

ANALYTICAL STUDY ON THE EFFECTS OF POLLUTANTS ON SILVER GELATIN PRINTS

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Abstract

Silver gelatin prints are composed of multiple materials giving such photographs a complex physical and chemical nature; and for this reason, they are more vulnerable to damage compared to other archival materials such as books and manuscripts. This paper studies the effects of pollutants on the properties of silver gelatin prints. Silver gelatin prints are attacked by pollutants in the form of gases and/or solid particles. Pollutants affect all components of a silver gelatin prints causing it to deteriorate and/or degrade. Gaseous pollutants have the most aggressive influence on photographic materials. Gaseous pollutants which are harmful to silver gelatin prints include oxidant, sulfiding and acidic gases. This paper focuses only on the effect of hydrogen peroxide as an internal pollutant and hydrogen sulfide as an external pollutant. The study included exposing photographic samples to both hydrogen peroxide and hydrogen sulfide for a period of 10 days and 15 days. The evaluation procedure was carried out using microscopic inspection, Fourier transform infrared spectroscopy and colorimetric measurements.

Keywords: *Silver gelatin prints; Pollutant; Damage; Visual inspection; Microscopic examination; FTIR; colorimetric measurement.*

Introduction

Photographic heritage, whether national, cultural or family, represents the history, knowledge and values that have developed overtime. Preservation of photographs materials has long been a challenge for collection holders. Egypt was a destination which attracted many pioneer photographers in the past [1]. This resulted in the existence of rare photographic collections held by museums, palaces, libraries and archives.

These photographic records contain images made on a variety of materials. However, photographs made during the last one hundred years belong to a class known as silver gelatin prints. A silver gelatin print is composed of three layers: the primary support, paper; the baryta layer, a layer of finely grounded barium sulfate in gelatin; the image layer; silver particles embedded in a gelatin binder layer [2-5]. This unique yet complex layer structure is to a large extent responsible for their long-term stability characteristics, and thus their permanence. It is therefore essential to consider the physical and chemical nature of such photographs and their role in the deterioration cycle [6]. There are two types of silver gelatin print depending on the method of image production: printed-out and developed-out prints [7, 8]. In this paper, we focus on developed-out silver gelatin prints since they are the most common among photographic collections in Egypt. Silver gelatin developed-out prints were popularized by Eastman Kodak Company in 1886 [9]. Developed-out silver gelatin prints contain filamentary silver particles,

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and these appear as twisted strains. Image silver is the most vulnerable part in silver gelatin prints. 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 [10]. Gelatin is a protein derived from fibrous insoluble protein, collagen, which is widely found as a major component of skin, bones and connective tissues [11]. Most of the stability problems associated with gelatin result from its physical and chemical properties (i.e. hygroscopic, organic, amphoteric and amorphous) [12, 13]. Early in the 19th century, photographic paper was manufactured from old linen and cotton rags. Around the 1840s, wood pulp paper was widely adopted for photographic purposes. Paper containing 50% rag and 50% purified wood pulp was manufactured by 1926. In 1929, paper was made from highly purified wood pulp [7, 14].

Agents which may affect the stability and permanence of silver gelatin prints include: intrinsic agents and extrinsic agents [15, 16]. Air pollution contributes heavily to the deterioration and/or degradation of silver gelatin prints [17]. A combination of high temperature, high relative humidity and pollutants are debilitating to paper support and the gelatin binder, but particularly to the image silver [18]. The severity of pollutant attack is determined by the levels of relative humidity and temperature in the surrounding environment, the concentration of gasses or fumes, and the presence of residual chemicals in the photographic prints [15]. Primary sources that affect the permanence of silver gelatin prints can be divided to: internal sources (i.e. improper storage and display materials) and external sources (i.e. the external environment and or the environment inside the storage or display space). The preservation of photographic prints is achieved by means of physical barriers (i.e. contact materials, storage and display furniture and storage and display area) [14, 16]. Improper selection or usage will cause silver gelatin print to deteriorate. Many available materials produce harmful compounds that are particularly damaging to silver gelatin prints [19]. The accumulation of harmful compounds of these harmful compounds or high relative humidity in a sealed container will cause undesirable microenvironments to develop [14]. Moreover, Cairo is a rapidly expanding city, which has led to many environmental problems. Air pollution has always been a matter of serious concern. Air quality in Cairo is more than 10 to 100 folds of acceptable world standards [20]. Gaseous pollutants which are harmful to silver gelatin prints include oxidants, sulfiding gases, acidic gases and environmental fumes [21, 22].

The issue of deterioration and degradation of silver gelatin prints by pollutants is not simple, it involves several concerns. This is mainly because the presence of different types of materials and pollutants. As a consequence, the chemical deteriorating reactions vary [3]. The visible signs of deterioration by atmospheric contaminants may appear in several forms. Most pollutants are oxidizing agents in different forms; and these include peroxides, nitrogen oxides, ozone, sulfur dioxide and hydrogen sulfide [23]. Sulfur dioxide and nitrous oxide are acidic gases since they react with water to produce acids [24]. Oxidation is the basis of image decay [25]. Symptoms of image decay include fading, silver mirroring, staining, and discoloration [7, 26]. Pollutants induce the hydrolysis of gelatin [27]. They further cause the discoloration and embrittlement of paper supports [22]. Silver has a strong tendency to react with sulfur [28].

The scope of this paper is to study the effect of pollutants on silver gelatin prints. Hydrogen peroxide has been selected as an internal pollutant and hydrogen sulfide as external pollutant. Many photographic prints have been degraded by the action of harmful ingredients in enclosures and adhesives that seal them [29]. For example, enclosures made from brown Kraft paper contain image damaging ingredients such as lignin which generate destructive peroxides. Cabinets made of inferior materials produce harmful chemicals. Wood and wood by-products contain lignin and oils and produce emanations of peroxides, organic acids and aldehydes. Additionally, hydrogen sulfide is produced by industrial activities that can produce the gas include petroleum/natural gas drilling and refining, wastewater treatment, coke ovens, tanneries, and Kraft paper mills [30]. Hydrogen sulfide and hydrogen peroxide are more damaging to silver gelatin prints above 35% RH [14].

Therefore, this research studies the effects of the two selected pollutants on silver gelatin prints in terms of the resultant degradation [31-34].

Materials and Methods

Sample preparation

Six samples were prepared by printing a Kodak enlarging exposure scale on a black and white photographic paper BH 0 Bromofort 6P0661 Tropical from Forte photochemical Company Vác, Hungary. This procedure was performed at the darkroom of the Contemporary Image Collective (CIC). Samples were exposed in the enlarger. All samples were developed in Fomatol LQN, fixed with hypo (sodium thiosulfate), and washed thoroughly with water following the conditions listed in Table 1. The samples were then allowed to dry over night, face up on a drying rack. To flatten the samples, they were placed between blotting paper and pressed in hydraulic press for two days.

Table 1. Processing conditions used for sample preparation

	BH 0 Bromofort 6P0661 Tropical
Exposure	9 seconds
Development	2 minutes using Fomatol LQN (250 ml) Ratio: 1:7 (dev: water) at 25° C
Contrast filter	5 + 4 Jessop contrast filter
Fixing	10 minutes using hypo (250 g. in 1L of water at 25° C)
Washing	20 minutes

The resultant greyscale contained ten different densities/steps (i.e., 2, 3, 4, 6, 8, 12, 16, 24, 32, and 48). The study was carried out on three densities: step 2 representing the highlight areas, step 12 representing the midtones and step 48 representing the shadow areas (Fig. 1).



Fig. 1. Prepared test material post processing.

Exposure conditions to selected pollutants

The test involved exposing the samples to hydrogen sulfide and hydrogen peroxide for 10 days and 15 days. The materials used for this test are:

- o Six greyscales, three for each pollutant.
- o Two desiccators.
- o Saturated salt of ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ to maintain 80% RH.
- o Neutral peroxide solution: 30% H_2O_2 .
- o Sulfide solution: 0.1% $\text{Na}_2\text{S}/\text{HCl}$.

The desiccators were conditioned for a period of 20 hours by mixing a saturated solution of $(\text{NH}_4)_2\text{SO}_4$ at room temperature. The salt was then poured in a Petri dish and placed in the bottom of the desiccators. The lid of one of the desiccators was removed and H_2O_2 (30%) was poured into a Petri dish which was then set into the bottom of the desiccator. For the preparation of the hydrogen sulfide environment, a solution of 0.1% of sodium sulfide in hydrochloric acid (37%) was mixed under the fumehood to make 200mL of solution. The solution was also poured into a Petri dish and placed in the bottom of the desiccator. Two photographic samples were placed in each desiccator and two samples remained as a control [35]. Samples S10 and S15 were exposed to H_2S for 10 and 15 days, respectively. Samples H10 and H15 were exposed to H_2O_2 for 10 and 15 days, respectively.

Assessment methods

Surface examination by digital microscope

A SUPEREYES PZ01 500X USB Digital Microscope was used to document the resultant damage forms due to the action of each pollutant.

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 10nm 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 $-a$ 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: $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ [36 - 41]. The analysis was carried out at the National Institute of Standards (NIS) in Cairo, Egypt.

Fourier transforms infrared spectroscopy

FT-IR spectroscopy was used to study the chemical changes which may have occurred after exposure. The FTIR instrument used is Jasco FT/IR-6100 Spectrometer under absorption mode. The analysis was carried out at the National Institute of Standards (NIS) in Cairo, Egypt.

Results and Discussions

Surface examination by digital microscope

Effect of hydrogen sulfide (10 days)

After 10 days of exposure to hydrogen sulfide, the samples showed a considerable change in image tones. The highlights and midtones became more yellow, while the shadow areas have shifted to a more brown tone (Fig. 2).

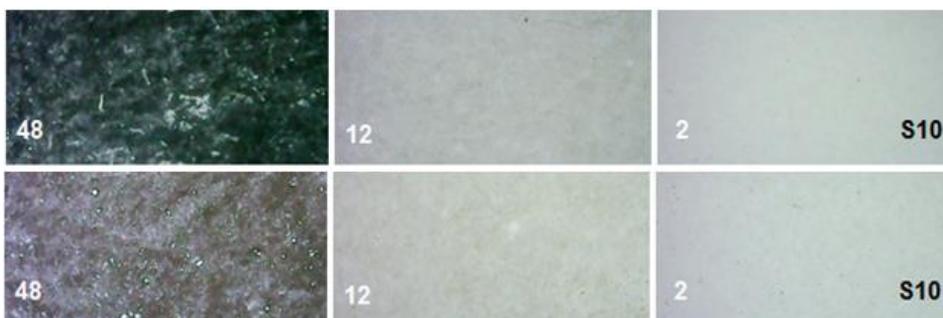


Fig. 2. Images taken by USB microscope showing the sample before exposure to hydrogen sulfide for 10 days (top) and after exposure (bottom).

Effect of hydrogen sulfide (15 days)

Prolonged exposure caused significant deterioration in the image silver and binder layer. The shadow areas showed fading (Fig. 3). They also showed initial signs of silver mirroring. Silver mirroring is a common form of image silver decay among silver-based photographic processes; particularly silver gelatin prints [24]. Image silver decay starts with the oxidation of the image silver particles (Ag_0) which are stripped off 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. Silver mirroring occurs when the mobile silver ions migrate to the surface [26, 42]. It was once assumed, that on the surface silver ions are reduced back to metallic silver [43]. However, several studies were carried out and concluded that it is result of the reaction between silver ions and an environmental sulfur-based compound [44], [45]. Silver mirroring appears as a bluish metallic sheen giving the shadow areas an iridescent appearance [46 - 49]. When very severe, it can appear green, violet or bronze in color [47].



Fig. 3. Images taken by USB microscope showing the sample before exposure to hydrogen sulfide for 15 days (top) and after exposure (bottom). The red arrows point to mirrored areas.

Effect of hydrogen peroxide (10 days)

Exposure to hydrogen peroxide for a period of 10 days has caused both fading and discoloration of the image silver, particularly in the midtones and shadow areas. Brown staining of unknown source was also observed on both the image layer and primary support. A network of fine cracks was also visible under magnification in the shadow areas (Fig. 4).

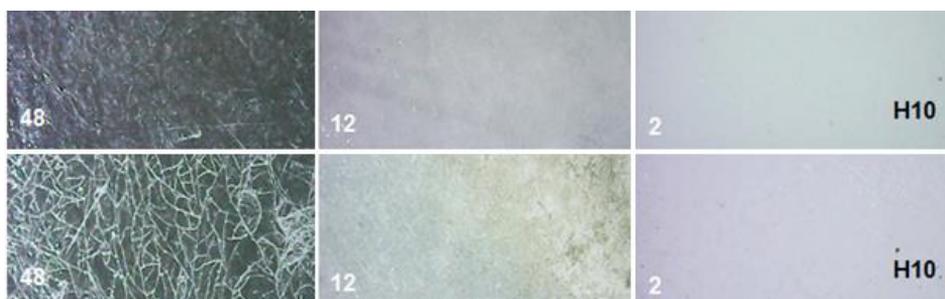


Fig. 4. Images taken by USB microscope showing the sample before exposure to hydrogen peroxide for 10 days (top) and after exposure (bottom).

Effect of hydrogen peroxide (15 days)

The gelatin appeared to be deleteriously damaged. Investigations also showed fading of the image silver and severe fungal infection of the gelatin binder layer carrying the image and paper support (Fig. 5). Several cracks were apparent under magnification in the midtones area represented in step 12.

A higher magnification was used to identify the present fungal colony according to its morphological characteristics (Fig. 6). Based on the results, the colony belongs to the group of *Aspergillus* sp. that have globular vesicles, conidiophores shaped translucent yellowish green, semi conidiospore round to round-shaped light green to brownish green [49].

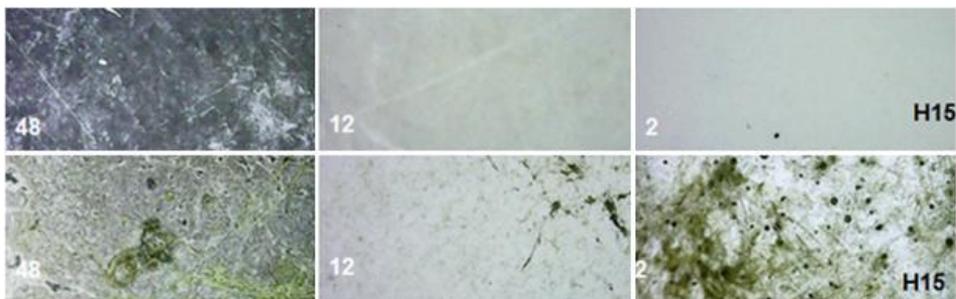


Fig. 5. Images taken by USB microscope showing the sample before exposure to hydrogen peroxide for 15 days (top) and after exposure (bottom).



Fig. 6. *Aspergillus* sp.

Colorimetric measurements

The total color difference (ΔE^*) is a value useful as an indicator of the difference between the sample and the reference. According to DIN EN ISO (super ceded by BS EN ISO 4628-1:2004), evaluation of ΔE^* is as follows:

- 0 – 1: color difference is not visible.
- 1-3: few people can recognize the difference.
- 3- 5: 66 % of people can recognize the difference.
- >5 everyone can recognize the difference [36, 37, 50, 51].

In literature, chromatic variation of 2-3 can be considered noticeable by human eye; however, it is clearly lower than the threshold limit required ($\Delta E^* = 5$) for the maintenance and restoration of historical surfaces [52]. Test results were illustrated using Color Math.

Effect of hydrogen sulfide (10 days)

Results listed in Table 2 show that minimal change in color occurred in the highlight areas (step 2), while both the midtones (step 12) and the shadow areas (step 48) showed a greater change in color with a total color change (ΔE^*) above 5. In breaking down the obtained data into CIE $L^*a^*b^*$, the lightness increased for the highlights (step 2) and decreased for the midtones (step 12) and shadows (step 48). Yellowing was also detected in all image tones (Fig. 7).

Effect of hydrogen sulfide (15 days)

All image tones showed ΔE^* values above 5 with the least total color change in the case of the highlight areas (step 2). Color representations of total color difference in all three tones as obtained by Color Math show that the image has shifted towards brownish tones (Fig. 7). The L^* axis shows that the shadow areas have become darker, while both the highlights and midtones have faded. The b^* axis reveals the yellowing of all image tones. Results are represented in Table 2.

Table 2. Measured values of L^* , a^* , b^* and total Color Change (ΔE^*) for samples S10 and S15 before and after exposure to hydrogen sulfide for 10 and 15 days, respectively

Sample No.	Exposure stage	L^*	a^*	b^*	ΔE^*
S10	Before	91.92	0.42	1.49	3.40
	After	93.28	-0.29	5.07	
	Before	80.71	0.14	2.98	7.98
	After	70.24	1.00	5.54	
	Before	43.58	0.10	-0.70	9.29
	After	32.83	0.31	0.41	
S15	Before	87.06	0.47	-0.14	5.56
	After	90.70	-0.13	5.36	
	Before	74.00	0.10	-0.51	7.42
	After	77.74	1.87	7.04	
	Before	43.40	0.79	-1.46	9.77
	After	33.29	2.14	2.94	

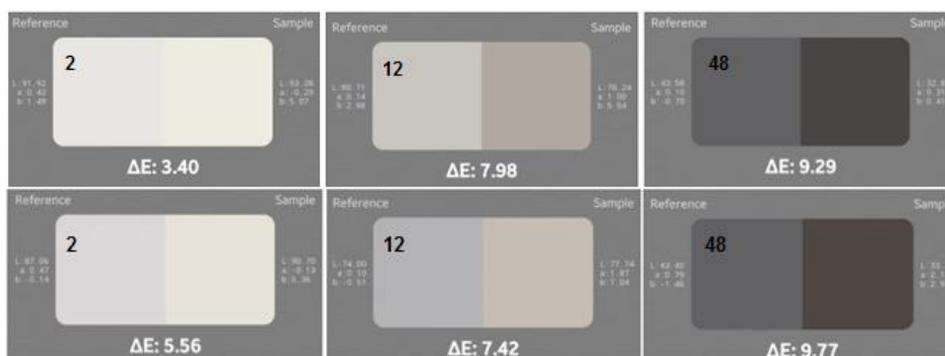


Fig. 7. Illustration of the total color difference in sample S10 (steps 2, 12 and 48) post exposure to hydrogen sulfide for 10 days (top) and sample S15 (steps 2, 12 and 48) post exposure for 15 days (bottom). Reference refers to the sample before exposure and sample is the sample after exposure.

Effect of hydrogen peroxide (10 days)

Results for the highlights showed slight color change. However, the L^* and b^* values show the occurrence of fading and very slight yellowing. Both the midtones and shadow areas showed a greater color change. The midtones have faded, while the shadow areas have become darker (Fig. 8). Results are shown in Table 3.

Effect of hydrogen peroxide (15 days)

Significant color change was observed in all image tones ($\Delta E^* > 5$), with the most color change in the shadow areas. The image has become darker and shifted to brownish tones (Fig. 8). Results are shown in Table 3.

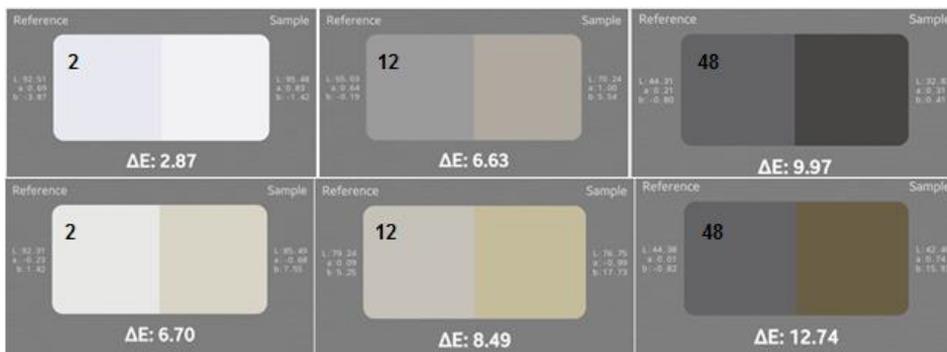


Fig. 8. Illustration of the total color difference in sample H10 (steps 2, 12 and 48) post exposure to hydrogen peroxide for 10 days (top) and sample H15 (steps 2, 12 and 48) post exposure for 15 days (bottom). Reference refers to the sample before exposure and sample is the sample after exposure.

Table 3. Measured values of L*, a*, b* and total Color Change (ΔE*) for samples H10 and H15 before and after exposure to hydrogen peroxide for 10 days.

Sample No.	Exposure stage	L*	a*	b*	ΔE*
H10	Before	92.51	0.69	-3.87	2.87
	After	95.48	0.83	-1.42	
	Before	65.03	0.46	-0.19	6.63
	After	70.24	1.00	5.54	
	Before	44.31	0.21	-0.80	9.97
	After	32.83	0.31	0.41	
H15	Before	92.31	-0.23	1.42	6.70
	After	85.49	-0.68	7.55	
	Before	79.24	0.09	5.25	8.49
	After	76.15	-0.99	17.73	
	Before	44.38	0.01	-0.82	12.74
	After	42.48	0.74	15.93	

Fourier transform infrared spectroscopy

Results for samples S15, H10 and H15 have shown the absorption bands characteristic of gelatin. Of these the amide I band (1600 – 1700cm⁻¹) and amide II (1500 – 1600cm⁻¹) are the most prominent vibrational bands of protein backbone [53]. Amide I is presided by the C=O stretching vibrations of the peptide linkage (70 – 85%) [54] Amide II is a combination of several types of vibrations within the peptide group; it originates from the in-plane N-H bending (40 – 60%), along with both the C-N stretching vibrations (18 – 40%) and C-C stretching vibrations (about 10%) [55 - 56]. With respect to degradation, hydrolysis of gelatin appears as an increase in amide I/amide II peak intensity ratio (I_{AI}/I_{AII}). On the other hand, decrease in amide I/amide II peak intensity ratio would reflect loss in protein level. Oxidation of gelatin results in the formation of carbonyl compounds and this can be seen as a slight shoulder on the amide I band or as an increase in the area of the amide I band [57]. Increase in amide I band intensity is related to an increase in random coil at expense of the ordered secondary structure [58]. Cellulose oxidation results in the increase of the intensity of the amide I band [59].

For FTIR study of the changes which has occurred in the photographic samples S15, H10 and H15 after exposure to H₂S for 15 days, H₂O₂ for 10 days and H₂O₂ for 15 days, respectively; results given in Table 4 show that the gelatin in all samples has been hydrolyzed as indicated by the increase in I_{AI}/I_{AII} ratio. All samples showed an increase in the intensity of the amide I band which indicates the occurrence of cellulose oxidation (Fig. 9).

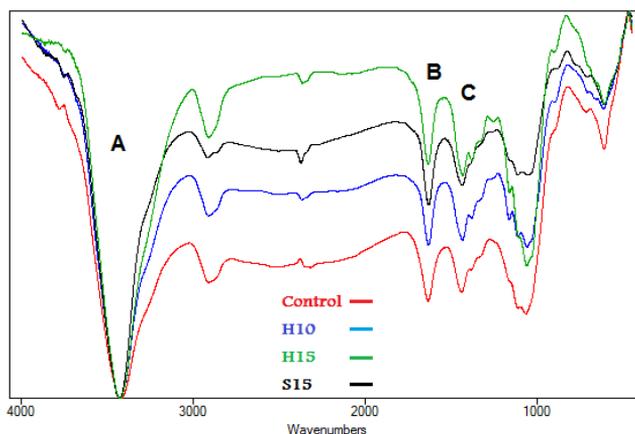


Fig. 9. FTIR spectra of samples S15, H10 and H15 after exposure to pollutants compared to a control sample.

Table 4. Comparison between the I_{AI}/I_{AII} ratio of samples exposed to pollutants

Sample no.	Control	S15	H10	H15
I_{AI}/I_{AII} ratio	1.3	2	1.4	2

Conclusions

Based on the results of this study, all components that make a silver gelatin print (i.e. metallic silver particles, gelatin binder, and paper) are greatly affected by pollutants in the form of hydrogen peroxide and hydrogen sulfide. Slight discoloration has occurred post exposure to hydrogen sulfide for a period of 10 days. Prolonged exposure to the same pollutant resulted in the mirroring of the shadow areas and discoloration of the highlights and midtones. On the other hand exposure to hydrogen peroxide led to the discoloration of midtones and shadow areas and the formation of a network of fine cracks on the image surface. Severe discoloration and damage to the binder and paper support was observed post exposure to hydrogen peroxide for a period of 15 days. Severe fungal infection of the gelatin binder layer carrying the image and paper support was perceptible. Based on the results, the existing colony belongs to the group of *Aspergillus sp.* FTIR study showed that gelatin has been hydrolyzed and cellulose has been oxidized in all samples.

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