NorCal Open Access Publications
Journal of Interventional Radiology and Nuclear Medicine
Volume 1; Issue 3
Shaeen RA et al.

Research Article

ISSN 2637-7152

Inquisition on the Photochemical Degradation of Silver Gelatin Photograph Print-Out

Rasha Ahmed SHAHEEN[1*], Mona Fouad ALI[2], Mohamed Osama SAQR[3], Sameh M. REDA[4], Ahmad M. LABEEB[5]

[1]Egyptian Textile Museum, Cairo, Egypt

[2]Faculty of Archaeology, Cairo University, Giza, Egypt

[3]Faculty of Applied Art, Helwan University, Cairo, Egypt

[4]Radiometry Department, National Institute for Standards, Giza, Egypt

[5]Physics and Dielectrics Department, National Research Center, Cairo, Egypt

[*]**Corresponding author:** Rasha Shaheen, Egyptian Textile Museum, Cairo, Egypt. Tel: +201287966610; **Email:** rashashaheen55@yahoo.com

Received: 27 November,2018; **Accepted:** 30th December, 2018; **Published:** 21 January, 2019

Abstract

This paper shows the experimental and analytical studies of gelatin behavior at photographic prints during the exposition to ultraviolet radiation. The test material used is black-and-white photographic paper. Different properties and characteristics of the prints have then been measured and compared before and after the irradiation. SEM used to study the surface topology of the gelatin. FTIR-ATR XRF analysis used to modify characteristic of the surfaces.

Mechanical performance used to study. Color change was studied. The obtained results indicate a strong effect of the UV radiation in the color characteristics of the silver image, a certain change in the mechanical properties of the supporting paper and only slight consequences on the chemical properties of gelatin, which may probably increase with time.

Keywords

Energy Quantum, Gelatin Silver Print, Photochemical Reactions, Polymer, tonal characteristics, UV radiation

Introduction

In museums and libraries, light is very essential for displaying the photographic materials, every common sources of light export forms of radiations, which include UV radiation the most harmful for photographic materials [1], the light levels exhibition for photographs have been determined, and classified in four levels which are lead to discolored, faded or exhausted image due to oxidation in light especially UV, and recommended to only facsimiles should be displayed [2]. Five hours of Microscal exposure has been approved roughly equal to 7×10^{20} visible-light photons/cm^2 and to about 10^{20} near-ultraviolet photons/cm^2, if this exposure caused a just-perceptible change, flash exposure of xenon studio should deliver no more than 0.01 of this amount, which contain near-ultraviolet wavelengths thus be the lifetime limit for prints [3]. So, this research aims to determine the ratio of deterioration of image in silver gelatin photographs (DOP) due to exposing to ultraviolet radiation. Photographic image is made by exposure of photosensitive emulsion to light, so it made during to a photo-chemical reaction that record the impression of light on a surface of the photographic print which coated with silver particles dispersed in a binder substance that is gelatin. This photographic print called monochrome which means that the image is dyed using a single color (black & white print) [4]. Silver gelatin photographic papers were available in two process printing-out paper (POP) and developing-out paper (DOP), even though they are similar in the internal chemical structure. Silver gelatin developing out-print paper (DOP) is consist of three layers they are a paper support, baryta and gelatin binder with silver particles which is sensitive to the light to make the image. The main different between DOP and POP is not in the structure of the photographic material but in the way that silver image is developed. POP paper is fully developed using light while DOP paper is fully developed using chemical development [4].

Experimental

Materials and Methods

Samples were prepared by printing a Kodak Enlarging Exposure Negative on a Black & White Photographic Paper (BN 8WL Bromofort 0211722 Tropical from Fort Photographical Company VÁC, Hungary). In the same circumstances, two samples were prepared. The processing chemicals were first prepared according to: developer bath was prepared by adding 44 gm of Sodium Sulfite, 59 gm of Sodium Carbonate, 4 gm of Hydroquinone, and 1 gm of Metol to 750 ml of water. The fixer bath was prepared by adding Sodium Thiosulfate, and Potassium Metabisulfate to 1 liter of water.

Thermal aging

The samples of photographs were studies in the National Institute for Standard, Ingram Frojd has shown that exposure photographs for 72 hours at a temperature of 100°C is equivalent to 28 years under normal circumstances, with the installation of humidity, but heat when used alone as a way of obsolescence accelerated methods, the results do not come an accurate because of changes due to heat alone do not represent changes that occur in the normal statute of limitations, so humidity must be an essential part in the statute of limitations [5]. So, in this study the print-out of photographs were accelerate aging by putting them in a thermal oven under the temperature of 80°C and relative humidity of 65% for 15 days.

Light fading test using UVA

The specimens were tested at a steady distance of UV rays in a conserved cabinet of 10 UV fluorescent lamps, 20 watts, 60 cm, three types of UVA lamps. This was done in the Radiation Measurement Section of the National Institute of Standards [6].

The display area was divided into three columns and rows resulting in nine levels of measurement. Measured radiation levels using UDT UVA at the sample level (30 cm) from sources.

In calculating the energy falling on the sample, the radiation level is multiplied at the time of exposure according to the following equation (1).

Energy (J) = Power (W) x Time (S) ---------- (1)

In this situation samples were exposed 150 minutes so the average energy received 4.3 J/cm^2 ± 0.75% [8].

The average irradiance level was 475μW/cm^2 ± 0.75%, and the average uniformity for field of exposure (min/ max) equals 0.8 ± 0.81%, calculated from the irradiance levels obtained using equation (2).

Uniformity = Maximum irradiance level / Minimum irradiance level ---------- (2)

The sample was prepared to be control without exposing to UV radiation was given the symbols (S0-S11), while the exposing samples to UV radiation was given the symbols (R0-R11).

Test methods

The test methods, which used to evaluate the damage of samples, were:

- Observe visual change by visual observation.
- Studying the variation in the chromatic characteristics of the samples because of exposure using the color scale.
- The rate of change in mechanical properties was assessed. The test was performed at National Institute of Measurement and Calibration, Cairo, Egypt.
- Electron Scanning microscopy (SEM-EDX) were used to assess the rate of change in the chemical properties of gelatin emulsion in photo samples after exposure to UVA. The instrument used for this analysis was (SEM-EDX) EMITECH - K550X sputter coater – England.
- XRF analysis was used to assess the concentration of the silver element after exposure which is the basic component of the image. The instrument used was Elio portable XRF Analyzer (PXRF). The analysis was implemented at Conservation and Restoration Laboratory of Egyptian Museum, Cairo, Egypt.
- the reduction of the gelatin emulsion was used to assess by (FTIR-ATR). The instrument used was JASCO FT/IR-6100 Spectrometer in reflection mode. The analysis was implemented at National Research Center, Cairo, Egypt.

Results and Discussion

Visual inspection

The result of light fading test declared the yellowing and fading in the image due to the high energy of UV after exposing to ultraviolet radiation (Figure 1). However, inconsiderable warping and yellowing in the supporting paper was noticed, it properly be the result of heat emitted from florescent lamps (Figure 1)

Mechanical properties

Tensile strength, the maximum tensile force per unit width developed in a test specimen at rupture or break under prescribed conditions, while Elongation, the tensile strain developed in the test specimen at maximum tensile strength before rupture under prescribed conditions.

Samples were cut up an area of 10cm × 5cm in the vertical direction, have been conducted measurements according to the American standard specifications ASTN 1682 in National Institute for Standards under the Ministry of Scientific Research [7]. This examination was made to samples before and after exposing, all of them in the longitudinal direction of the paper, Table

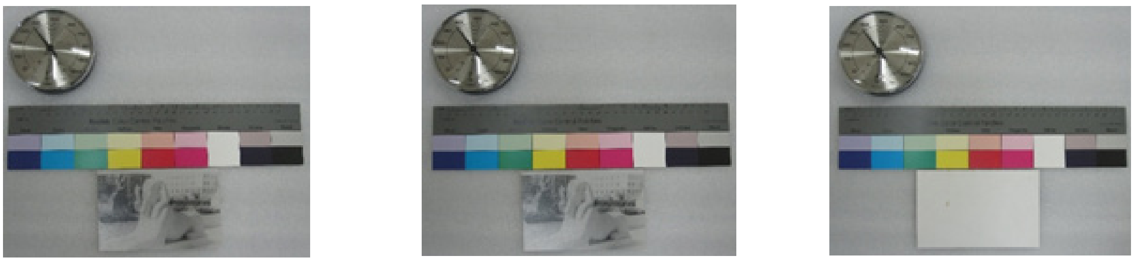

Figure 1: (A), (B): show the status of sample (S0-S11) and sample (R0-R11) after exposing to UVA. Compared to the control sample, yellowing and fading in the image have been declared. (C): show inconsiderable warping and yellowing in the supporting paper.

Sample	Tensile strength (N)	Elongation percentage (%)	Penetration Strength (PST), (N)
S0-S11	128	4.392	3.45
R0-R11	101.7	1.295	2.295
Ratio of mutation (degradation)	20.54%	70.5%	33.47%

Table 1: Average results of the light fading test in mechanical properities, compearing between before and sfter exposing

(1) shows the average results of samples.

To calculate the ratio of mutation (degradation) in the samples after exposure to UV radiation divided the difference between the value of control sample (S0-S11) and the value of sample (R0-R11) by the value of control sample (S0-S11) multiplying 100 as equation (3).

Value of sample (S0-S11) – value of sample (R0-R11) / value of sample (S0-S11) x 100 ---- (3)

Table (1) and (Figure 2) show compering average results of the light fading that done on samples (S0-S11) before exposing, and samples (R0-R11) after exposing to ultraviolet radiation which affected on the mechanical properties of (DOP), this decay appears in clear reduction of the force value of Tensile strength which changed from (128 N) in samples (S0-S11) to be (101.7) in samples (R0-R11). This shown in significant decrease percentage value of elongation which change from (4.392) in samples (S0-S11) to be (1.295) in samples (R0-R11). But regarding to the penetration strength test (PST) the decrease in the force value from samples (S0-S11) which was (3.45) then decrease in samples (R0-R11) to be (2.295).

This degradation is probably as a result of exposure (DOP) to

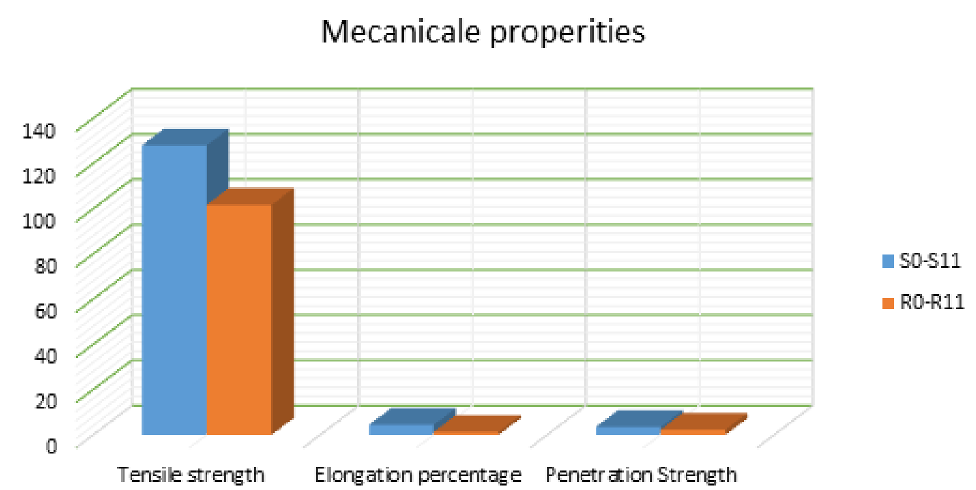

Figure 2: comparing between change values in mechanical properties for the samples before and after exposure

ultra violet radiation with high energy, and therefore its impact on the mechanical properties of gelatin silver print-out as a result of broken the bonds in cellulose which is the main component of paper that used as support to the image.

Tonal qualities (colored change)

Color change were measured of photographs samples before and after processes of exposure using the CIE Lab system a global scale is an approximately uniform color scale to measure the color change. In CIE Lab system color scale, the differences between points plotted in the color space correspond to visual differences between the colors plotted. CIE Lab color space is organized in a cube form, the L* axis runs from top to bottom, the maximum for L* is 100, which represents a perfect reflecting diffuser, the minimum for L* is zero, which represents black. The* and b* axes have no specific numerical limits, positive a* is red, negative a* is green. Positive b* is yellow, negative b* is blue [8].

These measurements have been developed to give color measurements of specific numbers in the form of units of optical nearly identical, and the difference in color between the two samples have specified using the symbol Delta Δ [9]:

Samples have been conducted measurements in National Institute for Standards using color meter, to study the change in tonal qualities that have occurred in the samples of (DOP) due exposure to ultraviolet radiation, and compering between samples before exposure (S0-S11) and samples after exposure (R0-R11), the result shown in the Table (2).

Table (2) and (Figure 3) show compering average results in tonal qualities of samples due to light aging that done on samples (S0-S11) before exposing and samples (R0-R11) after exposing to ultraviolet radiation, this abjection appears in clear declining in the value of color intensity and white test, noticeable rising up in the value of reflectance and yellowing test. CIE Lab system color scale shows decreasing in ΔL mean lacking of black, increasing negative in Δa mean excess green, and significant increasing in Δb mean excess yellowing.

SEM-EDX

The samples were analyzed at the Atomic Energy Commission and Nuclear Safety Laboratory, where were used Scanning Electron Microscope (SEM) with signal unit elemental analysis (EDX).

SEM scan in (Figure 4) shows the difference between the image of samples before exposed (S0-S11) and samples after exposed to UVA (R0-R11), where the image in sample (S0-S11) shows the clarity of image, as well as some of the impurities that are repre-

Sample	Color Intensity	reflectance	Yellowing	white	ΔL	Δa	Δb	ΔE
S0-S11	1.9977	22.636	- 6.56	46.26	- 0.04	- 0.14	0.58	0.60
R0-R11	1.496	32.29	- 0.77	- 44.32	8.05	- 0.47	2.06	8.32
Ratio of mutation (degradation)	25.1%	42.6%	88.26%	195.8%	8.9%	2.35%	2.55%	12.9%

Table 2: Average results of the tonal qualities due to light fading test, comparing between before and after exposing

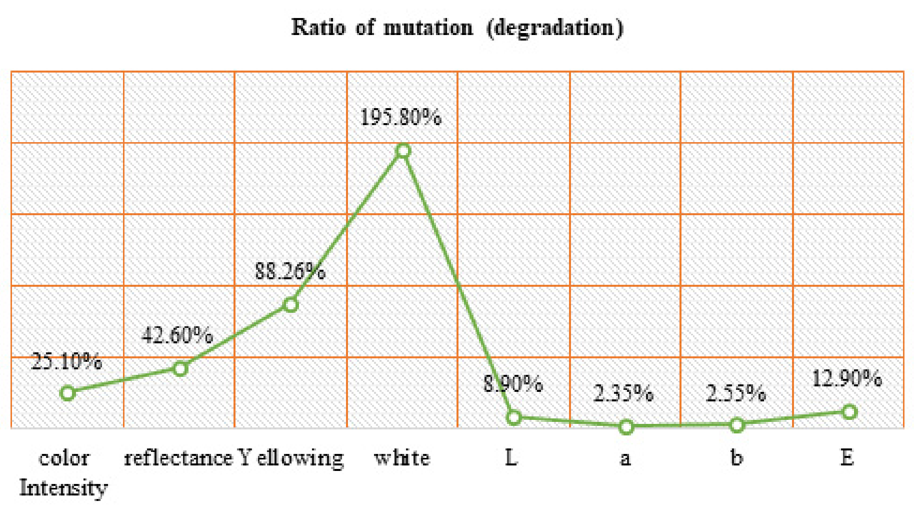

Figure 3: ratio of degradation in tonal qualities for the image in samples due to exposing to UV radiation

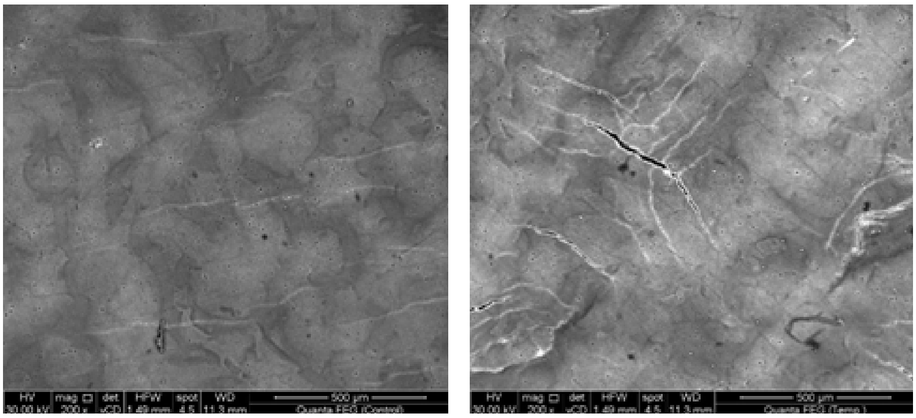

Figure 4: Thin section analysis of the experimental sample of silver gelatin photographic print after aging test, (A) before exposed to UVA, (B) after exposed to UVA.

sent in the composition of the gelatin layer appeared, while the sample (R0-R11) after exposed to UVA shows the lack of clarity as well as the fading and discoloration.

EDX analysis in (Figure 5) shows the sensitive layer of the sample which is photographic paper composed of the element carbon by (43.11), the main component of organic materials - paper and gelatin - and elemental chlorine by (3.82), this shows that the type sensitive silver halide was silver chloride (Ag CL), this type of halides silver is low sensitivity to light, and will be used on a large scale in operations Contact Print , the element of oxygen by (26.57), the element of calcium by (2.00) it shows that the sensitive emulsion who deposited the light-sensitive silver salts is gelatin, the element barium by (6.15), the element of sulfate by (1.05) which is the main component of the Baryta layer consisting of barium sulfate, the element of molybdenum by (5.49),

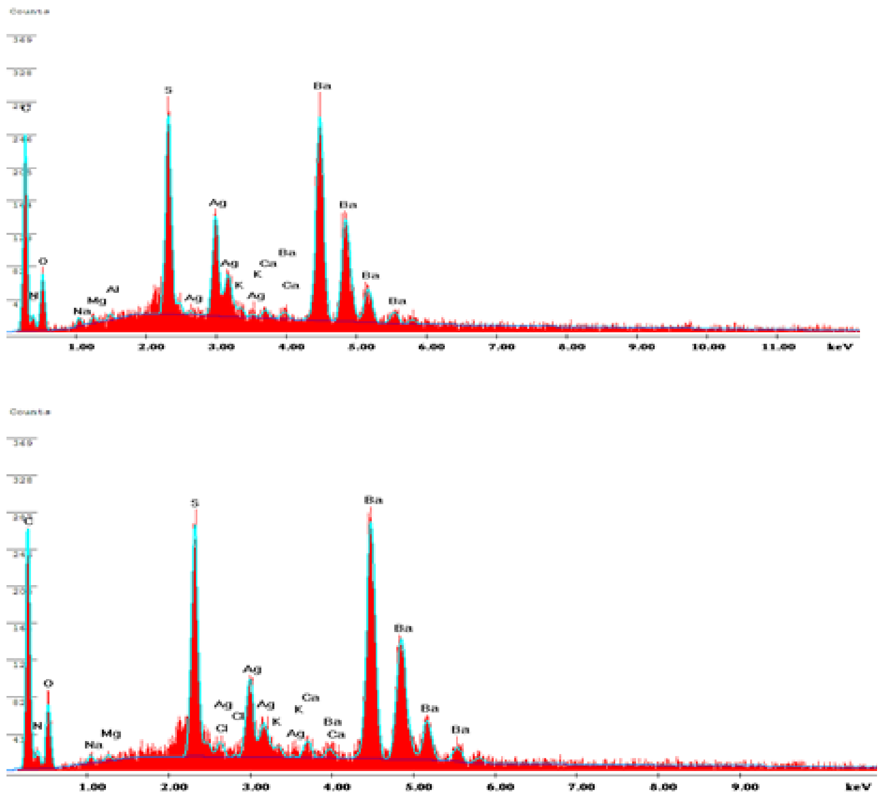

Figure 5: The EDX analysis indicated that, the elements arrangement for the first sample before exposing to UVA can be put in a decreasing order according to their concentration as follow: C (43.11), O (26.57), Cl (3.82), C (2.00), Ba (6.15), Mo (5.49), Na (11.2)

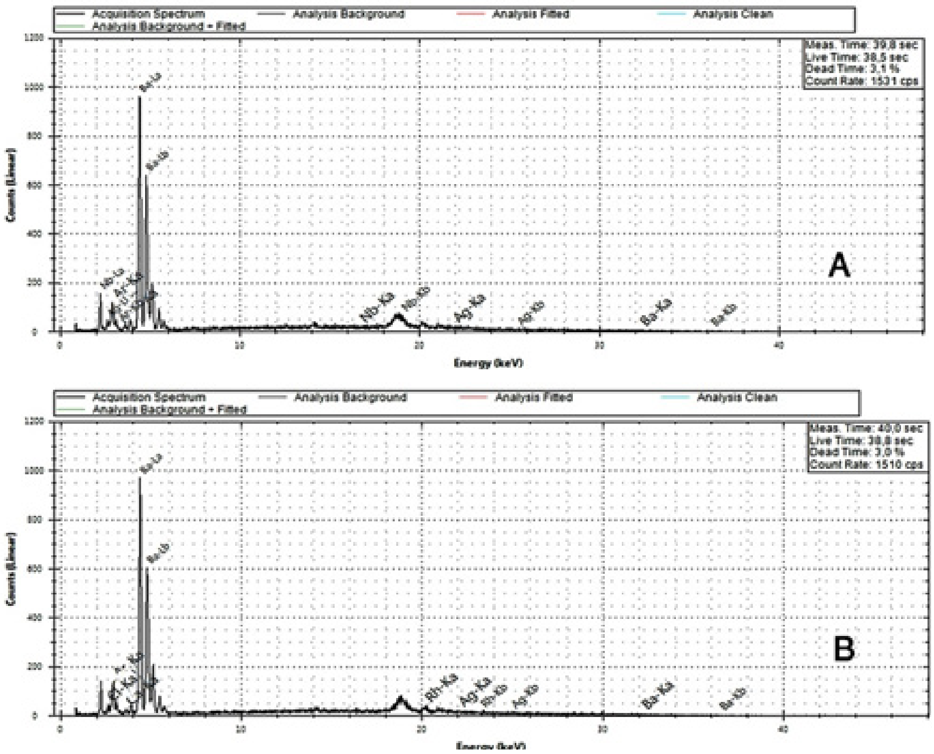

Figure 6: XRF spectrum result for the samples where (A) represent sample (S0-S11), (B) represent sample (R0-R11) show decrease in silver concentrate

	(A)			(B)	
Element	Concentration	Error	Element	Concentration	Error
Ba	88,43%	±0,95%	Ba	83,51%	±0,95%
Ag	9,75%	±6,76%	Cl	14,78%	±6,52%
Ca	1,73%	±8,28%	Ca	1,5%	±12,28%
Nb	0,09%	±3,47%	Ag	0,21%	±8,98%

Table 3: XRF analysis results of the samples, (A) represent sample (S0-S11) while (B) represent sample (R0-R11)

in addition to the presence of impurities of other elements of a sodium component by (11.22), and the element of aluminum by (1.63), while we did not seen these elements in sample (R0-R11), the percentage of the elements was decreasing due to the high energy of UV as seen in (Figure 5).

XRF analysis

Samples were analyzed at Conservation Lab of Egyptian Museum, XRF analysis results shows that a significant decrease in the concentration of the silver element after exposure which is the basic component of the image, thus threatening the image to fade and discolored over time, as shown in (Table 3), (Figure 6).

FT-IR spectroscopy

Fourier transform infrared spectroscopy (FT-IR) in National Research Center was used in the gelatin investigation of control sample [10] [11]. The IR spectrum was measured in IR region 400-4000 cm^{-1}. The spectrum revealed of functional groups of gelatin and their characteristic absorption frequency bands as shown in Table (4), there are several regions which identify the gelation had been observed clearly as N-H stretching peak at 3300 cm^{-1} for amide group (strong) overlapped with O-H 3200cm^{-1} stretching broaden peak (strong) for stretched H-bonded. Additionally, peak at 1630 cm^{-1} is typical for C=O stretching amide group. The peak at 1526 cm^{-1} represent the N-H bending which is strong due to many existences of this N-H bond in the gelatin. Moreover, there are weak N-H bend mode at 878 cm^{-1} but in opposite direction to previous strong 1526 cm^{-1} N-H bend mode due to chirality and helical structure of gelatin. The C-H bond has a bend mode vibration in plane at 1444 cm-1 while the stretching mode at 2924 cm^{-1}. Therefore, the bending vibration has lower energy than stretching vibration as seen in C-O-H which bends at 1396 cm^{-1} with medium strength, whereas, the

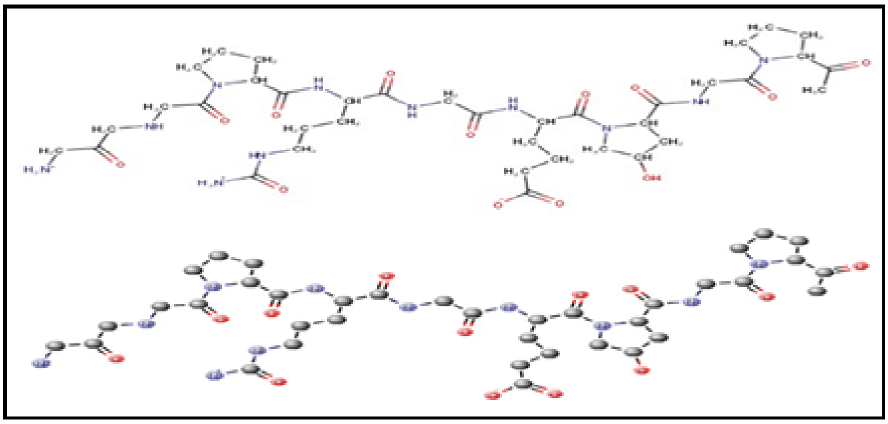

Figure 7: The structure unit of Gelatin is illustrated and confirmed by IR spectrum. There are several amide groups and a hydroxyl group as well which can be detected easily in IR spectroscopy. This chemical structure of one unit of gelatin which contain many units repeated in helical conformation

Functional Group	Characteristic Absorption(s) (cm-1)
Alkyl C-H Stretch	2950-2850 (m or s)
Alkenyl C-H Stretch	3100-3010 (m)
Aromatic C-H Stretch	~3030 (s)
Aromatic C-H Bending	860-680 (s)
Alcohol/Phenol O-H Stretch	3550-3200 (broad, s)
Carboxylic Acid O-H Stretch	3000-2500 (broad, v)
Amine N-H Stretch	3500-3300 (m)
Aldehyde C=O Stretch	1740-1690 (s)
Ketone C=O Stretch	1750-1680 (s)
Ester C=O Stretch	1750-1735 (s)
Carboxlic Acid C=O Stretch	1780-1710 (s)
Amide C=O Stretch	1690-1630 (s)
Amide N-H Stretch	3700-3500 (m)

Table 4: Basic functional groups and their characteristic absorption frequency bands in control sample.

C-O stretching only at 1232 cm^{-1} in medium–weak strength for hydroxyl group. The C-N bond was detected at 1323 cm^{-1} beside a weak peak at 1300 cm^{-1} for O-H bending in plane. Additionally, the bond C-C-C has two medium bending peaks at 1018 cm^{-1} and 1080 cm^{-1}. Finally, gelatin is good receptor to the chlorine atoms from photo sensitive material on the photographic papers such as AgCl2. Thus, peak at 540 cm^{-1} indicate to the presence of Cl atom although it is not in the structure unit of gelatin. The two bands 1500-1700 cm^{-1} and 3200-3450 cm^{-1} are identification of carbonyl (C=O) or amide (CONH2) and amine groups (NH) which specify the gelatin structure as illustrated in the gelatin structure [12] (Figure 7).

Thus, the obtained IR spectrum from FTIR confirmed the structure of gelatin, therefore, gelatin consists of different blocks of several and single polypeptides including from 50 to1000 amino acids in a helical structure of left-handed proline. Enrichment of pyrrolidines leads to strong gel structure which has helix with repeating unit 6 nm as tripeptides which had been proven since 10 years before [13] [14]. Thin Films from gelatin contains this kind or triple helical structure which its property is swelling less water and strongly tough [15]. The strong structure can be reproducing chemically by cross linking using trans-glutaminase which connect lysine with glutamine. There are another cross-linker such as glutaraldehyde which does network lysine to lysine [16].

FT-IR spectrum of the control sample without any treatments, then aging parameters as exposed to UV radiation applied later on gelatin layer. This parameter was studied by infrared spectrometry. Therefore, all obtained data had been enhanced and analyzed using a free software "Peak Fit".

The comparison of IR spectra before and after aging helps to understand the change could happen during aging processes for molecular structure of gelatin. The aim of these processes is examining the protection function of gelatin by investigate the extreme conditions of aging and their influence on the protective layer of gelatin on photographic materials.

FT-IR spectrum in (Figure 8) of the sample after exposing to UVA revealed that there wasn't any significant difference before and after UV exposure in IR spectra. This refers to the gelatin resistance to the UV light in short term. On the other hand, the UV accumulation influences on long term can be easily observed as an important parameter of aging process. The peak at 2350 cm-1 is decreased slightly due to possible rearrangements in the molecular structure network. The UV encourage gelatin network to for free radical with plays role in cross-linking and molecular rearrangement of the structure for individual gelatin molecules [17].

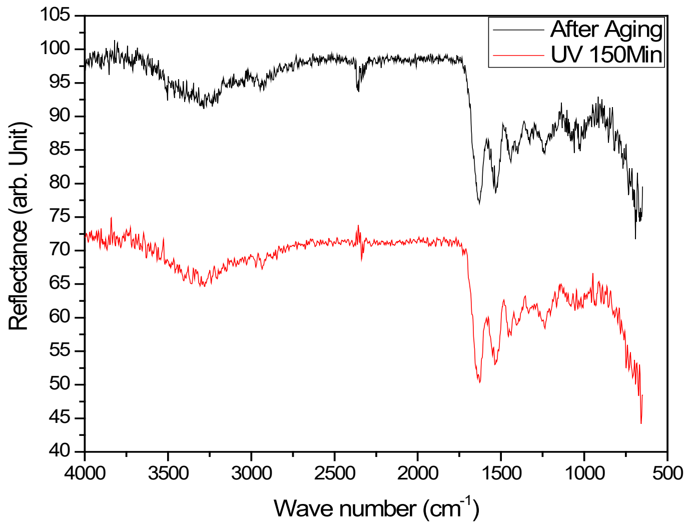

Figure 8: The IR spectra of aged gelatin before and after exposure to UV beam in UVA band. There is no significant difference between two spectra

Conclusion

The enquiring and analysis methods used in this paper show that silver gelatin photographs print-out (DOP) is greatly affected by ultraviolet radiation and that effect is depend on the quantity of energy which exposing to the photographs. Various properties of the silver gelatin photographic print-out have been studied. The result proves that this energy discoloring, fading, and yellowing the image and lost its clarity, farther for weakness in the mechanical properties of the supported paper. Result also revealed that the amount of change that occurs in photographs as a result of exposure to 4.3 joule of energy released from the ultraviolet radiation for 3600 hours at a rate of 12.9%± will be in the color characteristics of the image, 25.1% in the color intensity of the image, 0.41%± in the mechanical properties of the paper supporting a picture. However, the chemical properties have been affected slightly, which may increase over time.

Acknowledgments

The authors would like to thank to Dr. R.M. Ramadan (PhD. Liquid Crystals Physics, National Research Center), Mr. Moamen M. Othman (The General Director of Egyptian Museum), and Mrs. Eman H. Zidan (conservator at Egyptian Museum) for their great co-operation.

Reference

1. Standard for the Storage of Archival Records, National Archives of Australia, Australia, 2014.
2. Wagner S, McCabe C, Lemmen B (2001) Guidelines for exhibition light levels for photographic materials. AIC Topics in Photographic Preservation pp 9.
3. Schaeffer TT (2001) Effects of light on materials in collections: data on photoflash and related sources. Getty Publications.
4. Kodak publication M-1, Coping and duplicating: photographic and digital imaging techniques, CAT No. E1527969, Sterling Publishing, 1996.
5. Fröjd, I. (1992). Preservation research related to the Swedish R&D project on paper preservation. In Preservation Research and Development: Round Table Proceedings, September 28-29, 1992 pp. 110-117.
6. Robert L. Feller, Accelerated Aging: Photographic and Thermal Aspects, Getty Conservation Institute, Los Angeles, CA., 1994, pp. 71-113.
7. M. Jay Austin, Inorganic Anti–corrosive pigments, (Chapter 27), Paint and Coating Testing Manual (Editor: J.V. Koleske), 14th edition, Gardner-Sward Handbook 17, ASTM, Philadelphia, 1995, p. 241.
8. Billmeyer Jr FW (1983) Color Science: Concepts and Methods, Quantitative Data and Formulae, by Gunter Wyszecki and WS Stiles, John Wiley and Sons, New York, 1982, 950 pp
9. ALI, Maha Ahmed, ALI, Mona Fouad, SAKER, Mohammed Osama, ABDEL ALEEM, Abdel Azez El Bayoumi, et al. (2012) Investigations On The Chemical Degradation Of Silver Gelatine Prints. Int J Conserv Sci 3: 96-103.
10. Perkin Elmer Technical report, FT-IR Spectroscopy—Attenuated Total Reflectance (ATR), PerkinElmer, 2007.
11. Perron J, Siegel RE (1989) The use of FTIR in the study of photographic materials. In Topics in photographic preservation 3: 112-122.
12. T.W. Graham Solomon, C. Fryhle, S. Snyder, Organic Chemistry, 11th Edition, Wiley & Sons, Inc., United State of America, 2014, pp. 94-95.
13. Okuyama K, Wu G, Jiravanichanun N, Hong C, Noguchi K (2006) Helical twists of collagen model peptides. Peptide Science: Original Res Biomol 84: 421-432.
14. Okuyama K, Xu X, Iguchi, M, Noguchi K (2006) Revision of collagen molecular structure. Peptide Science: Original Res Biomol 84: 181-191.
15. Bigi A, Panzavolta S, Rubini K (2004) Relationship between tri-

ple-helix content and mechanical properties of gelatin films. Biomaterial 25: 5675-5680.

16. Babin H, Dickinson, E (2001) Influence of transglutaminase treatment on the thermoreversible gelation of gelatin. Food hydrocolloids 15: 271-276.

17. Masutani EM, Kinoshita CK,Tanaka,TT, Ellison A K, Yoza, BA (2014) Increasing thermal stability of gelatin by UV-induced cross-linking with glucose. Int J biomate Pp 1-9.