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INVESTIGATIONS ON THE CHEMICAL DEGRADATION OF SILVER GELATINE PRINTS

Maha Ahmed ALI[1*], Mona Fouad ALI[1], Mohammed Osama SAKER[2], Abdel Azez El Bayoumi ABDEL ALEEM[3], Khaled Ibrahim EL NAGAR[4]

[1)] Conservation Department, Faculty of Archaeology, Cairo University, Egypt.
[2)] Photography, Cinematography and Television Department, Faculty of Applied Arts, Helwan University, Egypt.
[3)] Analytical Chemistry Department, Faculty of Pharmacy, Cairo University, Egypt.
[4)] National Institute of Standards, Egypt.

Abstract

Photographs are considered composite objects with complex chemical and physical structures. Therefore they are more prone to damage as compared to other objects. Chemical degradation is by far the most common decay form found among photographic collections. This study investigates the chemical degradation of silver gelatin prints (DOP) and the reaction of the image, silver, gelatin, and paper to accelerated aging, to the action of light, and oxidizing gases, in terms of their physical and chemical nature. The test materials used are properly washed and poorly washed grayscale, black-and-white processed images on photographic paper (Black & White Photographic Paper BH 0 Bromofort 6P0661 Tropical from Forte Photochemical Company Vác, Hungary). After exposure, the results were studied by means of visual inspection, amino acid analyzer, Fourier transform infrared and transmission electron microscope. The results were compared with those of the control samples. Our study revealed that the image, silver, gelatin and photographic paper are greatly affected by oxidizing agents and that the effect increased if the photographic prints were inadequately washed at the time of their processing. Furthermore, our results indicated that an increased amount of ammonia and amino acid in the silver gelatin print is a reliable indicator of the degradation of its gelatine emulsion.

Keywords: *Chemical degradation; processed silver gelatine prints; accelerated ageing; FTIR; Amino acid analysis; TEM*

Introduction

A silver gelatin print is composed of three major components: the primary support material (paper), the binder (gelatin) and the photo-sensitive substance (silver salts) [1]. A fourth significant component which may be included is an interlayer between the support and the image layer known as the baryta coating [2]. Silver gelatin prints are prone to deterioration by numerous intrinsic and extrinsic agents. Improper handling, incorrect display location, storage materials and areas and improper levels or fluctuations in the levels of environmental factors will cause the prints to undergo varying degrees of deterioration and/or degradation [3] and [4]. Chemical degradation is by far the most common form of decay found among photographic collections.

The main aim of this study analyze the changes that occur with the aging of silver gelatin prints or upon their exposure to UV radiation and oxidants. It further investigates the effects

* Corresponding author: maha.ahmed@hotmail.com, +2 01115152803

that residual processing chemicals, resulted from insufficient washing, have on the chemical degradation of silver gelatin prints, compared to sufficiently washed silver gelatin prints. The study also aims to highlight the role played by oxidation in the chemical decay of the image silver, leading to discoloration, fading and staining.

Chemical reactions may occur in all components of a silver gelatin print, usually in the presence of chemically reactive substances, but they take place predominately in the image silver. The stability of silver salts depends, to a large extent, on their morphology [5]. Image silver particles found in developed silver gelatin prints are in the form of twisted strains known as filamentary silver [6]. The delicate silver images of silver gelatin prints are susceptible to low levels of chemical reagents according to the specific surface area concept [7]. Image silver particles have dimensions of the orders of microns and in silver gelatin prints, chemically developed, they take a complex dendritic form. Their small dimensions and the presence of kinks results in them having a large surface area, representing the surface that is accessible to chemical reagents in the atmosphere. The greater the specific surface, the greater the reaction. Consequently, most chemical reactions take place with the image-forming substance as a reaction partner [8]. Chemical changes in silver gelatin prints are usually the result of poor processing or adverse environmental conditions [9]. Upon aging of a silver gelatin print, the silver particles undergo changes in their shape and size and may react with sulfur to form silver sulfide. The change in particle size and the reaction with sulfur can produce dramatic changes in the color and density of the silver image [10]. According to the Oxidation-Migration-Re-aggregation model (OMR), the first step of image decay is the oxidation of the silver image particles [11]. In the process, metallic image silver particles (Ag^0) are stripped of electrons and converted to invisible silver ions (Ag^+). Silver ions may migrate throughout the gelatin emulsion layer. Once the silver ions have traveled away from their parent silver grain, one of the following image decay forms may occur: yellow/orange discoloration, silver mirroring, yellow/brown discoloration, fading [10], and the formation of redox blemishes [12].

Most of the stability problems associated with gelatin and paper result from their physical and chemical properties [13]. Gelatine is a natural protein which consists of amino acids chained together by a peptide bond (— CO — NH —) [14] and it is found in photographic emulsions in the form of long tightly coiled chains [15]. Gelatine and paper are hygroscopic, meaning they can contain moisture and exchange water vapor with the surrounding air [16]. They are both carbon sources and, therefore, they promote the growth of microorganisms under sustained conditions of high relative humidity [9]. Paper is highly susceptible to acid deterioration [17] and it can easily trap residual processing chemicals [18]. Light and UV radiation does not directly impact image silver, but it can degrade the image silver by causing the cellulose in the paper and the proteins in the emulsion to decompose [3]. It is important for conservators to understand the changes that can take place in a photograph, in order to be able to identify the changes and recognize the causes.

Many studies were carried out by Hendriks et al. [5], Nishimura [19], Hendriks and Ross [2], Reilly et al. [20], Burge, Reilly and Nishimura [12], Di Pietro [8], Poggi, Giorgi, and Baglioni [21] and Weaver [10] to investigate the chemical degradation of silver gelatin prints. This research provides information on the reaction of image silver and gelatin to accelerated aging, to the action of light and oxidizing gases, in terms of their physical and chemical nature. The results of accelerated aging tests were studied by means of visual inspection, amino acid analyzer, Fourier Transform Infrared (FTIR) and Transmission Electron Microscope (TEM). Amino acid analysis was used for the first time to study the changes in the amino acid composition of photographic gelatin, before and after artificial aging, to determine if this method can be employed as a damage assessment tool.

Experiment

Materials

Samples were prepared by printing a Kodak Enlarging Exposure Scale on a Black & White Photographic Paper (BH0 Bromofort 6P0661 Tropical from Forte Photochemical Company Vác, Hungary). Two sets of samples were prepared: sufficiently washed grayscales and insufficiently washed grayscales. The processing chemicals were first prepared and their temperature checked. Hypo was prepared by adding 250 gm of hypo to 1 liter of water. A KODAK PROFESSIONAL D-76 developer was prepared according to the instructions on the bottle. The stop bath involved rinsing in water at room temperature. Each grayscale consists of 10 different densities.

Methodologies

Accelerated ageing test

Two different combinations of conditions were used in this study: 60°C at 67.5% RH for 30 days and 105°C at 67.5% RH for 30 days. The first test did not cause any apparent changes and, therefore, the temperature was raised to 105°C at the same relative humidity level. The properly washed samples were given the symbols PP10IS-PP15IS, and the improperly washed samples were given the symbols IP10IS-IP15IS. This test was performed in an aging oven at the National Institute of Standard in Cairo. A saturated solution of sodium nitrate ($NaNO_3$) was prepared and placed in the aging oven for 20 hours prior to the introduction of the samples, which maintained a relative concentration of 67.5%.

Black-and-white light fading test

Samples PP16LF-PP21LF (properly washed) and samples IP16LF-IP21LF (improperly washed) were subjected to relatively high-intensity ultraviolet illumination (500 foot-candles for 45 days). This test was performed under normal room temperature and humidity conditions [5].

Gas fading test

The test involved exposing samples PP25GF-PP30GF (properly washed) and IP25GF-IP30GF to hydrogen peroxide and hydrogen sulfide for a period of 10, 12, and 15 days. Both tests were performed in desiccators. The desiccators were prepared by mixing a saturated solution of ammonium sulfate $(NH_4)_2SO_4$ at room temperature. This solution maintained an RH of approximately 80%. The salt was poured in a small flat dish and placed in the bottom of the desiccators. The desiccators were then conditioned for a period of 20 hours. Under the fume hood, laboratory grade H_2O_2 (30%) was poured in a shallow dish and was then set at the bottom of the desiccator. Samples PP25GF-PP26GF and IP25GF-IP26GF were arranged in that desiccator and the lid was sealed. Again, under the fume hood, a solution of 0.1% of sodium sulfide in hydrochloric acid was mixed to make 200 ml of solution. This solution was poured in a shallow dish and placed in the bottom of the other desiccator. Samples PP28GF-PP30GF and IP28GF-IP30GF were placed in the desiccator and then the lid was sealed [5]. Samples PP25GF and IP25GF were exposed to H_2O_2 for 10 days; samples PP26GF and IP26GF were exposed to H_2O_2 for 12 days; samples PP28GF and IP28GF were exposed to H_2S for 10 days; and samples PP29GF, IP29GF, PP30GF, IP30GF were exposed to H_2S for 15 days.

Test methods

The test methods used for the damage assessment of samples were:

- Visual observation to monitor unexpected visual changes.

- Fourier transform infrared spectroscopy (FT-IR) was used to study the decay of the photographic emulsion and paper after each test. The instrument used for this analysis was a JASCO FT/IR-6100 Spectrometer in reflectance mode. The analysis was performed at the Infrared Spectroscopy Laboratory, National Research Center (NRC) in Cairo/Egypt.

- Amino acid analysis was employed to study the changes in the amino acid composition of gelatin. The amino acid analysis was carried out on an Automatic Amino Acid Analyzer AAA 400 from INGO Ltd. At the Amino Acid Analyzer Lab/ Faculty of Agriculture Research Park (FARP), Cairo University. This analysis was run on samples PP12IS, IP12IS, PP16LF, IP16LF, PP26GF, IP26GF, PP29GF, and IP29GF. For amino acid analysis, acid hydrolysis was carried out according to the method of Block et al. [22]. The dried grinded sample (100mg) was hydrolyzed with 6N HCl (10ml) in a sealed tube at 110°C in an oven for 24 hours. The excess of HCl was then released from 1ml, hydrolyzed under vacuum of 80°C with occasional addition of distilled water, then evaporated to dryness. The HCl free residue was dissolved in exactly 2ml of loading buffer (6.2M., pH 2.2).

- A transmission electron microscope (TEM) was used to study the decay of image silver. A TEM is capable of examining fine details, even as small as a single column of atoms. The transmission microscope we used was a JEOL (JEM-1400) operated at 80 KV and with a MacroFire digital microscope camera. Images were recorded using Image Capture Engine Software Version 600.124. Small portions (1×3 mm^2) of discolored emulsion were removed from the samples under study before and after aging. The pieces of control sample step (4), control sample step (12), control sample step (24), control sample step (48), PP12IS step (4), IP12IS step (4), PP12IS step (24), IP12IS step (24), PP25GF step (12), IP25GF step (12), PP25GF step (24), IP25GF step (24), PP25GF step (48), IP25GF step (48), PP28GF step (24), and IP28GF step (24) were prepared for examination at the Electron Microscope Lab, Central Lab, the National Research Center (NRC). The samples were fixed in a solution of 1 part of sodium cacodylate buffer and 24 parts of glutardehyde for 6 hours. The samples were then washed with the buffer, preserved in the buffer and placed in the refrigerator for the next day. This was followed by fixing the samples in a solution of osmium tetra oxide (½ an ampoule) and 50 cm³ of a sodium cacodylate buffer. The samples were placed in this solution for 2 hours in the refrigerator. Then the samples were rinsed and underwent a dehydration procedure in alcohol solutions (alcohol concentration increasing from 30% to 100 %). In the final steps a mixture of 50% ethyl alcohol and 50% propylenoxid was used. The samples were then placed in 55% propylenoxid. This was followed by resin preparation (SPI-PON 812 Epoxy Embedding Kit). The kit included four substances, which were mixed together in the following order 9.8 grams of SPI-Pon 812, 3.3 grams of DDSA, 0.3 grams of DMP-30, and 6.9 grams of NMA. The samples were embedded in a mixture of 50% resin and 50% propylenoxid for one hour and then embedded in 100% resin for the next day. The samples were placed in an oven for 2 days at 45ºC and 60ºC respectively (Fig. 4). After embedding, 100 nm thick slices were cut in cross-section with an ultra-microtome (the Reichert-Jung ultra-cut ultra). The slices were transferred on a grid and they were inserted under the microscope available at the Electron Microscope Lab of the Faculty of Agriculture Research Park, Cairo University.

Results and discussions

Visual inspection

The results of the accelerated aging test revealed the high stability of properly processed samples compared to improperly processed samples. The residual fixer left in the IP samples caused the binder and support to turn yellow and brown respectively and the image silver to slightly discolor. Moreover, the test confirmed that physical forms of damage (i.e. cracks) are affected by the processing procedure. Inherent acidic components such as hypo cause the embrittlement of the paper support through an acid deterioration process, which is accelerated

by heat and humidity. The cracks present in the improperly processed samples were probably caused by this mechanism (Fig.1) and (Fig.2). As for the light fading test, both properly and improperly processed samples showed good stability to high-intensity illumination and only very slight yellowing was observed in both cases. The paper support was in good condition with very slight yellowing (Fig. 3).

Fig. 1. (a): shows the status of sample PP10IS (properly processed) and sample IP10IS (improperly processed samples) after aging. Compared to the control sample, PP10IS they were slightly yellowed, while IP10IS shows severe discoloration. The aging condition is 105°C at 67.5% RH; (b): the verso of the samples showing slight discoloration in the case of the properly processed sample and severe discoloration in the case of the improperly processed sample.

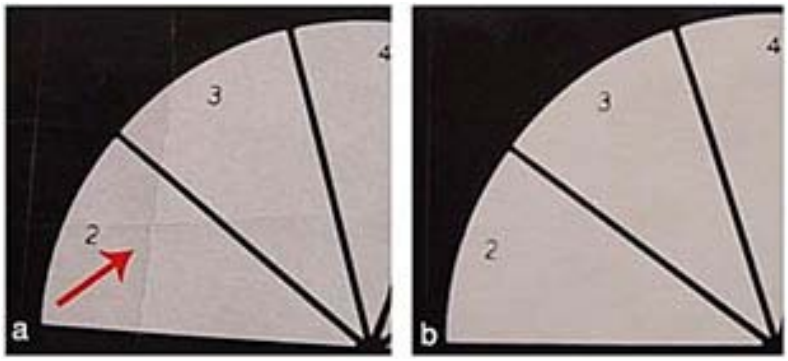

Fig. 2. (a): a close-up shot of the crack pattern that has developed after ageing improperly processed sample after ageing at 105°C and 67.5% RH; (b): a properly processed sample aged in the same condition showing no visible signs of cracking.

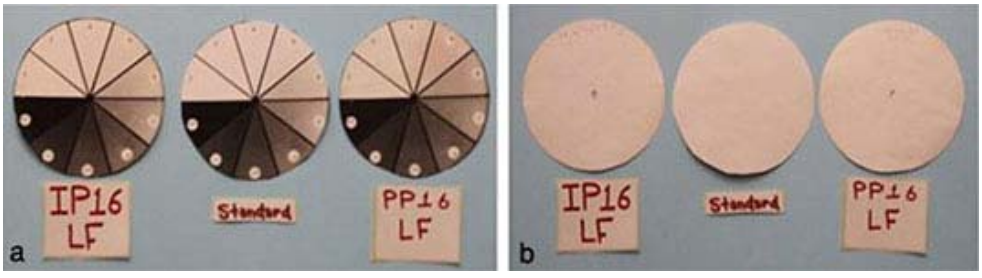

Fig. 3. (a): the back of sample IP16LF and PP16LF after light fading test showing slight discoloration when compared to the control sample; (b): the verso of the same samples. The change in the color of the paper bases is indistinguishable except around the edges where slight yellowing has occurred.

However, the edges of the samples exhibit minor warping and wrinkling, likely caused by the heat emitted by the fluorescent lamp. The results of the gas fading test confirmed the fact that contaminants, along with high relative humidity, cause the degradation of the delicate

image silver, the gelatin binder and the paper support and that the brutality of the attack is affected by the presence of processing chemicals in the materials, such as residual thiosulfate complexes (fixer) and silver-thiosulfate, which are left behind due to inadequate washing (Fig. 4). For example, samples PP26GF and IP26GF were exposed to the same oxidizing agent (H_2O_2) for the same period of time (12 days), yet this test was more aggressive on the latter sample, resulting in severe image decay and embrittlement of the support. Hydrogen peroxide caused fading of the IP samples and yellow/orange discoloration of the PP samples, while hydrogen sulfide exposure resulted in a warm brown discoloration (Fig. 5). Silver mirroring occurred in sample PP25GF in the shadows after exposure to hydrogen peroxide for 10 days and another one month outside the desiccator. Yet, it did not appear in sample IP25GF which was exposed to the same conditions (Fig. 6). This happened mostly because the cause of discoloration in this case was faulty processing and when faulty processing is the cause, silver mirroring will not occur [10]. The forms of decay found in each sample are shown in Table 1.

Table 1. Results of the gas fading test (visible decay forms).

Sample No.	Test	Forms of decay and observations made during visual inspection
PP25GF	H_2O_2 for 10 days	• Yellow/orange discoloration of the image silver. • Embrittlement of the paper support. • Silver mirroring. • The gelatin is intact.
IP25GF	H_2O_2 for 10 days	• Fading. • Severe embrittlement of the paper support. • Cracks. • Discoloration of the paper support. • The gloss of the sample has decreased.
PP26GF	H_2O_2 for 12 days	• Decay of the gelatin binder. • Yellow/orange discoloration and fading. • Fragility of the paper support. • Discoloration of the paper support. • The gelatin is intact.
IP26GF	H_2O_2 for 12 days	• Severe degradation of the image silver in the form of fading. • Yellowish brown staining. • Extreme fragility of the support. The sample can no longer be safely handled. • Discoloration and staining of the paper support.
PP27GF	H_2O_2 for 15 days	• Decay of the gelatin binder. • The gloss of the sample has decreased greatly. • Yellow/orange discoloration and fading. • Fragility of the paper support. • Discoloration of the paper support. • The gelatin is intact.
IP27GF	H_2O_2 for 15 days	• Severe decay of the image silver, gelatin binder, and support. • The paper support was extremely fragile and the sample was lost while being removed from the desiccator.
PP28GF	H_2S for 10 days	• Slight discoloration (warm hue). • The paper and gelatin binder is in good condition. • Discoloration (warm hue).
IP28GF	H_2S for 10 days	• The paper and gelatin binder is in good condition. • Discoloration (warm hue).
PP29GF	H_2S for 15 days	• Flaking of the photographic emulsion. • The paper base remained in good condition. • Discoloration.
IP29GF	H_2S for 15 days	• Severe decay of the emulsion due to high relative humidity. • Slight yellowing of the paper base. • Fungal growth. • Discoloration (warm hue).
PP30GF	H_2S for 15 days	• Flaking of the photographic emulsion. • The paper base remained in good condition. • Discoloration.
IP30GF	H_2S for 15 days	• Severe decay of the emulsion and fungal growth. • Yellowish brown staining. • Slight yellowing of the paper base.

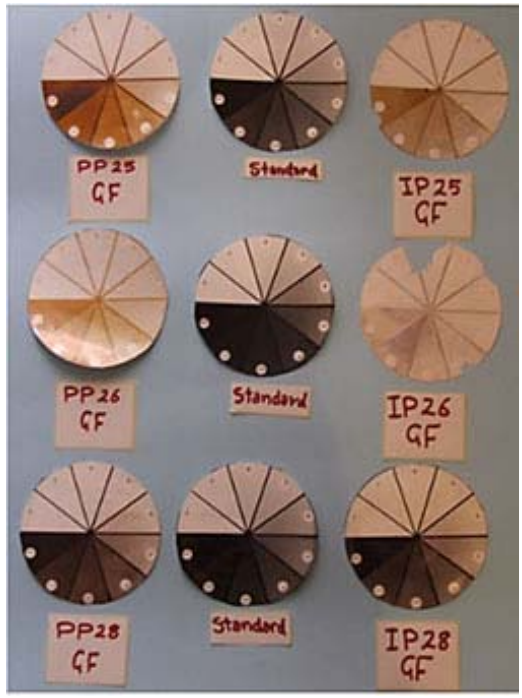

Fig. 4. Gas fading test samples after exposure to oxidizing gases. The image silver decay is noticeable in all samples; however, the effect of the gases is much more severe in the case of the improperly processed samples (i.e. IP25GF, IP26GF, and IP28GF compared to PP25GF, PP26GF, and PP28GF respectively).

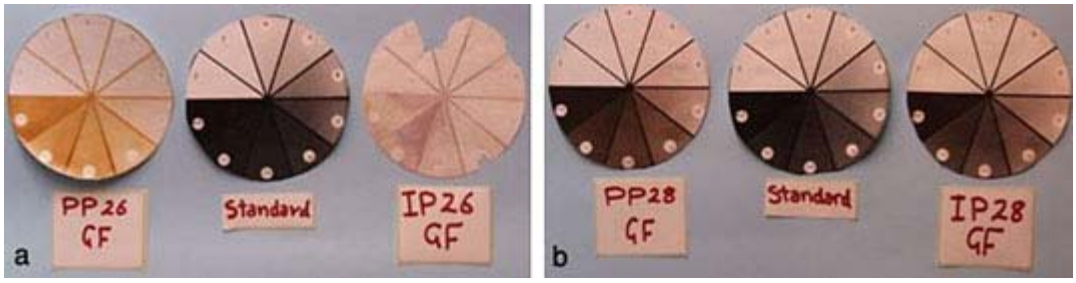

Fig. 5. (a): comparison between the condition of sample PP26GF and sample IP26GF after exposure to hydrogen peroxide for 12 days. Image decay is apparent in both samples; however, hydrogen peroxide caused yellow/orange discoloration in sample PP26GF and fading of sample IP26GF. The paper support in sample PP26GF is still intact, while it has become extremely brittle in sample IP26GF; (b): samples PP28GF and IP28GF after exposure to hydrogen sulfide for 10 days. Both samples have slightly discolored taking warm tones.

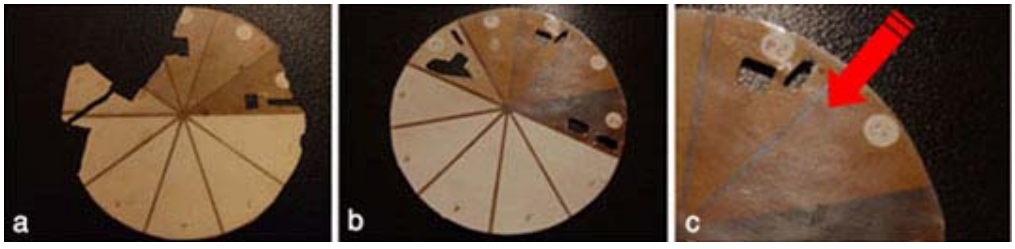

Fig. 6. (a): sample IP25GF after exposure to hydrogen peroxide for 10 days showing embrittlement of the paper base but no visible signs of silver mirroring; (b): sample PP25GF showing silver mirroring decay in shadow areas after to the same gas fading test; (c): close-up shot of silver mirroring decay found in sample PP25GF.

Fungal Test

In silver gelatin prints, the organic components are considered potential carbon sources for the growth of microorganisms, if environmental conditions are adequate [23]. Out of the fifteen species most frequently identified in photographic collections, the most representative belong to the *Aspergillus*, *Penicilluim*, *Mucor*, *Cladosporium*, *Trichoderma*, and *Phoma* species [24]. A study was done to identify the biological activity of both *Aspergillus niger* and *Aspergillus flavus* on paper and gelatin. The two fungal species were isolated from samples IP29GF and IP30GF (Fig. 7). The isolated species were propagated in the Microbiology Lab at the Conservation Department, Faculty of Archaeology/Cairo University. They were inoculated to a medium containing carboxymethylcellulose (CMC) and a second medium containing gelatin and beef extract (Fig. 8). After 48 hours of incubation, the radius of fungal growth was measured (Fig. 9). The fungal growth rate was detected by studying the increase or decrease in colony radius. The growth rate of both *Aspergillus niger* and *Aspergillus flavus* was faster in the case of the CMC medium.

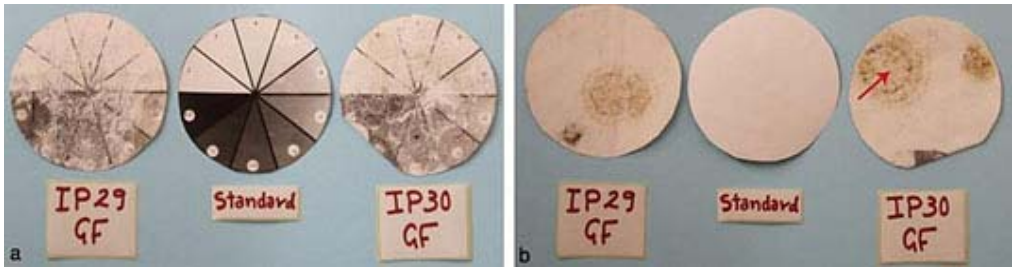

Fig. 7. (a): samples IP29GF and IP30GF after exposure to hydrogen sulfide for 15 days at 80%RH. High relative humidity (80%) caused severe degradation of the gelatin binder; (b): the growth of microorganisms on the verso of samples IP29GF and IP30GF after exposure to hydrogen sulfide for 15 days at 80%RH.

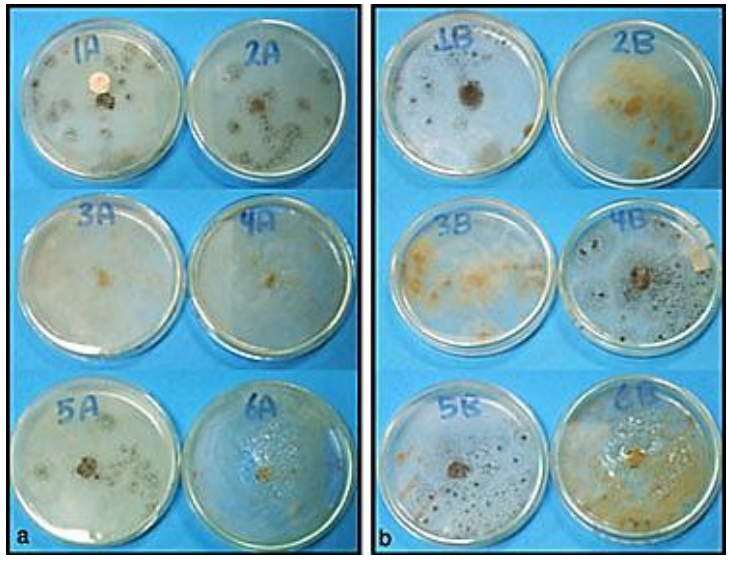

Fig. 8. (a): Petri dishes 1A-6A containing *Aspergillus niger (black)*and *Aspergillus flavus (green)* on a gelatine and beef extract media; (b): petri dishes 1B-6B containing *Aspergillus niger (black)* and *Aspergillus flavus (green)* on CMC media.

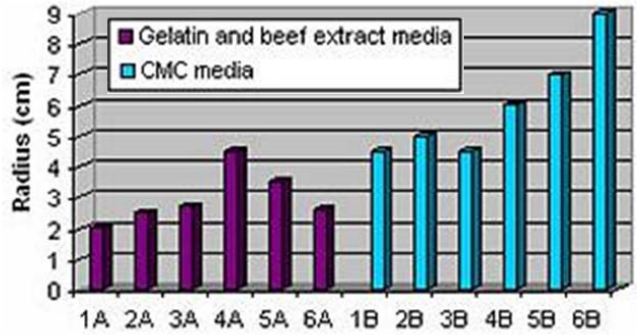

Fig. 9. Radius of fungal growth in samples (1A-6A) and samples (1B-6B). The growth rate of both *Aspergillus niger* and *Aspergillus flavus* was faster in the case of the CMC media.

FTIR

The FTIR spectrum of the control sample, before aging, consisted of the characteristic spectra of gelatin, cellulose, and barium sulfate. The results revealed that photographic paper and gelatin are greatly affected by oxidizing agents and that this effect is increased if the photographic prints were inadequately washed at the time of their processing. The FT-IR spectrum of PP29GF shows complete degradation of paper cellulose which was indicated by the increase in the intensity of carbonyl stretching bands at 1640.16 cm^{-1}, and the absence of the characteristic bands at 3277.43 cm^{-1}; 3071.08 cm^{-1}; 2931.27 cm^{-1}; 1233.25 cm^{-1}; 1163.83 cm^{-1}; and 1076.08 cm^{-1}. The increase of the intensity of the amide I and amide II bands compared to that of the standard ones, indicate that the photographic emulsion has been severely damaged. The FT-IR spectrum also shows the presence of an additional characteristic band at 602.64 cm^{-1} which is attributed to the SO_4^{2-} bending band. This could be due to the breakdown of barium sulfate, a reaction induced by high relative humidity (80%). The damage is more severe in the case of the IP29GF sample (Fig. 10) and Table 2. Furthermore, hydrogen peroxide caused major decay to photographic prints compared to hydrogen sulfide (Fig. 11) and Table 3.

Table 2. Functional groups found in the control sample, PP28GF and IP28GF.

Band No.	Functional group of the control sample	Wave number of the functional group cm-1 of the control sample	Intensity	Sample PP28GF/ Intensity and Wave no.	Sample IP28GF/ Intensity and Wave no.
1	OH stretching broad band due to inter molecular hydrogen bonding.	3277.43 cm-1	84.096	present 84.82 3279.36 cm^{-1}	present 88.45 3280.32 cm^{-1}
2	C-H stretching.	3071.08 cm-1	86.75	present 88.40 3076.87 cm^{-1}	present 90.96 3074.94 cm^{-1}
3		2931.27 cm-1	86.65	present 88.21 2931.27 cm^{-1}	present 90.77 2931.27 cm^{-1}
4	C=O stretching of gelatin (amide I).	1628.59 cm-1	67.77	present 68.53 1630.52 cm^{-1}	present 73.81 1632.45 cm^{-1}
5	C-N stretching + N-H bending (amide II) of gelatin	1531.2 cm-1	69.67	present 72.14 1536.02 cm^{-1}	present 77.08 1535.06 cm^{-1}
6	C-H bending (amide III) of gelatin	1446.35 cm-1	77.72	present 80.98 1447.31 cm^{-1}	present 84.60 1447.31 cm^{-1}
7	C-O stretching of various (C-OH) hydroxyl groups present in paper cellulose.	1233.25 cm-1	77.80	present 83.11 1239.04 cm^{-1}	present 85.72 1237.11 cm^{-1}
8		1163.83 cm-1	82.56	disappeared	Disappeared
9		1076.08 cm-1	85.39	present 88.97 1077.05 cm^{-1}	present 88.60 1077.05 cm^{-1}

10		1076.08 cm-1	85.39	present 88.97 1077.05 cm^{-1}	present 88.60 1077.05 cm^{-1}
	SO_4^{2-} stretching of $BaSO_4$.			present	present
11		1028.84 cm-1	86.51	89.83 1036.55 cm^{-1}	89.43 1032.69 cm^{-1}
12		964.233 cm-1	88.03	disappeared	Disappeared

Table 3. Functional groups found in the control sample, PP25GF and IP25GF.

Band No.	Functional group of the control sample	Wave number of the functional group cm-1 of the control sample	Intensity	Sample PP25GF/ Intensity and Wave no.	Sample IP25GF/ Intensity and Wave no.
1	OH stretching broad band due to inter molecular hydrogen bonding.	3277.43 cm-1	84.096	present 97.53 3261.36 cm^{-1}	Disappeared
2	C-H stretching.	3071.08 cm-1	86.75	disappeared	Disappeared
3		2931.27 cm-1	86.65	disappeared	Disappeared
4	C=O stretching of gelatin (amide I).	1628.59 cm-1	67.77	present 82.67 1627.63 cm^{-1}	Disappeared
5	C-N stretching + N-H bending (amide II) of gelatin	1531.2 cm-1	69.67	present 83.29 1535.06 cm^{-1}	Disappeared
6	C-H bending (amide III) of gelatin	1446.35 cm-1	77.72	present 85.99 1444.42 cm^{-1}	Disappeared
7	C-O stretching of various (C-OH) hydroxyl groups present in paper cellulose.	1233.25 cm-1	77.80	present 85.17 1240 cm^{-1}	present 77.32 1277.61 cm^{-1}
8		1163.83 cm-1	82.56	disappeared	Disappeared
9		1076.08 cm-1	85.39	disappeared	Disappeared
9	SO_4^{2-} stretching of $BaSO_4$.	1076.08 cm-1	85.39	disappeared	Disappeared
10		1028.84 cm-1	86.51	disappeared	Disappeared
11		964.233 cm-1	88.03	disappeared	Disappeared

Both light fading test and accelerated aging test had less effect on photographic paper and gelatin (Fig. 12) and (Fig. 13).

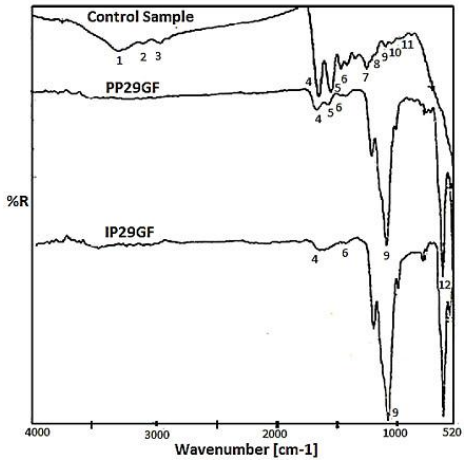

Fig. 10. FT-IR spectra of samples PP29GF and IP29GF after exposure to hydrogen sulfide for 15 days compared to the control sample.

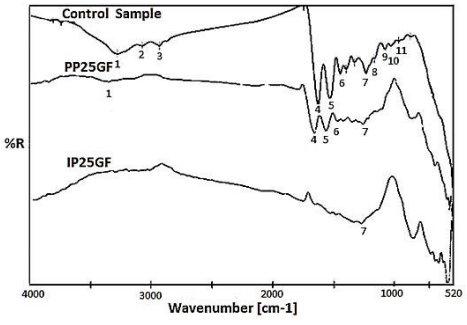

Fig. 11. FT-IR spectra of samples PP25GF and IP25GF after exposure to hydrogen peroxide for 10 days compared to the control sample.

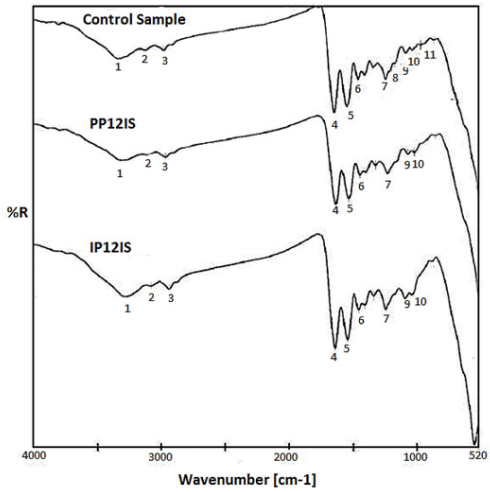

Fig. 12. FT-IR spectra of samples PP12IS and IP12IS after ageing at 105°C and 67.5%RH for 30 days compared to the control sample.

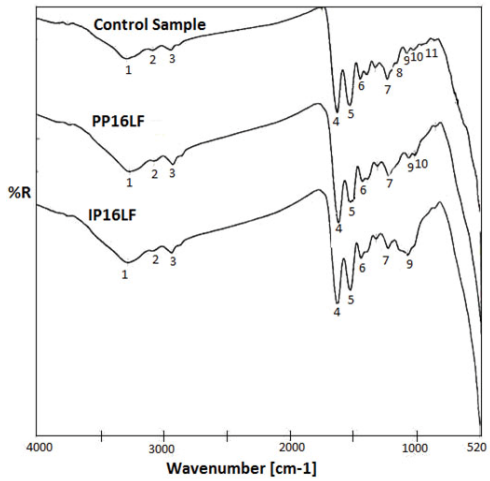

Fig. 13. FT-IR spectra of samples PP16LF and IP16LF after light fading test compared to the control sample.

Amino Acid Analysis

The decay mechanisms of photographic gelatin received less attention than those of image silver decay. Chemically speaking, the reactive groups on the side chains of amino acids are capable of a wide range of alterations, leading to various forms of degradation. The common reactions of amino acids are deamination (which indicates the loss of the amine group) decarboxylation (which indicates the loss of carboxyl group), dehydrogenation (which involves the elimination of hydrogen) and transamination (which involves the conversion of one amino acid to another). These reactions cause changes in the amino acids and also form products, each specific to a certain deterioration form.

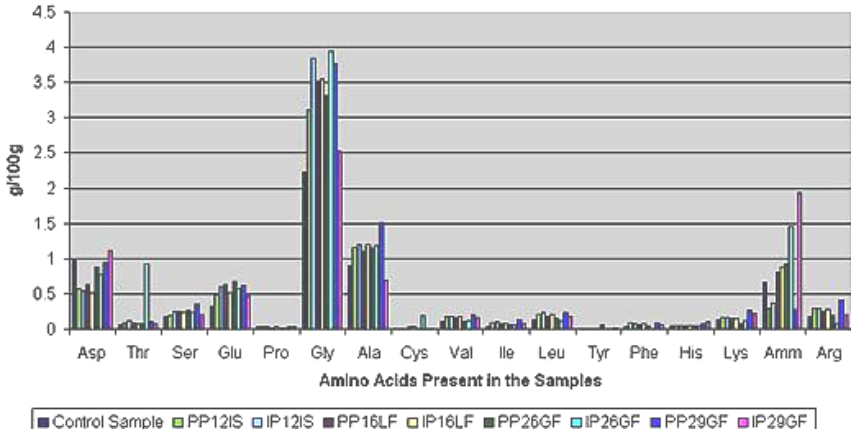

Fig. 14. Amino acid composition of the control sample and the artificially aged samples (g/100g).

Therefore, these products and alterations are considered indicators of deterioration [25]. The route of protein deterioration is as follows:

- In oxidative decarboxylation, the carboxylic acid group is lost and the amino acid is converted to the corresponding amine, i.e. glutamic acid is converted to amine glutamine and, eventually, ammonia is formed.

- In oxidative deamination and non-oxidative decarboxylation, the amino acid is converted to the corresponding α-Keto acid, and then to ammonia.
- In dehydrogenation, amino acids with β,γ-, or γ,δ- unsaturated bands are formed (i.e. γ-butyric acid). The end product is ammonia.
- The formed ammonia is capable of reacting with the sulfuric acid present in the protein and the result is the formation of ammonia sulfate. Therefore, the presence of sulfate is an indication of the occurrence of a hydrolytic deterioration.

Our results revealed that photographic gelatin is severely affected by oxidizing agents and by inadequate washing during processing and the result is the increase in the amount of ammonia and acidic amino acids, as shown in (Fig. 14).

Transmission Electron Microscopy

Transmission electron micrographs showed that the discoloration of the silver gelatin prints was always accompanied by a migration mechanism resulting in the formation of small silver particles. When compared to high temperatures and relative humidity, oxidizing agents plus high relative humidity (i.e. hydrogen peroxide and hydrogen sulfide) have the most aggressive effect on the size and distribution of the silver particles (Fig. 15).

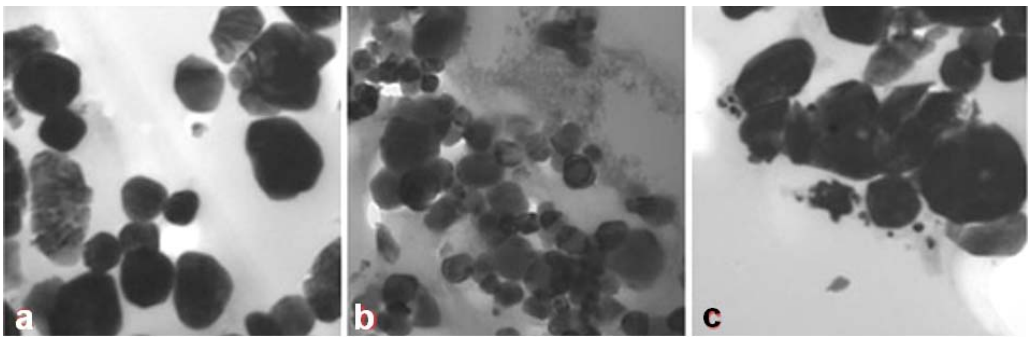

Fig. 15. (a): TEM micrograph of processed silver grains from sample IP25GF step (24) at magnification 50000 X. The image shows the erosion of silver particles; (b): TEM micrograph of processed silver grains from sample IP12IS step (24) at magnification 30000 X. The image shows no significant changes; (c): TEM micrograph of processed silver grains from sample IP25GF step (24) at magnification 50000 X. The image shows the breakdown of silver particles and the formation of numerous silver particles in new sites.

Conclusions

The investigation and analysis methods used in this study show that image silver, photographic paper and gelatin are greatly affected by oxidizing agents and that effect is increased if the photographic prints were inadequately washed at the time of their processing. Light was found to have a minor effect on silver gelatin prints, causing only slight yellowing in both samples. The effects were most dramatic in the case of the gas fading test, resulting in severe discoloration and embrittlement. The results proved that hydrogen peroxide causes more serious decay to photographic prints, compared to hydrogen sulfide. Both hydrogen sulfide and hydrogen peroxide caused the image silver to discolor to a warm brown tone and a yellow orange tone respectively. Hydrogen peroxide was found to cause silver mirroring in the shadow areas of properly processed samples. Results also revealed that physical forms of damage such as cracks were affected by the processing procedure and that hypo caused the embrittlement of the paper support, through an acid deterioration process, causing cracks to develop. The fact that gelatin is highly prone to oxidation is also confirmed by the results of the amino acid test. The oxidation of the side chains of amino acids that compose gelatin caused the amount of ammonia and acidic amino acids to increase. Therefore, the increased amount of ammonia and

acidic amino acid in silver gelatin prints is a reliable indicator of gelatin emulsion degradation. Amino acid analysis was performed because this method has not been used earlier to measure the degradation of the gelatin emulsion. The results from the transmission electron micrographs showed the erosion of silver particles and their breakdown to smaller particles, upon oxidation. However, much more erosion and breakdown was expected in the case of the samples which were exposed to hydrogen peroxide. Therefore, further investigations are needed to reveal the behavior of silver particles during aging. Oxidation was found to have deleterious effects on all three components of the silver gelatin prints, in terms of their physical and chemical properties and nature. The paper deals only with one of the many sides of chemical degradation in silver gelatin prints and much more studies are needed to analyze all of them.

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