

EVALUATION OF CONVENTIONAL TREATMENTS FOR MIRRORED SILVER GELATIN PRINTS: EXPERIMENTAL AND APPLIED STUDY

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Abstract

Silver gelatin prints are found abundantly among photographic collections. They are composed of three main components: the final image material, filamentary silver particles; the binder, gelatin; and the primary support, paper. Due to this complex structure, silver gelatin prints are very vulnerable to the surrounding environment, particularly to air pollutants. As a result, silver gelatin prints commonly suffer from an image decay form known as silver mirroring, a bluish metallic sheen found on the surface of such photographs. The aim of this study is to assess several treatments to determine which is efficient and safe for use to treat silver mirroring. The following treatments were tested: ethyl alcohol (100%), ethyl alcohol and distilled water (80:20%), Magic Rub vinyl eraser, Faber Castell eraser, and gelatin coating. Treatments were evaluated using visual inspection, microscopic inspection, Fourier transform infrared spectroscopy and colorimetric measurements. Long-term effect of the treatments on the photographic samples was studied using artificial aging. Samples were exposed to humid heat aging conditions at a temperature of 80°C and 65% RH for 5 day. The paper also presents the conservation of a historical silver gelatin print suffering from mirroring. Treatment carried out included: disinfection, mechanical cleaning, and dismantlement of secondary support, deacidification, tear mending, remounting and retouching.

Keywords: *Silver gelatin prints; Oxidation; Mirroring treatments; Artificial aging; Microscopic examination; FTIR; Colorimetric measurement; SEM; Remedial conservation.*

Introduction

Silver gelatin developed-out prints were popularized by Eastman Kodak Company in 1886. Chemical development of positive photographic images formed the basis of modern photography [1]. Basically, a silver gelatin print is composed of three major components: the primary support material which provides the physical support to the photographic image, paper; the binder, gelatin; and the final image material, metallic silver [2-4]. A fourth component which is commonly included is an interlayer between the support and the image layer, the baryta layer [5]. The baryta layer consists of finely grounded barium sulphate, a white pigment, in gelatin [6].

Silver gelatin prints are a complex product of their manufacture, processing and subsequent display and storage conditions [7]. The complexity of silver gelatin prints make them one of the most vulnerable types of objects held by museums, libraries and archives [8].

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The more recent the photographs, the more chemically unstable they are. Therefore, we find that the majority of damaged photographs are likely to be those made in the early 20th century [9]. There are other terms used to describe this form of damage including sulfiding out, mirroring and silvering out [10]. Silver gelatin prints are prone to deterioration and/or degradation by numerous agents [11]. Agents which may affect the stability and permanence of silver gelatin prints include: intrinsic agents (i.e. natural decay, poor manufacture, built-in properties, multiple layer structure and poor processing) and extrinsic agents (i.e. temperature and relative humidity, atmospheric pollutants, light and irradiation, biological threats, inappropriate handling and misuse, and disasters) [12, 13]. At improper levels or fluctuations in the levels of extrinsic agents, silver gelatin prints that are either displayed or stored can undergo varying degree of deterioration and/or degradation [14].

The main concern in this work is image silver decay, particularly silver mirroring. Image silver comprises the final image. Image silver is found as microscopic grains embedded in the binder layer, gelatin [15]. Silver is reactive towards a number of chemical reagents than one would expect for its classification as a noble metal [6]. The stability of silver grains depends to a large degree on their morphology [16]. In silver gelatin developed-out prints, image silver is found in the form of twisted strains known as filamentary silver [17, 18]. Image silver is the most vulnerable part in silver gelatin prints. Silver particles have dimensions of the order of microns and in developed-out silver gelatin prints, a complex dendritic form. Their small dimensions and the presence of kinks result in them having a large surface area. This explains their susceptibility to undergo reactions and corrosion processes [19].

The first stage of image silver decay is the oxidation of the silver particles; the metallic particles (Ag^0) are stripped of electrons and converted to invisible silver ions (Ag^+). These silver ions may migrate away from their parent silver grain in all directions within the gelatin binder. Once the silver has been oxidized to silver ions and travelled away from the silver particle, it has four possible fates. However, silver mirroring occurs when the mobile silver ions migrates to the surface [7, 20]. On the surface, it is assumed that silver ions are reduced back to metallic silver [21]. However, X-ray photoelectron spectroscopy (XPS) results allowed 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 [22], [23]. Nearly most 19th and 20th century silver gelatin prints are affected by this type of image decay [24]. Silver mirroring appears as a bluish metallic sheen giving the shadow areas an iridescent appearance [9, 10, 25, 26]. When very severe, it can appear green, violet or bronze in color [25]. Silver mirroring can occur locally or overall depending on the source of pollutant attacking the image silver [7].

The treatment of silver mirroring is a controversial issue among conservators. Some conservators argue that mirroring should not be removed as it is a sign of authenticity and should be valued as a patina. Others suggest that it should only be removed if it disfigures the image rather than enhance it. However, while this damage form can be appealing now, one should consider that the continuation of the same decay process will result in undesirable appearance in the future.

Since it is not possible to return the silver particles in the surface mirror to its original location in the binder layer, methods of reduction or removal have been performed and several have been investigated [27]. Chemical restoration has been used to convert mirrored silver salts to black elemental image silver. However, attempt to carry them out may cause serious damage, and even when successful can alter the tone of the photograph changing the integrity of the object [1]. One of the previously investigated treatments involved immersion of the damaged photographic print in a solution of iodine/alcohol for a short time. This treatment was introduced by *Edith Weyde* in 1972 [28]. Another treatment involving the use of Thiourea and

ammonium thiosulfate was performed to remove mirroring from aged negative material [29]. Two types of PVC erasers were examined and their effects on both silver gelatin and albumen prints were evaluated [30]. The author recommended more studies to be carried out. PVC erasers, ethanol/water solution and iodine/ethanol solution, methyl cellulose and coating microcrystalline wax coating were evaluated and the results show that they have affected the surface characteristics of the tested images [31].

The main aim of this study is to evaluate the efficiency of the following selected treatments: ethyl alcohol (100%), ethyl alcohol with distilled water (80: 20%), Magic Rub vinyl eraser, Faber Castell vinyl eraser, and a gelatin coating in removing silver mirroring. Both the immediate and long-term effects of the treatments have been examined. The second part of the study involves the treatment of a selected vintage silver gelatin print suffering from silver mirroring based on the result obtained from the experimental study.

Materials and Methods

Samples

Three naturally aged developed-out silver gelatin fiber-based prints were selected as test materials. This would give the study a more practical approach rather than a theoretical one. All three samples suffered from overall silver mirroring (Fig. 1).

A vintage photograph of an unknown man dressed in a black suit and a tie was selected for this study. In terms of structure, the photograph 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 poor-quality wood pulp. The integral support carries the signature of the photographer. Due to the appearance of silver mirroring in the images and the likelihood of a gelatin binder layer, the researchers concluded that the image is most likely a silver gelatin print. It appears 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. The general condition of the photograph prior to treatment is poor (Fig. 2).

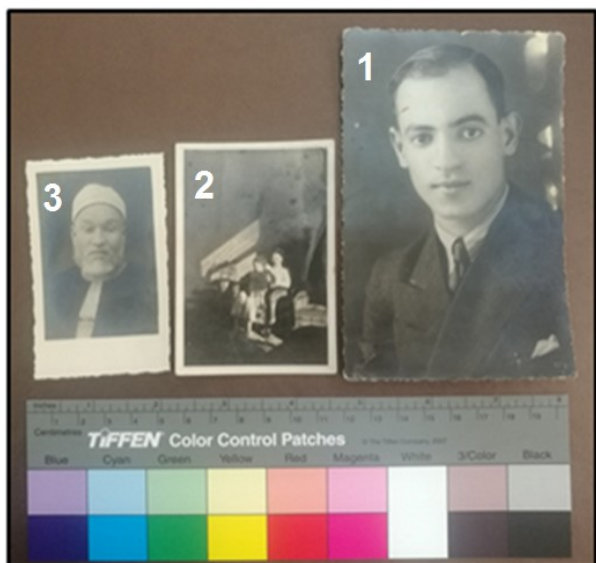


Fig. 1. Silver gelatin photographic samples showing signs of silver mirroring



Fig. 2. A 20th century silver gelatin print showing signs of silver mirroring visible in the shadow areas

The surface characteristics of the photograph are represented in Table 1.

Table 1. Surface characteristics of the selected photograph

Texture	Sheen	Image size (cm × cm)	Support size (cm × cm)
Smooth	Matt	24 × 17.5	34 × 25

Treatments

Five treatments were selected for this study based on their common used by photograph conservators. Eraser treatments included two types of erasers: Magic Rub and Faber Castell. Ethyl alcohol was used in two concentrations [31-33]. Furthermore, the study evaluated one type of coating, gelatin. The solvent treatments were applied using sterilized cotton swabs, while the coatings were applied by a soft brush to avoid scratching the surface. Samples were each assigned a code according to the treatment. For example, in sample 1, the area treated with ethyl alcohol was given the code 1E, where 1 is the sample number and E is the treatment used. In the same sample, the area treated with ethyl alcohol and distilled water was given the code 1EW, where 1 is the sample number and EW is the treatment used and so on. Table 2 below lists the different treatments and samples used.

Table 2. Samples and applied treatments

Sample number	Dimensions (cm × cm)	Treatment	Application method
Photograph no. 1		Ethyl Alcohol	
1E		Alcohol 100%	
1EW	13 × 8.5	Alcohol 80% + distilled water 20%	Cotton swab
Photograph no. 2		Eraser	
2MR	8.8 × 6	Magic Rub	A light circular motion.
2FC		Faber Castell	
Photograph no. 3		Coatings	
3G	8.2 × 5.2	Gelatin coating (2%) in distilled water	Brush

Visual inspection

Visual observation is included to monitor unexpected visual changes. A photographic survey was carried out before and after each treatment in ambient light also to highlight the surface characteristics of the photograph as well as the present damage forms.

Surface examination by digital microscope

A SUPEREYES PZ01 500X USB Digital Microscope was used to document surface characteristics of the tested photographic samples before and after each treatment and after artificial aging.

Colorimetric measurements

The change in color due to treatments was measured using an Optimatch 3100® spectrophotometer from SDL Company. All samples were measured in a visible region, with an interval of 10 nm using D65 light source and an observed angle of 10 degrees. The CIELAB color parameters (L^* , a^* and b^*) were used, where L^* defines lightness and varies from 0 (black) to 100 (white); a^* represents the red/green axis, where $+a^*$ means red and $-a^*$ means green; b^* represents the yellow/blue axis, where $+b^*$ means yellow and $-b^*$ means blue. All values of L^* , a^* , and b^* were obtained before treatment and after treatment and artificial aging. Each reading was the average of three measurements. The total color difference ΔE^* was also calculated from the following formula: $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ [34-36]. The analysis was carried out at the National Institute of Standards (NIS) in Cairo, Egypt.

Fourier transform infrared spectroscopy

FT-IR spectroscopy was used to study the chemical changes which may have occurred after treatment and artificial aging, also the photographic process, the binder and the damage present. The FTIR instrument used is Jasco FT/IR-6100 Spectrometer under transmission mode

in the range of $4000 - 400\text{cm}^{-1}$. The analysis was carried out at the National Institute of Standards (NIS) in Cairo, Egypt.

Ninhydrin test

Ninhydrin is a chemical used to detect protein [37]. When it reacts with an amino acid, it produces a deep violet, resonance-stabilized anion called Ruhemann's purple [38]. The reagent was prepared by dissolving 1.25g of ninhydrin crystals in 200mL of acetone [39]. One drop of the reagent was placed on the swaps and a piece of each eraser) post silver mirroring removal, and was then heated on a tacking iron for several minutes before a color appeared [40]. The test was performed to study if the tested treatments disturb the gelatin binder layer. The same test was performed on a blank to ensure that the test was being conducted correctly.

Scanning electron microscopy

Scanning electron microscope with an energy dispersive X-ray Microanalysis system (EDX) was used to identify the photographic process used and to study the changes that have occurred as a result of natural aging and/or deterioration. Samples were examined using a Zeiss LEO Supra 55VP Field Emission with EDX Oxford Instrument X-act PentaFET Precision model 51-ADD001. All samples were first coated in gold using EMITECH K450X Sputter coater. Sputtering was performed under an argon gas flow at a working distance of 50mm at 0.05mbar and a current of 40mA for 30 seconds and then observed using the scanning electron microscope operated at an accelerated voltage of 5 – 15kV. The SEM - X-ray microanalysis was performed at the SEM Laboratory, Department of Chemical Sciences, University of Catania, Italy.

Fungal testing

Microbiological studies were carried out at the Microbiology Laboratory of the National Archives in Cairo, Egypt. A methodology was developed to isolate the fungi. There are several methods to obtain samples; however, due to the historical value of the print, swab sampling technique was used to minimize damage since it is considered a non-invasive sample prelevation method [41]. Sterile cotton swabs were used to gently wipe the infected areas of the print then transferred to the lab in sterile tubes to be used for fungal culturing and identification [42]. Samples were kept frozen until isolations were made in the laboratory [43]. 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) [44]. 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 [45]. 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.

pH value measurement

The pH of the secondary support was evaluated using pH paper strips. Using a pipette, a drop of water was placed on the secondary support and the pH paper strips was placed over it and left for a few minutes. The color of the strip was then compared with that of the standard to determine the pH value integral of the secondary support.

Results and Discussions

Evaluation of Silver Mirroring Treatments

Visual inspection

Treatments performed using a pure solution of ethyl alcohol solution and a mixture of ethyl alcohol and distilled water (80:20%) yielded good results showing no visible signs of damage to the tested photographic surfaces (Fig. 3). Eraser treatments gave good results in terms of silver mirroring removal; however it caused apparent mechanical damage to the

photographic surface, particularly in the case of the Faber Castell eraser. Fine minor scratch marks were created probably by the abrasives contained in the eraser (Fig. 4). The application of a gelatin coating on the surface effectively removed the silver mirroring appearance; however, it led to the swelling and peeling of the gelatin layer (Fig. 5). Based on the obtained results, all treatments were effective in removing silver mirroring. Ethyl alcohol treatments were the effective in reducing silver mirroring without causing further visible damage. Removing silver mirroring with erasers required the greatest physical effort; and therefore is a lengthy procedure compared to other tested treatments.



Fig. 3. Photographic sample 1 before treatment (left) and after treatment with pure ethyl alcohol (red square) and after treatment with a solution of 80:20% of ethyl alcohol and distilled water (blue square)



Fig. 4. Photographic sample 2 before treatment (left), after cleaning with Faber Castell eraser (red square) and after cleaning with Magic Rub eraser (blue square)



Fig. 5. Photographic sample 3 before coating (left) and after coating with a 2% solution of gelatin in distilled water (right). Generally, good results were obtained (blue square); however, loss in the gelatin binder has occurred in some areas as a result of the treatment (red square)

Surface examination by digital microscope

Obtained images show slight change in surface sheen for the pure ethyl alcohol treatment. No change was observed for the sample treated with 80:20% solutions of ethyl alcohol and distilled water. Post artificial aging result showed no major alterations. The gelatin coating gave good results in terms of mirroring removal and the revealing of the original dark surface of the photograph. No significant visible change was observed post artificial aging. As for the eraser treatments, major scratching was observed after treatment. After artificial aging, a loss in the gelatin binder was observed in the case of the sample treated with the Faber Castell eraser (Fig. 6).

Colorimetric measurements

In the cultural heritage field, the maximum acceptable difference of ΔE_{ab}^* has to be such to not compromise reading of the artworks. In particular, for the quantification of the colour

difference after aging tests [CIE 157: 2004], the ΔE_{ab}^* , 10 quantity is selected. The choice is based on the assumption that it represents the most used in the cultural heritage field [46, 47]. All treatments showed some degree of color change after treatment and artificial aging. However, in this case, it could be an indication of the efficiency of the tested treatments.

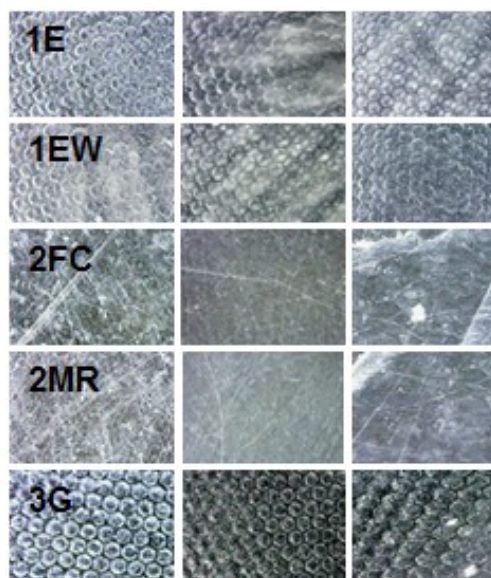


Fig. 6. Photographic samples before treatment (left column), after treatment (middle column) and after artificial aging (right column).

This is mainly because the removal of silver mirroring will result in the revealing of the original darker surface and for this reason it was necessary to study the change in the lightness of the sample, the L^* parameter. The decrease in the L^* value for ethyl alcohol treatments reveals their efficiency in removing the mirroring. The gelatin treatment also gave good results in terms of its effectiveness in removing silver mirroring. Although, the eraser treatments showed excellent results visually speaking, colorimetric measurements proved otherwise. L^* value results for both Magic Rub and Faber castell erasers indicate the minimal fading of the sample post treatment and artificial aging. The results are represented in Table 3.

Table 3. Colorimetric values for the tested samples and the total color change post treatment and artificial aging

ΔE^*	b^*	a^*	L^*	Sample
8.82	1.27	0.05	49.81	Reference sample 1
	2.49	0.21	40.61	Ethyl Alcohol 100% (treated and aged)
11.22	1.71	0.21	37.75	Ethyl Alcohol/ distilled water
	2.64	0.30	44.15	80: 20% (treated and aged)
16.48	9.30	0.28	59.97	Reference sample 2
6.47	1.01	-1.35	50.09	Magic Rub (treated and aged)
16.08	5.16	0.07	60.75	Faber castell (treated and aged)
	3.25	-0.12	44.36	Reference sample 3
				Gelatin coating (treated and aged)

Fourier transform infrared spectroscopy

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 [48]. Amide I band is mainly related with the $C=O$ stretching vibration and it occurs in the range of $1660 - 1600\text{cm}^{-1}$, while amide II band is relates with the N-H bending

and C-H stretching vibration and it occurs in the range of $1565 - 1500\text{cm}^{-1}$ [49]. Characteristic signals from cellulose fibres (i.e. the primary support) were observed, with absorption bands at around $3600 - 3100\text{cm}^{-1}$, corresponding to OH stretching vibrations; 2894cm^{-1} corresponding to CH_2 stretching symmetrical; 1369cm^{-1} corresponding to CH deformation stretching; and $1160 - 898\text{cm}^{-1}$ corresponding to C-O stretching of COH/C-O-C. The spectrum for the sample treated with pure ethyl alcohol showed an increase in the intensity of the amide I band and the broadness of the OH band indicating the occurrence of oxidation of cellulose which led to the formation of carbonyl and carboxyl groups [50]. The increase in the width of the amide I band indicates the oxidation of the gelatin binder [49]. As for the sample treated with 80:20% solutions of ethyl alcohol and distilled water, insignificant change in the identified functional groups has been observed. Very slight oxidation of the cellulose has occurred as indicated by the minor increase in the intensity of the amide I band. Results for the eraser treatments revealed that the change in the functional groups was more evident in the case of the Faber Castell treatment (Fig. 7).

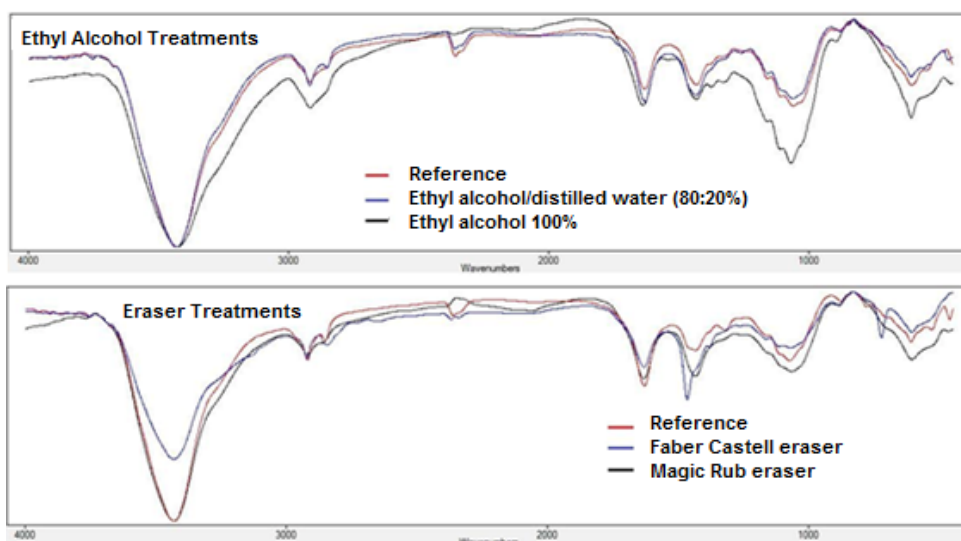


Fig. 7. FT-IR analysis results for ethyl alcohol and eraser treated samples before treatment and after treatment and aging

Ninhydrin test

Based on the results of this test, samples treated with ethyl alcohol were barely affected as the swab gave a faint purple color, whereas the samples treated with ethyl alcohol and distilled water (80:20%) and Magic Rub eraser was more affected by the treatment. However, in all previous cases the change was insignificant. Samples which were cleaned using Faber Castell eraser appear to have been affected the most.

Conservation of Mirrored Silver Gelatin Print

Visual inspection

The integral support was in poor state of preservation. It appeared to be acidic, yellowed and embrittled. It also suffers from structural damage such as tears, cracks and losses. These forms are typical of cellulose degradation. Paper undergoes inevitable aging process that causes cellulose to decay. Acid substances and moisture present in the print (acid hydrolysis), air pollutants (oxidation), microorganisms (biodegradation) and light (photodegradation) act together and led to the breakage of the polymeric chains of cellulose [51, 52].

The binder layer was also damaged. It suffered mainly from insect attack. Some scratches are also visible which are more likely due to improper handling of the print.

With regard to the image, the photograph appeared to suffer severely from irregular pattern of mirroring. Mirroring has mainly occurred due to the attack of the toxins such as lignins, sulfurous gases, and peroxides released from the poor quality integral support. These toxins have also caused the fading of the silver image (Fig. 8).

Microscopic inspection

Images obtained by USB microscope revealed the absence of the paper fibers of the primary support. This indicates the presence of a baryta layer within the structure of the print (Fig. 9).

SEM-EDX analysis

SEM examination of the primary support revealed that it was made from cotton, while the source of cellulose fibers of the integral secondary support has been identified as wood pulp. Image of the secondary support shows a high degree of degradation as indicated by the broken fibers (Fig. 10). EDX analysis of the print surface detected the presence of carbon, calcium, and silicon that forms the fillers of paper. The analysis also revealed silver as the image forming substance and detected the presence of a baryta coating (Fig. 11).

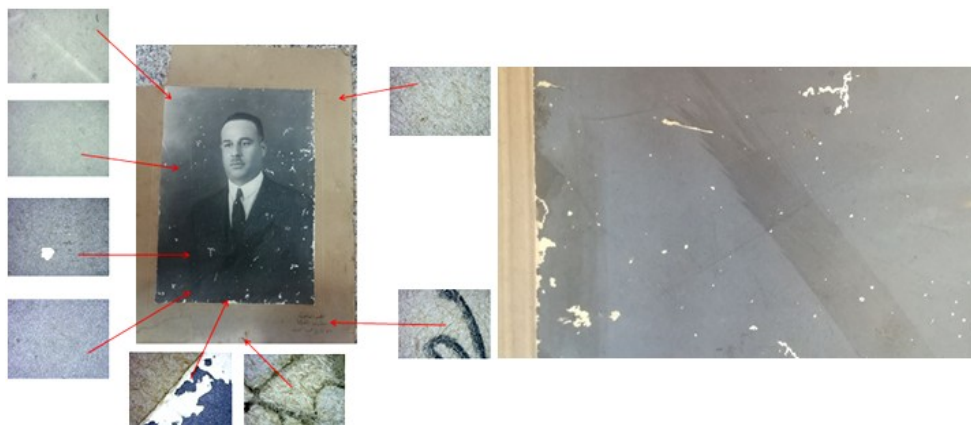


Fig. 8. Photo-documentation of the state of preservation of the silver gelatin print before treatment. The print shows sign of physical, chemical and biological deterioration. The print appears to suffer from severe mirroring.



Fig. 9. The silver mirrored surface (left). The baryta coating which is responsible for the absence of the primary support fibers (center). The brittle fibers of the secondary support (right).

Fourier transform infrared spectroscopy

The FT-IR spectrum of the print reveals the presence of amide I band at 1645cm^{-1} and amide II band at 1540cm^{-1} . Characteristic signals from the primary support were identified, with absorption bands at around 3438cm^{-1} , corresponding to OH stretching vibrations; 2926cm^{-1} corresponding to CH_2 stretching symmetrical; and 1070cm^{-1} corresponding to C-O stretching of COH/C-O-C. Results of visual examination, SEM-EDX analysis and FT-IR analysis confirm that the photograph is a silver gelatin print. Based on the obtained FT-IR data, the gelatin has been oxidized as indicated by the formation of a slight shoulder on the amide I carbonyl band [49] (Fig. 12).

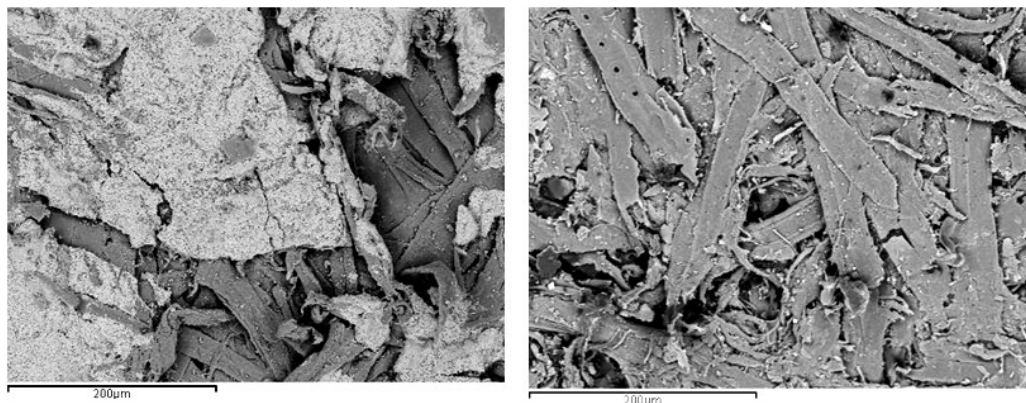


Fig. 10. SEM micrographs of the cotton fibers used to make the primary support (left) and the secondary support showing severe deterioration (right).

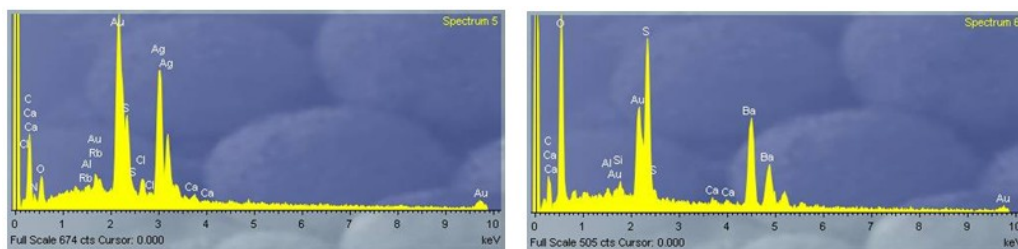


Fig. 11. X-ray spectrum showing the presence of silver as the final image material (left) and the baryta layer is identified by the presence of barium and sulfur (right).

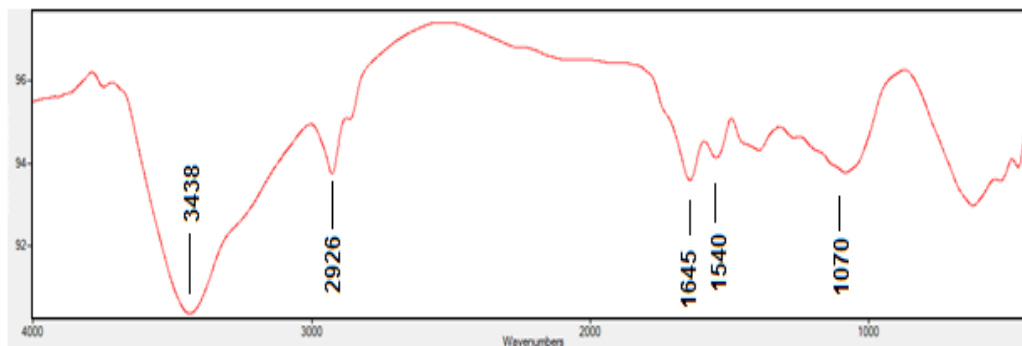


Fig. 12. FT-IR spectrum for the case study.

Taxa identification

For characterization and identification, the isolates were studied under the light microscope and identified according to the morphological characteristics of the fungal colonies.

The following species were isolated from the photograph (Fig. 13):

- *Aspergillus flavus*.
- *Aspergillus niger*.
- *Penicillium chrysogenum*.
- *Penicillium coryophilum*.

Fungal genera isolated from the photograph are frequently mentioned as being typical of photographic materials [26, 53].

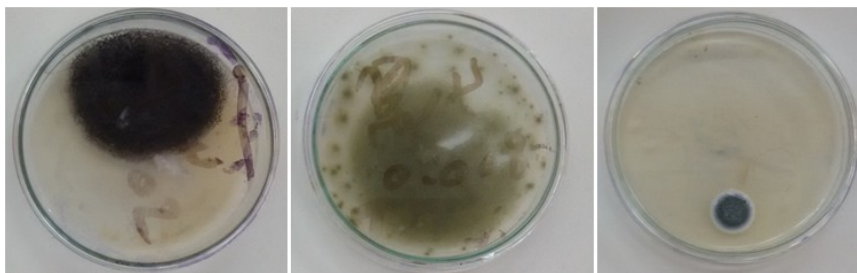


Fig.13. Inoculated plates showing fungal growth after two weeks of incubation at 28°C.

pH Value Measurement

The state of preservation of the integral secondary support (i.e. brittle and yellowed) indicates that it is acidic. pH value measurement confirmed the previous finding as the measured pH value for the secondary support was around 4.5.

Interventive conservation

Based on the examination and analysis results, we decided that the conservation treatments would involve disinfection, mechanical cleaning, dismantlement of secondary support, deacidification, tear mending, remounting and retouching.

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 since it has antimicrobial antiseptic, and disinfecting action, given by its content in terpenes, aromatic aldehydes, terpenic aldehydes and phenolic compounds, among other components [54].

Mechanical cleaning

Dry cleaning was carried out on the recto and verso of the secondary support and the image side of the print using a very fine brush (Fig. 14). This step is very important prior to mount removal in order to avoid the penetration of dirt inside the paper fibres. Silver mirroring was removed using 80:20% solution of ethyl alcohol and distilled water. Only minor cleaning was carried out using a Magic Rub eraser to avoid physically damaging the surface.

Dismantlement of the secondary support

Due to the poor condition of the secondary support and its contribution to the degradation of the photographic print, we decided to remove the bottom layer of secondary support, which was not historically significant and did not contain any information.

The wet removal method was used to demount the secondary support. It 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 (Fig. 15).

Deacidification

The facing paper was immersed in an alkaline solution until the acidity has been neutralized and the pH has been raised to 7.5. The treatment involved immersing the facing paper of the secondary support in subsequent baths of 2% solution of calcium hydroxide and magnesium hydroxide in distilled water [55].

Tear mending

Structural repair of the facing papers was necessary in order to limit further damage. For tear mending, a small strip of Japanese paper was placed on the tears found on the verso of the facing paper and secured in place using carboxy methyl cellulose (Fig. 16).



Fig. 14. The photograph during surface cleaning using a fine brush.



Fig. 15. Dismantlement of the secondary support in a bath of warm distilled water and ethyl alcohol

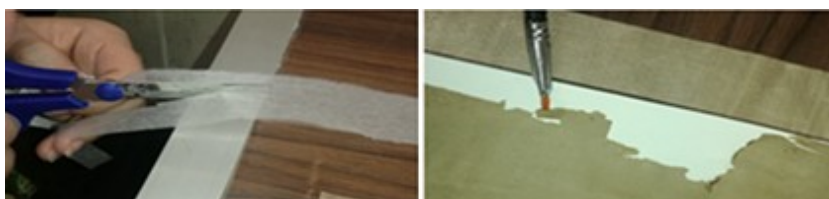


Fig. 16. Tear mending using Japanese paper and carboxy methyl cellulose as an adhesive

Remounting

The restored facing paper was fixed to an acid-free board using carboxy methyl cellulose. This was followed by securing the photographic images in place using the same adhesive. Finally, the mounted print were dried between two sheets of polyester webbing, followed by sheets of blotting paper under light pressure for several days.

Retouching

Retouching was done using a Faber-Castell Art and Graphic Polychromos set. 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 (Fig. 17).



Fig. 17. The photographic print before (left) and after treatment (right)

Conclusions

The main aim of this work was to evaluate the efficiency of selected treatments in the removal of silver mirroring and document their immediate and long-term effects on silver gelatin prints. All treatments appeared to have affected the tested photographic samples to some degree.

Visible inspection revealed that ethyl alcohol was the least to affect the surface of the photograph, while the use of eraser resulted in physical damage in the form of minor scratches. The application of gelatin coating while very successful in silver mirroring reduction; it caused the swelling and peeling of gelatin in certain areas.

Chromatic measurements showed some degree of color change after all tested treatments; however, this finding could be an indication of the efficiency of the tested treatments, since the removal of silver mirroring will result in the revealing of a darker surface. Ethyl alcohol and gelatin treatments gave good results. On the other hand, the erasers appear to have caused minimal fading.

FT-IR analysis results showed insignificant chemical change for the 80:20% ethyl alcohol and distilled water treated sample. Gelatin showed no change. Both types of erasers and pure alcohol treatment appeared to have caused change in the form of oxidation.

Ninhydrin testing results showed that the gelatin binder was most affected by Faber Castell eraser and least affected by pure ethanol treatment.

Based on the previous results, the researchers recommend the use of 80:20% solution of ethyl alcohol and distilled water for the treatment of mirrored silver gelatin print. In addition to its efficiency in removing silver mirroring without causing considerable damage, it is also efficient in removing surface dirt.

The treated case study was identified as a developed-out silver gelatin print dating back to the 20th century. The print has the following characteristics: three layer structure (i.e. image layer, baryta layer and primary support), neutral black and white tones since the final image material is filamentary silver and silver mirroring. Several decay forms have been identified via visual inspection such as silver mirroring, image fading, loss in gelatin binder, and embrittled and yellowed secondary support.

Results of SEM-EDX analysis revealed a three layer structure of the image consisting of an image layer, a baryta layer, and a paper support. The final image material was identified as metallic silver. SEM investigation also proved that primary support was made from cotton, while secondary support was made from wood pulp. The secondary support was found to suffer from severe embrittlement. The measured pH value for the secondary support was around 4.5.

FT-IR data showed that the gelatin has been oxidized as indicated by the formation of a slight shoulder on the amide I carbonyl band.

Based on microbiological studied, the fungi isolated from the photograph were identified as *Aspergillus flavus*, *Aspergillus niger*, *Penicillium chrysogenum*, and *Penicillium coryophilum*.

The conservation of the photographic collection was effectively performed following several interventive treatments. The print was disinfected using clove oil. Surface cleaning was carried out using a soft brush. Silver mirroring was mainly removed using 80:20% solution of ethyl alcohol and distilled water. The secondary support was dismantled using a bath of warm distilled water and ethanol. Deacidification was carried out using a mixture of calcium hydroxide and magnesium hydroxide (2%) in distilled water. Tear mending was done to consolidate the structure of the secondary support. The restored facing paper of the secondary support was fixed on an acid-free board. The photograph was remounted using carboxy methyl cellulose. Only minor pencil retouching was carried out to enhance the appearance of the photographic print.

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