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Ethyl Lactate: A New Prospective Eco-friendly Cleaner for Silver Gelatin Prints

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Abstract

This study is the first involving the use of ethyl lactate as a green solvent on vulnerable photographs in an endeavour to protect the environment by using eco-friendly economic materials and methods in photograph conservation field. The paper is an experimental study aims at evaluating the efficiency of Ethyl lactate (E.L.) as an eco-friendly solvent in the removal of adhesive stains found on developed-out (DOP) silver gelatin prints. For achieving the paper objectives, three silver gelatin prints were stained with an adhesive and treated with three concentrations of E.L. The study assessment was implemented by digital microscope, atomic force microscope, and spectrophotometer to observe the changes which may occur on the surface post treatments; in addition to the use of attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy to investigate the gelatin binder layer after treatment. Moreover, the mechanical properties and the pH value were measured. The three concentrations of ethyl lactate were efficient in cleaning the surface without causing any damage to the structure of photographs. The paper proved the success of ethyl lactate treatments as an eco-friendly solvent in cleaning adhesive stains from developingout silver gelatin prints.

Keywords: Ethyl lactate; Adhesive stains; Silver gelatin prints; Eco-friendly; Cleaning.

1. Introduction

Silver gelatin prints were the dominant black-and white photographic process of the 20th century until the color revolution in 1970s [1, 2]. There are two types of silver gelatin prints: printed-out silver gelatin prints (POP) and developed-out silver gelatin prints (DOP) [3]. The DOP silver gelatin prints exist in abundance numbers in collections of archives, museums, libraries, historical societies, and family photograph worldwide. The layered structure of DOP silver gelatin print contains mainly three layers [4]: a paper support on which other layers are attached. It physically supports the photographic binder of gelatin, a highly purified protein produced mainly from hides and bones of animal wastes which holds the silver particles (i.e., the final image material) [5, 6]. In addition to an interlayer consisting of barium sulfate, an opaque pigment, grounded in gelatin [7] and exists between the paper support and the final image layer.

Figure (1): Illustration of DOP silver gelatin prints' main layers

Photographic prints are susceptible to irreversible
damage if mounted or preserved negligently due to their delicate surfaces, in particular those containing gelatin. Adhesives can be delivered to the surfaces of photographs throughout inappropriate materials that are employed in preserving and mounting processes. The adhesives (i.e., rubber-based adhesive) existing in paperboards and magnetic albums stain

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photographs driving them to adhere to the pages overtime. Adhesive residues from self-adhesive notes, pressure-sensitive tapes, and double-sided tapes become difficult to remove and overtime degrade and damage the photographic prints [8, 9]. Other adhesives used in mounting and for mending torn photographs (i.e., glues, pastes, etc.) may cause irreversible stains and yellow the binder layer. Furthermore, sulfur-containing adhesive may react with the image silver. [10-12]. The purpose of removing adhesives from photographs is to protect the photographs from damage such as being torn or being stuck to adjacent surfaces. Adhesives also disfigure the image surface by collecting grime and dirt and overtime it becomes stiff and difficult to remove without causing irreversible damage to the surface [13]. Likewise, water-based adhesive such as adhesive seams which exist in paper enclosures are hygroscopic in nature and attract moisture, that raises the water content in thephotograph which is likely to increase the ability of pollutants to penetrate the gelatin layer and ease the migration of silver ions within the gelatin binder. Additionally, water is considered the medium for oxidation/reduction reactions and mold growth, which result in the production of stains and distort the surface [11]. Moreover, in fluctuating temperature and relative humidity conditions, adhesive attached to the image surface may threaten the object's condition due to frequent expansion and contraction which affect the strength properties [10, 11].

However, valuable or irreplaceable photographs require an accurate and appropriate cleaning process that does not cause damage or extensive deterioration. A variety of materials and techniques were employed in attempting to reduce adhesive with dirt and grime layers from photographic surfaces. For example, mechanical cleaning (i.e., non-sticking knife and spatula) [9] probably scratches the surface, changes the surface gloss, and causes discoloration; cleaning spray and wipes dissolve and remove surface coatings [8]; and steamers may negatively affect the components of the photograph. Enzymes attack the gelatin binder; poultices require the use of solvents to prevent fast evaporating [14]; and the removal of some adhesives requires prolonged immersion in a water bath which is known to be damaging. Other techniques such as excessive heat may soften or burn the photographs or even harden some adhesives making their removal more difficult [9]. The use of organic solvents is not favorable since they are toxic and harm the environment as well as the object if they penetrate into it, causing chemical reactivity and the possibility of irreversible visual alteration and deterioration.

In the last decade, numbers of publications have focused on green solvents as a global endeavor to replace toxic solvent regarding to economic and ecological issues [15]. These green solvents are nontoxic, economically viable, and eco-friendly solvents which are obtained from biomass (renewable sources) and can be used safely [16].

Ethyl lactate, lactic acid ethyl ester, or 2-Hydroxypropanoic acid ethyl ester with molecular formula $C_5H_{10}O_3$ is the main member of the lactate esters family and one of the most encouraging green solvents. It is a natural product derived from the renewable sources (biomass crops) including agricultural wastes of starch or cellulosic feedstocks [17, 18]. It is formed by the esterification of lactic acid with ethanol, which makes it environmentally benign and economically viable [19]. Ethyl lactate is noncorrosive, non-carcinogenic and fully and rapidly 100% biodegrades to water and carbon dioxide. This means the ecotoxicity is very low and it is easily recyclable without causing any health issues. Generally, it is recognized as safe and affirmed by the U.S. Food and Drug Administration (FDA) and European Food Safety Authority (EFSA) as a pharmaceutical and food additive [17-21]. It has a low vapor pressure and the vapors released from are a non-ozone depleting. Ethyl lactate has a high boiling point, low surface tension and high solvency power [22].

Ethyl lactate has properties that make it a proper alternative for the conventional solvents and suitable for numerous applications. For example, it has been found to be effective for a variety of fields such as food [23, 24], fragrances [25], pharmaceutical [26, 27] medicinal chemistry [21], and agricultural as a remover of contaminants in soils [28, 29]. Nevertheless, its main application is using it as a safer alternative to traditional organic solvents [19] and a range of halogenated and toxic solvents. It clearly proved that the green solvent is effective compared to petroleum-based solvents [21]. Furthermore, it has been used for graffiti removal, a cleaning agent for metal surfaces, and efficiently

removing greases, oils, and adhesives [30]. Moreover, it safely cleaned artworks as a neat solvent applied by swab [17] and an excellent cleaning solvent with almost no cleaning residues or film [31].

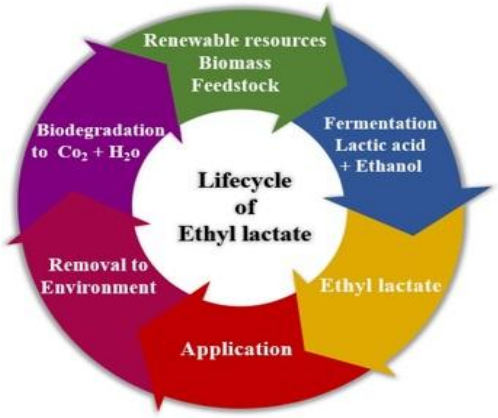

Figure (2): Illustration of Ethyl lactate lifecycle

2. Materials and Methods

2.1. Materials 2.1.1. Silver gelatin prints

Three silver gelatin prints with no historic or artistic value date back to 1946 AD were used for this study. These photographs were numbered as follows P30, P50, and P70 (see figure 3). Each photograph was assigned to a single concentration of ethyl lactate. Their size ranged between 13 cm long and 9 cm wide.

2.1.2. Ethyl lactate

An ethyl lactate solvent 99% was purchased from LOBA CHEMIE PVT. LTD. Company. Three concentrations {i.e., 30%, 50%, 70% (v/v)} were selected for the treatments after a pre-test on a photograph.

2.2. Methods 2.2.1. Sample preparing:

Various types of commercial adhesives and candle wax were tested to check which adhesive would be the most coherent to the photographs' surface.

Figure (3): The three DOP silver gelatin prints from left (P30, P50, P70), respectively.

Based on the results, "I stick glue" was selected and applied using a soft brush on the three photographs (P30), (P50), and (P70) on different color areas (i.e., shadow, mid-tone, and highlight). The three photographs were then exposed to water vapor for more adhering then left in ambient air at room temperature for 2 days for complete dryness (see figure 4,5).

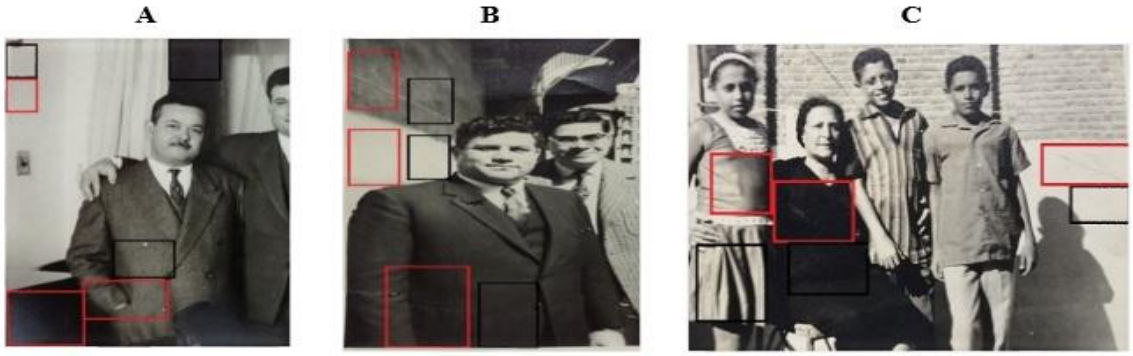

Figure (4): displays the stained areas and the unstained control areas on the three photographs: A is P30, B is P50, and C is P70. The red squares define the stained areas and the black squares signify unstained ones.

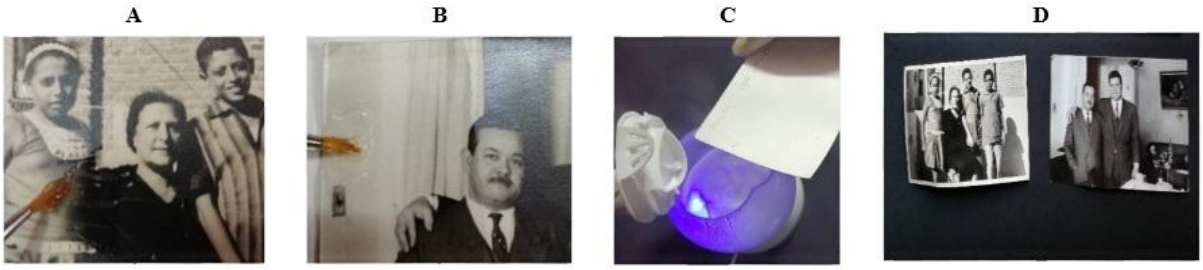

Figure (5): shows the preparation steps: A and B: 1st step: Applying the adhesive on the surface with a brush on different color areas, C: 2nd step: exposure the photographs after staining to water vapor, and D: 3rd step: the photographs in ambient air for complete dryness.

2.2.2. Artificial aging:

The three photographs were artificially aged at a temperature of 80˚C ± 2 ˚C and relative humidity of 65% for a period of 72 hours as per the international standards, ISO standard 5630-3:1996 [32] to accelerate the age of the stains and promote the connection between stains and the photographs' surface, as the stain becomes older, it is harder to remove. The accelerated aging was carried out at the National Institute for Standards, Cairo, Egypt.

2.2.3. Treatment method sets as follows:

Each of the three photographs was appointed to each of the concentrations; P30 for 30%, P50 for 50%, and P70 for 70%. Treatment processes were carefully performed with precautions, avoiding contact with the gelatin layer of the surrounding areas which were covered with tissues to prevent any damage to the surrounding binder. Stain removal was implemented using cotton-swabs. The removal process started from the edges of the stains towards the center removing layer by layer. The process progressed in less than 1 minute to the fully clean by the naked eye. The removal time decreased as the concentration increased. The surface felt sticky post treatments; thus, the treatments were followed by one cycle of cotton-swab slightly wet with distilled water for a complete removal of ethyl lactate and stain residues (See column B figure 6).

2.2.4. Test assessment

2.2.4.1. Digital microscope

A USB digital microscope with microscopic lens 200× magnification up to 500×, 5 mega pixel sensor, and measurement of software (1/1000 mm) was used to investigate the surface of photographs after the cleaning processes.

2.2.4.2. pH measurement

Two methods were employed to measure the pH Value: 1. Paper strips (MColorpHast™). On the support layer, paper, a drop of water was dropped by a pipette, and then a pH strip was situated over it. Once the color of the strip changed, it was compared to the pH standard indicator. 2. Portable pH meter was used according to ASTM D778-97 (2002) [33]. Samples weighing 0.5 g were soaked in 40 ml of distilled water (pH = 7) for 6 hours at room temperature according to ISO 187 1990 [34, 35].

2.2.4.3. Color change

The color change of samples was evaluated using the CIEL*a*b* (CIE76) system as it is more suitable for archaeological applications [36, 37]. An Optimatch 3100 Model No. CE 3100. Serial No. 31013780698, SDL, UK, was used to investigate the color changes induced by the cleaning treatments. The analysis was conducted in the visible region, i.e., the wavelength range from 400 nm to 700 nm, with an interval of 10 nm utilizing a D65 light source, observed angle 10° and The CIELAB color space was organized in a cubic form. The CIELAB colorimetric parameters (L*a*b*) were used to represent the color change. The data of L*, a*, b* coordinates were measured and the (ΔE^*_{ab}), total color difference, was calculated by the equation: $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{½}$ [38, 39]. This analysis was performed at the Wood Conservation Laboratory, Faculty of Archaeology, Cairo University.

2.2.4.4. Atomic force microscope

The atomic force microscope was used to study the surface topography post the application of selected cleaning treatments since it is an efficient analytical technique for assessing the effectiveness of cleaning treatments and for studying the changes which occur on the surface post these treatments [40]. The Thermomicroscope Autoprobe CP-Research head model MLCT manufactured, operated in contact mode utilizing silicon nitride probe. Results are provided in 2D and 3D images companied with a histogram. The IP 2.1 software was employed for

image analysis with color scale (false). The scanning applied on area 20 x 20 μm^2 with scan rate 1 Hz and resolution 256 x 256.

To control the scan parameters, the Proscan 1.8 software was used. This analysis was implemented at (NIS) National Institute for Standards, Giza, Egypt.

2.2.4.5. FTIR-ATR analysis

The FTIR-ATR spectra were obtained using Nicolet 380 under transmission mode in the wavelength range of 4000 – 400 cm^{-1} at the National Institute of Standards (NIS), Giza, Egypt. FTIR analysis was employed to detect any potential changes post treatments in chemical structure, and intermolecular crosslinking of the gelatin layer as an organic material [41].

2.2.4.6. Mechanical properties

Tensile and elongation test was employed to investigate the strength properties of treated samples using the dynamometer H5KT130-500N/E139- 34A –

strip method at the National Institute for Standards (NIS), Giza, Egypt, according to ISO 13934-1;1999 [42]. This test measures the maximum tensile force per unit area of the tested sample before it breaks and the maximum outstretch ability of the linear length of the tested sample under the maximum tensile stress before refraction at stable conditions [43].

3. Results and Discussion

3.1. Treatment of stained silver gelatin prints with ethyl lactate (30%, 50%, 70%)

Visually speaking, the three concentrations of ethyl lactate (30%, 50%, and 70%) were successful in removing the adhesive stains as displayed in figure (6).

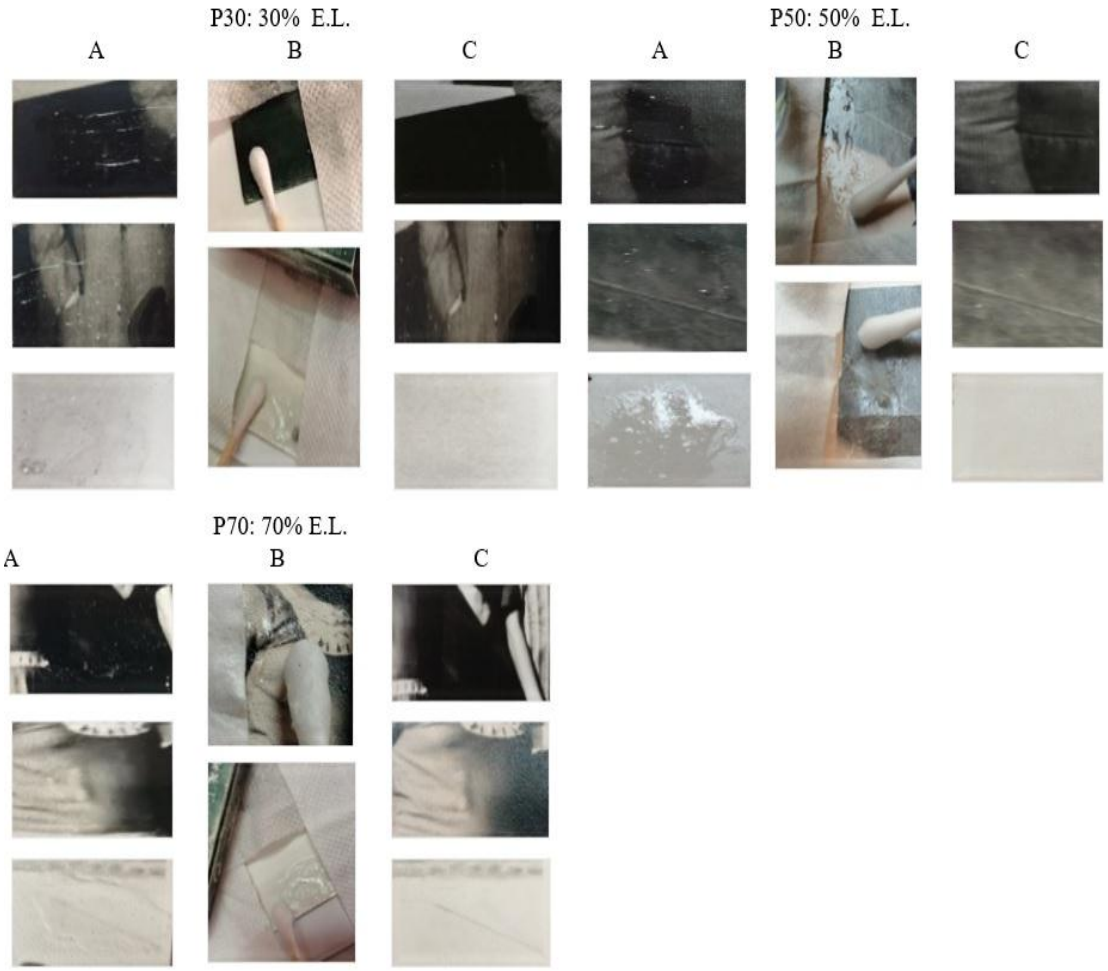

Figure (6): Demonstrates digital camera images of 30%, 50% and 70% treatments for photographs P30, P50, and P70, respectively. Column A represents prior treatments of the three-color stained areas of each photograph, Column B views the process during the stain removal of each photograph, and C column displays the three-color stained areas after the cleaning treatments.

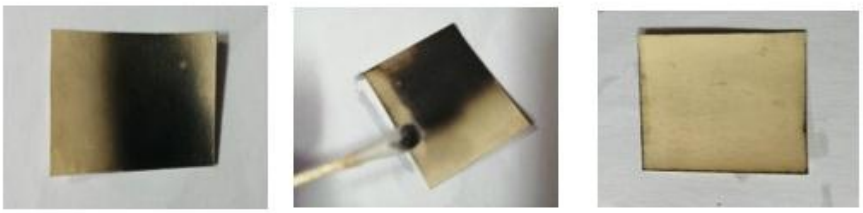

Figure (7) displays the removal of the smudge from the photograph's surface using E.L. 70%

3.2. Cleaning assessments

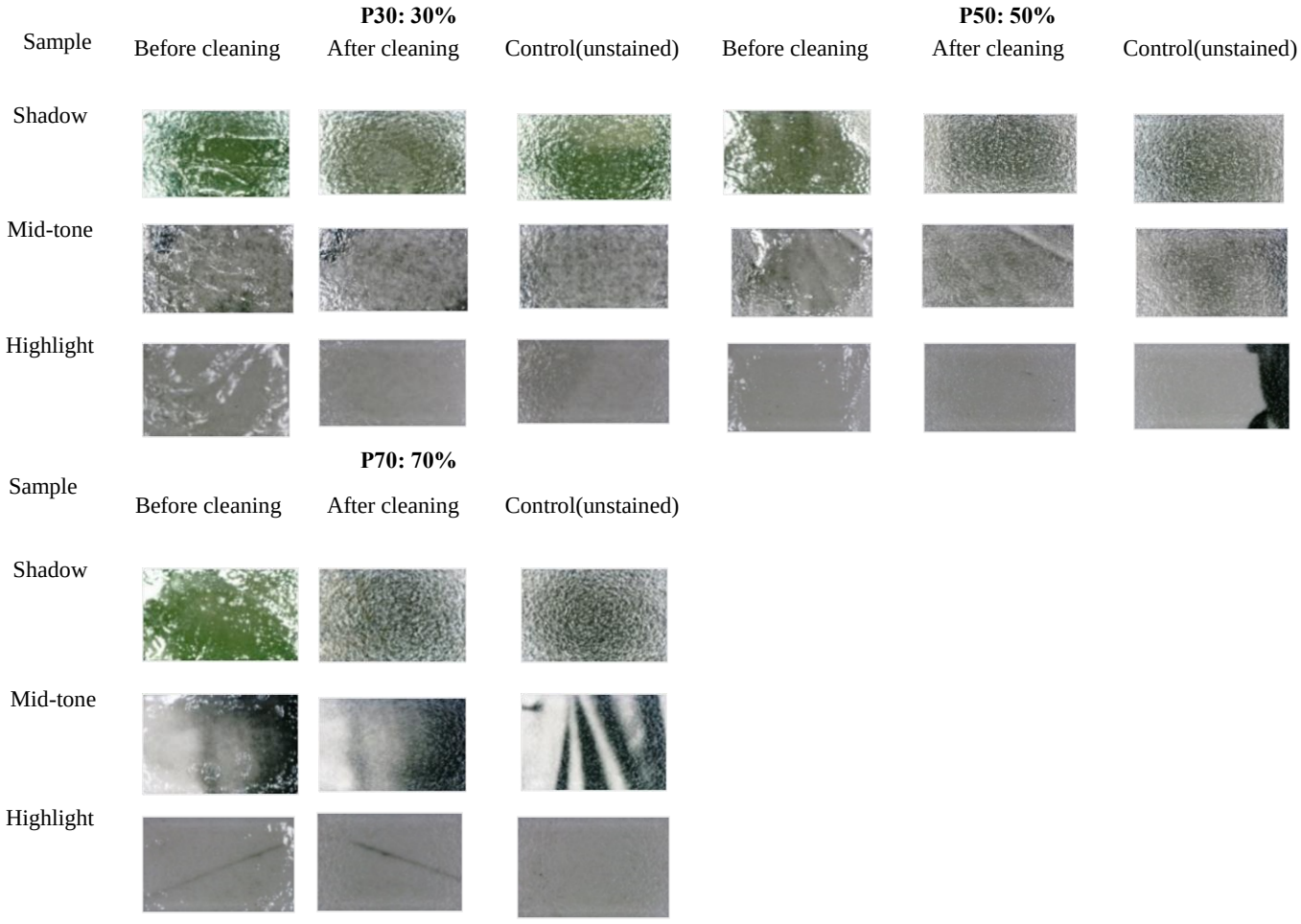

Figure (8): shows the digital microscope of 30%, 50% and 70% treatments for photographs P30, P50, and P70 for stained, treated and control samples.

3.2.1. Digital microscope

The visual analysis of digital microscope was carried out on stained samples before and after treatments and unstained control samples with 500× magnification. The results in figure (8) demonstrates the digital microscope investigations after treatments which revealed that all concentrations have accomplished full cleaning as the treated samples appeared to be very similar to the unstained samples without showing any residues of the E.L. or the stains.

3.2.2. pH measurements

The pH measurements were carried out on stained samples, treated samples, and control (unstained) samples to determine any change in pH value post treatments. The results in table (1) show that the three photographs (P30, P50 and P70) have decreased in pH values post staining procedure, while post treatments the three concentrations of E.L. have provided satisfying results and the acidity values nearly reverted to their original values of the unstained samples (control).

Table (1): displays pH measurements and change % of stained and treated samples compared to unstained samples

	Sample	Control (unstained)	Stained	Change* %	Treated	Change %
Ethyl lactate 30%, 50%, 70% treatments	P30: 30% E.L.	6.3	4.7	- 25.3**	5.9	- 6.3
	P50: 50% E.L.	5.9	4.5	- 23.7	5.8	- 1.7
	P70: 70%E.L.	6.4	4.8	- 25	6.2	- 3.1

*pH change % of stained and treated samples compared to unstained samples

**-ve charge means a decrease in pH value and the sample tends to be more acidic.

3.2.3. Color change measurements

This analysis was carried on stained, treated and control (unstained) samples. Each axis of CIEL*a*b* system runs from positive to negative. The axis L+ = 100 indicates white, while L- = 0 denotes black. The axis a+ means red and the a- is green. The b+ equals yellow and b- indicates blue [39, 44]. Data of the three axes were calculated to obtain the total color difference ΔE* according to the formula $\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{½}$ [36, 38]. Table 2 shows that the ethyl lactate treatments achieved satisfied color change values i.e., lower ΔE* values after treatment compared to the control means better cleaning.

Table (2): shows L*, a*, b* and total color change (ΔE*) values after 30%, 50% and 70% of ethyl lactate treatments

	Samples		L*	a*	b*	ΔE*	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*
			30%				50%				70%			
Ethyl lactate 30%, 50%, 70% treatments	Shadow area	Stained	15.38	1.20	1.57	3.96	22.28	0.43	3.95	7.35	14.53	0.36	2.20	3.94
		Treated	18.19	0.51	2.77	0.87	27.29	0.17	3.58	2.47	18.97	0.07	1.60	0.71
		control	19.03	0.31	2.83		29.62	0.26	4.38		18.37	0.29	1.30	
	Mid-tone area	Stained	44.18	0.59	4.55	6.49	51.74	1.24	7.14	2.95	61.06	2.65	12.36	9.32
		Treated	50.20	0.43	4.44	0.51	49.03	1.09	6.05	0.08	68.80	2.74	14.27	1.42
		Control	50.67	0.42	4.63		48.98	1.06	6.10		70.21	2.70	14.11	
	Highlight area	Stained	70.18	1.25	3.26	12.69	82.80	3.16	10.29	2.62	79.54	2.52	10.99	3.56
		Treated	83.60	0.97	3.29	0.84	84.31	3.28	8.88	1.27	83.76	2.71	11.48	0.89
		Control	82.86	1.05	3.67		83.63	3.50	7.83		83.10	2.57	10.90	

The limit of colour difference ΔE* = 5

None of the three treatments overtopped the limit of color difference (i.e., ΔE* = 5) [45]. In shadow and highlight areas, it was noticed that the treatment of 50% concentration exhibited the highest ΔE* value, 2.47, 1.27, respectively, among all the treatments. On the other hand, the 70% treatments recorded the lowest ΔE* value (i.e., 0.84) in the highlight areas. Conversely, in the mid-tone areas, the 50% treatment recorded the lowest ΔE* value (i.e., 0.08) compared to the ΔE* value of 30% and 70% treatments (i.e., ΔE* 0.51, 1.42) respectively.

3.2.4. Atomic force microscope (AFM)

The AFM was used to investigate the state of treated photographs' surface compared to the unstained control photographs. This analysis depends on measuring roughness parameters. The roughness average (Ra) and Rms (root-mean-squared-rough)

(Rq) were measured to determine the achievable extent of cleaning treatment, any stain residues exist, or any change which may have occurred to the photograph's surface due to treatments. Accordingly, the highest concentration (70%) of ethyl lactate was selected for this examination. Brighter regions define the higher roughness. Table (3) shows the percentage (%) difference between the (Rq) and (Ra) of the treated samples and unstained samples. The 70% of ethyl lactate treatment exhibited an approaching roughness to the unstained samples with (Rq) + 46.7 and (Ra) + 35.8. In figure (9), the 2D and the 3D images of unstained control samples show a uniform surface while the 2D and the 3D images of treated samples show a less smooth surface. This may be due to the presence of some adhesive residues that got stuck to the gelatin binder during the 2nd step of sample preparation, exposure of the photographs to water vapor; this is in accordance with the sticky feeling that was observed after cleaning. Additional study is required in this area. However, the variation in roughness was moderate.

Samples		Rms Rough (Rq)	Change %	Ave Rough (Ra)	Change %
P70: 70% E.L.	Control (unstained)	74.20 nm	----	56.73 nm	----
	treated	108.9 nm	+ 46.7	77.04 nm	+ 35.8

Table (3) displays the change % of (Ra) and (Rq) of 70% of E.L. treated and unstained samples

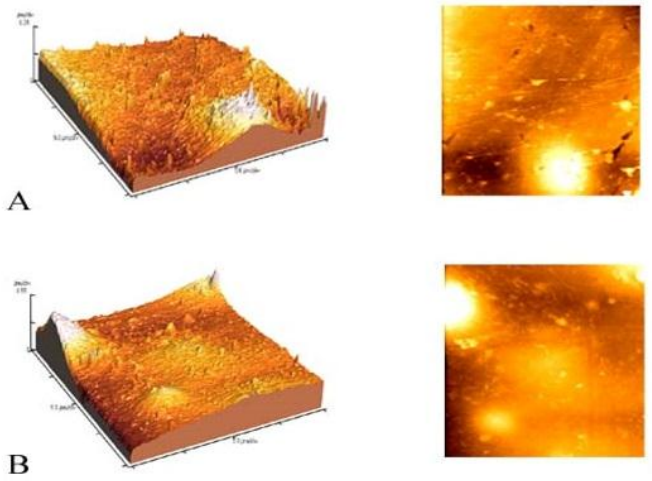

Figure (9): views AFM surface morphology of ethyl lactate 70% samples: (A)3D and 2D of treated samples, (B) 3D and 2D of unstained Control samples

3.2.5. FTIR-ATR analysis

Protein, such as gelatin, is characterized by the presence of amide groups, namely, amide I and amide II bands. The amide I band ranges between (1600 – 1700 cm^{-1}) and is mainly related with C=O stretching vibrations. The amide II band falls between (1500 – 1600 cm^{-1}) and is associated with N—H bending vibration plus C—N stretching vibration. Both amides are considered the major bands of IR spectra of protein and the most used IR spectrum to reveal the conformational changes of the protein [46]. The spectra of treated samples were compared with untreated ones to detect any changes occurred after cleaning. FTIR - ATR results displayed in table (3) and figure (10) showed almost no deterioration with amide I and amide II after both treatments. After the 30% of ethyl lactate treatment, the amide I showed the same position and approximately the same transmittance intensity; and similarly, the amide II band showed approximately the same transmittance intensity yet a slight shift to higher wavenumber (i.e., from 1526 to1532 cm^{-1}) was observed compared to

the unstained control samples. Similarly, post the 70% of ethyl lactate treatment, a slight shift has occurred in the position of amide I (i.e., from 1635 to 1640 cm^{-1}) and of amide II (from 1535 to 1542 cm^{-1}), while the transmittance intensities for both were approximately at the same range. This indicates a breakdown of little hydrogen bonding between protein chains which did not make the protein more vulnerable to chemical reactions or deterioration.

Table (4): shows the effect of Ethyl lactate 30% and 70% treatments on the chemical bonds of the gelatin binder

Sample	Amide I				Amide II			
	Wavenumbers cm^{-1}		Transmittance %		Wavenumbers cm^{-1}		Transmittance %	
	Control	Treated	Control	Treated	Control	Treated	Control	Treated
P30: 30% E.L.	1628	1628	81	76	1526	1532	80	77
P70: 70% E.L.	1635	1640	87	86	1535	1542	88	85

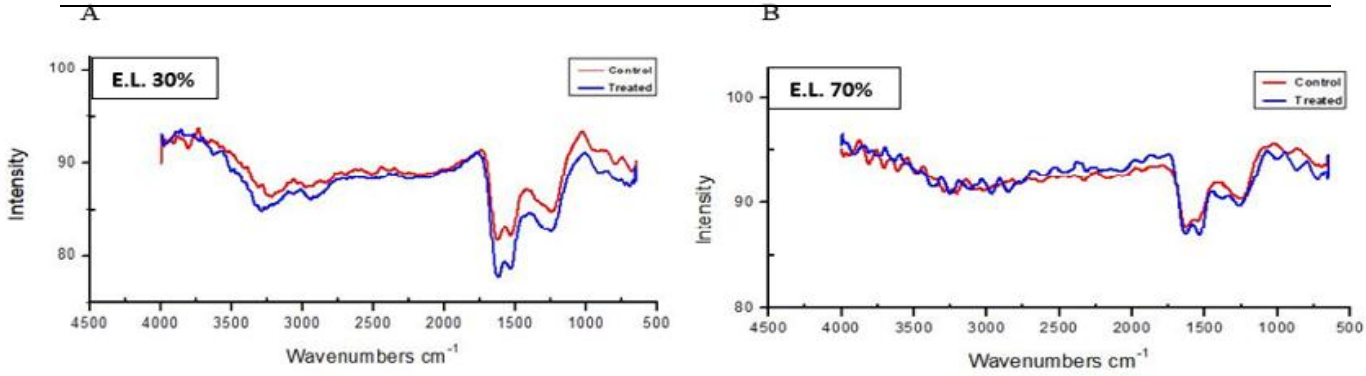

Figure (10): Shows FTIR- ATR spectra of the samples treated with Ethyl lactate; A: 30%of E.L. treatment compared with control sample. B: 70% of E.L. treatment compared with control sample.

3.2.6. Mechanical properties

For this analysis, the samples were cut in the dimensions of 2 cm × 15 cm and held between two clamps to be pulled according to a preset rate. The analysis was performed on treated samples of 30% and 70% of ethyl lactate before and after treatments and unstained control samples. Table (5) clarifies that both treatments of E.L. (30% - 70%) have ability in improving the mechanical properties of the treated photographs. Both treatments have strengthened the bonds of the cellulose chains of the paper support which has been revealed through the improvement of tensile strength and elongation % values of the treated samples. The 70% of E.L. presented superiority in increasing the tensile strength value by 63.04%, while the 30% of E.L. improved the tensile strength by 12.69% compared to stained sample. For elongation %, the 70% highly improved the value by 49%, while the 30% of E.L. raised the value by 29.69% compared to stained sample.

Table (5): displays tensile strengths and elongation % of samples treated with 30% and 70% of Ethyl lactate treatments compared with unstained control samples

Experiment	Sample	Tensile strength		Elongation %	
		alue	Value change %	Value	Value change %
Ethyl Lactate 70%	Control (unstained)	181.0	-------	2.800	-------
	Stained	55.5	-69.33	1.140	-59.28
	Treated	169.6	-6.29	2.512	-10.28
Ethyl lactate 30%	Control (unstained)	163.8	-------	1.600	-------
	Stained	165.0	0.732	0.635	-60.31
	Treated	185.8	13.43	1.110	-30.62

(-ve %= decrease, +ve % = increase)

4. Conclusion

Ethyl lactate will have a vital contribution in cleaning applications. It will anticipate in solving a wide range of issues generated by the hazardous solvents in cleaning vulnerable photographs. Ethyl lactate is inexpensive, non-hazardous, and nontoxic solvent for the environment, conservators, and the object. Test results proved that it can be safely used to remove different types of stains from photographs without causing any harm to the object or leaving residues as aforementioned. No changes have occurred to prints post treatments with all concentrations in pH, color change, also the topography of the photographs'surface. The organic component of the prints, gelatine binder, has not been affected or degraded after the treatments as given in FTIR results. Furthermore, the mechanical properties have shown substantial strength after dealing with ethyl lactate.

5. Conflicts of interest

"There are no conflicts to declare".

6. Acknowledgments

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