Symposium*.

Borrego, S., Valdés, O., Vivar, I., Lavin, P., Guiamet, P., Battistoni, P., Gómez de Saravia, S., Borges, P. (2012) Essemtial Oils of Plants as Biocides against Microorganisms Isolated from Cuban and Argentine Documentary Heritage, *International Scholarly Research Network Microbiology*.

Ciolacu, D., Ciolacu, F., Popa, V. (2011) Amorphous Cellulose – Structure and Characterization. *Cellulose Chemistry and Technology*, Vol. 45.

Clark, S., and Frey, F. (2003) *Care of Photographs*. European Commission on Preservation and Access. Retrieved from http://www.knaw.nl/ecpa/sepia/linksandliterature/CareOfPhotographs.pdf

Cycleback, D. (2010) *Judging the Authenticity of Photographs*, Hamerweit Books.

da Silva, N., Taniwaki, M., Junqueira, V., Silveira, N., do Nascimento, M., Gomes, R. (2013) *Microbiological examination Methods of Food and Water: A Laboratory Manual*, Taylor and Francis Group, London, United Kingdom.

Derrick, M. (1991) Evaluation of the State of Degradation of Dead Sea Scroll Samples Using FT-IR Spectroscopy, *The Book and Paper Group Annual*, Vol. 10.

Donaldson, J. (2000) *Preservation Notes: Caring for Photographs and Paper Workshop*, New South Wales. Retrieved from http://www.magsq.com.au/_dbase_upl/training_pres_photospaper.pdf

Durant, F. (2005) *Albumen Prints: Their History, Conservation, and Care*, 2005. Retrieved from http://www.ischool.utexas.edu/~fdurant/Project_pages/Albumen%20Final.doc

Eastman Kodak Company (1985). *Conservation of Photographs*, Eastman Kodak Company.

Egunnike, L. (2003) *Preservation of Works on Paper*. Arts Torque.

Ferrer, N., Sistach, C. (2007) FTIR Technique Used to Study Acidic Paper Manuscripts Dating from the Thirteenth to the Sixteenth Century from the Archive of the Crown of Aragón, *The Book and Paper Group Annual*, Vol. 26.

Giorgi, R., Dei, L., Ceccato, M., Schettino, C., Baglioni, P. (2002) Nanotechnologies for Conservation of Cultural Heritage: Paper and Canvas Deacidification, *Langmuir*, Vol. 18.

Griffith, G., Easton, G., Detheridge, A., Roderick, K., Edwards, A., Worgan, H., Nicholson, J., Perkins, W. (2007) *Copper Deficiency in Potato Dextrose Agar causes Reduced Pigmentation in Cultures of Various Fungi*, Federation of European Microbiological Societies Letter, Blackwell Publishing Ltd., Vol. 276, 2007, p. 165.

Havermans, J. B. G. A., and Dufour, J. (1997) Photo Oxidation of Paper Documents: A Literature Review, *Restaurator*, Vol. 24.

Held, B., Jurgens, J., Arenz, B., Duncan, S., Farrell, R., Blanchette, R. (2012) Environmental Factors Influencing Microbial Growth inside the Historic Expedition Huts of Russ Island, Antarctica. *International Biodeterioration and Biodegradation*, Vol. 75.

Hendriks, K. (1984) The Preservation and Restoration of Photographic Materials in Archives and Libraries: A Ramp Study with Guidelines, UNESCO, Paris.

Hendriks, K., Ross, L. (1998) The restoration of Discolored Black-and-White Photographic Images in Chemical Solutions. *Reprint from preprints of papers presented at the 16th Annual Meeting of the American Institute for Conservation of Historic and Artistic Works*, New Orleans, Louisiana.

Hendriks, K., Thurgood, B., Iraci, J., Lesser, B., Hill, G. (1991) *Fundamentals of Photograph Conservation: A Study Guide*. Lugus Publications, Canada.

Jablonský, Holúbková, S., Kazíková, J., Botková, Ház, A., Bajzíková, M. (2013) The Treatment of Acid Newsprint Paper: Evaluation of Treatment by MGO or by a Mixture of MGO and Methyl Methoxy Magnesium Carbonate. *Wood Research*, Vol. 58, Issue 2.

Lattuati-Derieux, A., Bonnassies-Termes, S., Lavédrine, B. (2006) Characterization of Compounds Emitted during Natural and Artificial Ageing of a book: Use of Headspace-Solid-Phase-microextraction/Gas Chromatography/Mass Spectrometry. *Journal of Cultural Heritage*, Vol. 7.

Lavédrine, B. (2003) *A Guide to the Preventive Conservation of Photograph Collections*, Getty Publications, USA.

Lionetto, F., Del Sole, R., Cannoletta, D., Vasapollo, Maffezzoli, A. (2012) Monitoring Wood Degradation during Weathering by Cellulose Crystallinity. *Materials*, Vol. 5.

Montanari, M., Mellomi, V., Pinzari, F., Innocenti, G. (2012) Fungal Biodeterioration of Historical Library Materials Stored in Compactus. *International Biodeterioration and Biodegradation*, Vol. 55.

Łojewska, J., Miśkowiec, P., Łojewska, T., Proniewicz, L. (2005) Oxidative and Hydrolytic Path of Paper Degradation Studied by In-situ FTIR Transmission Spectroscopy. *Polymer Degradation and stability*. Vol. 88.

McArthur, S., Mishra, G., Easton, C. (2014) Applications of XPS in Biology and Biointerface Analysis, *Surface Analysis and Techniques in Biology*, V.S. Smentkowski Ed., Springer International Publishing.

Morris, P. (2003) Photographic Media: Care and Handling. *Public records information leaflet no. 19*, South Carolina Department of Archives and History.

Nishimura, D. (1993) *Sulfiding of Silver Images*. Conservation Distlist Archives. Retrieved from http://palimpsest.stanford.edu/byform/mailing-lists/cdl/1993/0386.html

Porck, H., Teygeler, R. (2000) *Preservation Science Survey: An Overview of Recent Developments in Research on the Conservation of Selected Analog Library and Archival Materials*. Council on Library and Information Resources, Washington, D.C.

Princi, E., Vicini, S., Marsano, E., Trefiletti, V. (2008) Influence of the Artificial Weathering on Thermal Stability of Paper-based Materials, *Thermochimica Acta*, Vol. 468.

Reilly, J. (2005) *Stability Problems of 19th and 20th Century Photographic Materials*. Rochester Institute of Technology, New York. Retrieved from http://albumen.conservation-us.org/library/c20/reilly-stability.html

Roosa, M. (2004) Handling and Storage of Photographs. International Preservation Issues, No. 5, the International Federation of Library Associations and Institutions (IFLA) Core Activity on Preservation and Conservation.

Ryhl-Svendsen, M (1999). An Introduction to the Factors which Deteriorates Photographic Materials, and to Basic Preventive Conservation. *Seminar notes: Western African Museums Program (WAMP)*, Saint Louis, Senegal, Retrieved from http://www.iaq.dk/papers/wamp_photo.htm

Stulik, D., Kaplan, A. (2013) *The Atlas of Analytical Signatures of Photographic Processes: Silver Gelatin*, The Getty Conservation Institute, USA.

Teygeler, R. (2001) *Preservation of Archives in Tropical Climates: An annotated bibliography*. Retrieved from http://www.knaw.nl/ecpa/grip/pdf/tropical/tropical.pdf

Vanea, E., Simon, V. (2011) XPS Study of Protein Adsorption onto Nanocrystalline Aluminosilicate Microparticles. *Applied Surface Science*, Vol. 257, Issue 6.

Vasconcelos, A., Freddi, G., Cavaco-Paulo, A. (2008) Biodegradable Materials Based on Silk Fibroin and Keratin, *Biomacromolecules*, Vol. 9.

Vivar, I., Borrego, S., Ellis, G., Mareno, D., Garcia, A. (2013) Fungal Biodeterioration of Color Cinematographic Films of the Cultural Heritage of Cuba. *International Biodeterioration and Biodegradation*, Vol. 84.

Weaver, G. (2008) *A Guide to Fiber-Base Gelatin Silver Print Condition and Deterioration*, Adobe Calson, Pro, Catriel, and Tandelle.

Wilhelm, H., Brower, C. (1993) *The Permanence and Care of Color Photographs: Traditional and Digital Color Prints, Color Negatives, Slides, and Motion Pictures*. Preservation Publishing Company.

Xiang, Q., Lee, Y. (2003) Heterogeneous Aspects of Acid Hydrolysis of α-Cellulose. *Applied Biochemistry and Biotechnology*, Vol. 105-108.