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SOLVENT CLEANING OF ANTIQUE CHROMOGENIC PRINTS: AN ANALYTICAL COMPARATIVE STUDY

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ABSTRACT

Chromogenic prints were the classic form of color photography in the latter half of the 20th century. Overall, photographs are considered composite objects with complex structures. However, color photographs are much more complex in structure than black and white; and therefore present special preservation challenges. Since photographs are in high demand due to their numerous applications, they often suffer from damage as a result of improper and frequent handling. Particulates, which may be greasy, grimy, abrasive, and chemically or biologically active, settle on shelves and on collection materials causing both physical and chemical damage. Accordingly, photographs may benefit greatly from surface cleaning treatments. Treatments chosen for this experiment were based on the following solvents: acetone, toluene, ethyl alcohol and isopropyl alcohol. Changes promoted in the binder and image silver, as a result of these treatments, were measured in order to evaluate the benefits and potential problems of each treatment and estimate if they can be used without unacceptable change in the original image now and in the future. The tests are based on the consideration of the following criteria: changes in the surface characteristics through digital imaging, atomic force microscopy (AFM); changes in the density of image silver through densitometric measurements; changes in the chemical structure of the gelatin binder through attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), changes in color and gloss through spectrocolorimetric measurements; and disturbance of the binder (i.e. ninhydrin test). Data obtained from naturally and artificially aged samples were compared with those of the control samples.

KEYWORDS: Chromogenic prints, solvents, digital microscope, AFM; ATR-FTIR, densitometer, spectrophotometer, ninhydrin test.

1. INTRODUCTION

A vast amount of photographs are of historical and artistic value, and their preservation is a significant task. Almost from the beginning of photography, there was a quest for color. It was first applied by hand. Chromogenic prints were the classic form of color photography in the latter half of the 20th century. Color prints are much more complex in structure than black and white photographs; and therefore present special preservation challenges to archivists, librarians, and conservators.

Chromogenic prints are composed of (from top to bottom) yellow, magenta, and cyan organic dyes, distributed in three superimposed layers of gelatin (Lavédrine, 2003). This is the conventional layer order used when Kodacolor negative-positive system was introduced in 1942. In 1954, the dye layer order was reversed (from top to bottom) cyan, magenta and yellow (Weaver et al., 2009). Chromogenic images are made up of spherical dye clouds measuring a few tenth of a micron in diameter (Lavédrine, 2003). The binder which holds the dye clouds to the support is gelatin (Roosa, 2004), a protein derived from the fibrous, insoluble protein, collagen, which is widely found as the major component of skin, bones, and connective tissues (Sailaja, 2011). Gelatin is a polymer built of amino acids that are joined together by peptide bonds (Brodsky et. al., 2005; Sturge, 1977). The three binder layers are supported on a paper support. Prints were first made with a low-cost fiber-base paper. In 1968, a low-cost polyethylene resin-coated support was introduced as a substitute (Wilhelm et. al., 1993). Fiber-base paper consisted of paper, also known as raw base, and a baryta coating (Weaver et al., 2009). On the other hand, resin-coated prints have a paper support coated on the back and directly below the emulsion with polyethylene. A white pigment, usually titanium dioxide, is added to the polyethylene layer on the emulsion side of the print (Hendriks, 1984). Chromogenic dyes have extremely poor light fading stability, and they also have poor stability when stored in the dark (Wilhelm et. al., 1993; Fenech, 2011)

Since photographs are in high demand due to their numerous applications: for study and research, publications, exhibitions, etc., they often suffer from damage from improper and frequent handling. Particulates, which may be greasy, grimy, abrasive, and chemically or biologically active, settle on shelves and on collection materials causing physical and chemical damage. Dust, dirt and other solid particles can contribute to surface damage as they may abrade the surface and eventually lead to cracking and other physical damage. Generally, gritty dust causes physical damage, while sticky dust (i.e. soot) will stain most surfaces.

A major objective of all conservation treatments is to increase the physical and chemical stability of the objects being treated. Cleaning treatments often form an important part of the stabilization process. The use of conventional cleaning treatments on photographic prints is an area that requires further research, in particular their long-term effects since they have not received much attention until recently. There are no standardized effective methods for cleaning photographs, and hence the importance of this research.

Treatment of chromogenic prints is particularly challenging due to their inherent instability, their degradation process and the complex multi-component of their composition. The complexity of the problem under examination, which is to assess the validity of conventional cleaning treatments, requires an appropriate experimental approach. Selections of cleaning treatments have been examined with regard to their immediate physical effects on the gelatin binder surfaces (i.e. image layer) of naturally aged chromogenic photographic prints. All aqueous cleaning treatments have been excluded since they were found to severely swell the gelatin and can cause cracking, pitting and loss in the image layer. It also lowers the efficiency of organic solvents.

Solvent molecules are held together by Van der Waals, dipole, and hydrogen bonds of various strength and portions, depending on the polarity of the solvents. A solvent will dissolve a soil which has a similar polarity to the solvent itself. (Timar-Balazsy et al., 2011). Contaminants can be divided into surface contaminants and contaminants embedded in the gelatin layer. If the contaminant is embedded in the gelatin binder layer, it could be beneficial to slightly swell the gelatin to remove it. Superficial dirt or contaminants do not require this property and swelling the gelatin will be of no benefit and will do more harm than good (Morrison, 2005).

The present study evaluated cleaning treatments often used by conservators to clean chromogenic prints, in terms of efficiency of cleaning as well as the potential damage caused to the photograph, focusing on the changes which occur in the photographic binder and final image substance. The following treatments: ethyl alcohol, isopropyl alcohol, acetone, and toluene, were selected based on their common use in the conservation of photographic materials.

Changes promoted in the photographs, as a result of these treatments were measured and registered in order to evaluate the benefits and potential problems

of each treatment and estimate if they can be used without unacceptable change in the original image now and in the future. Several physical and chemical properties were measured before and after treatment as well as after artificial aging in naturally aged chromogenic prints with different degrees of degradation to determine if any changes had occurred. Only personal photographs were used in this study.

2. MATERIALS AND METHODS

2.1. *Test Materials*

Five naturally aged chromogenic prints were chosen as samples in order to give a more practical, rather than theoretical focus to this experiment. Kodacolor prints, the first commercially available chromogenic print process, were selected for this research. All cases are fiber-based prints with an F surface (glossy). They date back to 1960s. They mainly suffer from superficial dirt and minor cracking (as shown in Fig.1). The photographs were soiled and aged at 80 °C ± 2 °C and 65% RH for 10 days based on the conditions described in specification ISO 5630-3:1996 for paper-based materials (Kamińska et al., 2004; Pentzien et al., 2011; Arias et al., 2013). Each photograph was assigned a number prior to treatment (9-13). Mylar templates were made to mark the precise area on each photographic print to measure with the densitometer and spectrophotometer before and after treatment and after artificial aging. Three areas were selected on each sample (A, B, and C). The area to measure with the FTIR spectrometer was also marked on Mylar templates.

Figure 1. Sample 12 exhibiting superficial dirt.

2.2. *Treatment Application Methods*

Five solvents were selected: acetone (100%), toluene (100%), acetone/toluene (50:50%), ethyl alcohol (100%), and isopropyl alcohol (100%). The numbering system for the samples represents the number of the sample (9-13) and the type of treatment used (i.e. E for ethyl alcohol, I for isopropyl alcohol, A for acetone, T for toluene, and TA for toluene/acetone). For example, a completely numbered sample may have been identified as 13-TA, where 13 is the number of the photograph and TA is the treatment used. The photographs were treated with swabs lightly dampened with the solutions. The swabs were gently rolled in a consistent manner. One photograph was treated at a time and then put under weight to compensate for some of the planar deformation that can occur as a result of wetting. The swabs were saved in a holder which kept them separated by treatment and photographic print for further testing. The swabs were preserved in plastic bags to avoid contamination by airborne particulates, etc. Treated photographs were artificially aged at 80 °C ± 2 °C and 65% RH for 10 days.

2.3. *Analytical Methods*

Measurements were made before and after treatment and after artificial aging process. The surface, optical and chemical properties of the tested samples were determined as follows:

2.3.1. Examination by Digital Microscope

A SUPEREYES PZ01 500X USB Digital Microscope was utilized to document the surface characteristics of the image side of the photographs and the changes which have occurred upon treatment (i.e. immediate effects) and after artificial aging (i.e. long-term effects).

2.3.2. Atomic Force Microscopy

To monitor and analyze the effectiveness of the treatments, the atomic force microscope (AFM) was employed. The combination of this technique with the precious surface monitoring techniques (i.e. digital microscope) allowed a complete characterization of the tested surfaces (Pereira et al., 2013). The atomic force microscope used was a Thermomicroscopes Autoprobe® CP Research head operated in contact mode using nonconductive silicon nitride probe. AFM images acquisition (i.e. scan area) was performed on each sample (0.5cm × 0.5cm) using 5×5 μm^2 or 15×15 μm^2 frames depending on the topography of the sample. The resolution was 256 by 256 lines at a scan rate of 1 Hz. Proscan1.8 software was used for controlling the scan parameters and IP 2.1software was used for image analysis. The images are shown in false color scale, where brighter areas present higher areas. Atomic Force Microscopy scans were performed on untreated and treated historic samples. AFM

utilization, a novelty in the research of photograph conservation, provides the following information on the photograph surface: 2D and 3D images and surface histograms. Degradation effects can be evaluated by means of surface roughness parameters Ra and Rq since they are the most commonly used roughness parameters. In this paper, only a qualitative study has been provided. The procedure was carried out at the Atomic Force Microscope Laboratory at the National Institute for Standards (NIS), Cairo, Egypt.

2.3.3. Densitometric Measurements

The action of the treatments on the image layer of the prints was evaluated by measuring the average optical density of the image layer of each sample before and after treatment and aging using a Densitometer T/RT120 TECHKON GmbH, Germany. Three readings were taken for each area (A, B and C) and were then averaged for a single measurement of that area. The procedure was performed at the Conservation Department, Faculty of Archaeology, Cairo University.

2.3.4. Colorimetric Measurements

Color changes due to treatments were measured using an Optimatch 3100® spectrophotometer from the SDL Company. All samples were measured in a visible region, i.e., a wavelength range from 400-700nm, with an interval of 10nm using a D65 light source and an observed angle of 10 degrees. The CIELAB color parameters (L* a* b*) were used to express color change. These data were used to calculate the total color difference parameter (i.e. ΔE^*). Each reading was the average of three measurements. This analysis was carried out at the National Institute for Standards in Cairo, Egypt.

2.3.5. Surface Gloss

For this surface analysis, an Optimatch 3100® spectrophotometer from the SDL Company was used in preference to a gloss meter to measure diffuse reflectance at different wavelengths. All samples were measured in a visible region, i.e., a wavelength range from 400-700nm, with an interval of 10nm using a D65 light source and an observed angle of 10 degrees. Each sample was measured in triplicate before and after treatment and after artificial aging. This procedure was carried out at the National Institute for Standards in Cairo, Egypt.

2.3.6. ATR-FTIR Analysis

Spectra were obtained by using a Nicolet 380 FT-IR Spectrometer, in the frequency range of 4000 - 400 cm^{-1}. The ATR accessory was a Thermo Scientific ™ Performer Plate ZnSe Crystal with an angle of incidence of 45°. The diamond has an active area of 1 mm in diameter, and the depth of each scan was approximately 2 microns below the surface. No preparation of the samples was necessary. The analysis was performed at the National Institute for Standards in Cairo, Egypt.

2.3.7. Ninhydrin Test

Ninhydrin is a common reagent for detecting proteins. When ninhydrin reacts with an amino acid, one of the products is a deep violet, resonance-stabilized anion called Ruhemann's purple. Ninhydrin produces this purple dye regardless of the structure of the original amino acid (Wade, 2010). The ninhydrin reagent was prepared by dissolving 1.25 gm of ninhydrin crystals in 200 ml of acetone (The North Carolina State Crime Lab and Forensic Laboratories, 2013). To perform the ninhydrin test, one drop of the reagent was placed on the swabs, and allowed to rest several minutes before heating on a taking iron. The swaps had to be heated for several minutes before a color appeared (Adams et al., 2009). The test was performed to understand whether or not the binder layer was disturbed during cleaning. The same test was performed on a blank to ensure that the test was being conducted correctly. Gloves must be worn during the test, as the resulting stains are difficult to remove.

3. RESULTS AND DISCUSSION

3.1. Examination by Digital Microscope

Samples were examined to determine the immediate effect of the treatments and to check for changes in surface qualities (as shown in Figure 2). Results are given in Table I.

Table I. Preliminary evaluation of the immediate effect of tested cleaning treatments

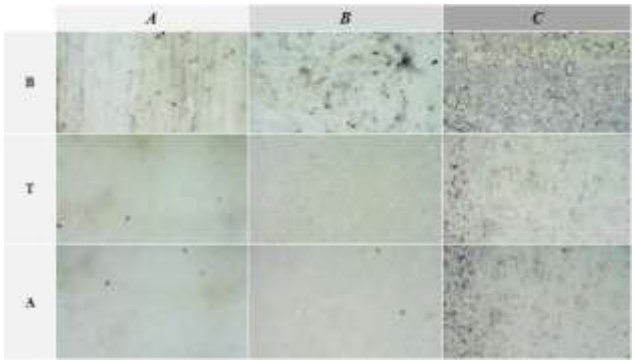
Sample No.	Tested Treatment	Immediate Effects
9-A	100% Acetone	Moderately cleaned off the surface dirt.
10-E	100% Ethyl alcohol	Moderately reduced surface dirt.
11-I	100% Isopropyl alcohol	Moderately reduced surface dirt.
12-T	100% Toluene	Successfully removed surface dirt.
13-TA	50:50% Toluene/acetone	Moderately removed surface dirt.

Figure 2. Sample 12 before (top) and after (bottom) cleaning with a 100% solution of toluene.

All samples were investigated and photographed using a digital microscope before and after treatment and after artificial aging in order to study the long-term effects of the tested cleaning treatments.

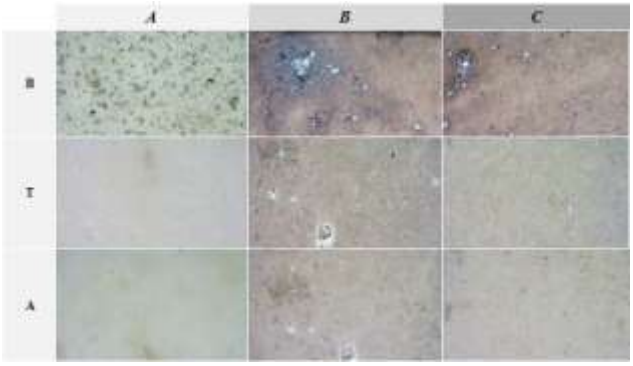
Samples treated with acetone, ethyl alcohol and isopropyl alcohol showed moderate to good results in terms of treatment efficiency, leaving on the surface a very thin layer of dirt. In the case of acetone treated sample, a change in color was observed in the shadow area after aging. No visible change in the surface sheen or color was detected in both alcohol treated samples. Results are given in Table II.

Table II. Surface examination of historic sample 11 treated with 100% solution of isopropyl alcohol, where B is the soiled sample before treatment, T represents the sample after treatment and A is the sample after treatment and artificial aging



As for the toluene treated sample, excellent results were obtained in terms of treatment efficiency in removing surface dirt while preserving the surface characteristics of the image. Compared to the previous treatment, sample treated with a solution of acetone and toluene (50:50%) showed less efficiency in reducing the surface dirt. Nevertheless, the results were good and no visible change in surface characteristics was observed after treatment or after artificial aging. Results are given in Table III.

Table III. Surface examination of historic sample 12 treated with 100% solution of toluene



3.2. *Atomic Force Microscopy*

Sample 9-A treated with a 100% solution of acetone was not efficiently cleaned as indicated by the high roughness; however, the after treatment 2D and 3D images showed a more uniform surface (as shown in Fig.3). Conversely, surface roughness decreased for sample 10-E treated with a 100% solution of ethyl alcohol indicating the efficiency of the treatment in reducing surface dirt. 2D and 3D images confirm this result showing a smoother surface post treatment (as shown in Figure 4). Similar results were obtained for sample 11-I with a 100% solution of isopropyl alcohol. 2D image and 3D image of sample 12-T treated with a 100% solution of toluene reflected the high efficiency of the treatment. The surface topography appeared more uniform and smoother (as shown in Fig. 5). Sample 13-TA showed no significant changes post treatment indicating that this treatment failed to reduce the surface dirt (as shown in Fig. 6). This was only a preliminary study to test the possible use of atomic force microscopy in evaluating photograph conservation treatments. A quantitative study regarding the change in surface roughness needs to be performed and further experimentation is required to study the long-term effects of the tested treatments.

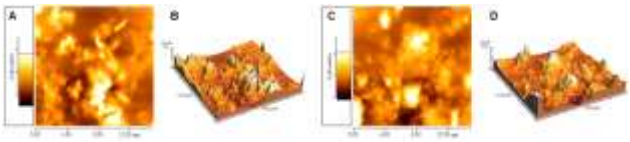


Figure 3. AFM surface morphology of sample 9-A. (A) and (B) 2D and 3D views prior treatment, and (C) and (D) 2D and 3D views post treatment.

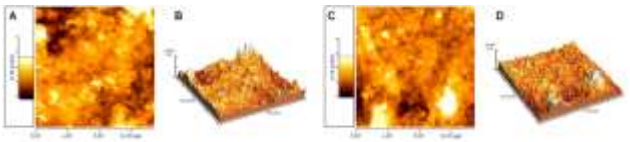


Figure 4. AFM surface morphology of sample 10-E. (A) and (B) 2D and 3D views prior treatment, and (C) and (D) 2D and 3D views post treatment.

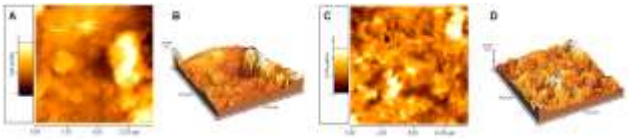


Figure 5. AFM surface morphology of sample 12-T. (A) and (B) 2D and 3D views prior treatment, and (C) and (D) 2D and 3D views post treatment.

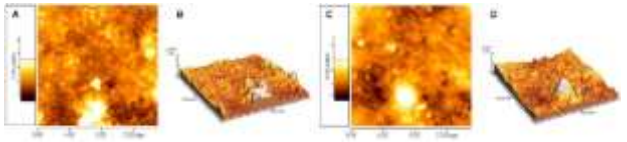


Figure 6. AFM surface morphology of sample 13-TA. (A) and (B) 2D and 3D views prior treatment, and (C) and (D) 2D and 3D views post treatment.

3.3. Densitometric Measurements

Changes in the optical density of the samples before treatment, after treatment and after artificial aging were followed to measure any changes in the image tones. Changes within the range of 0.00 – 0.03 were considered measuring errors (Hanus et al., 1999). The outcomes of this test are given in Table IV.

Table IV. Optical density changes (ΔD) of the untreated, treated and aged treated historic chromogenic prints. Results expressed are the average of three measurements.

	Densitometric Measurements For Historic Chromogenic Prints		
	Dmin (A)	Midtones (B)	Dmax (C)
	9-A: 100% Acetone		
Untreated	0.20	0.30	0.59
Treated	0.19	0.38	0.61
Immediate	-0.01	0.08	0.02
Aged	0.18	0.33	0.57
Long-term	-0.02	0.03	-0.02
	10-E: 100% Ethyl Alcohol		
Untreated	0.42	0.32	0.58
Treated	0.42	0.32	0.63
Immediate	0.00	0.00	0.05
Aged	0.40	0.28	0.63
Long-term	-0.02	-0.04	0.05
	11-I: 100% Isopropyl Alcohol		
Untreated	0.22	0.34	0.51
Treated	0.31	0.63	0.66
Immediate	0.09	0.29	0.15
Aged	0.23	0.32	0.55
Long-term	0.01	-0.02	0.04
	12-T: 100% Toluene		
Untreated	0.30	0.60	0.62
Treated	0.31	0.63	0.66
Immediate	0.01	0.03	0.04
Aged	0.29	0.56	0.59
Long-term	-0.01	-0.04	-0.03
	13-TA: 50:50% Toluene/Acetone		
Untreated	0.42	0.31	0.50
Treated	0.47	0.31	0.50
Immediate	0.05	0.00	0.00
Aged	0.42	0.31	0.45
Long-term	0.00	0.00	-0.05

All five investigated organic solvents yielded successful results in terms of preserving the optical density of chromogenic prints for the three areas selected for testing (i.e. A, B and C) , after treatment and after artificial aging. The highest change in density was recorded for sample 11-I after treatment, where the three areas A, B, and C showed an increase in optical density with a ΔD value of 0.09, 0.29, and 0.15, respectively. Nevertheless, all treatments showed no to very minimal change in optical density after aging.

3.4. Colorimetric Measurements

An important issue of conservation treatments is the impact of the treatment on the original color of the object treated. When a color is expressed in CIELAB (L*a*b*), L* defines lightness and varies from 0 (black) to 100 (white). a* denotes the red/green value, where +a means red and -a means green. The b* scale measures yellow/blue, where +b means yellow and -b means blue (Nemtanu, 2008).

The total color difference ΔE* between treated and untreated samples and aged treated and untreated samples can be calculated from the following formula: $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{½}$ (Kamperidou et al., 2012; Čermák et al., 2013). The total color difference, ΔE*, is a value useful as an indicator of the difference between a sample and a reference. In literature, ΔE* values of 2-3 are thought to be observable and

unacceptable color difference (Nematanu, 2008; Sahin et al., 2011); however, it is clearly lower than the threshold limit (ΔE* = 5) required for the maintenance and restoration of historical surfaces (Goffredo et al., 2015). Another study also mentions that a ΔE* <<4 is a value normally accepted as limit for the visual impact of surface treatments (de Ferri et al., 2013).

Table V. Measured L*, a*, b* and total color change (ΔE*) values for historical chromogenic prints used for testing the efficiency of selected cleaning treatments.

Sample	**Colorimetric Measurements for Historic Chromogenic Prints**			
	L*	**a***	**b***	**ΔE***
	9-A: 100% Acetone			
	Color Values and Color Difference for the A Area			
Untreated	78.03	2.66	21.95	
Treated	81.75	1.75	22.15	**3.83**
Untreated	79.55	2.12	24.69	**3.18**
	Color Values and Color Difference for the B Area			
Untreated	68.36	9.01	23.53	
Treated	70.43	9.94	27.37	**4.46**
Untreated	69.40	8.31	26.15	**2.90**
	Color Values and Color Difference for the C Area			
Untreated	64.45	9.02	20.43	
Treated	59.27	9.35	22.26	**5.50**
Untreated	51.39	13.20	27.26	**9.31**
	10-E: 100% Ethyl Alcohol			
	Color Values and Color Difference for the A Area			
Untreated	68.23	7.87	25.22	
Treated	66.02	6.68	25.31	**2.51**
Untreated	67.10	7.80	28.63	**3.59**
	Color Values and Color Difference for the B Area			
Untreated	70.54	4.94	24.39	
Treated	71.39	4.61	24.80	**1.00**
Untreated	69.63	5.12	26.69	**2.73**
	Color Values and Color Difference for the C Area			
Untreated	59.43	8.41	21.64	
Treated	54.92	10.34	23.12	**5.12**
Untreated	62.10	8.38	30.18	**8.95**
	HS11: 100% Isopropyl Alcohol			
	Color Values and Color Difference for the A Area			
Untreated	71.92	4.43	25.25	
Treated	76.81	3.53	26.39	**5.10**
Untreated	73.85	4.61	27.74	**3.16**
	Color Values and Color Difference for the B Area			
Untreated	64.37	7.50	24.67	
Treated	69.05	7.68	28.10	**5.81**
Untreated	67.37	7.77	29.52	**5.71**
	Color Values and Color Difference for the C Area			
Untreated	61.23	8.94	26.72	
Treated	57.91	8.74	25.24	**3.64**
Untreated	59.49	9.54	29.12	**3.02**
	HS12: 100% Toluene			
	Color Values and Color Difference for the A Area			
Untreated	69.98	6.40	25.41	
Treated	71.81	5.91	26.49	**2.18**
Untreated	70.84	6.55	28.98	**3.68**
	Color Values and Color Difference for the B Area			
Untreated	55.38	12.12	22.22	
Treated	53.72	14.54	26.39	**5.10**
Untreated	53.28	15.33	27.36	**6.41**
	Color Values and Color Difference for the C Area			
Untreated	54.70	12.33	22.49	
Treated	54.08	12.62	22.86	**0.78**
Untreated	55.13	13.91	26.18	**4.04**
	HS13: 50:50% Toluene/Acetone			
	Color Values and Color Difference for the A Area			
Untreated	64.36	6.05	20.82	
Treated	66.87	6.70	23.83	**3.97**
Untreated	64.72	7.09	25.77	**5.07**
	Color Values and Color Difference for the B Area			
Untreated	70.01	4.41	23.80	
Treated	71.33	4.21	24.66	**1.59**
Untreated	69.43	5.20	27.12	**3.46**
	Color Values and Color Difference for the C Area			
Untreated	62.66	9.76	26.90	
Treated	65.13	8.89	28.25	**2.95**
Untreated	66.89	8.15	29.80	**5.38**

Based on the results given in Table V, samples 9-A and 10-E showed great color change in the shadow areas (C) after treatment and after aging. Conversely, the midtones (B) of sample 11-I exhibited ΔE* values slightly exceeding the acceptable limit. Similarly, sample 12-T showed a great color change for the midtones after aging. For sample 13-TA, the ΔE* was within the acceptable limit after treatment; however, after aging, the highlight (A) and shadow areas showed a change in color that is slightly above the allowed limit.

In breaking down the data to L*a*b* values, most investigated samples showed a trend towards an increase in L* for areas A and B and a decrease in the C area. This could be explained by the fact that the color of the surface dirt affect the before treatment color measurement result; consequently the lightness increase for light areas and decreases for dark areas. Sample 10-E showed the slight darkening of area A and B after aging. The toluene treatment caused the darkening of the B area, both after treatment and after aging. Sample 13-TA showed an increase lightness in all three areas (i.e. A, B, and C), after treatment. However, after aging, areas A and B have darkened, while area C exhibited fading.

All investigated sample exhibited yellowing as indicated by the positive Δb* values, the highest being the C area of aged sample 10-E (Δb* >8). The next sample with high amount of yellowing in the C area is aged sample 9-A. The highest amount of yellowing in the A area was observed I aged sample 13-TA, while the highest amount of yellowing recorded for the B area was found in aged sample 12-T.

3.5. *Surface Gloss*

Results for the chromogenic prints show that area (A) of photograph 9-A has suffered a loss in surface reflectance after treatment at most wavelengths. After aging, an increase in reflectance was observed. As for area (C), it exhibited an increase in reflectance after treatment, and a significant loss was noticed after aging. Photograph 10-E showed a significant increase in surface reflectance for spot (A), both after treatment and after aging. Spot (C) also showed a significant increase in surface reflectance after treatment; however, post aging, a decrease was observed. As for photograph 11-I treated with a 100% solution of isopropyl alcohol, results showed that both investigated areas (A) and (C) suffered from a similar decrease in surface reflectance (as shown in Fig. 7). Photograph 12-T, showed a significant decrease in surface reflectance after treatment for the two tested areas (A) and (C). Post aging, area (A) showed an increase in reflectance at most wavelengths; whereas area (C) showed a considerable overall increase in reflectance. Finally, photograph 13-TA showed an overall decrease in surface reflectance for area (A), post treatment and post aging. Area (C) exhibited an increase in surface reflectance after treatment; however, after aging, a significant decrease was observed.

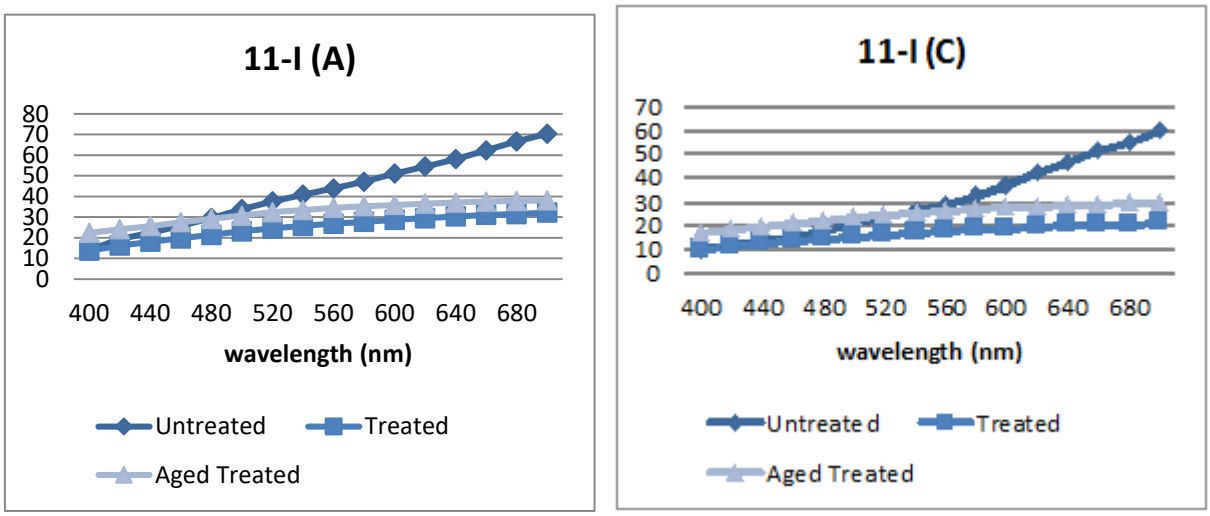


Figure 7. Average change in percent reflectance for sample 11-I treated with 100% solution of isopropyl alcohol.

3.6. *ATR-FTIR Analysis*

The main objective of this study was to investigate the effect of the selected cleaning processes on the gelatin binder, through the use of ATR-FTIR spectroscopy, in order to determine possible interactions that might occur. Spectra were recorded before and after treatment and artificial aging. Essential FTIR software was used to process the obtained spectra.

Protein gives rise to nine characteristic IR absorption bands, namely, amide A, B, and I-VII (Adochitei et al., 2011). According to literature, the information needed to predict the chemical changes which take place in gelatin is contained in the amide I and amide II absorption bands of the peptide bonds centered at ~1650 and 1550 cm^{-1}, respectively (Goldberg et al., 2005).

Obtained results show a slight increase in the intensity of the amide I and II bands for sample 9-A treated with 100% solution of acetone (as shown in Fig. 8).

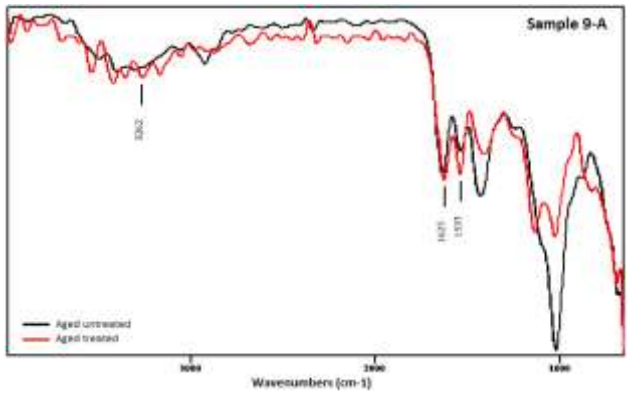


Figure 8. ATR-FTIR spectra of sample 9-A after treatment and after artificial aging.

This is an indication of the hydrolysis and oxidation of gelatin (Ishida et al., 1993; Derrick, 1991). Further studies show that an increase in amide I band intensity is related to an increase in random coil at the expense of the ordered secondary structure (Al-Saidi et al., 2012). On the other hand, the I_{AI}/I_{AII} ratio exhibited a decrease. Loss in amide I/II ratio is primarily related to the decrease in protein level of the sample (Karthikeyan, 2012).

Sample 10-E showed a slight increase in the OH stretching band which is also an indication of the hydrolysis of gelatin (Ishida et al., 1993). A significant increase in the intensity of amide I band was observed as well as a slight increase in the bandwidth. The I_{AI}/I_{AII} ratio decreased after treatment and aging.

ATR-FTIR spectra for sample 11-I showed minor change in the intensity of the OH stretching band. The protein characteristic bands significantly decreased. As for the I_{AI}/I_{AII} ratio, it also showed a decrease after treatment and ageing.

A marked decrease in the intensity of the amide I and II bands was observed upon treatment and aging of sample 12-T. The intensity of the OH stretching band was also reduced. The I_{AI}/I_{AII} ratio also decreased after treatment and aging (as shown in Fig. 9).

As for sample 13-TA, an increase in OH stretching, amide I and amide II bands was observed upon aging; however, the I_{AI}/I_{AII} ratio showed a decrease. ATR-FTIR results for the samples are given in Table VI.

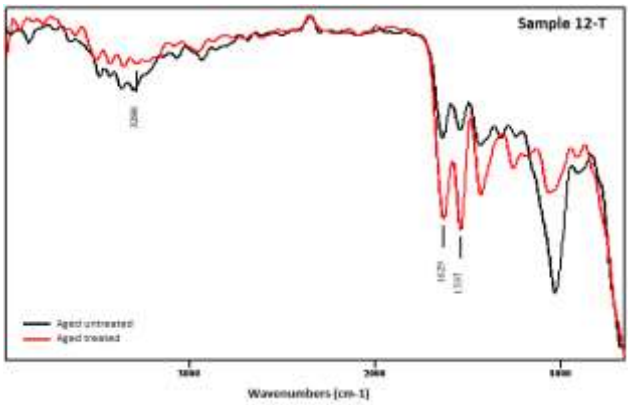


Figure 9. ATR-FTIR spectra of sample 12-T after treatment and after artificial ageing.

3.7. Ninhydrin Test

Table VII. lists the results of the ninhydrin test for the historic samples referring to the extent the samples were affected by the treatments compared to each other, where + refers to the least affected and ++ refers to the most affected. Based on these results, the sample treated with acetone showed a medium purple color. Samples treated with ethyl alcohol and toluene showed no change upon testing. Samples treated with isopropyl alcohol and toluene/acetone mixture showed a faint purple color (as shown in Fig. 10).

Table VI. The IAI/IAII ratio for the samples before treatments and after treatment and artificial ageing, where W is the wavenumber of the band (cm-1), I is the band intensity, AI refers to the Amide I band and AII refers to the Amide II band.

Sample Number		Before Treatment			After Treatment and Aging		
		AI	AII	(I_{AI}/I_{AII}) Ratio	AI	AII	(I_{AI}/I_{AII}) Ratio
9-A	W	1635	1535	2.28	1625	1537	1.84
	I	3.51	1.54		4.11	2.23	
10-E	W	1630	1529	3.46	1630	1537	1.42
	I	2.32	0.67		4.89	3.43	
11-I	W	1635	1535	3.45	1622	1539	1.34
	I	4.14	1.20		2.58	1.92	
12-T	W	1634	1539	2.04	1629	1537	1.16
	I	3.56	1.74		7.02	6.04	
13-TA	W	1625	1520	6.81	1631	1539	1.33
	I	1.50	0.22		5.97	4.48	

Table VII. Results of the ninhydrin test.

Sample No.	Test results
9-A	++
10-E	No change observed
11-I	+
12-T	No change observed
13-TA	+

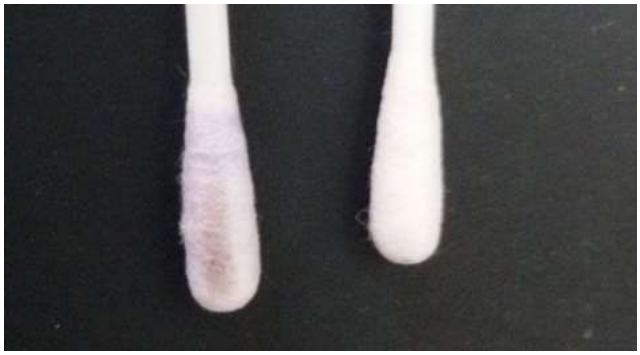


Figure 10. Testing result for the acetone treated sample 9-A compared to a blank.

4. CONCLUSION

In this research, different cleaning treatments were applied on chromogenic prints in order to

evaluate their effects on the surface. Treatments which have been experimented include:

- Acetone.
- Ethyl alcohol.
- Isopropyl alcohol.
- Toluene.
- Toluene/acetone (50:50%).

Samples were studied before and after cleaning by means of digital camera, USB microscope, AFM microscope, densitometer, spectrophotometer, ATR-FTIR and ninhydrin test in order to the treated surfaces with their untreated counterparts. Analysis results led to the following remarks:

- All tested treatments reduced surface dirt; however, acetone seems to have dehydrated the surface causing the samples to curl.
- Based on digital microscope examination, successful results were yielded using a 100% solution of toluene, followed by the toluene/acetone treatment. Ethanol and isopropanol treatments produced moderate results. Acetone treatment seemed to alter the color of the shadow areas post aging.
- AFM results showed the high roughness of the surface post acetone treatment. The roughness decreased for surfaces treated with ethanol and isopropanol. The obtained results also confirmed the efficiency of toluene; however, the results for the toluene/acetone mixture showed no changes in terms of surface morphology, topography, and roughness.
- All tested organic solvents yielded successful results in terms of preserving the optical density of prints.
- As for colorimetric measurements, acetone and ethanol caused great color change in the shadow areas after treatment and after aging. Isopropanol and toluene treatments affected the midtones. For sample toluene/acetone, the ΔE^* was within the acceptable limit after treatment; however, after aging, the highlight and shadow areas showed a change in color that is slightly above the allowed limit.
- All treatment seemed to affect surface gloss after treatment and after aging apart from toluene which showed minor impact on the gloss of silver gelatin prints after aging.
- ATR-FTIR results show that tested treatments had a negative impact on the chemical structure of gelatin as indicated by the increase or decrease of the amide I/amide II intensity ratio.
- Ninhydrin testing results showed that the gelatin binder was most affected by acetone, and no change was observed for pure toluene and ethanol treatment.

From the previous results one can conclude that all treatments negatively affected the tested chromogenic prints in one way or another. Accordingly, it is advised to perform solvent cleaning only when necessary. Toluene treatment showed the least negative effect on the investigated prints. Acetone should not be used since it severely dehydrates the gelatin and paper causing their rapid deterioration. Further experimentation is required on a larger set of samples.

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