

THE EVALUATION OF AGAROSE-BASED GEL SYSTEMS FOR SURFACE
CLEANING ALBUMEN PRINTS VS THE CONVENTIONAL WATER
TREATMENT

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Abstract:

The albumen process was the main positive printing photographic process of the 19th century. Albumen prints form a significant part of historical collections, whether on display or in storage. Since photographs are in high demand, they often suffer from improper and frequent handling, resulting in dirt and stains. Accordingly, albumen prints may benefit from surface cleaning. However, conventional treatments are very risky procedures which may cause severe damage to albumen prints. Recently, many gel-based systems have been developed and tested for possible use to surface clean different cultural materials. Given that the use of gelled systems proved to have several advantages over common treatments, the suitability of agarose-based gel systems and their effects on treated albumen surfaces was thoroughly assessed using visual inspection, UV fluorescence imaging, digital microscopy, scanning electron microscopy, atomic force microscope, Fourier transform infrared spectroscopy, colorimetric measurements, pH value measurements, ninhydrin test, mechanical testing, thickness measurements, and fungal testing. In this study, agarose-based gel was prepared in three concentrations (2, 3, and 4% in distilled water), without and with a solvent (i.e. ethanol or toluene). For studying long-term effects of the selected treatments, prepared test samples were exposed to humid heat aging for a period of five days as described in the ISO 5630-3:1996 standard. For color change measurements, vintage albumen prints were used. The conventional water treatment was also carried out for comparative purposes. Based on the obtained results, the tested agarose-based systems are less aggressive than the water treatment conventionally used to clean albumen prints.

1. Introduction

Photographic images are very valuable and powerful resources that visually document objective information on individuals, social groups, places, and events that have shaped our history; but also our identity by reflecting the values, beliefs and aspirations of the particular nation they were created in [1]. Preserving photographic heritage and passing it on to future

generations strengthens it and contributes to giving us a sense of identity, responsibility and continuity [2]. Nevertheless, it does present special preservation challenges to conservators due to their complex physical and chemical structure which varies from one photographic process to another [3]. This study is dedicated to albumen prints. The albumen process was

the main positive printing photographic process of the nineteenth century [4]. It was invented by Louis-Désiré Blanquart-Evrard, a French cloth merchant from Lille who became a student of photography in the 1840s [5]. In 1850, Blanquart-Evrard presented his process to the French Academy of Sciences. The process dominated photographic printing for approximately 40 years, from 1850-1890, but survived in various forms into the late 1920s [4]. This process involved coating a thin smooth sheet of rag paper with albumen, egg white, containing sodium chloride or ammonium chloride [6]. The paper was then sensitized by floatation using a solution of silver nitrate forming silver halide grains [7]. The albumen binds the light-sensitive silver halide salt to the paper substrate [8]. Images are made by placing the desired negative on sensitized albumen paper in a copy or printing frame [9]. Prolonged exposure to light forms a print-out image composed of photolytic silver, the final image material. After exposure, the image was toned, fixed in hypo, washed and dried [10]. Albumen prints have a warm brown image tone (i.e. very light brown, brown, and reddish brown to dark violet-black) [4]. Albumen paper produced a sharp image retaining all the quality contained in the original negative [10]. Generally, earlier albumen prints, created before about 1870, were usually less glossy than double-coated albumen photographs and albumen photographs that were made glossy by surface burnishing and varnishing [4]. Most albumen prints were often affixed to cardboard mounts of varying sizes. The typical sizes are the carte de visite and the cabinet card. Many albumen prints form a significant part of historical collections around the globe, whether on display or in storage [8]. The primary mission of institutions holding photographic collections is to acquire, document, preserve, and appreciate significant images,

making them accessible to as many people as possible [11]. Albumen prints are among the least stable silver-based photographs [12]. Their inherent instability is a result of the silver and gold image and the chemical characteristics of the albumen itself [13]. Overtime, albumen prints will deteriorate due to many factors including natural aging, poor processing, inappropriate temperature and relative humidity levels, inappropriate light levels, biological threats, pollutants, inappropriate storage and display, mishandling and misuse, disasters, and inappropriate conservation treatments [14]. Fortunately, the lifespan of albumen prints can be prolonged provided that proper remedial conservation and preventive conservation measures are taken, these can help stabilize or at least slow down the rate of deterioration [15]. Since photographic materials are in high demand, they often suffer from improper and frequent handling, particularly when accompanied by uncontrolled environmental conditions. Particulates, which may be greasy, grimy abrasive and chemically or biologically active, settle on shelves and on collection materials and create dust that spread to other items when they are handled [4]. The reduction or removal of these particulates may be desirable for aesthetic reasons or long-term preservation as they may contribute to further damage [16]. In view of that, albumen prints may benefit greatly from surface cleaning which is already a fundamental stage of the conservation of photographic collections. Nonetheless, surface cleaning treatments are very risky procedures which may cause severe damage to soiled albumen prints, altering their surface characteristics and reducing their physical and chemical stability; if not carried out a skilled conservator [16, 17]. The challenge to photo conservators is to address this problem in an effective, safe, and controllable way [18], particularly since the albumen layer of historic

prints is generally brittle and often exhibits a network of fine cracks [19]. The purpose of surface cleaning is to reduce potential damage to photographic materials/artefacts by removing foreign material which, overtime, can be very harmful [20]. Traditional cleaning methods such as mechanical cleaning, aqueous cleaning, solvent cleaning, enzyme cleaning, and others involve several drawbacks. Mechanical cleaning involves the use of brushes, sponges, erasers, scalpels, spatulas, and vacuums, all of which can be unselective and abrasive for sensitive surfaces [21]. Aged albumen prints are very fragile, and in most cases cannot endure the rough impact of mechanical cleaning [22]. Aqueous treatments are conventionally used to surface clean albumen prints. However, water-based systems can be invasive [23]. One study assessing the effects of aqueous cleaning on albumen prints showed that aqueous treatments, whether surface cleaning or immersion, increase the cracking of the albumen layer and reduce the surface gloss [24]. The use of four different baths was selected for evaluation (i.e. deionized water, deionized water ammoniated to pH 3, deionized water: ethanol mixture 1:1 v/v and deionized water followed by ethanol). Results showed that all treated prints lost gloss, regardless of initial gloss or emulsion thickness. The water followed by ethanol showed the greatest decrease in gloss, while the water: ethanol (1:1 v/v) bath showed the least decrease in gloss [25]. These results are in conformance with a more recent study which additionally stated that other physical forms of damage were observed post aqueous cleaning such as roughening and pitting [26]. Organic solvents, both aliphatic and aromatic, are notably used within the conservation field due to their efficiency in dirt removal, rapid-action and low-cost [27]. Many solvents, whether used pure or in mixtures,

are able to solubilise surface dirt; but can also rapidly penetrate into the substrate and cause some degree of damage [28]. Overall, organic solvents are often aggressive, poorly controllable and toxic to the conservator and environment [29]. Another problem is flammability; using a volatile solvent fills the air with the solvent's fumes and a small spark or the lighting of a match can cause combustion [30]. One could imagine what this would do to paper and photographic collections since they are highly flammable materials. The conservation of photographs, particularly when as sensitive as albumen prints, requires a technical and scientific approach. Gelled systems are reported to be the most promising green and sustainable cleaning methods. In this study, innovative and non-invasive surface cleaning methods based on the use of gels are addressed. The use of gelled systems is not new; and today, its use is quite common and widespread in cultural heritage applications [31]. The use of liquid cleaning agents entrapped in gel matrices was introduced by Richard Wolbers at the beginning of the 1990s as an innovative approach to minimize the problems arising from the contact of solvents and painted surfaces [32]. The systems introduced by Wolbers consist of five components: water, pH buffer, chelating agent, surfactant, and gelling agent [33]. Nonetheless, there are two basic components for a producing a gel: the gelling agent and the solvent. Other components are subsidiary to these and are intended either to make the solvent and the gelling agent compatible or to alter the effect of the gel on the solute (i.e., surfactants, pH buffers, etc...) [34]. Based on the previous studies, the use of a proper gelled system provides a simple, effective and non-invasive solution for many of the challenges faced by conservators reducing possible resultant damage, through a

controlled release of liquid cleaning agents to the object. It assures easy application and removal [35]. The application of gels has the advantage of reducing the efficacy of strong solvents and increasing the efficacy of milder solvents. Removal of foreign substances such as fats, waxes, proteins, and others requires gel systems with solvents of different polarities. Anyhow, namely, organic solvents, water, enzymes and chelating solutions can be gelled [36]. Gels of high viscosity allow the gradual release of solvents, reducing their solubilising action, reducing the solvents' evaporation and consequently limiting their penetration within the original substrate [31]; and moreover, minimizing the exposure of conservators to harmful and possibly toxic substances [37]. The main problem associated with the use of gel-based systems is the long-term effects of their residues [38]. Recently, many gel-based systems have been developed and tested for possible use to remove contaminants from different cultural materials [39]. However, this study is primarily dedicated to gelled systems applied on paper artifacts since albumen prints have paper primary and secondary supports; but also to those applied on paints given that, in some cases, albumen prints were hand-colored with different coloring agents [40]. A gel is a polymer network that can absorb a large quantity of solvent and swell due to a physical or chemical stimulus [41]. Gels are divided into two categories, depending on the nature of their bonds: **1)** chemical gels - the bonds linking the subunits are covalent chemical bonds, **2)** physical gels - the subunits are linked by weak secondary bonds (i.e. van der Waals interactions, hydrophobic, electrostatic and hydrogen bonds). Physical gels (e.g. polysaccharide, cellulose ethers, etc.) are generally viscous systems that respond to heat or be disrupted by mechanical forces. They tend to leave residues on the

treated surface because cohesion forces inside the gel have similar magnitudes as adhesion forces with the treated substrate [23,42]. One solution was to employ a clearing rinse using water after gel application. However, this rinse could create a problem on water-sensitive surfaces, considering that the gel had originally been selected to avoid the use of free water. To overcome the drawback of conventional fluid gels, the so-called rigid gels, such as gellan gum and agarose-based gels, have been used since they do not require an after treatment due to their physical form and their limited adhesive strength [43]. The assessment of different agar-based solvent gel formulations showed a number of significant advantages that make them suitable as cleaning agents. However, a number of disadvantages were also reported such as the necessity of using water first for gel preparation; using certain solvents can be tricky due to the difference in polarity; the risk of biological damage if full removal of the gel is not achieved; and others [44]. Generally, gels can be applied as pre-formed solid bricks on planar surfaces or brushed onto objects in a semi-solid state [45]. As multiply pointed out earlier, cleaning is one of the most controversial procedures in the field of conservation, particularly in the case of solvent- or water-sensitive materials such as albumen prints. In view of that, the principle aim of this study was to develop innovative and non-invasive surface cleaning practices for use on albumen prints. Given that the use of gelled systems proved to have several advantages over the use of solvents, the suitability of agarose-based gel cleaning systems and their long-term effects on treated albumen surfaces were thoroughly assessed. The efficacy of selected treatments was evaluated in terms of the efficiency of cleaning, absence of aesthetic alteration, long-term effects on the physical and

chemical properties of albumen prints, ease of removal, durability and sustainability. A multi-analytical approach was conducted during this study using visual inspection, UV fluorescence imaging, digital microscopy, scanning electron microscopy (SEM), atomic force microscope (AFM), Fourier transform infrared spectroscopy (FTIR), colorimetric measurements, pH measurements, ninhydrin test, mechanical testing, thickness measurements, and fungal testing.

2. Materials and Methods

2.1. Materials

2.1.1. Preparation of test materials

Two sample sets were prepared for this study: artificially aged albumen prints and naturally aged albumen prints. The vintage albumen prints were not selected as the main test materials to eliminate the influence of any potential variables (i.e. processing, surface characteristics, etc.). Producing controlled sample set of albumen prints provided a wide range of silver density from highlights to shadows. This will ensure to a large extent that all variables in the experiments are controlled and that the results are due to the effect of the variable being tested, which in turn increases the reliability of the obtained results. Albumen prints were prepared by gently mixing 500 ml of egg whites, 2 ml of 28% acetic acid, 15 ml of distilled water and 15 gm of sodium chloride in a glass beaker. The mixture was beaten into a fine froth for a period of 30 minutes using an electric hand mixer. The beaker was then covered with plastic wrap and left in the refrigerator until the mixture had settled leaving froth on top. After removing the froth, the mixture was filtered through cheesecloth. Resultant albumen/salt mixture was poured into a glass jar with a lid. The mixture was then left in the refrigerator for a week to further denature it. The coating step involved pouring the albumen into a tray.

After scraping away tiny bubbles, a sheet of paper, front side down was placed and floated on the surface of the albumen/salt mixture for 3 minutes. The sheet of paper was then lifted from the mixture allowing the liquid to drain. The paper was hung lengthwise, blotting off any excess as the coating dries. For sensitization, 37.5 gm. of silver nitrate was added to 250 ml of distilled water in an amber glass bottled to make 15% solution. The 15% silver nitrate solution was poured into a tray. The albumen- coated paper was then floated on the surface of the solution for 3 minutes, lifted, and hung to dry. A proper negative with a density range of 1.8 to 2.0 was selected. The image was printed-out in a contact printing frame for a period of 15 minutes. After exposure to an acceptable level, the print was rinsed in running water for 30 seconds and fixed using sodium thiosulfate fixer (i.e. hypo bath) for a period of 10 minutes. The print was then thoroughly washed for 60 minutes in running water and left to dry [46]. Three samples were aged and remained unsoiled as a reference and nine samples were artificially soiled with dirt and self-adhesive tape. Accelerated aging was applied to the soiled samples in a Binder dry oven with digital indicator, model no. 92403000002000 at the National Institute of Standards (NIS) in Cairo. The aging was conducted at a temperature of 80°C and 65% RH for 10 days, which is equivalent to aging of paper under natural conditions for 50 years. The aging procedure was in conformance with the ISO 5630-3:1996 standard [47]. Mylar templates were made to mark the precise areas on each sample to examine and analyze before treatment and after treatment and artificial aging. FTIR analysis was done on two areas (i.e. Dmin & Dmax) of each sample.

2.1.2. Agarose-based gel systems

Agarose-based gel systems were selected for this study based on their efficiency in

cleaning paper artifacts and other artistic and historical substrates. Agar-based gels are classified as reversible sol-gels; this reversibility is induced by the application of heat [48]. The sol-gel process begins with a colloidal solution (i.e. the sol) that acts as the precursor for an integrated network of polymers (i.e. the gel) [44]. Agar, a polysaccharide complex derived from a species of red algae of the Gelidium family, consists of two polysaccharides: agarose, which forms approx. 70% of the mixture and is responsible for the gelling properties of agar, and agaropectin [48]. Agarose consists of an alternating (1,3) - linked- β -D-galactopyranose and 1,4-linked-3, 6-anhydro- α -L-galactopyranose [49]; while Agaropectin is a complex mixture of low-weight saccharide molecules and contains all the charges units, such as sulfate, pyruvate and carboxilate [50]. Agar powder is available in a number of purities, ranging from highly purified agarose to food grade agar [44]. Agarose forms more transparent gels compared to the cloudy agar gels; however it is very expensive. On the other hand, agar controls the water release efficiently due to the presence of agaropectin which reduces the pore size of the polymer thus retarding the expulsion rate of water from the gel thus making a good humidifier [48]. Advantageously, melting and re-gelification of the gel improves its homogeneity and transparency [50]. Therefore, agar is commonly used for conservation purposes [48]. Agar-based gels are prepared by mixing agar powder and distilled water; then it is heated and cooled [51]. The sol-gel process, gelation, involves the shift of randomly coiled polymer chains in solution to a double helix in the initial stages of gelation, and then agglomerate into a three dimensional network with large pores [52]. The minimum temperature at which the polymeric chains cross-link to

cause gelation is 85°C, and agar-based sols need to be cooled to below 40° C to form the gel [44]. This process is thermo-reversible for several cycles [50]; it can be repeated multiple times without causing a change in the working properties of the gel. Agar-based gels are natural and non-toxic prior to the addition of other cleaning agents. They are stable in both highly alkaline and acidic conditions. The porosity of agar gels depends on the concentration of agarose within the dispersion phase. Accordingly, it is possible to control viscosity, absorption, and dispersion by altering the concentration. The average pore size for a prepared gel between 2-7% (w/v) is typically between 100 and 300 nm. This porosity allows the agar gel to act as a molecular sponge [44]. Agar-based cleaning systems can be applied as a warm viscous fluid (i.e. sol) at a temperature of 50-60° C using a brush or spatula, or as a rigid gel after cooling at room temperature [44,50]. The rigidity of agar is very beneficial for water sensitive surfaces as it has the ability to confine the water action and entrap removed soiling into the gelled matrix itself [53]. It also magnifies the details of the surface on which it is applied thus creating a lens effect which can be useful for conservators to see the magnified details which is not visible to the naked eye [50]. Gelled agar can be cut to the desired shape and size and applied as cleaning poultices. After treatment, the gel pad can be easily peeled off by lifting the edges of the pad. Any small residues will detach from the substrate and spontaneously flake off after drying. Those that do not can be moistened with warm water and brushed off. The gel efficiency can be improved by altering the agar and solvent concentration, the application temperature, the application time and the number of applications on the surface [44]. Lower

concentrations permit a higher degree of water diffusion into the object, while higher concentrations allow a lower degree of water diffusion based on capillary forces [54]. In this study, agarose-based gel was prepared in three concentrations (2, 3, and 4% in distilled water). A weighted amount of agarose powder from Vivantis was placed into a closed vessel filled with a known volume of water, and then the vessel was heated to 85° C using an electric heater. After heating, each concentration is poured in three non-stick molds. Then, for each concentration, a measured amount of solvent was added to the agarose sol-gel and stirred in to achieve homogeneity. One mold of each concentration remained solvent-free. The agarose sol-gels were mixed with ethanol and toluene. The agarose-based formulations were allowed to cool into a rigid gel form of 0.5 cm thickness [44, 50].

2.2. Methods

2.2.1. Treatment application

The resultant sheets of rigid agarose gels were cut into squares with the size of 1×2 cm in order to allow a comparable surface coverage. Samples were pre-humidified in a humidity chamber for 15 minutes. Each sample was placed on a larger piece of Mylar. The gel was then placed on the recto of the samples and covered with another piece of Mylar. To provide some pressure and even contact of the gel to the treated surface, a piece of Plexiglas was placed on top of the sandwich [55]. The contact time was 30 minutes for all samples [48]. The selected concentrations were applied on un-soiled samples and on soiled samples. A blank sample was also prepared and analyzed for comparison. Three samples were studied for each concentration. A total of nine samples were prepared for each gel, fig. (1). One sample was treated with distilled water for comparison. The samples are as shown in tab. (1).

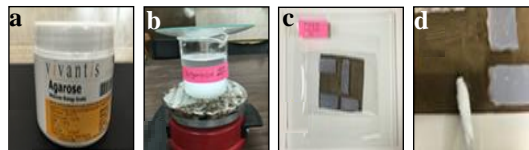


Figure (1) Shows preparation steps of rigid agarose gel sheets and application method. **a.** Vivantis Agarose, **b.** heating the agarose using an electric heater to a temperature of 85°C, **c.** application of the gel pads, **d.** removal of remaining adhesive residues using a cotton swap

Table (1) Treated samples

Conc.	Agarose gel Distilled Water	Agarose gel Ethyl alcohol	Agarose gel Toluene	Distilled water
2%	AG2	AGE2	AGT2	-
3%	AG3	AGE3	AGT3	-
4%	AG4	AGE4	AGT4	-
100%	-	-	-	DW100

2.2.2. Artificial aging

To assess the long-term effects of the selected treatments, the treated samples were exposed to humid heat aging for a period of five days as described in the ISO 5630-3:1996 standard [47].

2.2.3. Assessment methods

2.2.3.1. Visual & microscopic inspection

Resultant changes were documented using a 1000-X ROHS USB Digital Microscope. Examination was carried out at the Conservation dept., Faculty of Archaeology, Cairo University, Egypt.

2.2.3.2. UV fluorescence imaging

The surfaces of the treated albumen prints were visualized under ultra violet light using a Liper UV light bulb, model: HSD.LG, voltage: ~ 220V, power: 36W, frequency: 50Hz.

2.2.3.3. Scanning electron microscope

Microscopic examination was performed using a scanning electron microscope, Model Quanta FEG 250 with accelerating voltage of 20 kV. Samples were not gold-coated. This procedure was carried out at the National Research Center (NRC), Cairo, Egypt.

2.2.3.4. Atomic force microscope

To monitor and analyze the effectiveness of the treatments, the atomic force microscope (AFM) was employed. The atomic force microscope used was a Thermo-microscopes

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 (0.5 cm×0.5 cm) using 20×20 μm² frames. The resolution was 256 by 256 lines at a scan rate of 1 Hz. Proscan 1.8 software was used for controlling the scan parameters and IP 2.1 software was used for image analysis. The images are shown in false color scale, where brighter areas present higher areas. AFM scans were performed on untreated and treated aged samples. AFM utilization 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. The procedure was carried out at the Atomic Force Microscope Laboratory at the National Institute for Standards (NIS), Cairo, Egypt.

2.2.3.5. Colorimetric measurements

The change in color was measured using a MiniScan Model No. EZ MSEZ0693. All samples were measured in a visible region, with an interval of 10 nm using D65 light source and an observed angle of 10 degrees. The CIELAB color parameters (L*, a*, b*) were used, where L* defines lightness and varies from 0 (black) to 100 (white); a* represents the red/green axis, where +a means red and -a means green; b* represents the yellow/blue axis, where +b means yellow and -a means blue. All values of L*, a*, and b* were obtained before treatment and after treatment. The total color difference ΔE^* was also calculated using the following formula: $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$ [56]. Measurements were carried out on a vintage albumen print at the Faculty of Archaeology, Cairo University due to the extreme color change that has occurred in the experimental samples as a result of

artificial aging. The albumen print was photographed by Luigi Fiorillo, a well-known Italian photographer who migrated to Alexandria, Egypt around 1870 and opened a successful photography studio. The image dates back to 1895 and documents the funerary Khanqah of Sultan Al-Nasir Faraj Ibn Barquq which was built from 1400 to 1411 CE. The Khanqah is located in the Northern Cemetery which is a part of Cairo's historic necropolis districts and is considered to be one of the most accomplished works of Mamluk architecture in Cairo. The agarose-based poultices were 0.3 cm thick. A Mylar template was made to mark the precise areas on the image to measure before and after treatment. Ten areas were selected. Each area was measured in triplicate before and after treatment. Agarose-based poultices were applied as described previously. However, a piece of Japanese tissue paper was placed under the gel-based poultices to avoid direct contact with the photographic surface given the fact that it is a valuable photograph. On the other hand, the water treatment was applied using a cotton swab. Visible inspection of the photograph post treatment did not show any sign of surface damage, fig. (2). Nevertheless, the cotton swab and the gel-based poultices were placed in a container for further testing (i.e. ninhydrin test).

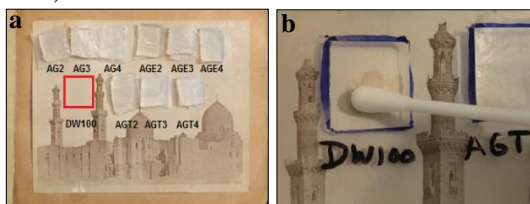


Figure (2) Shows an albumen print of the Mamluk funerary Khanqah of Sultan Al-Nasir Faraj Ibn Barquq (Cairo, Egypt) taken by Luigi Fiorillo in 1895; **a.** application of the agarose-based gel poultices on a vintage albumen print, **b.** application of water treatment using a cotton swab.

2.2.3.6. *Attenuated total reflectance Fourier transform infrared spectroscopy*

FT-IR spectroscopy was used to study the chemical changes which may have occurred after treatment and artificial aging. Spectra were obtained 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 sample preparation was necessary before scanning. The analysis was carried out at the National Institute of Standards (NIS) in Cairo, Egypt.

2.2.3.7. *pH value measurements*

The pH values were measured according to the cold extraction method described in TAPPI T 509 using a martini Mi 180 Bench Meter provided with a micro electrode. 1 gm of each sample was immersed in 70 ml of water for 1 hour in room temperature [57]. Measurements were carried out in triplicates before aging and after treatment and aging. The measurements were carried out at the National Institute of Standards (NIS) in Cairo, Egypt.

2.2.3.8. *Ninhydrin test*

Ninhydrin is used to detect the presence of proteins as it produces a deep violet resonance-stabilized anion called Ruhemann's purple when it reacts with any amino acid [58]. The test was used to determine if the tested treatments negatively affect the albumen binder layer. The ninhydrin reagent was prepared by dissolving 1.25 gm of ninhydrin crystals in 200 ml of acetone [59]. To perform the test, one drop of the reagent was placed on the cotton swab in the case of

the water treatment and on the poultices in the case of the gel-based treatments. The swab and poultices were briefly exposed to heat (i.e. hair dryer) for the color to appear [60]. Gloves must be worn during the test, as the resulting stains are difficult to remove. Test was carried out on Fiorillo's albumen print from Francis Amin's collection.

2.2.3.9. *Mechanical testing*

The influences of the treatments were also examined in terms of changes in the mechanical properties of the samples before and after treatment and aging. Results were expressed by tensile strength and elongation. Tensile strength is indicative of fiber strength, fiber bonding and fiber length. The tensile strength of a paper-based object is the maximum force per unit width that the paper strip can resist before breaking when applying the load in the direction parallel to the length of the strip [61]. Elongation is the ability of materials to increase its linear length under the action of external mechanical forces; the increase of linear length is attributed to elastic and plastic deformations [62]. The mechanical behaviour of the samples were studied using the dynamometer produced by SDL ATLAS, H5KT according to TAPPI T 494. Samples were cut in the machine direction to strips of 2.5 cm × 18 cm [63]. The results reported are the average of three measurements. This study was carried out at the National Institute of Standards (NIS), Cairo, Egypt.

2.2.3.10. *Thickness measurements*

Five thickness measurements were made for each treated and aged sample using a 0.001 mm High Accuracy BY02 Digital Thickness Gauge Meter with a measuring range of 0~12.7 mm and compared to the thickness of the control sample. Measurements were carried out at the National Institute of Standards (NIS), Cairo, Egypt.

2.2.3.11. Fungal testing

Microbiological studies were conducted at the Microbiology Lab, Faculty of Archaeology, Cairo University, Egypt to detect the presence of microorganisms on albumen prints post gel treatment. 3M™ Petrifilm™ Yeast and Mold Count Plates (3M Company, Minneapolis, Minn.) were used since they are sample-ready selective culture systems that are marketed for rapid yeast mold isolation [64]. These Petrifilm plates contain nutrients, antibiotics, and a water-soluble gelling agent. Mold colonies on these plates can be distinguished by variably-colored colonies with foci and distorted edges, where yeasts appear as blue-green colonies with defined edges and no foci [65]. The procedure involved spreading 1 mL of dis-tilled water on the gel. The plates were then inoculated by placing them in contact with the treated samples and a control sample. The plates were incubated at a temperature of 25°C for 5 days [66].

3. Results

3.1. Visual and microscopic inspection

The samples treated with agarose/distilled water poultices (i.e. AG2, AG3, and AG4) showed good results in terms of dirt removal, and as expected poor results were obtained for adhesive removal. Sample AG4 was the most efficient in dirt removal. All samples showed slight curling post treatment. On the other hand, samples treated with agarose/ ethyl alcohol poultices (i.e. AGE2, AGE3, and AGE4) showed good results for dirt and adhesive removal without causing apparent surface changes. Samples treated by agarose/ toluene poultices showed the best results for adhesive removal, particularly sample AGT4. Conventional cleaning of albumen prints using distilled water resulted in the curling of the sample, fig. (3). Surface modification was only observed in the

case of the water treated sample which exhibits cracking. On the other hand, no cracking or any other surface changes were observed in the case of the gel treated samples as revealed through microscopic examination, fig. (4).



Figure (3) Shows; **left** sample treated with 100 % solution of distilled water, **right** samples post gel-based treatments and artificial aging.

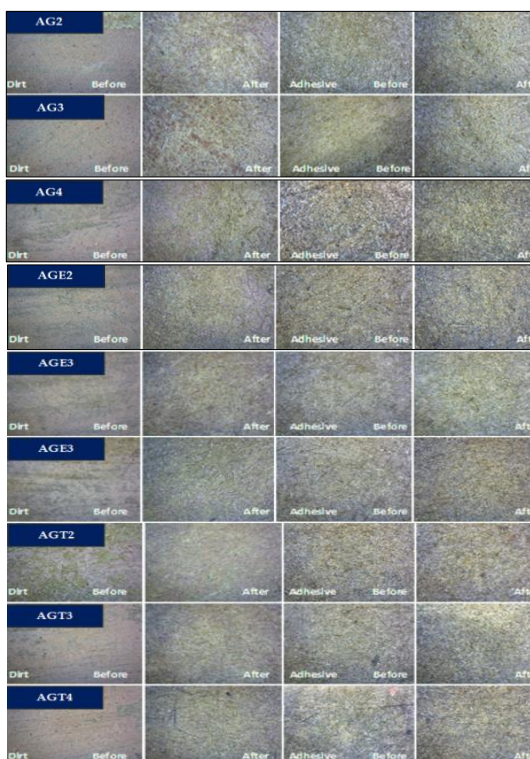


Figure (4) Shows surface examination of all treated samples with a USB digital microscope.

3.2. UV fluorescence imaging

The removal of agarose-based gels from the photographic surfaces was extremely simple and did not leave any residues as confirmed by surface examination under UV light, fig. (5).

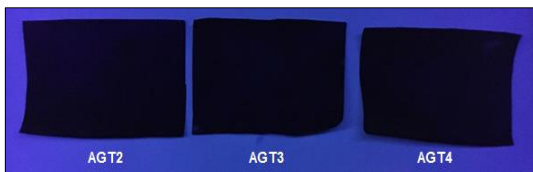


Figure (5) Shows surface examination of photographic surfaces under UV light.

3.3. Scanning electron microscope

SEM images of the photographic samples after treatment and artificial aging show severe cracking in the case of the water-treated sample DW100 compared to the other samples treated with the agarose-based formulations at 250-x magnification. SEM image for sample AG4 treated with agarose gel poultice reveals the treatment efficiency in the removal of dirt particles, and satisfactory results were obtained for the removal of the adhesive residues using the agarose gel/toluene poultice on sample AGT4, fig. (6-a,b,c,d). Cracking is a typical microscopic characteristic of albumen prints [4], fig. (7-a,b,c,d,e,f). All albumen prints exhibit similar network of surface micro-cracks due to the several cycles of wetting and drying they go through during manufacture [67]. The albumen binder layer does not expand in the same manner as the primary paper support as the former exhibits behavior characteristic to denatured, filtered, egg albumen: it shrinks and curls; and this causes strain in the albumen later, creating cracks. Average crack width is approx. 10 μm [4]. Crack width measurement results for the treated albumen surfaces show an increase in the number and dimensions of minute cracks post water treatment compared to the pre-existent cracks found in the control sample, fig. (7-a). The cracks measure approx. 10-15 μm in width. However, although agarose gel poultices contain water, a decrease in crack width is observed, compared to water treatment, with cracks measuring approx. 6-12 μm . On the other hand, agarose gel/ solvent

treated samples show a decrease in both crack width and number, compared to water treatment, with cracks measuring 4-8 μm , fig. (7). Crack width measurement

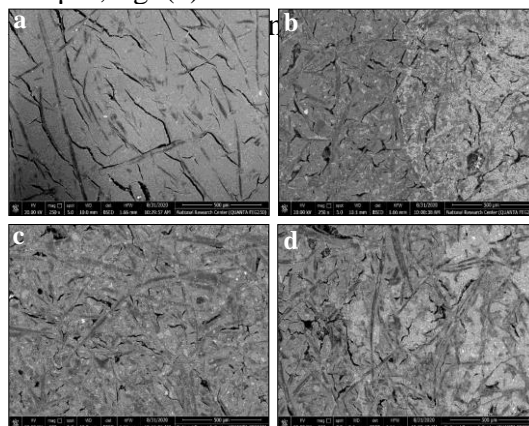


Figure (6) Shows SEM images; of the surface of the treated samples after artificial aging at 250-X; **a.** water treatment, **b.** agarose gel poultice, **c.** agarose gel+ethanol poultice, **d.** agarose gel+toluene poultice

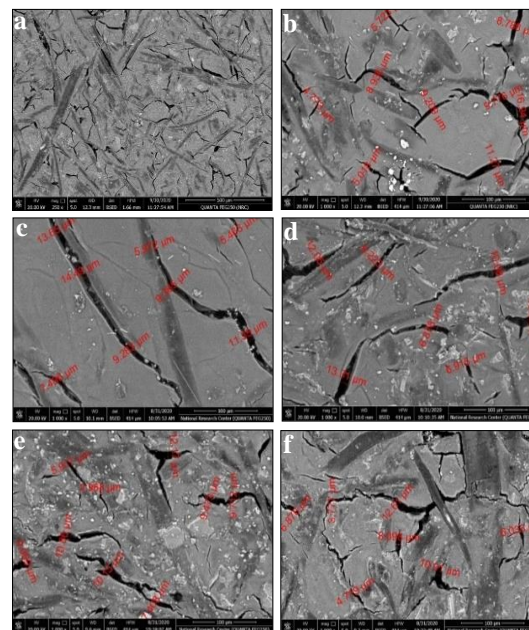


Figure (7) Shows SEM images; **a.** albumen print sample before treatment at 250-X, **b.** 1000-X and the photographic surfaces of the treated albumen print samples after treatment and artificial aging at 1000-X magnification showing the cracks width measurements; **c.** Water treatment (DW 100), **d.** Agarose gel poultice (AG4), **e.** Agarose gel+ethanol poultice (AGE4), **f.** Agarose gel+toluene poultice (AGT4).

Table (2) Crack width measurements of treated albumen photographic surfaces compared to untreated sample

Treatment	Crack width (nm)
Control sample (untreated, aged)	9.20
	8.93
	5.72
Water-treated sample (DW100) (treated, aged)	14.49
	13.65
	11.35
Agarose gel treated sample (AG4) (treated, aged)	10.08
	8.22
Agarose gel/ethanol treated sample (AGE4) (treated, aged)	6.91
	10.13
	7.40
Agarose gel/toluene treated sample (AGT4) (treated, aged)	5.91
	8.08
	6.87
	4.71

3.4. Atomic force microscope

The 2D AFM images across the scanned area of $20 \times 20 \mu\text{m}^2$ of the control sample and treated albumen surfaces show a surface with linear aggregation of particles. The size of the agglomerate is big compared to other photographic processes (i.e. silver gelatin prints) and presents linear and circular patterns. The white spots in the surface micrographs indicate elevated regions, fig. (8) [68]. 3D AFM examination results show that agarose gel and agarose gel/toluene treated samples have a smoother surface compared to the control sample and water and agarose gel/ethanol treated samples. 3D AFM image for the agarose gel/ethanol treated samples revealed a rough surface topography, fig. (9). However, surface roughness results, tab. (3) indicate that the surface roughness has increased for the water-treated albumen surface, decreased for the agarose gel and agarose gel/ethanol treated albumen surface and remained the same for the agarose gel/toluene treated albumen surface.

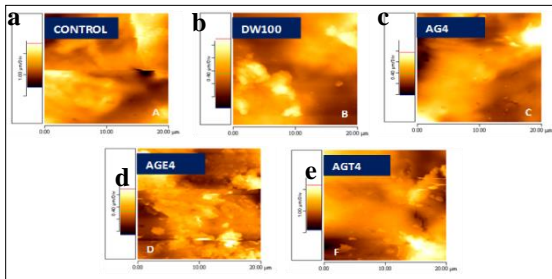


Figure (8) Shows 2D AFM images of surface areas of $20 \times 20 \mu\text{m}^2$; **a.** control sample, and treated surfaces by **b.** water, **c.** agarose gel, **d.** ag-arse gel/ethanol, **e.** agarose gel/ toluene.

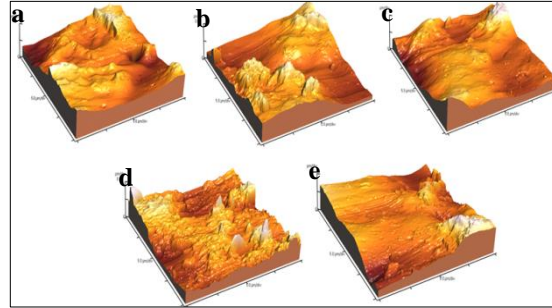


Figure (9) Shows 3D AFM images of surface areas of $20 \times 20 \mu\text{m}^2$; **a.** control sample, and treated surfaces by **b.** water, **c.** agarose gel, **d.** agarose gel/ethanol, **e.** agarose gel/ toluene.

Table (3) Roughness values in different parameters for control sample and treated albumen surfaces

Samples/treatments	Rq (nm)	Ra (nm)
Control sample (untreated, aged)	348.8	271.2
Water-treated sample (DW100) (treated, aged)	360.6	311
Agarose gel treated sample (AG4) (treated, aged)	262.5	206.6
Agarose gel/ethanol treated sample (AGE4) (treated, aged)	253.4	201.6
Agarose gel/toluene treated sample (AGT4) (treated, aged)	346.8	267.5

3.5. Colorimetric measurements

An important issue of conservation treatments is the impact of the treatment on the original color of the object treated. The total color difference, ΔE^* , is a value useful as an indicator of the difference between a sample and a reference. Evaluation of ΔE^* according to DIN EN ISO 53230 (super ceded by BS EN ISO 4628-1:2004) is as follows: 0-1: not perceptible difference; 1-2: minimal color difference; 2-4: visible color difference; 4-5: great color difference; and >5 : extreme color difference [69]. Based on the obtained results, all treated samples showed ΔE^* values below the threshold limit ($\Delta E^* = 5$) required for the maintenance and restoration of historic surfaces as listed in tab (4) [70]. Nevertheless, most treated samples showed no visible color difference, while the agarose gel/ethanol treated samples (i.e. 3% and 4%) and the agarose gel/toluene treated samples (i.e. 3% and 4%) showed minimal color difference. Total color difference representations shown in tab. (4) were obtained using the *ColorMine Delta-E calculator*.

Table (4) Results of the colorimetric study obtained for treated samples

Samples/treatments	Colorimetric measurements								
	Before			Color	After			Color	ΔE^*
	L*	a*	b*		L*	a*	b*		
Water-treated sample (DW100) (treated, un-aged)	70.76	3.64	14.38		70.92	3.68	14.54		0.23
Agarose gel treated sample (AG2) (treated, un-aged)	73.48	3.52	14.92		73.29	3.60	15.18		0.33
Agarose gel treated sample (AG3) (treated, un-aged)	71.71	3.74	14.95		71.46	3.83	15.15		0.33
Agarose gel treated sample (AG4) (treated, un-aged)	72.01	3.68	14.87		71.85	3.69	15.25		0.41
Agarose gel/ethanol treated sample (AGE2) (treated, un-aged)	72.07	3.83	14.89		72.80	3.96	14.80		0.75
Agarose gel/ethanol treated sample (AGE3) (treated, un-aged)	71.27	3.81	15.45		72.49	3.84	15.52		1.22
Agarose gel/ethanol treated sample (AGE4) (treated, un-aged)	71.04	3.98	15.31		72.08	3.91	15.97		1.23
Agarose gel/toluene treated sample (AGT2) (treated, un-aged)	71.11	3.67	14.76		72.03	3.72	14.86		0.93
Agarose gel/toluene treated sample (AGT3) (treated, un-aged)	70.84	3.47	14.70		72.06	3.61	15.01		1.27
Agarose gel/toluene treated sample (AGT4) (treated, un-aged)	71.54	3.55	14.98		73.01	3.61	15.31		1.51

3.6. FT-IR spectroscopy

As indicated previously, albumen is a protein characterized by the presence of amide groups, namely, amide I and amide II bands of the peptide bonds located at ~ 1650 and 1550 cm^{-1} , respectively [4]. The amide I corresponds to the vibrations of the C=O group with very minor contributions of the C-N groups, and the amide II band originates from the in-plane N-H bending, along with both the C-N stretching vibrations and the C-C stretching vibrations [71]. The spectra also show the presence of a broad band at $\sim 3400 \text{ cm}^{-1}$, which is assigned to the N-H and hydrogen bonded O-H stretching vibrational frequencies [72]. The band at $2800\text{-}3000 \text{ cm}^{-1}$ is assigned to C-H stretch region of the FTIR spectrum, while the band at $1000\text{-}1200 \text{ cm}^{-1}$ is assigned to the C-O stretching region [73]. There are no notice-

able changes in the FTIR spectra of the treated albumen surfaces indicating that all treatments did not cause changes in chemical structure of the binder layer. A minor change was observed in the intensity of the O-H stretching band in albumen surfaces treated with agarose gel poultices excluding the agarose gel/toluene treated samples, fig. (10). The absence or presence of agarose residues on albumen surfaces treated with agarose gel and agarose/solvent gels could not be confirmed since agarose also gives rise to O-H stretching vibrations, C-H stretching vibrations and C-O stretching vibrations at wave numbers similar to albumen prints [74]. Accordingly, further testing was required to determine if the tested agarose gel treatments induce microbial growth on the surface of albumen prints.

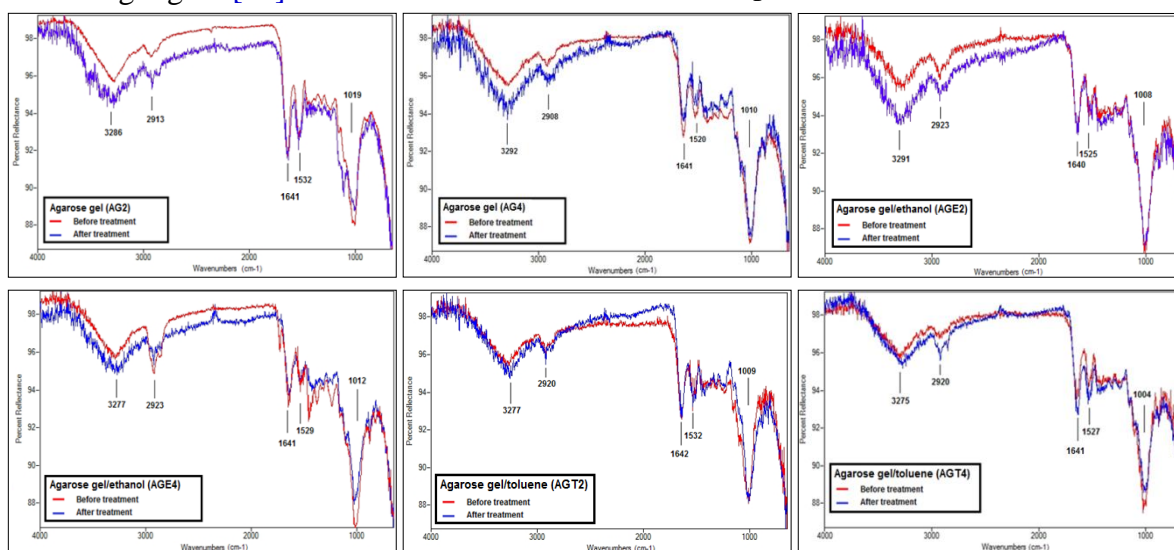


Figure (10) Shows ATR-FTIR spectra of the image layer of the albumen prints before treatment (red) and after treatment and artificial aging (blue).

3.7. pH value measurements

The pH value of the control sample was 8.57 and a very slight change was observed for all treated samples. Results are listed in tab. (5).

Table (5) pH value measurements for control sample and treated albumen surfaces

Samples/treatments	pH value
Control sample (untreated, aged)	8.57
Water-treated sample (DW100) (treated, aged)	8.55
Agarose gel treated sample (AG4) (treated, aged)	8.63
Agarose gel/ethanol treated sample (AGE4) (treated, aged)	8.62
Agarose gel/toluene treated sample (AGT4) (treated, aged)	8.63

3.8. Ninhydrin test

Results of Ninhydrin test listed in, tab. (6), where (+) refers to the least affected and (++) refers to the most affected. Based on these results, no change was observed in agarose-based gel treatments, while the sample treated with water showed a purple color. The test was also performed on a control sample to ensure that the test was being conducted correctly, fig. (11).

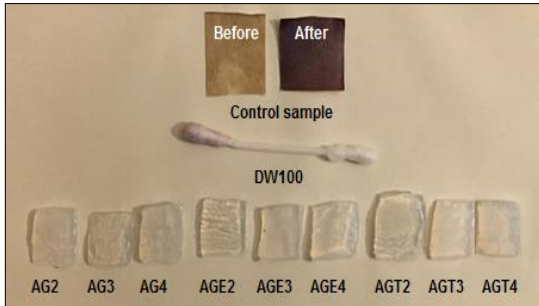


Figure (11) Shows Ninhydrin test results

3.9. Mechanical testing

The changes in mechanical properties (i.e. tensile strength and elongation) representing long-term effects of the investigated cleaning treatments are illustrated in the following diagram, fig. (12). The water treated sample DW100 showed a great decrease in tensile strength and elongation compared to the control sample, while all gel-treated samples showed a slight change in both tensile strength and elongation compared to the control sample. The least change was observed in the case of the agarose-treated sample.

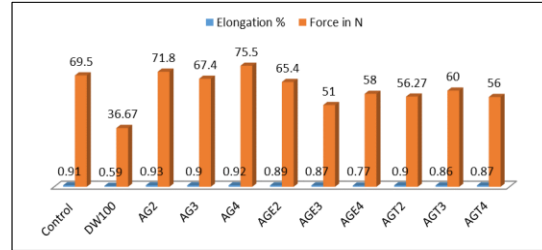


Figure (12) Shows tensile force (Fmax) and elongation (%) diagram comparing treated and aged samples to the control sample.

3.10. Thickness measurements

The thickness of the prints after treatment and aging tab. (7) proved that the change ranged from no change for the gel-based treatments to slight change in the case of the water-treated sample.

Table (7) Change in sample thickness after treatment and artificial aging

Samples/treatments	Measurements					Average
	1	2	3	4	5	
Control sample (untreated, aged)	0.191	0.190	0.191	0.193	0.196	0.192
Water-treated sample (DW100) (treated, aged)	0.186	0.191	0.191	0.188	0.190	0.189
Agarose gel treated sample (AG2) (treated, aged)	0.192	0.189	0.192	0.193	0.191	0.191
Agarose gel treated sample (AG3) (treated, aged)	0.191	0.196	0.194	0.192	0.189	0.192
Agarose gel treated sample (AG4) (treated, aged)	0.196	0.192	0.189	0.190	0.191	0.191
Agarose gel/ethanol treated sample (AGE2) (treated, aged)	0.193	0.190	0.189	0.191	0.192	0.191
Agarose gel/ethanol treated sample (AGE3) (treated, aged)	0.195	0.192	0.190	0.192	0.191	0.192
Agarose gel/ethanol treated sample (AGE4) (treated, aged)	0.192	0.191	0.192	0.191	0.194	0.192
Agarose gel/toluene treated sample (AGT2) (treated, aged)	0.194	0.192	0.190	0.193	0.191	0.192
Agarose gel/toluene treated sample (AGT3) (treated, aged)	0.191	0.189	0.194	0.194	0.192	0.192
Agarose gel/toluene treated sample (AGT4) (treated, aged)	0.192	0.192	0.191	0.192	0.193	0.192

3.11. Fungal testing

Visually and microscopically speaking, no agarose gel residues were observed on the treated albumen surfaces. Moreover, one can neither confirm nor deny their presence by means of ATR-FTIR spectroscopy as pointed out earlier. However, three days after the application of selected treatments, all 0.5 cm thick agarose-based gel poultices used for surface cleaning the experimental samples showed visible signs of mold growth as expected. This issue did not show up in the case of the 0.3 cm thick agarose-based gel poultices applied on the vintage albumen print. In view of that, microbiological studies were carried out six months post treatment application to isolate fungi that may be present on treated albumen surfaces. After two days, two small circle of mold growth began to form in the water-treated sample Petrifilm plate. Colonies were obtained after 5 days, fig. (13).

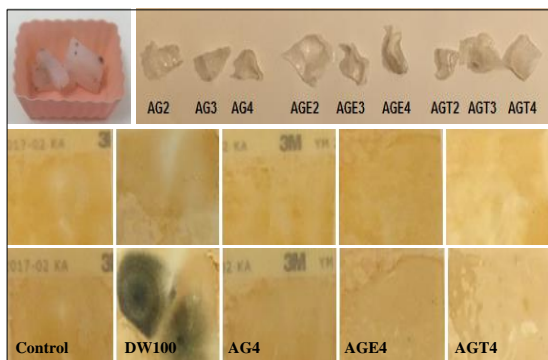


Figure (13). Shows fungal growth on agarose gel poultrices (**top**). The inoculated Petrifilm plates (**center**) and the formation of mold growth after 5 days at 25 °C (**bottom**).

4. Discussion

Gel-based systems have been successfully used in surface cleaning different types of materials of significant value. However, it wasn't until recently that a reference evaluated the use of gellan gum hydrogel for the treatment of 19th century albumen prints; and results showed that this gel-based treatment has significantly enhanced the cracking of the albumen layer [75]. In search for a more delicate alternative method, the author selected agarose-based gel systems. The agarose-based gel was prepared in three concentrations (2, 3, and 4% in distilled water). For each concentration, agarose gel/solvent formulations were also prepared by adding a measured amount of solvent (i.e., ethyl alcohol and toluene) to the agarose sol-gel. The resultant gel was applied in the form of a poultice for a period of 30 minutes. Visual and microscopic inspection results showed the efficiency of agarose gel-based systems in removing common surface deposits such as dirt and adhesive residues. Solvents are to be selected according to the type of dirt or stain. Since the agarose gel-based poultices allow for the gradual release of solvents limiting its penetration, they have limited the formation of new cracks and the increase of the width of pre-existent cracks as observed in the SEM images. The use of a polar

solvent (i.e., ethyl alcohol) affected the surface roughness of the albumen binder layer based on the obtained 3D AFM image; this may be attributed to the dehydration of the sample. On the other hand, a non-polar solvent (i.e., toluene) preserved the surface roughness based on the obtained 3D AFM image and measurements of the surface roughness parameters Ra and Rq listed in tab. (3). Color change is not an issue here since the total color difference (ΔE^*) caused by all tested treatments is within the accepted limit. However, for comparison purpose, agarose/solvent gel-based poultice caused minimal color change that requires skilled eyes to be observed. The main concern for conserve-ators with regard to gel-based treatments is that many tend to leave residues on treated surfaces. ATR-FTIR analysis was not helpful to detect the presence of residues on the surface since both the binder and the gel-based systems give rise to O–H stretching vibrations, C–H stretching vibrations and C–O stretching vibrations. Accordingly, further analysis and examination were required. Surface examination under UV light showed no residues for all tested gel-based systems. The fungal testing confirmed the validity of the previous results. This finding was expected since agarose-based formulations form rigid gels. In terms of chemical change, ATR-FTIR results showed insignificant change in all treatments. The minor change in the intensity of the O-H stretching band in albumen surfaces treated with agarose gel poultices and the agarose gel/ethanol treated samples may be attributed to the introduction of water to the surface, which means more hydrogen bonding [73]. The pH value measurements supported all tested treatments. On the other hand, the ninhydrin test results and thickness measurements were in favour of the agarose gel-based poultices. The ninhydrin test reveals if the albumen binder layer has been affected by the used treatment. With regard to mechanical testing, the mechanical behavior of paper is known to be very com-

plicated [76]. The tensile properties (i.e. tensile strength and elongation) of paper-based materials are strongly affected by their moisture content. The tensile strength of paper-based materials generally decreases when they are exposed to high humidity [76,77]. Water also causes the elongation of paper to decrease [78]. Organic solvents tend to swell cellulose less than water: ethanol (83%) and toluene (2%) [79]. This explains the decrease in tensile strength and elongation for the water treated sample as opposed to the gel-treated samples which showed a slight change in both tensile strength and elongation compared to the control sample. The results obtained through this study is promising; however, further studies are required using different exposure time periods, different additives, and new gels.

5. Conclusion

Agarose gel/distilled water without and with a solvent (i.e. ethanol or toluene) poultices were prepared in three concentrations (i.e. 2%, 3%, and 4%) for testing the possibility of their use to surface clean albumen prints as an alternative to the conventional water treatment used by photograph conservators since the later treatment is known for its damaging effect, particularly in increasing the cracks commonly found in this type of photographic prints. The efficiency of the agarose-based gel treatments in removing surface dirt and adhesive has been evaluated as well as their long-term effects on treated albumen surfaces using visual inspection, UV fluorescence imaging, digital microscopy, scanning electron microscopy (SEM), atomic force microscope (AFM), Fourier transform infrared spectroscopy (FTIR), colorimetric measurements, pH value measurements, ninhydrin test, mechanical testing, thickness measurements, and fungal testing. A sample was treated with distilled water for comparison. Visual and microscopic inspection show the efficiency of the agarose gel/distilled water and to some extent the agarose gel/ ethanol poultices in removing surface dirt, particularly at the concentration of 4%. Adhesive residues were efficiently removed by the agarose gel/ toluene poultices. However, in all cases, agarose-based gel treatments were followed by gentle mechanical cleaning using cotton swabs to remove the remaining soil. All samples showed slight curling post treatment. The removal of agarose-based gels from the photographic

surfaces was extremely simple and did not leave any residues as confirmed by surface examination under UV light. Crack width measurement results for the treated albumen surfaces show an increase in the number and dimensions of minute cracks post water treatment compared to the control sample. On the other hand, the crack widths were not slightly affected in the case of the agarose gel-based treatments. AFM results show that the surface roughness has increased for the water-treated albumen surface, decreased for the agarose gel and agarose gel/ethanol treated albumen surfaces and remained the same for the agarose gel/ toluene treated albumen surface. Colorimetric measurements for all treated samples showed ΔE^ values below the threshold limit ($\Delta E^* = 5$) required for the maintenance and restoration of historic surfaces. The pH value and thickness measurements show insignificant change. In terms of chemical change, ATR-FTIR results show unnoticeable changes in the spectra of all the treated albumen surfaces. The albumen binder has been disturbed by the water treatment as indicated by the ninhydrin test. The change in mechanical properties (i.e. tensile strength and elongation) was significant in the case of the water-treated sample. Minor change was observed in the case of the agarose-based gel treatments. Based on the results of the microbiological studies, no fungal growths were observed for the agarose-based gel treated samples. Accordingly, the tested agarose-based cleaning systems are less aggressive than the water treatment conventionally used to clean albumen prints. Nevertheless, toluene poses a threat to human health, a fact that must be taken into consideration.*

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