

RESTORATION OF SILVER GELATIN PRINTS IN THE DIGITAL ERA: AN INNOVATIVE APPROACH

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Abstract

One of the most common physical damage in silver gelatin prints is losses which occurs due to many deterioration factors (i.e. rodent attack, improper handling, fire, etc.). Conventionally, conservators compensated for the losses by making paper infills. While this method improves the physical structure of the treated print, it creates an unacceptable appearance due to the large contrast between the tone of the original photograph and the blank paper. Manual retouching of the missing part does not provide a better solution either, since it is achieved using a different medium (i.e. watercolors, ink washes, conté crayons, pastels, and graphite). Many conservators are now aware of the advantages of digital restoration in treating old photographs. Hence, the importance of this study, which focuses mainly on modifying conventional methods used to treat losses by combining it with a digital restoration technique. The concept of this idea is solely based on the authors' vision. Accordingly, the main aim of this paper is to evaluate the efficiency of the proposed novel technique. Experiments were carried out on two old photographs of no significant value. Both photographs suffered from losses, particularly around the edges. Missing parts were digitally restored using Adobe Photoshop Software. Restored image data was then printed on Japanese paper using two types of printers: inkjet and laser. Samples on each printing process was exposed to artificial aging at a temperature of 80° and 65% relative humidity for a period of 120 hours to study the long-term efficacy of the proposed technique; as well as the effects it has on silver gelatin prints. Several examination and analysis methods were carried out for technique evaluation including: visual inspection, scanning electron microscope equipped with an EDX unit, attenuated total Reflectance Fourier transform Infrared (ATR-FTIR), colorimetric measurements, pH value measurement, and the Oddy test. Based on obtained results, laser printing is much more stable compared to inkjet printing; and therefore, it is considered the best option for this technique. All in all, one can conclude that the proposed technique is a very promising technique which can be efficiently used to restore losses in damaged photographic prints with slight effects on the original photograph.

Keywords: Silver gelatin prints; Losses; Infills; Digital restoration; Inkjet printing; Laser printing; Japanese paper.

Introduction

Silver gelatin prints were the form of nearly most of twentieth-century photography. These prints are present in large numbers not only in fine art collections, but in archives, historical societies, and family photograph collections. Silver Gelatin prints were introduced by Richard Leach Maddox in 1871 with subsequent considerable improvements in sensitivity

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obtained by Charles Harper Bennett in 1878 [1]. Silver gelatin prints were produced as printed-out and developed-out prints. Printed-out prints have warm tones, while developed-out prints has a neutral black-and-white tone [2, 3]. Both photographs are composed of a three-layer structure: the paper support and it serves as the substrate onto which the subsequent layers are attached; the baryta layer, a white opaque coating made primarily from gelatin and barium sulfate used to cover the paper fibers and form a smooth surface upon which to coat the gelatin; the gelatin binder that holds the silver grains of the photographic image [4].

Silver gelatin prints are one of the most vulnerable objects held by museums, archives and libraries due to their complex physical and chemical nature. They often display problems that reflect their manufacture, processing and surrounding environment. Factors that affect the permanence of silver gelatin prints are inherent vice, improper temperature and relative humidity levels, atmospheric pollutants, light and irradiation, biological threats, poor display and storage conditions, improper handling and disasters [4, 5]. Forms of damage can be divided according to their origin into physical, chemical, biological and deposited matter [6].

Dealing with losses in silver gelatin photographic prints continues to be a challenging issue facing photograph conservators. Conventionally, this procedure involves using a piece of paper that is of similar weight, texture, and color to the original. The prepared fill is secured in place with adhesive. However, it is difficult to repair losses in silver gelatin prints, because the refractive index and texture of silver gelatin binder are difficult to simulate [7]. The practice of restoring missing parts is either called inpainting or retouching. Inpainting defines the work carried out by a conservator/restorer to reinstate damaged areas in a photographic layer, in a way that blends with the surrounding colors without covering any of the original paint. On the other hand, retouching originally referred to corrections or changes made by an artist in his or her own artwork as final adjustments, in order to conclude a painting. Currently, the term has, to some extent, changed its meaning, becoming in some instances a synonym for inpainting [8]. Retouching materials in the early twentieth century included watercolors, ink washes, conté crayons, pastels and graphite.

Conservator often debate ethical issues involved in retouching photographs after repair and in-filling treatments. The argument revolves around the question of photographer's original intentions and the integrity of the original image. The Photograph Conservation Laboratory of the Metropolitan Museum takes a middle ground approach conservators, retouch to the point where in-fills, repairs and abrasions blend into their surrounds. It is only acceptable to reduce the visual impact of losses in damaged areas [9]. Retouching colors are applied to photographs using a very fine brush in a series of tiny dots. The eye sees the dots as blended. For large fills, an airbrush may be used [10]. One of the common disadvantages of this process is inhomogeneity that arises due to changes in the photographic image or the inpainting media or both. At times, skillfully applied original inpainting becomes unsightly when the surrounding image fades and discolors, leaving the retouched areas extremely obvious.

Nowadays, most photograph conservators prefer digital restoration over manual restoration for several reasons; some of which are: the ability to use a variety of image editing techniques and programs to remove visible damage and aging effects (i.e. scratches, losses, cracks, tears, stains, etc.) achieving outstanding results from a fully deteriorated prints, the possibility to print an infinity number of copies, and ease of application as many tutorials and softwares are available online. With regard to digital restoration, this study focuses only on one of the significant digital techniques which is inpainting. Inpainting in the digital world is an application of advanced algorithms using geometric approaches for filling missing areas or corrupted parts of images resulting from the impact of various factors. This practice is as old as artistic creation itself. Using this approach, one is able to obtain digitally retouched areas that are non-detectable to an observer who had not seen the original image. The algorithms mainly focus on the consistency of the geometric structure. The structure of the area surrounding the missing part (i.e. image information) is used as a reference to fill in the missing image

information of only this part. The problem is one may get good results if the missing regions are small; but in the case of large damaged areas, the process will be time consuming and the results are not so good.

Digital printing is a process that utilizes digital data to control certain electronic printing devices such as laser printers or inkjet printers. LaserJet printing is an electrostatic printing process that is nearly identical to the xerographic copy process the difference being that laser prints come from a digital source. Black and white laser prints tend to be very stable and permanent since the toner is essentially black carbon pigment in a resin carrier. However, color laser prints may fade on light or water exposure due to the colored pigments used in the CMYK toner. On the other hand, the inkjet printing process involves the application of tiny droplets of ink onto the paper surface. This super-fine dot structure produced by the printer's ink spray will be visible under low magnification. As inkjet printers evolved, the dot structure became finer and less distinguishable to the naked eye. Deterioration of inkjet prints depends greatly on the quality of the paper and type of ink. All inkjet prints are also highly sensitive to surface abrasion due to the ink's shallow, and also will quickly discolor and fade to a yellowish-brown color if it exposed to high humidity, intense light or atmospheric pollutants like ozone. Ink bleeding, streaking, and distortion may occur if exposed to moisture. Pigment-based inks are considerably more stable than dye-based, but they may also be water-based and therefore sensitive to moisture [11].

The main aim of this paper is to evaluate the efficiency of merging both manual and digital restoration techniques. This way one is able to obtain accurate and excellent retouching results, an advantage of digital restoration; while preserving the value of the original photograph, an advantage of manual restoration.

Materials and Methods

Graphic Editing Software

A set of old photographs (approx. 100 years old) exhibiting a variety of deterioration forms (scratches, loses, cracks, tears, stains) were randomly selected. A small data set was made to determine the different categories of the photographs and also the percentage of photographs in the collection suffering from each identified damage form (Fig. 1).

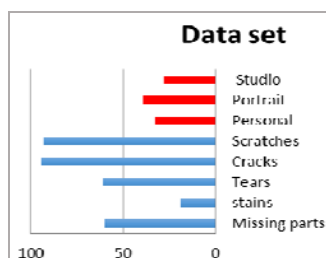


Fig. 1. Data set for a 100 randomly selected photographs suffering from various damage forms

A group of photographs displaying various physical damage forms (i.e. scratching, tears, losses) was chosen for digital restoration in order to decide which graphic editing software to use in our experiments. Two softwares were tested: Adobe Photoshop and an automated software (i.e. ISCNO) which has been created by Virgilio Ragazzi, Department of Mathematics and Informatics, University of Catania [12]. A comparative study revealed that Adobe Photoshop has the following advantages: it quickly and easily imports photos into the software; once imported, everything is neatly organized on the screen. This makes it easy to handle numerous photos; proper organization of the workspace makes it easy to find editing tools and other features; and quick editing. However, the disadvantages of this software include: its high

price more than most of the other photo-editing software; it was not built for the novice user; it requires a well-equipped computer. It is a heavyweight program and many of the tools are computationally intensive (Fig. 2a).

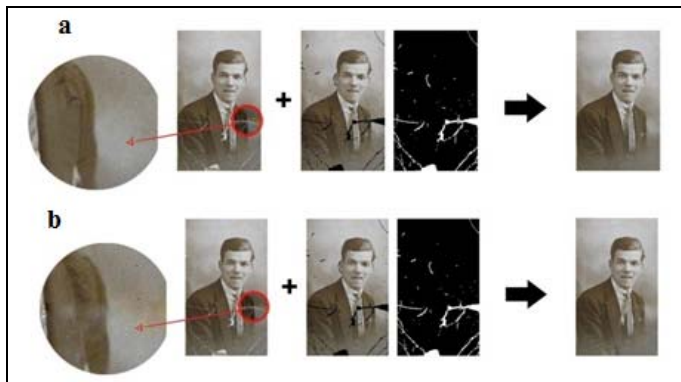


Fig. 2. Photograph processed with Adobe Photoshop (a) and photograph processed with automated software (b)

On the other hand, the automated software, ISCNO, has the following advantages: quick and automatic process; it is suitable for the novice user; good and fast result can be obtained in the case of digital restoration; economic friendly since it is a free application. However, it has many disadvantages: it is not possible to enlarge the original photograph to select a specific area; it is not easy to restore all details; the program has limited tools; good results are obtained in the shadow areas; however, poor results are obtained for textured areas; it is not possible to specify the treated area for printing purpose like as in the case of Adobe Photoshop; all the structural inpainting methods are not able to restore texture. It is not possible to perform restoration by continuing the level lines into the gap and it is not possible to save the image in an active file to use it again if any modification is needed (Fig. 2b). Based on the previous obtained results, it was decided to use Adobe Photoshop for digital restoration.

Test Materials

Two old developed-out silver gelatin prints of no significant values were selected for this study in order to give a more practical focus to these experiments. The two photographs are in good conditions of preservation; however, they suffer from losses, particularly around the edges (Fig. 3).

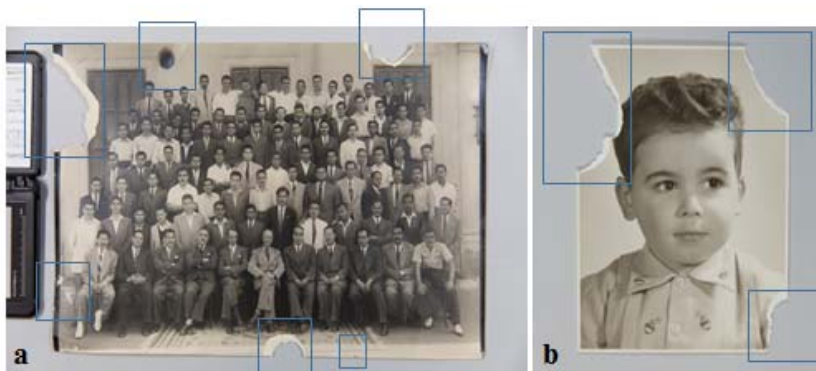


Fig. 3. An old silver gelatin print of AUC students with their professors, dating back to 1955: a - the photograph is in a good state of preservation; however, it suffers from tears, cockling, abrasions and losses; b - second photograph is also a silver gelatin print of Dr. Yusuf Froez in his childhood, the print dates back to 1960, is in very good condition but suffers from losses

Printers

As mentioned earlier two types of printers were used. LaserJet printing was carried out using a Ricoh Aficio MP C2800 MP C3300 and an HP Deskjet Ink Advantage 1515.

Digital Camera

A photographic survey was carried out before, during and after treatment using a Canon EOS 5D Mark III DSLR Camera.

Japanese Paper

Restored areas were printed on an off-white Japanese paper with the weight of 2g/m². Japanese tissue is a thin, strong paper made from vegetable fibers.

Adhesive

TYLOSE® MH 300P was used in concentration ranging between 2-3% to secure the infills in place. Tylose is a white powder composed of methyl hydroxyethyl cellulose. It is soluble in cold water and insoluble in warm water and organic solvents. And its aqueous solutions have a neutral pH value. Conservators have traditionally used methyl hydroxyethyl cellulose for the mending of photographs. This water-based adhesive is known to be reversible and not to fade or darken the silver image, although it generally gives good results, there are some inherent problems in the use of a water-based adhesive [13].

Methodology**Treatment Application**

The main concept behind this new technique is to digitally restore the missing parts of the photographs using Adobe Photoshop Software, and then print only this missing data on Japanese paper using printers. The resultant patches were then used as infills for the missing parts in the original photographs. Infills were fixed in place using Tylose adhesive. The steps of the proposed techniques were as follows:

- documentation and preparation of the photographic prints for digital restoration. A color patch from X-rite was used in order to modify the color of the scanned image;
- Adobe Photoshop was then used to digitally restore the missing parts;
- a test scale was printed in order to determine the suitable color.

In order to analyze the absolute color a CM-2600d Spectrophotometer was used. It is a handheld, portable measurement instrument designed to evaluate the color, relative gloss, and UV characteristics of samples

All samples were measured in the visible spectra, i.e., a wavelength range from 400 – 700nm, with an interval of 10nm using a D65 light source and observed angle of 10 degrees. The CIELAB color space was used to express color change. The total color change (ΔE^*_{ab}) is a value useful as an indicator of the difference between the sample and the reference (Fig. 4).



Fig. 4. A printed scale to distinguish the suitable color using a spectrophotometer

According to DIN EN ISO (super ceded by BS EN ISO 4628-1:2004), evaluation of ΔE^*_{ab} is as follows:

- values from 0 to 1: color difference is not visible;
- values from 1 to 3: few people can recognize the difference;
- values from 3 to 5: 66 % of people can recognize the difference;
- values greater than 5: everyone can recognize the difference [14-16].

A thickness meter was used to select a Japanese paper of suitable weight. The missing data was then printed on the selected Japanese paper using an inkjet printer and a laser printer (Fig. 5).

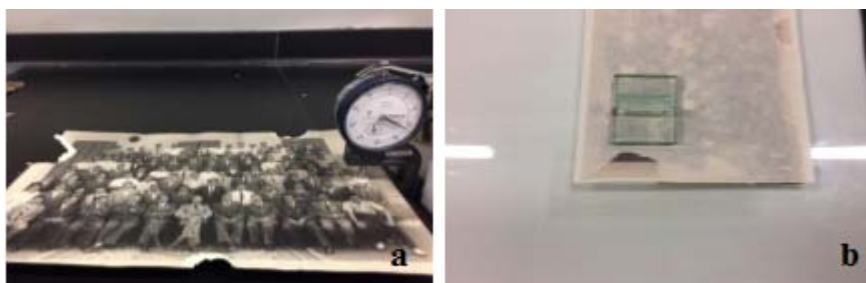


Fig. 5. Measurement of the photograph thickness to select a suitable Japanese paper (a).
Preparing the print for manual restoration on the light table (b)

Losses in both were restored using the printed Japanese paper (Figs. 6 to 12).

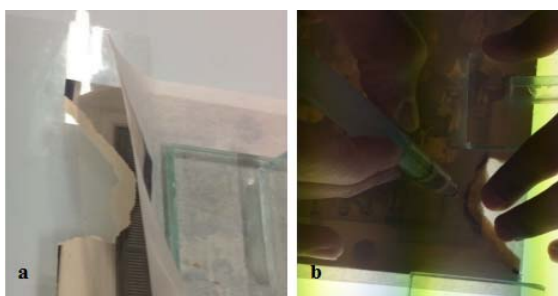


Fig. 6. Placing a polyester sheet between the photograph and the printed Japanese paper to avoid any damage (a).
Wetting the required area with a water pen (b)

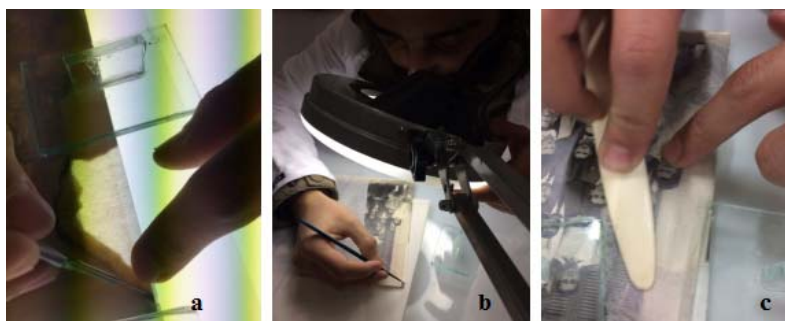


Fig. 7. Cutting the selected area using a scalpel (a);
applying the Tylose adhesive by brush to secure the infills in place (b);
and using the bone folder to ensure the infills are secured in place (c)

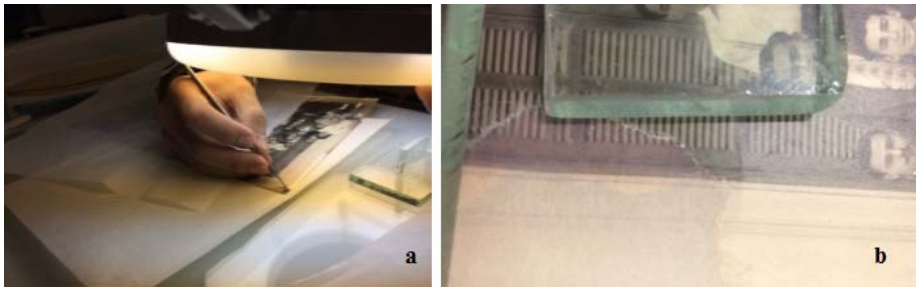


Fig. 8. Refining the edges after manual restoration (a). The digitally restored data printed on Japanese paper and secured in place with an adhesive (b)



Fig. 9. Flattening the photograph under press

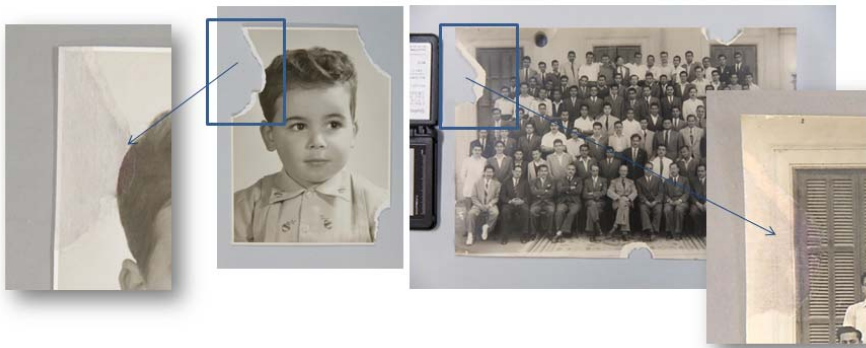


Fig. 10. The restored photographs before and after digital and manual restoration

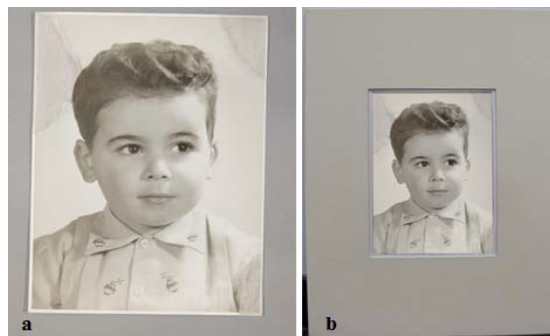


Fig. 11. Restored photograph after the proposed restoration technique (a) and after housing (b)



Fig. 12. Restored photograph after the proposed restoration technique (a) and after housing (b)

Accelerated Aging

Accelerated aging was carried out to determine the stability of the two tested printing processes and to study the effect they have on the original photographs. The following conditions were used to perform artificial aging for the experimental samples: a temperature of 80°C, a relative humidity of 65%, irradiation of 26,948kJ/m² and a period of 120 hours. Accelerated aging was applied to the samples and also an untreated (reference) sample in a closed climatic chamber with previous conditions which is equivalent to aging of paper objects under natural conditions for 25 years. The aging procedure is in conformance with the ISO 5630-3:1996 standard [17]. This procedure was carried out in a climatic chamber at the University of Catania, Italy.

Examination and Analysis Techniques

Visual inspection

A photographic survey was carried out before and after artificial aging using a Canon EOS 5D Mark III DSLR Camera in ambient light.

SEM-EDX

Scanning electron microscopy was carried out using environmental scanning electron microscope model Quanta200 emission with EDX unit. It can produce extremely high magnification images (up to 200,000×) at high resolution up to 2nm combined with the ability to generate localized chemical information (EDX). The purpose of using this technique was to detect the presence of new element in the original photographs which may have been formed as decay products or from the printing procedure as it was used to study the areas of the original photographs that were fixed to the Japanese paper. This procedure was carried out at the Scanning Electron Microscope Lab, the Ministry of Antiquities, Cairo.

ATR – FTIR

Attenuated Total Reflectance (ATR) is today the most widely used FTIR sampling tool. ATR generally allows qualitative or quantitative analysis of samples with little or no sample preparation, which greatly speeds sample analysis. The instrument used is a portable Perkin Elmer Spectrum Two™ IR Spectrometer, spectral range of 8300 – 350cm⁻¹, which utilizes a 10™ software and a LiTaO₃ MIR detector with a SNR of 9,300:1. This analysis was carried out at the University of Catania, Italy. FTIR analysis was used to identify the type of photograph and the binder before and after treatment, and detect the presence of degradation as a result of treatment aging.

pH value measurement

pH test strips were used to identify the approximate change in pH value after artificial aging.

The Oddy Test

The Oddy test was developed by Andrew Oddy with colleagues at the British Museum in the 1970s [18]. It is a non-specific test that indicates the release of volatile compounds with corrosive properties under accelerated aging conditions. In the conservation field, the Oddy test is usually applied for the analysis of materials used for storage and display. This test was used to measure the long-term effects of chemical compound that may be emitted from restored areas on the original photographs. In general, analytically pure lead, copper, iron and silver foils are used as test coupons. Degradation of silver indicates sulfur containing compounds and decay of lead indicates the presence of organic carbonyl compounds. Copper is also sensitive to these compounds but also indicates alkaline compounds and iron is for detecting nitrogen oxides, acidic gases and sulfur compounds [19, 20]. The test was performed as follows:

- approximately 2g were taken from the test samples and cut into small pieces;
- metal coupons were cut in a size of 35×10mm with thickness of 0.1mm, which were then soaked in acetone for a few minutes, handled with a tweezer and left to dry between two pieces of blotting paper;
- a small tube filled with 0.5ml distilled water and covered with a piece of cotton wool was placed inside each tube;
- four slots were cut in the bottom of the silicon stopper with a scalpel about 5mm depth and 10 mm across;
- metal coupons were placed inside the glass tube;
- the tubes were then placed inside an oven at a temperature of 60°C for 28 days;
- after 28 days, the metal coupons were taken out from the tube and compared with standard coupons.

Results and Discussion

Visual inspection

Both printing processes were affected post artificial aging. However, the ink in the inkjet sample was completely removed, while it faded in the laser sample (Fig. 13).

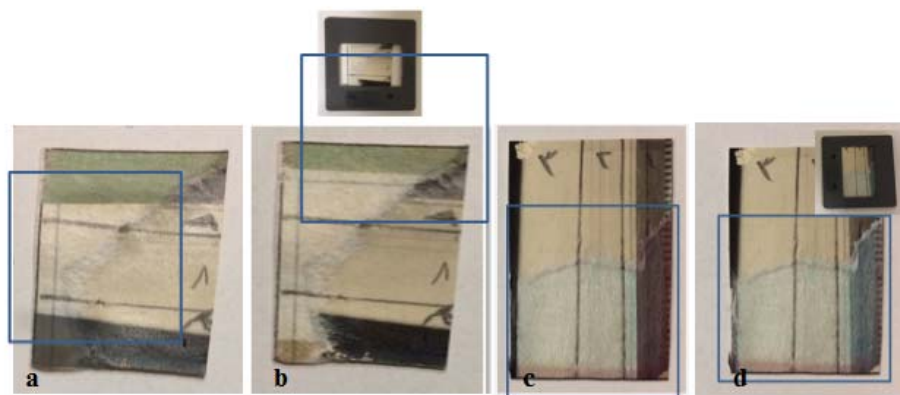


Fig. 13. Inkjet sample before aging (a), inkjet sample after aging (b), laser sample before aging (c), and laser sample after aging (d).

SEM-EDX

The EDX analysis revealed the presence of a number of chemical elements. Silver (Ag) was detected and it refers to the final image material. Samples also showed the presence of barium (Ba) and sulfur (S) indicating the presence of the baryta layer. Elements related to paper manufacture such as carbon (C), calcium (Ca), aluminum (Al) and magnesium (Mg) were also

detected. The instrument did not detect any uncommon elements in all samples (Fig. 14 and 15). No signs of deterioration was detected and there is no sign of ink migration.

ATR – FTIR

Protein gives rise to nine characteristic IR absorption bands. Of these, the Amide I and Amide II are the most prominent vibrational bands of the protein backbone. The Amide I is within the 1600 – 1700cm⁻¹ region is presided by the C=O stretching vibrations. Amide II is within the 1500 – 1600cm⁻¹ region and it originates from the in-plane N-H bending, along with both C-H stretching vibrations and C-C stretching vibrations [21].

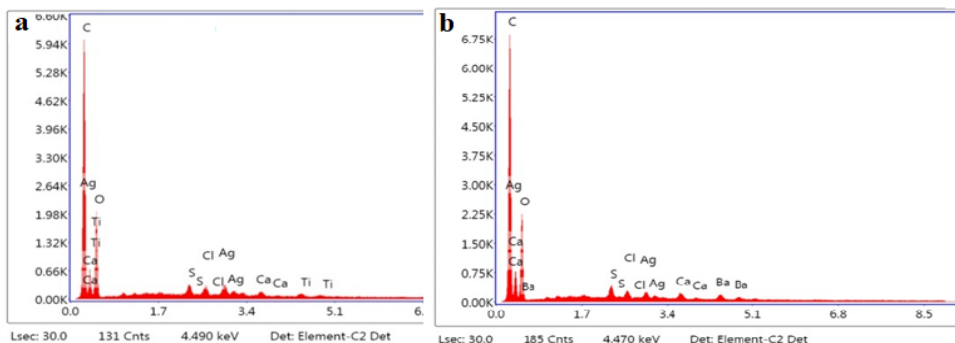


Fig. 14. X-ray spectrum of the photograph standard sample (a), X-Ray spectrum of the photograph standard sample post aging (b)

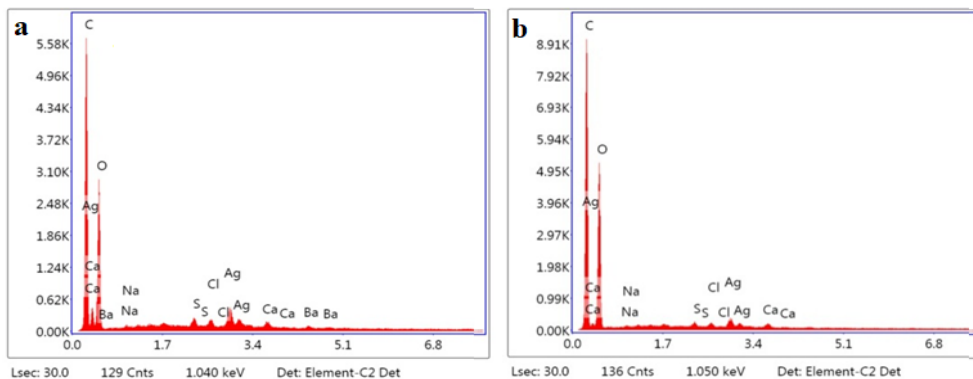


Fig. 15. X-ray spectrum of the restored photograph: a - inkjet print infill, post aging, b - laser print infill, post aging

With respect to degradation, hydrolysis would be apparent as an increase in the OH stretching or bending frequencies found at 3400 and 1650cm⁻¹, respectively since the Amide I band also occurs near 1650cm⁻¹, an increase in the -OH band at 1650cm⁻¹ would result in an increase in the absorption intensity or height of the Amide I band. Oxidation results in the formation of the carbonyl compounds which would absorb in the 1700 - 1750cm⁻¹ 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. The Amide I/Amide II intensity ratio (I_{AI}/I_{AII}) was also measured to predict the possibly occurring chemical changes due to treatment and/or artificial aging [22].

Obtained results reveal that no change in the position of the carbonyl group has occurred for all investigated samples. The increase of the intensity of C=O vibrational group assigned to amide I for both the laser ink sample and the inkjet sample indicates that the gelatin has been hydrolyzed (Fig. 16). Furthermore, the I_{AI}/I_{AII} intensity ratio for the same samples also

increased after treatment, this finding indicates that the gelatin has been hydrolyzed confirming the previous results. It also indicates that there has been an increase in the random coils. Results are listed in Table 1.

pH measurement

The pH value measurements were carried out on the samples using pH paper indicators to determine if any change in pH value has occurred post artificial aging. Results showed that there is a very slight change in the treated samples, pH between 7 and 8 (Fig. 17).

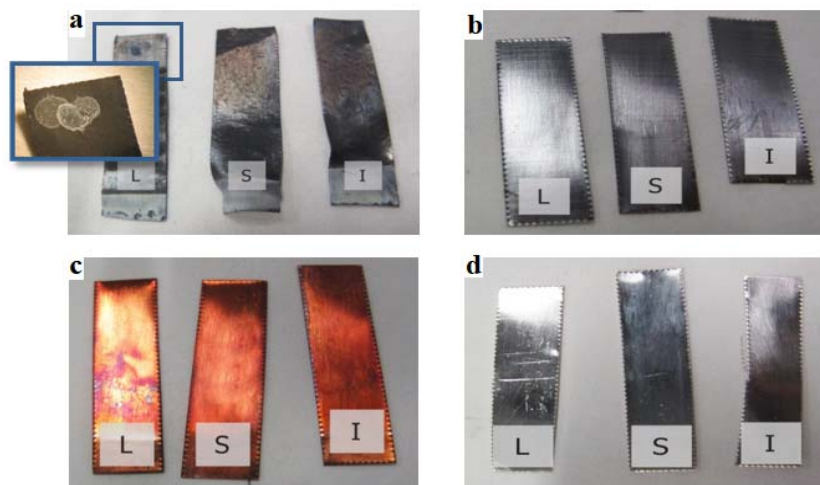


Fig. 18. Reference photograph for lead coupons (a), reference photograph for iron coupons (b), reference photograph for copper coupons (c), and reference photograph for silver coupons (d)

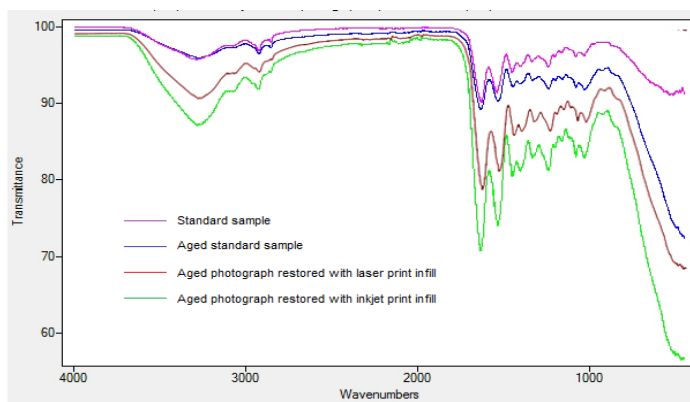


Fig. 16. ATR spectra representing a comparison between the four samples

Table 1. Results of the ATR-FTIR spectroscopy analysis. Comparison between the I_{AI}/I_{AII} ratio in photographic samples

Sample	Band	Wavenumber (cm ⁻¹)	Intensity	I_{AI}/I_{AII}
Standard	Amide I	1628	6.27	1.51
	Amide II	1538	4.14	
Aged Standard	Amide I	1632	5.81	1.62
	Amide II	1532	3.58	
Photograph with inkjet ink	Amide I	1631	15.5	1.7
	Amide II	1530	8.5	
Photograph with laser ink	Amide I	1634	16.02	1.68
	Amide II	1537	9.49	

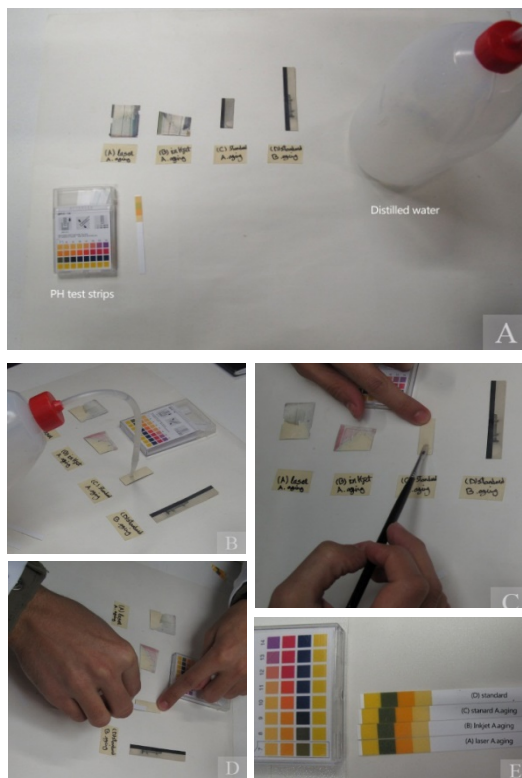


Fig. 17. pH value measurement using pH paper indicators

The Oddy test

Result for the Oddy test are listed in Table 2, where the letter P refers to suitability of the material for permanent use, T for temporary use. Results show that both tested inks are between temporary and permanent, which indicate that both types are suitable for usage and storage (Fig. 18).

Table 2. Results of the Oddy Test

Sample	Pb	Fe	Cu	Ag
Standard	P	P	P	P
LaserJet	T	P	T	T
Inkjet	P	P	T	P

Conclusion

Based on the obtained results of this study, one can conclude that the proposed technique is a very promising technique which can be efficiently used to restore losses in damaged photographic prints with slight effects on the original photograph. ATR-FTIR analysis showed very slight degradation in all cases. SEM-EDX analysis showed elements related to the composition of silver gelatin prints, the final image material and paper base. No uncommon elements have been detected in the treated samples. pH value measurements were neutral, showing normal ranges.

Results of the artificial aging proved the stability of laser printing compared to inkjet printing; and therefore, it is considered the best option for this technique.

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