Research & Reviews: Journal of Ecology and Environmental Sciences

e-ISSN:2347-7830
p-ISSN:2347-7822

Investigation on the Photo-Chemical Degradation of Silver Albumen Photographs Due to Exposing to UV-A Radiation

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Research Article

Received: 30/10/2017
Accepted: 17/11/2017
Published: 24/11/2017

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Keywords: Albumen photographic prints, UV radiation, Energy quantum, Photochemical reactions

ABSTRACT

Light is an essential for displaying albumen photographic prints which considered a photographic culture heritage, which is become the most important photographic printing process of the 19th century. Each source of light emit several radiations with different of energy, the most one harmful of albumen photographic prints is ultraviolet radiation. A high level of energy in UV radiation and high sensitivity of the photographic material for the light makes the display process in the museums of the difficult things that lead to the decay of the image with age. This paper presents the results of experimental and analytical studies of albumen performance at photographic print-out during of exposing to ultraviolet radiation. The test material used are albumen photographic print that had prepared. The morphology and properties of albumen binder have been analyzed. The surface topology of the albumen has been studied by scanning electron microscopy. The modified surfaces was characterized by infrared spectroscopy. The chemical constituents of the albumen was estimated according to ASTM standards. Mechanical performance of the albumen was also investigated. Mutation in tonal quantity has been specified. The theoretical change of the albumen was also calculated and compared with the experimental results. Comparison between the experimental results and those of analytical results indicate that at a rate of 23.64% ± will be in the color characteristics of the image, 1.07% ± in the color intensity of the image, 7.34% ± in the mechanical properties of the paper supporting a picture, the chemical properties has been affected slightly, which may increase over time.

INTRODUCTION

The albumen silver positive printing process was the most important positive photographic process of the second part of the nineteenth century. It was the invention of Louis Desire Blanquart-Evrard, a pioneer French photographer who made many important contributions to photography. Albumen photographs were often mounted on mounting boards. Many, but not all, of existing cartes de visite (CDV), cabinet cards (CC), and a number of later variants of card photographs contain albumen prints. Albumen photographs were also mounted in early photographic albums and printed in large numbers for trade as portraits of famous people or royalty, as curiosities, or as tourist souvenirs [1]. The discovery of albumen paper came in the late 1840's as Blanquart-Evrard searched for improvements in Talbot's collotype process. Blanquart-Evrard tried and was somewhat successful in using albumen as a carrier for the light-sensitive salts on paper negatives, and he went further and adapted it to the usual method of making positives on plain salted paper. It worked splendidly as a positive material, and provided a deeper, bolder image than could be obtained on the matte salted papers of the day [2]. Albumen for photographic purposes may be taken to mean the clear white of a hen’s egg. Actually many specific proteins can be identified in egg white, but when used collectively they are

e-ISSN:2347-7830
p-ISSN:2347-7822

referred to as albumen. Albumen has a specific gravity of 1.040, and at room temperature it dries to a brittle, transparent mass [3]. Albumen is insoluble in alcohol, and in fact alcohol will coagulate albumen, a property that is useful to obtain multiple coatings of albumen on a single sheet. Albumen is also coagulated by temperatures above 65°C and by contact with salts of metals. The reason why albumen does not dissolve off the sheet during processing is because contact with silver nitrate in the sensitizing bath coagulates it and forms a new insoluble silver-albumen complex called silver albumenate. This substance itself is light sensitive and makes an important contribution to image formation in albumen paper. The pH of native egg white is 7.8. Albumen is used in this fresh alkaline condition only for matte papers, and for these it is always mixed with starch or other substances. Glossy papers are prepared with partially decomposed acidic albumen, because in that condition it creates a glossier surface and more even coating, and has less tendency to yellow after sensitization. Albumen is never used in the strictly native condition; before any photographic use may be contemplated, the egg whites must be beaten to a froth and allowed to settle back to a liquid state. This beating process denatures the various proteins — all of which have different viscosities — and results in a homogeneous liquid which will form an even layer on the sheet of paper. Photographic materials are very sensitive to the change of surrounding environment, where even with the best processing of protection and preservation procedures Albumen photographic prints could be deteriorate and damaged. For this reasons, it is important for photographic conservator to understand the change which could take place in a photographic image, to be able to diagnose the case to identify the changes and recognize the causes. Light has no significant effect upon the silver of an image in ordinary circumstances. However, light can reduce silver ions to metallic silver after oxidizing gases and moisture have acted upon the image. Constant exposure to light can cause Albumen to turn yellow and tend to make it brittle. Paper also yellows with exposure especially papers used in photographs prior to 1926. Any considerable discoloration is more likely to be caused by oxidation or by the decomposition of residual processing chemicals than by light. Valuable prints that are placed on display should not be exposed to strong daylight for any length of time. Tungsten light is preferable to most types of fluorescent light for display purposes [4].

MATERIALS AND METHODS

Experimental

Two samples were prepared in the same circumstances. The 500 ml of egg white, 2 mL of 28% acetic acid, 15 mL of distilled water, and 15 g Ammonium Chloride was poured in to a large bowl. The paper (cotton paper of 18 × 24 cm) was floated on the mixture for three minutes, and the sheet was lifted from the surface of the albumen, allowing the liquid to drain. To sensitize the paper 37.5 g of silver nitrate have been used with 250 ml of distilled water to make a 15% solution in a darkroom. To brush coat tip the glass, to which the paper has been taped, at a 45 degree angle and paint the silver nitrate coating from top to bottom, negative glass have been used with a density range of 1.8 to 2.0, using contact printing frame with a split back. Have been exposed to sunlight for 12 minutes. Before washing, soak in a hypo clear (use Kodak HCA or one tablespoon EDTA plus one tablespoon sodium sulfite to a gallon of water) bath for two to three minutes [5]. Wash prints for 60 to 90 minutes (only about 30 minutes is required if using hypo clear) in running water. Prints was hanged to dry, and straighten in a dry mounting press.

Light Fading Test Using UVA

The samples was subjected to UV radiation using an exposing cabinet which consists of set of 10 UV fluorescent lamps., 20 W, 60 cm length, three types of lamps can be installed UVA. UVB, and UVC, and /or mix of it, in our case UVA lamps only was used, at fixed distance from the samples. This cabinet was in Radiometry Department, Photometry & Radiometry Division, National Institute for Standards [6]. For accurate measurements of the irradiance levels, the exposing area was divided to three columns and three rows resulting in 9 measuring positions irradiance levels at each point measured five times. Irradiance levels measured using UVA radiometer from UDT at the sample level (30 cm) from the sources. The total energy received by the sample can be calculated by multiplying the irradiance level by the time of exposing as equation (1).

$$\text{Energy(J)} = \text{Power(W)} \times \text{Time(S)} \quad (1)$$

In our case the samples was exposed 20 hours [7-9].

The average energy received is 216 J/cm^2 ± 0.75%

The average irradiance level was 3 mW/cm^2 ± 0.5%

$0.003\ \text{W/cm}^2 \times 20\ \text{hours} \times 60\ \text{min} \times 60\ \text{s} = 216\ \text{Joule/cm}^2$

The average uniformity for field of exposure (min/ max) equals 0.8 ± 0.81%, calculated from the irradiance levels obtained using equation (2).

$$\text{Uniformity} = \text{Maximum irradiance level} / \text{Minimum irradiance level} \quad (2)$$

Control samples (with no exposing) was given the symbol (Sb), while exposed samples was given symbol (Eb).

Test Methods

Numerous methods was used to assess the change of the samples:

- Visual observation to detect the visual changes of the albumen layer and the supported paper.
- Tensile strength, elongation, and penetration strength test was used to assess the rate of degradation in the mechanical properties of silver albumen photographs print-out.
- Color meters was used to assess the rate of color change by studying the change in (ΔE) that have occurred in the sample photographs as a result of the exposure processes.
- Electron Scanning Microscopy (SEM-EDX) was used to assess the rate of change in the chemical properties by studying the morphology of albumen layer surface in the photograph samples after an exposure to UVA.
- Fourier transform infrared spectroscopy (FT-IR) was used to assess the decay of the albumen emulsion.

RESULTS AND DISCUSSION

Visual Inspection

The result of the light fading test indicates the yellowing and fading of the image due to exposing it to the ultraviolet radiation. As well as, in considerable warping and yellowing of the supporting paper was noticed, it may be the result of heat emitted from fluorescent lamps.

Tensile Strength, Elongation And Penetration Strength Tests (Mechanical Properties)

The examinations procedure was done at the National Institute of Standard under the Ministry of Scientific Research. The instrument used for this measurement is tensile strength, elongation device, and Penetration Strength Test (PST) device Code: PARAM-XLW-PC. The samples was prepared by cutting it to a fixed sizes and according to the type of device used, the samples was cut up an area of 10 cm × 5 cm, it was prepared two samples in the vertical direction was the recording medium between them, have been conducted measurements according to the American standard specifications ASTN 1682 [10]. This examination was done to the samples before and after exposing them to the ultraviolet radiations, all in the longitudinal direction of the paper. **Table 1** shows the average results of samples. To calculate the ratio of change in the mechanical properties of the samples after exposure to UVA, divided the difference between the value of control sample and the value of sample after exposure by the value of control sample multiplying 100 as equation (3).

$$\text{(value of control sample -value of exposured sample)/(value of control sample)} \times 100 \quad (3)$$

Table 1. Average results of the light fading test in mechanical properties, comparing between samples before and after exposing.

Sample	Tensile strength (N)	Elongation percentage (%)	Penetration Strength (PST), (N)
Sb	190.0	5.08	6.52
Eb	177.9	4.387	5.76
Ratio of change (degradation)	6.36%	13.64%	11.65%

Colored Change (ΔE)

Color changes was evaluated by spectrophotometer Optimatch 3100® from the SDL Company in National Institute for Standards. The dimension of the measured area of each sample equals to (1 × 1) cm^2, to study the change in tonal qualities that have occurred in the samples of silver albumen photographs due to the exposure to ultraviolet radiation by studying (ΔE), and comparison between samples before exposure (Sb) and samples after exposure (Eb), the result are shown in **Table 2**. According to Italian guidelines for the restoration of stone buildings, (ΔE) value must be <5, other authors state that this beginning value should be <10 [11-13]. According to Limbo and Piergiovanni, which put (ΔE) scale in order as follow (0.5<ΔE<2: small difference, 3<ΔE<6: perceptible difference, 6<ΔE<12: strong difference, ΔE>12: different colors) [14,15].

Table 2. Average results of the color change due to light fading test, comparing samples between before and after exposing to Ultraviolet Radiation.

Sample	ΔL	Δa	Δb	ΔE	Observations
Eb	- 22.77	4.91	4.05	23.64	(*ΔE*) > 12, i.e., different colors were obtained. (*ΔL*) value proved that when the surface of silver albumen photographs epoxsing to UV radiation they darkened, (*Δa*) proved that they become more reddish, and (*Δb*) proved that they becom yellowish.

In this regard, samples after exposing to UVA for 20 hours (Eb) have average results in ΔE values where it ranges between 23.64 depending on their chemical composition. These values indicate that ultraviolet radiation energy induced chromatic variations resulting from its photo-breakdown and thermal oxidative decomposition. These data are listed in **Table 2**.

Sem-Edx

The morphology of surface of samples before and after exposing to UVA radiation was investigated using Scanning Electron Microscope (SEM). The samples was analyzed in the central administration of the coefficient plant of the Egyptian General Authority for Mineral Resources - Ministry of Petroleum, where he was to use electron microscope scanner with signal unit elemental analysis (EDX). Using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30K.V. magnification14x up to 1000000 and resolution for Gun.1n), FEI company, Netherlands. The goal of such testing and analysis study of surface change of albumen emulsion samples photographs after an exposure ultraviolet radiation compared with sample standard, through the examination by (SEM) of surface layer of albumen emulsion. Types of damaged aspects were identified in most of the studied samples with examples shown in **Figure 1** that shows thermal effect decreases the viscosity of albumen and shows the formation of blistering and micro-cracks on the surfaces of the albumen, while **Figure 2** shows the chemical change in the elements (Ag, Ca) and some impurities which are the basic component of the image, the percentage of Ag, Ca element in the sample is decrease while O_2 element is increase as a result to oxidation process which occurred during photo-break down from ultraviolet radiation energy, that is lead to disappearance of image and threatens to fade image over time.

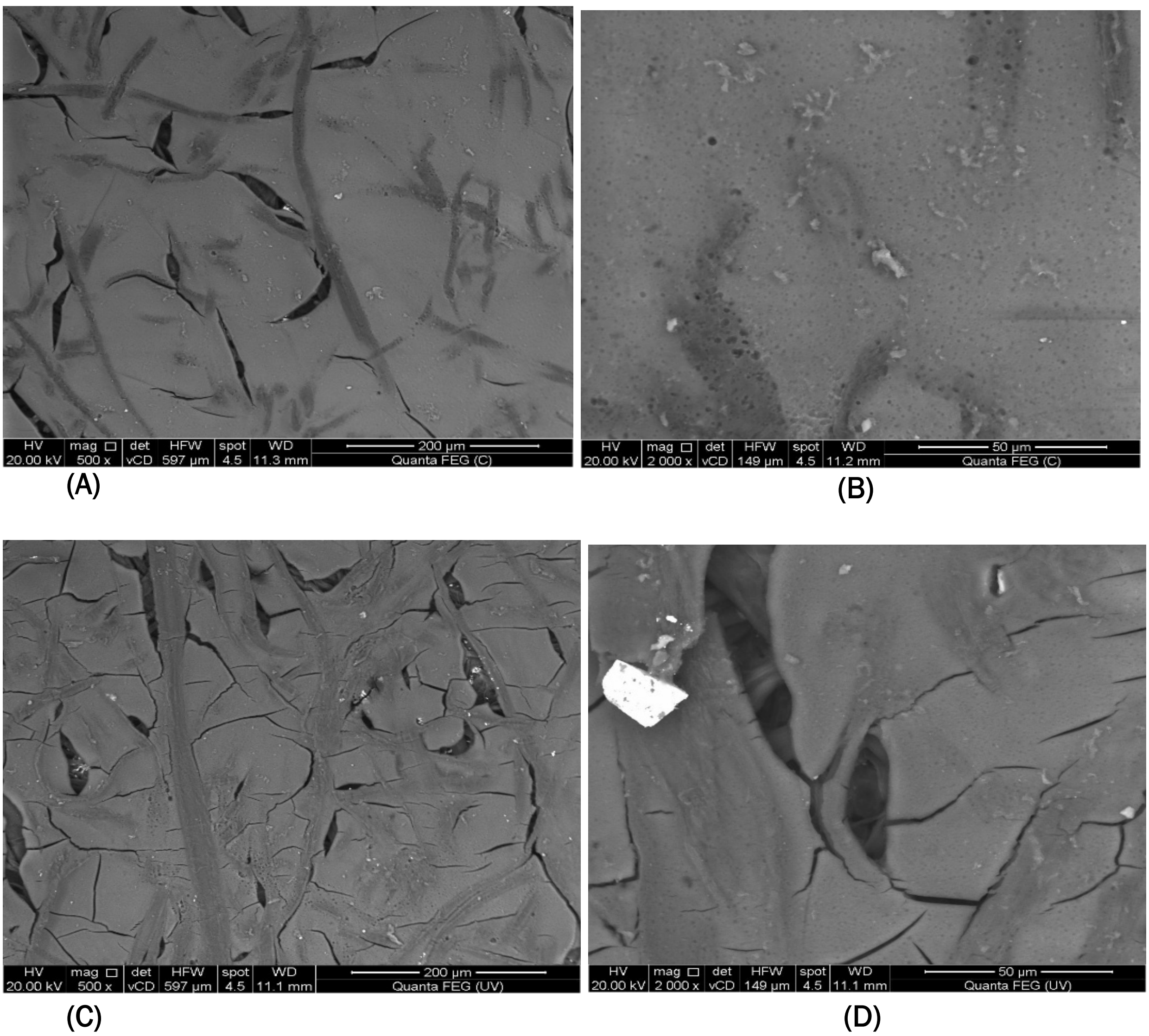

Figure 1. SEM photomicrographs of the silver albumen photgraphs sample: A: SEM photomicrogrphs (500X) and B: SEM photomicrogrphs (2000X) of samples befor exposing to UV (Sb) we note serenity emulsion Albumen where impurities appear in Albumen clear; C: SEM photomicrogrphs (500X) and D: SEM photomicrogrphs (2000X) of samples after exposing to UV (Eb).

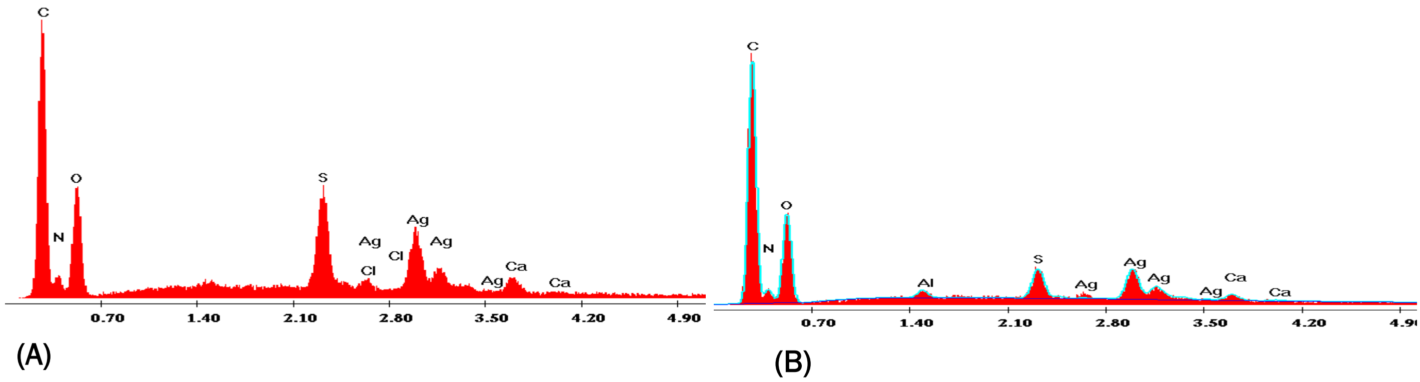

Figure 2. Analysis pattern of unit elemental analysis (EDX): A- shows the elements in the sample taken from the emulsion Albumen photo before the exposure to UV; B- shows the elements in the sample after.

FT-IR Spectroscopy

The FT-IR ATR instrument used for this analysis is Spectrum 100 with a Universal Single bounce Diamond ATR attachment, PerkinElmer. Albumen was investigated on paper as binding material for photograph. These photographs papers were investigated using a non-destructive ATR IR-spectroscopy technique [16,17]. The IR spectrum was measured in IR region 400-4000 cm^{-1}. The IR spectrum of Albumen on paper was measured using Bruker FT-IR spectrometer model Vertex 70. The ATR-FTIR spectrum of the photograph shows the presence of a proteinaceous binding medium that can be identified by the Amide I spectral value at about 1632 cm^{-1} and the Amide II spectral value around 1537 cm^{-1} **(Figure 3)**. Moreover, there are several regions which identify the albumen had been observed clearly as N-H stretching value at 3429 cm^{-1} for amide group (strong). Additionally, value at 1428 cm^{-1} is typical for C=O stretching amide group. The value at 1651 cm^{-1} represent the N-H bending which is strong due to many existence of this N-H bond in the Albumen. The C-H bond has a bend mode vibration in plane at 1055 cm^{-1} while the stretching mode at 2918 cm^{-1}.

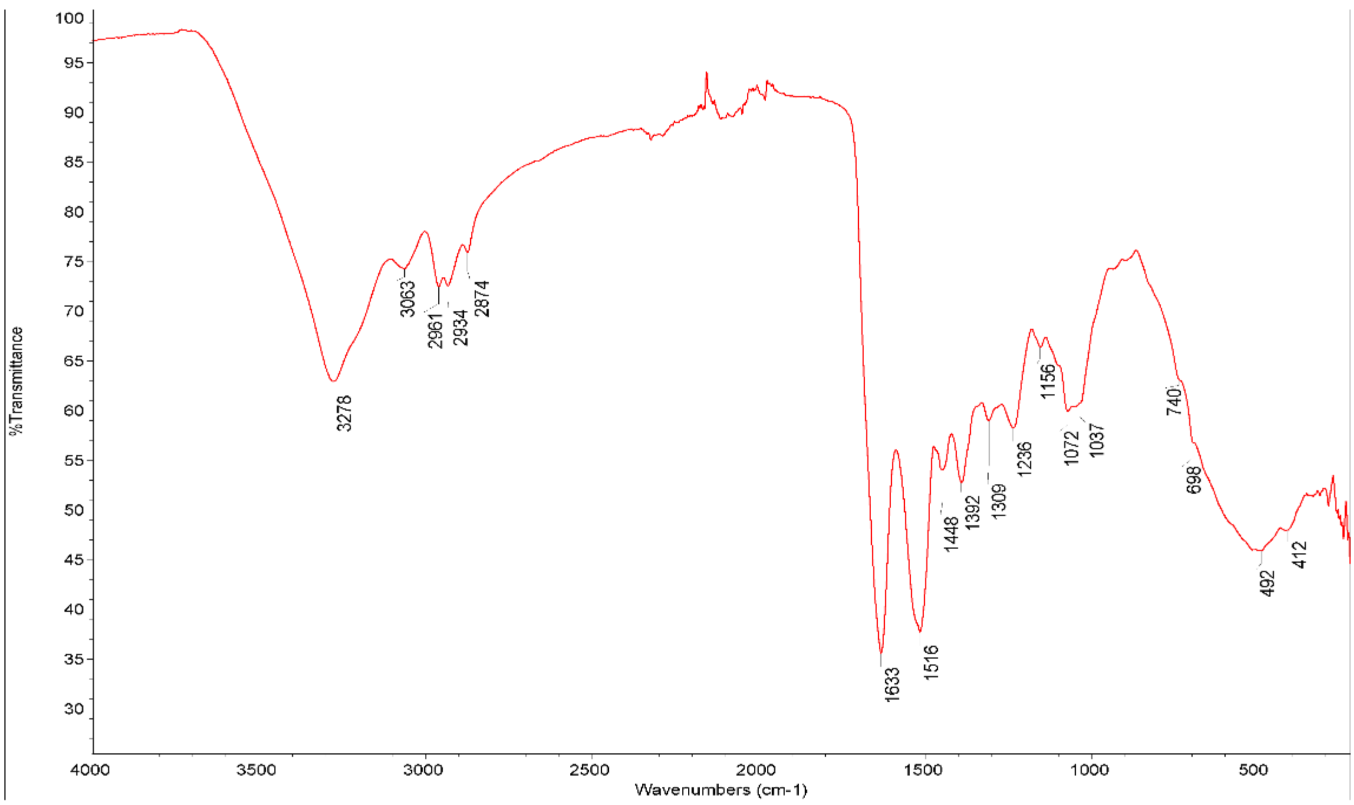

Figure 3. The IR spectrum of albumen on photographic paper is measured by ATR technique.

The ATR-FTIR spectrum of the albumen photograph shows two spectral values of about the same intensity at 1428 and 1372 cm^{-1}. The relative thickness of the albumen layer can be assessed by measuring the ratio between the Amide I (~1632 cm^{-1}) spectral value, representing albumen, and the spectral envelope of the cellulose substrate around 1034 cm^{-1} of the albumen print [18]. The thicker albumen layer attenuates the signal of cellulose and makes it less intense. The spectrum also shows unusually intense CH spectral values (CH, CH2, and CH3 bonds around 2918 cm^{-1}). The presence of these spectral values in the spectra of albumen photographs indicates the presence of organic molecules other than those belonging to the albumen layer [19]. The ATR-FTIR spectrum of the matte photograph shows the well-developed and sharp groups of C-H spectral values that are typical for coating with long and straight chains of hydrocarbons as seen in **Table 3**. Finally, Albumen is good receptor to the chlorine atoms from photo sensitive material on the photographic papers such as $AgCl_2$. Thus, value at 532 cm^{-1} indicate to the presence of Cl atom although it is not in the structure unit of Albumen. Thus, the obtained IR spectrum from FTIR confirmed the structure of Albumen.

Table 3. FTIR-ATR characteristic absorptions bands of white egg.

Functional Group	Characteristic Absorption(s) (cm^{-1})
N-H stretching	3429 vs
N-H stretching (Amide)	3673 m
N-H stretching (Amide)	3715 m
CH stretching	2918 vs
Amide I (C=O stretching)	1632 m
Amide II (N-H bending)	1537 m
C=O stretching	1428 s
C≡N stretching	2356 m
N-H bending	1651 m
CH bending	1055 s
CH bending	1372 w
CH rocking	560 m
C-O-C (ester) stretching	1113 m

Note: vs: very strong; s: strong; m: medium; w: weak; sh: shoulder

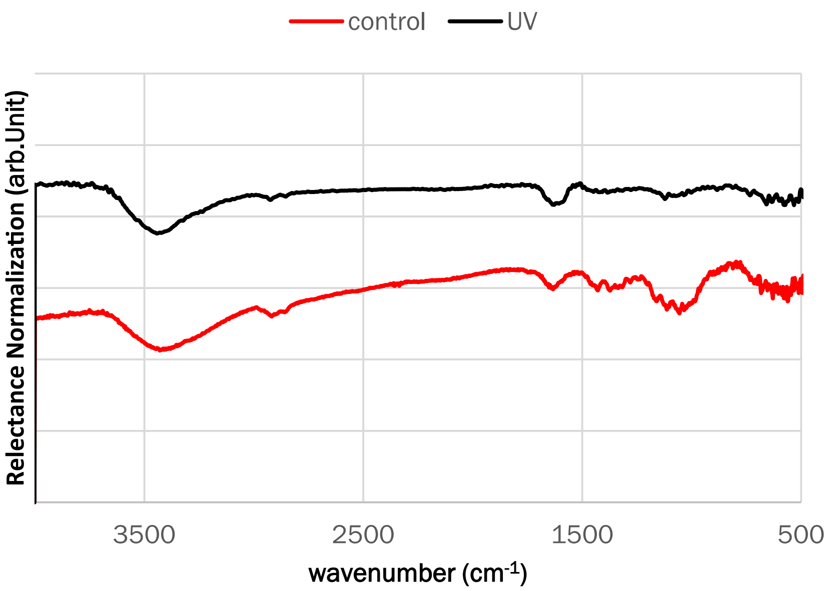

Figure 4. The IR spectra of albumen before and after exposure to UV beam in UVA band.

The aim of these processes is examine the protection function of Albumen by investigate the extreme conditions of aging and their influence on the binder layer of Albumen on photographic materials. All these parameter were studied by infrared spectrometry. Therefore, all obtained data had been enhanced and analyzed using a free software "Value Fit". In **Figure 4** the infrared spectroscopy was measured after exposure to UV beam which was produced from UVA lamp 20 W/h power for duration 20 hours, and the average energy received is 216 J/cm^2 ± 0.75%. The value at 1632 m Amide I (C=O stretching), 1537 m Amide II (N-H bending), 1428s C=O stretching, 1055s CH bending, and 1372w CH bending were clearly decreased that maybe due to the high energy of UV which beaked the bond in the structure of albumen that refer to oxidation in albumen structure.

e-ISSN:2347-7830
p-ISSN:2347-7822

CONCLUSION

The paper showed the importance of studying the bad effect of exposing silver albumen photographs print-out to ultraviolet radiation, where that silver albumen photographs print-out are greatly affected by ultraviolet radiation and that the effect depends on the quantity of energy which the photographs are exposed to. Physical and chemical properties of the silver albumen photographs print-out have been studied. According to the result obtained, the energy of ultraviolet radiation causes discoloring, fading, and yellowing of the image and leads to the loss of the image's clarity, further weakening the mechanical properties of the supported paper. Moreover, results revealed that the amount of change that occurs in photographs as a result of exposure to 216 Joule/cm^2 of energy released from the ultraviolet radiation will affect the color properties of the image at a rate of ± 23.64%, and in the mechanical properties of the supported paper at a rate of ± 10.6%. However, the chemical properties have also been affected slightly, which may increase over time. From these results, we can suggest avoid displaying and storage silver albumen photographs print-out away from sunlight or light lamps that contain ultraviolet light or use filters to block ultraviolet radiation, In order to preserve the cultural heritage of the photographs.

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