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ACIDIFIED MOUNTED SILVER GELATIN PRINTS: EVALUATION OF THE EFFICIENCY OF NEW AND CONVENTIONAL TREATMENTS

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Abstract

Acid-attack is the main enemy of paper-based materials, including photographic materials. Accordingly, the primary aim of this study is to evaluate the efficacy of different deacidification methods in decreasing the acidity level in mounted silver gelatin prints, as well as to study their effect on the properties of such unique photographs. Selected methods include the use of conventional methods (i.e., calcium carbonate and barium hydroxide) and new methods (i.e., calcium carbonate and barium hydroxide loaded on gellan gum gel, and magnesium hydroxide nanoparticles). Several testing methods have been employed such as: USB digital microscope, scanning electron microscope (SEM), pH value measurements, and Fourier transform infrared spectroscopy (FTIR). The obtained results indicate that the gellan gum gel loaded with barium hydroxide treatment yielded the best results compared to the other treatments, in terms of efficiency and having the lowest effect on the properties of the acidified mounted silver gelatin prints.

Keywords: Acidity; Mounted silver gelatin prints; Deacidification; SEM; pH measurement; FTIR

Introduction

Photographs are an essential part of the Egyptian cultural heritage for their historical, social, and artistic value and as documentary tools, as well as records of the history of photography [1].

Silver gelatin prints were considered the classic form of black-and-white photography in the 20th century [2]. Silver gelatin prints were either printed-out (POP) or developed-out (DOP). DOP silver gelatin prints form an essential part of photographic collections since they exist in large numbers in archival collections in museums, libraries, and archives worldwide [3]. A developed-out silver gelatin print comprises a primary support material, paper; a baryta coating, a finely ground white barium sulfate in gelatin; a binder, gelatin; and the image forming substance, filamentary silver grains [4]. In many cases, photographs are mounted on a secondary support, the original mount [5].

The lifespan of silver gelatin prints is greatly affected by many factors, such as natural decay, poor processing, improper or fluctuating temperature and relative humidity levels, light, biological threats, inappropriate handling and misuse, atmospheric pollutants, and inappropriate

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display and storage materials [6]. These factors can lead to deterioration and/or degradation ranging from mild to severe. Acid is a common cause of damage to photographs with their high cellulose content [7].

Paper is one of the most common primary support materials used for positive images. It was introduced in 1840 for use in making salt prints and is still in use today [5, /8]. In the early 1900s, photographic paper was made almost entirely from rag pulp (i.e., linen or cotton). In 1923, 75% rag fiber and 25% sulfite pulp were used for making photographic paper. In 1924, paper was made using 75% rag fiber and 25% alpha cellulose pulp [9]. In 1929, highly purified, 100% wood cellulose was produced. Paper was sized with gelatin, starch or rosin solutions in the 19th century. In 1926, sodium stearate was used as a sizing agent. In 1885, baryta-coated paper was used for photographic purposes [10]. By 1931, all raw paper bases, with one exception, had been converted to 100% high alpha wood pulp and stearic acid sizing [9]. The secondary support involves both the mount itself and an adhesive. Many mounts are composed of a laminate of good quality top and bottom sheets with a center which contained highly lignified fibers. Starch, gelatin, and sulfur-containing adhesives such as rubber cement were used such as adhesives [5].

Paper is a multi-component material with a structure that depends considerably on the manufacturing process and raw materials used. In all cases, cellulose is the main component of paper. Cellulosic fibers form three-dimensional structures, whose molecules are linear polymers of β -D–glucopyranose monomers linked by β -1, 4–glycoside bonds. In addition to cellulose, the paper may also contain hemicelluloses, lignin, and additives (i.e., binders, inorganic fillers, dyes, pigments, metal ions, etc.) in varying amounts, depending on the cellulose source and the intended use of the material [11]. Rags make strong paper structures due to their long cellulose chains (i.e., a degree of polymerization around 3500 for linen and 1000–3000 for cotton), where the chains are tightly bound into the fibrils and fibers by extensive hydrogen bonding, as opposed to wood pulp which produces paper with shorter cellulose chains (i.e., a degree of polymerization around 600–1000) and a weaker structure [12].

The main causes of paper degradation are hydrolysis and oxidation. These are inherent in the natural polymer but can be significantly accelerated by factors such as additives, temperature, relative humidity, light, pollution, poor-quality display and storage materials and others. Cellulose, its derivatives and lignin are all susceptible to oxidation. Lignin, hemicellulose and hydrolyzed cellulose (i.e., all basic to the cellular structure of wood pulp) oxidize and produce substantial amounts of acidic degradation products [13]. In cellulose, the hydroxyl groups are oxidized to aldehydes, ketones and carboxylic acids, causing the paper to discolor. On the other hand, lignin is responsible for the distinctive yellowing of paper since it contains several chromophores with conjugated aromatic rings and carbonyl groups, these chromophores absorb light and can decompose into yellow-colored ketones and quinones. Moreover, these molecules act as secondary chromophores and can react further, exacerbating the yellowing and degradation processes. For this reason, paper made from rags degrades slower than wood pulp paper [12]. Additives added during the manufacturing process (i.e., rosin-alum) result in the formation of oxidizing agents and provide a source of acid, leading to acid-catalyzed hydrolysis. As a result, the paper becomes severely fragile and yellow [13]. On this basis, discoloration and loss of strength are significant indicators for the chemical stability of paper.

Deacidification, using aqueous or nonaqueous chemical treatments, mainly aims at decreasing the rates of acid-catalyzed hydrolysis and other changes leading to embrittlement in paper-based materials by neutralizing acids and depositing a buffer in the paper that will protect it from the formation of acid in the future [14]. This article focuses on assessing the efficiency of selected deacidification methods in reducing the acidity of mounted silver gelatin prints and evaluating their effect on their properties. Selected methods include the use of conventional

methods (i.e., calcium carbonate and barium hydroxide) and new methods (i.e., calcium carbonate and barium hydroxide loaded on gellan gum gel, and magnesium hydroxide nanoparticles).

Calcium carbonate is one of the most abundant materials [15], and it is considered as a leading candidate for deacidification in terms of its chemical simplicity, relatively low cost, high brightness, and suitability for use as a paper filler. However, CaCO₃ and carbonates in general tend to be insoluble in neutral water as well as in organic solvents, a factor that limits its manner of distribution in paper-based artifacts. Although that magnesium carbonate was found to impart a higher pH than calcium carbonate [16], it was also found to cause accelerated aging of pure cellulose paper, whereas calcium carbonate did not [17]. It is known, however, that some precipitated CaCO₃ products contain some residual calcium hydroxide (Ca (OH)₂), such that when they are equilibrated with water the pH can rise well above 9. By contrast, relatively pure calcium carbonate products, as well as essentially all limestone and chalk products tend to buffer the pH in a more moderate range of about 7.5 to 8.5 [18]. Barium hydroxide is used in analytical chemistry to titrate weak acids, particularly organic acids. It forms clear aqueous solutions that are free from carbonate, unlike those of the alkali hydroxides since barium carbonate is insoluble in water. This allows the use of indicators such as phenolphthalein or thymophthalein without the risk of titration errors due to the presence of weakly basic CO_3^{-2} ions [19]. Barium hydroxide (Ba (OH)₂) has been used as an alkaline agent, primarily in non-aqueous deacidification, and it is reported that the British Museum had used Ba(OH)₂ for deacidification as early as 1890 with the primary disadvantage that the barium hydroxide solute is toxic [18].

Gellan gum is a high molecular mass polysaccharide gum produced by a pure culture fermentation of carbohydrates by Pseudomonas elodea, purified by recovery with isopropyl alcohol, dried, and milled. With a molecular mass of approximately 500 000, it consists of approximately glucose 60 %, rhamnose 20 % and glucuronic acid 20 %. There are three types of gellan gum: 1) native gellan gum which consists of a backbone of repeating unit of b-1,3-D-glucose, b-1,4-D-glucuronic acid, b-1,3- D-glucose, a-1,4-L-rhamnose, and two acyl groups, acetate and glycerate, bound to glucose residue adjacent to glucuronic acid; 2) acetylated gellan gum which is produced by removing The acetyl groups in native gellan gum by alkaline treatment; and 3) clarified gellan gum which is produced by filtering hot, deacetylated gellan gum for enhanced removal of cell protein residue [19]. Gelling agents are used in surface cleaning artifacts, particularly, fragile objects which are highly water-sensitive, to increase the viscosity of water by means of hydrophilic polymers. The disadvantage of this method is that it tends to leave gel residues on the surface and accordingly requires a clearing rinse with water. To overcome this issue, Richard Wolbers developed the so-called rigid gels which do not require any treatment afterwards due to the rigid gels' physical form and limited adhesive strength [20].

In the last few decades, nanomaterials have received particular attention in the field of cultural heritage conservation due to their unique properties. Nanomaterials (1–100 nm) with higher surface areas than similar larger-scale materials have the possibility to penetrate deep into the damaged artifacts due to their particle size. The efficacy of these nanoparticles has been tested on different materials [21]. In this article, magnesium hydroxide nanoparticles, Mg(OH)₂NPS, were explored as an effective material in the deacidification of acidified mounted silver gelatin prints. This treatment was found to preserve the mechanical properties of paper; gave a higher efficacy in the deacidification treatment; are less aggressive since they are easily converted into the carbonate; can be applied by spraying, brushing, and immersion; their use does not require any special safety procedures; the method is environmentally safe; and cheaper than the conventional methods for paper deacidification [22].

For scientific assessment of previous treatments, several testing methods have been employed such as: USB digital microscope, scanning electron microscope (SEM), pH value measurements, and Fourier transform infrared spectroscopy (FTIR).

Experimental part

Materials

A silver and gelatin print dating back to the 20th century suffering from high acidity was selected for this study as shown in Figure 1. The print was cut into several samples in different sizes according to the application of the materials as well as the types of tests and analysis as shown in Table 1.



Fig. 1. Sample preparation

Table 1. The samples prepared for this study

Tests	Sample size	Number of samples
USB	$5 \times 5 \text{ cm}^2$	12 (6 rectos & 6 versos)
pН	$7 \times 2.5 \text{ cm}^2$	12 (6 rectos & 6 versos)
SEM	$2 \times 2 \text{ cm}^2$	12 (6 rectos & 6 versos)
FTIR	$2 \times 2 \text{ cm}^2$	12 (6 rectos & 6 versos)

Both conventional and modern materials were selected for this study. Conventional materials included: barium hydroxide and calcium carbonate, which were applied loaded on gellan gum and by brush. Novel materials included: magnesium hydroxide nanoparticles, which was also loaded on gellan gum.

Methods

Preparation methods

Preparation of gellan gum gel: 4g of calcium acetate were added in two stages to 30g of gellan gum, also added in two stages to 1000 ml of distilled water. The mixture was heated using a Bunsen burner flame to a temperature of 80°C [22], after which the resultant gel was poured into Petri dishes and sterilized with alcohol for protection against fungal infection as shown in Figure 2.



Fig. 2. Preparation of gellan gum gel

Preparation for barium hydroxide: 2.5 g of barium hydroxide were added to 500 mL of ethyl alcohol and well stirred as shown in Figure 3.



Fig. 3. Preparation of barium hydroxide

Preparation of calcium carbonate: Similarly, 2.5g of calcium carbonate were added to 500 millimeters of distilled water, and well stirred.

Preparation of magnesium hydroxide nanoparticles: 4g of magnesium oxide nanoparticles were added in two stages to 500 millimeters of distilled water, and well stirred and flipped. (Fig. 6).

Application methods

Application of gellan gum gel with barium hydroxide dispersion: In this method, the barium hydroxide dispersion was loaded on the surface of the gel by brush and then the samples were placed in the Petri dish for treatment. As shown in Figure 4.



Fig. 4. Application of gellan gum gel with barium hydroxide dispersion

Application of barium hydroxide dispersion by brushing technique: barium hydroxide dispersion was conventionally applied to the surface of the samples by brush.

Application of gellan gum gel with calcium carbonate dispersion: the calcium carbonate dispersion was loaded on the surface of the gel by brush and then the samples were placed in the Petri dish to treat acidity.

Application of calcium carbonate dispersion by brushing technique: the calcium carbonate dispersion was conventionally applied to the surface of the samples by brush.

Application of magnesium hydroxide nanoparticles dispersion by brushing technique: the magnesium hydroxide nanoparticles dispersion was conventionally applied to the surface of the samples by brush as shown in Figure 5.



Fig. 5. Application of magnesium hydroxide nanoparticles dispersion using a brush

Assessment methods

Changes in samples post treatment were studied using visual inspection, microscopic inspection using digital microscope, scanning electron microscope (SEM), pH value measurement, and Fourier transform infrared spectroscopy (FTIR).

Microscopic inspection: a ROHS Digital USB microscope 1000X was used to monitor the visual changes which have occurred due to the effect of acidity and treatments.

Scanning electron microscope (SEM): the samples were examined using a JEOLJSM 5400 LV EDX LINK ISIS – (Oxford Detector High Vacuum).

pH value measurement: pH values were measured by a cold extraction method according to ASTMD778-97(2002) at room temperature using a PH meter. The samples were cut into 25g pieces for each treatment and put in 20ml of distilled water (a pH of 7) for 1 h to measure the acidity of the paper [23].

Fourier transform infrared spectroscopy (FTIR): this analysis was performed using the Nicolet 380 FT-IR Spectrometer. This analysis provides information on the chemical nature of materials and the changes that occur to them as a result of the treatment and the aging processes. Grounded FTIR technology absorbs the material for some infrared regions, which have a wavelength of 400 to 4000 cm-1, which is the field corresponding to the energies of vibration of the particles inside the material. This analysis was conducted at the National Institute of Standards (NIS) [24].

Results and discussion

Microscopic inspection

Digital microscope examination of the photographic samples before treatment showed reddish brown spots on different regions on the surface of the photograph which is mostly a color change caused by the high level of acidity [25] and some white spots can be seen which are likely salt deposits that maybe caused by the deposition of chlorine ions from the hydrochloric acid. A large peeled off spot can be seen on one of the samples besides some faded grayish spots that may be caused by the HCL fumes. It is also likely to have been caused by the high acidity level that led to weakness and bombardment of the cellulose fibers as shown in Figure 6 [11].



Fig. 6. Reddish-brown spot and white spots on a photograph sample prior to treatment (left) and a large peeled off spot on the surface of a standard photograph sample and some grayish spots (right)

Photographic samples treated with calcium carbonate using the brush method showed a faded reddish spot on the photograph sample which is most likely remaining acidity or a color change which have resulted from the high acidity level the samples were exposed to. No remaining acidity was observed in the case of gel-based treatments as shown in Figure 7. Furthermore, small white spots were observed on both the gel and the brush samples which is probably due to the excess CaCO₃ salt that was deposited on the surface of the samples [11, 26];

and it can also be calcium chloride salt resulting from the reaction between calcium carbonate and hydrochloric acid [27] as shown in Figure 8.



Fig. 7. The sample treated with calcium carbonate by brush, (a) with a faint reddish spot; sample treated with the gel method (b) with no obvious acidity remaining



Fig. 8. White spots thought to be crystallized salt in the case of both treatment applications, where (a) is the brushing method; (b) is the gel-based method

Photographic samples treated with barium hydroxide showed small faded reddish spots in the brush-treated samples and large reddish areas in the gel-treated samples which also may be caused by the remaining acidity as shown in Figure 9. It also showed deposited salt with a medium amount in the brush samples and a very small amount in the gel samples as shown in Figure 10.



Fig. 9. Reddish spots on the samples treated with Ba (OH)₂, where(a) is the brush-treated sample showing small faded spots;(b) is the gel-treated sample with a large reddish area



Fig. 10. Salt crystallization on both treatment methods, where (a) is the brush-treated sample; (b) is the gel-treated sample.

Photographic samples treated with magnesium hydroxide nanoparticles showed large gray spots spreading in many parts of the samples. There was also salt deposited in some areas. In addition to some residual acidity color change traces (Fig. 22) as shown in Figure 11.



Fig. 11. Photograph samples (a, b) show the treated with Mg (OH)₂ NPS suffering from grey spots; (c) shows salt deposition on the photograph sample treated with Mg(OH)₂ NPS, and (d) shows remaining discolored spots post treatment with Mg(OH)₂ NPS

Untreated cardboard samples showed brown spots darker in color than the support itself which is likely due to the high prevalence of acidity in most of the samples. There were large peeled off areas on some of the samples which is likely caused by the high acidity level or some mechanical impact on the support. Some dark spots can also be seen which can also be the effect of the high acidity level as shown in Figure 12.



Fig. 12. Acidity of the cardboard support samples before treatment where (a) shows a large brown spot; (b, c) show a large brown spot around a peeled off spot in the sample, (d) shows a small black dot on one of the samples; and (e) shows some larger black spots on another sample

Cardboard samples treated with calcium carbonate showed dark brown spots on the samples treated using the brush application method which could mean that the acidity was not fully neutralized or that these spots are just an unrecovered color change that the acidity has caused. At the same time, there were no brown spots on the samples treated with the gel-based application method. The examination also showed some salt spots deposited on the samples, whether treated by brush or gel as shown in Figure 13. Fungal growth was observed on the

samples treated by gel. The fungal species were identified using the USB microscope as *Aspergillus niger*, *Aspergillus tamarii* and *Aspergillus fumigatus* [28] which is due to the gel remaining on the samples because the gel consists of a molecular mass of polysaccharides which fungi feed on [29] as shown in table 2 and Figures 14 and 15.



Fig. 13. The acidity treatment results of the two treatment application methods, where (a, b) are the samples treated by brush showing brown spots; (c, d) are the samples treated by gel showing no spots; and (e, f) show the deposited salt spots on samples treated using both selected application methods, where (e) is the sample treated by brush and (f) is the sample treated by gel.

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I able 2.	SHOWS	morphology	characteristics	or me	lunguses	growing c	m me	samples.

Fungi	Morphology	images
name		
Aspergillus niger	Conidiophores 0.5-2 mm X 16-22(-30) μ m conidial heads globose to radiate, 300-500 (-1000) μ m in diameter. Conidiophores smooth, long and coarse, vesicles globose, 25-75 μ m, metulae cylindrical, (10-) 20-40 (-75) X 6-8 μ m. phialides cylindrical tapering to a diatinct neck, 7-10 X 3-3.5 μ m. conidia globose, 3.5- 4.5 μ m, rough-walled, with black bars.	
Aspergillus fumigatus	Conidiophores hyaline or slightly coloured, short, green, particularly in the upper part, smooth-walled, 100-500 X 5-8 μ m. conidial heads radiate to nearly globose, 100-150 μ m in diameter, biseriate. Conidiophores vesicles broadly clavate, 20-30 μ m. phialides with a short neck, often greenish pigmented, 6-8 X 2-3 μ m. conidia colourless, globose to subglobose, 2.5-3 μ m, green, rough-walled to echinulate. The teleomorph is produced with difficulty.	
Aspergillus tamari	Conidiophores hyaline, long and coarsem 0.5-2 mm X 10-20 μ m. conidial heads radiate, splitting into separate columns, 500-600 μ m in diameter. Conidiophore vesicles globose, 25-50 μ m, metulae present, cylindrical 7-10 X 4-6 μ m. phialides cylindrical tapering to a distinct neck, 10-15 X 4-8 μ m. conidial heads often biseriate, but heads with only phialides also present. Conidia cylindrical to pyriform when young, later globose to subglobose, 5-6.5 (-8) μ m, conspicuously roughened from prominent tubercles and bars of brownish yellow colouring matter, the outer and inner conidial wall visible.	



Fig. 14. A fungus infection on some of the samples treated with gel



Fig. 15. A clearer image of the fungus infection on some samples treated by gel where:
(a) is Aspergillus niger; (b) is Aspergillus fumigatus; (c) is Aspergillus niger in its early formation;
(d) is Aspergillus tamarii; (e) is Aspergillus niger in its early and late formation;
(f) is Aspergillus niger and Aspergillus tamari

Cardboard samples treated with barium hydroxide showed some remaining brown spots in the samples treated by brush, while in the samples treated by gel there were none as well as some deposited salt spots in both brush and gel-treated samples, but it was very minor in geltreated samples as shown in Figure 16.



Fig. 16. The acidity treatment results of the two treatment application methods, where:
(a, b) are the samples treated by brush showing dark brown spots can be seen;
(c, d) are the samples treated by gel showing no spots can be seen; (e, f) show the deposited salt spots on both treatment application methods - where (e) is the sample treated by brush and (f) is the sample treated by gel

Cardboard samples treated with magnesium hydroxide nanoparticles showed some faint brown spots, as well as some deposited salt spots in several places of the samples as shown in Figure 17.



Fig. 17. Faint brown spots on some of the samples treated with Mg $(OH)_2$ NPS (a, b); and (c, d) show deposited salt spots

Scanning electron microscope (SEM)

Scanning electron microscopy was used to examine the morphology of fibers, the effect of acidity, and also to detect the effect of each treatment. SEM images show the rough and uneven surface of the standard photograph sample, where some particles are present on the surface, which may be dirt particles as shown in Figure 18. The SEM images also reveal fractured wood fibers of the cardboard support's standard sample where cracks appear on the surface due to the acidity as shown in Figure 19 [14]. In the samples where calcium carbonate was applied to the photograph with a brush, the result was satisfactory as shown in Figure 20, and in case of the supports, calcium carbonate seemed to cover the fibers and link them together as shown in Figure 21. In the samples treated with gellan gum gel with calcium carbonate, no negative impact was

detected on the photograph samples, and small white particles which seem to be the treatment's salt particles appear on the surface of the sample as shown in Figure 22. On the other hand, fungus growth can be seen on the support samples due to the gel residues as shown in Figure 23 [30]. In the samples treated with barium hydroxide applied with a brush or as gel, the results were good and there was little to no significant change in the photograph; however, in the gel-treated support sample, small particles appear to be covering the wood fibers as shown in Figure 24. In the samples treated with magnesium hydroxide NPS, the nanoparticles appear to fill in the gaps between the grains of the photograph and improve its surface heterogeneity and enhance the surface overall due to the deposition of the nanoparticles since nanoparticles smaller than 10 nanometers have shown to act similar to gas molecules and can penetrate through the surface and get into fibers as shown in Figure 25 [31]; however, for the photograph sample, the treatment does not seem to enhance the surface at all; cracks can still be seen between the fibers and also some of the fibers appear to be ripped off as shown in Figure 26.



Fig. 18. The uneven surface of the standard photograph sample, where some particles can be seen between the surface grains



Fig. 19. The fractured surface of the standard support sample where cracks can be seen in the structure of the support



Fig. 20. The photograph sample treated with CaCO3 applied with brush



Fig. 21. The support sample treated with CaCO₃ applied with brush, where the treatment salt appears covering the ends of the fibers and linking them together



Fig. 22. The photograph sample treated with CaCO₃ applied with gel, where no physical change can be detected except for some white particles that seems to be the treatment salt particles



Fig. 23. The support sample treated with CaCO3 applied with gel, where fungal growth is obvious



Fig. 24. The support sample treated with Ba $(OH)_2$ applied with gel, where the treatment salt appears to be enveloping the fibers



Fig. 25. The photograph sample treated with $Mg(OH)_2$ NPS, where the nanoparticles can be seen between the surface grains



Fig. 26. The support sample treated with Mg (OH)₂ NPS, where cracks can still be seen between the fibers and some fibers are ripped

pH value measurements

The pH value of the treatments' dispersions was measured before starting the treatment as shown in table 3; two measurements were taken for each photograph and support sample and the mean of the measurements was calculated as shown in tables 4 and 5. In the measurement of the standard samples, the support sample was found to be far lower compared to the photograph sample as shown in tables 4 and 5; and that's due to the cardboard nature since it is made out of wood pulp that contains lignin and naturally produces acids. pH measurement showed that the treatment that increased the pH level the most was calcium carbonate [32] as shown in table 6. The barium hydroxide treatment was also effective in increasing the pH level when applied with gellan gum gel [18], while it was less effective when applied by brush as shown in tables 4 and 5. In general, when comparing between the gel and brush application methods, the gel-based treatments were more effective in increasing the pH level as shown in table 6. As for the samples treated with magnesium hydroxide nanoparticles, their pH values were low as shown in tables 4 and 5, which may be due to the low pH level of the treatments dispersion itself as mentioned in table 3.

By comparing the average values of the measurements shown in Tables 3 and 4, it was concluded that the more to less effective treatments are: magnesium hydroxide NPS, calcium carbonate applied by brush for the photograph samples, and calcium carbonate applied by brush, barium hydroxide applied by brush, and magnesium hydroxide NPS for the secondary supports.

Solution	pH measurement				
CaCO ₃	10.5				
Ba (OH) ₂	13.2				
Mg (OH) ₂ NPS	5.5				

Table 3. The	oH measurements	of the treatment	t solutions
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Sample	Measurement 1	Measurement 2	Mean
Standard	5.7	5.7	5.7
CaCO ₃ (brush)	4.7	6.4	5.6
CaCO ₃ (gel)	5.9	6.9	6.4
Ba $(OH)_2$ (brush)	5.4	6.6	6
Ba (OH) ₂ (gel)	6.2	6.2	6.2
Mg (OH) ₂ NPS	6	4.6	5.3

Table 4. The pH measurements results of the photograph samples.

Table 5. The pH measurements results of the support samples

Sample	Measurement 1	Measurement 2	Mean
Standard	4.2	3.1	3.7
CaCO ₃ (brush)	2.8	4.8	3.8
CaCO ₃ (gel)	6.1	6	6.1
Ba (OH) ₂ (brush)	3.2	4.4	3.8
Ba (OH) ₂ (gel)	4.3	5.6	5
Mg (OH) ₂ NPS	4.6	3.3	4

Table 6. The arrangement of the different treatment methods from best to worst results in increasing the pH level in both sample types

Order	Photograph samples	Support samples
1	CaCO ₃ (gel)	CaCO ₃ (gel)
2	Ba (OH) ₂ (gel)	Ba (OH) ₂ (gel)
3	Ba (OH) ₂ (brush)	Mg (OH) ₂ NPS
4	CaCO ₃ (brush)	CaCO ₃ B. / Ba (OH) ₂ (brush)
5	Mg(OH) ₂ NPS	

Fourier transform infrared spectroscopy (FTIR)

The samples were treated with different substances to remove acidity and were divided into paper support samples and silver gelatin photographic samples. The treatment with calcium carbonate and its application with a brush to remove acidity from the paper support caused a decrease in the wavelength of the band of O-H stretching from 3431 to 3415cm⁻¹, which led to a decrease in the water content of the treated sample [33]. At the same time, there was no noticeable change in the intensity and wavelength of the photos when treated with the gel loaded with calcium carbonate. Samples treated with barium hydroxide applied by a brush showed a decrease in the intensity of O-H stretching band from 48.7 to 34.6; however, loading that substance on a gel of gellan gum showed no change in the water content of the samples as shown in table 7 and Figure 27.

Functional groups	Standard		Calcium carbonate by brush		Calcium carbonate on gel		Barium hydroxide carbonate by brush		Barium hydroxide carbonate on gel		Nano magnesium hydroxide by brush	
	Wave length	Intensity	Wave length	intensity	Wave length	intensity	Wave length	intensity	Wave length	Intensity	Wave length	intensity
OH stretching	3431	48.7	3415	51.5	3431	47.2	3413	34.6	3431	49.1	3431	46.6
C H stretching	2922	56.1	2922	57.8	2922	55.3	2911	44.4	2922	56.1	2922	53.2
C=O ester carbonyl	1632	58.3	1655	59.6	1641	57.1	1657	46.6	1641	58.4	1641	56.3
CH ₂ banding	1429	58.6	1458	58.9	1429	57.3	1430	43.7	1429	57.7	1429	55.7



Fig. 27. The comparison between the standard sample and samples treated with calcium carbonate applied by brush and loaded on gellan gum gel on the paper support

The use of calcium carbonate and barium hydroxide applied by brush caused the highest rate of oxidation in the paper support samples as the wavelength and intensity of the C=O carbonyl group of the samples treated with calcium carbonate increased from 1632 cm⁻¹ to 1655 cm^{-1;} and from 58.3 to 59.6, respectively. While the samples treated with barium hydroxide, showed an increase in the wavelength of C=O carbonyl group from 1632 cm⁻¹ to 1657 cm⁻¹, and a decrease in the intensity from 58.3 to 46.6. The treatment with calcium carbonate achieved the highest rate of increase in the crystallinity index of cellulose as the intensity of the CH₂ band increased from1429cm⁻¹ to 1458 cm⁻¹. The barium hydroxide applied by brush decreased the intensity from 58.6 to 43.7 compared to the standard sample as shown in figure 28 and 29. The photographic samples treated with nano Mg(OH)₂ exhibited the highest rate of oxidation by increasing the wavelength of the OH stretching from 1641 to 1647 cm⁻¹ and increasing the intensity from 47.1 to 66.1. Deacidification using nano magnesium hydroxide and barium hydroxide applied by brush caused hydrolysis and oxidation at the amide I and amid II region, which led to the degradation of the photographic samples, but all the changes that occurred post treatment with the gel loaded with barium hydroxide were not noticeable, which indicate that the use of the barium hydroxide bearing gel technique is the best in deacidification of the photos without causing any effects on their properties or changes in the functional groups of the samples [34] as shown in table. 8 and figures 30, 31 and 32.



Fig. 28. The comparison between the standard sample and samples treated with barium hydroxide applied by brush and loaded on gellan gum gel on the paper support



Fig. 29. The comparison between the standard sample and sample treated with nano magnesium hydroxide applied by brush on the paper support

Table 8. The changes in functional groups of the treated samples from the photographic layer

Functional groups	Standard		Calcium carbonate by brush		Calcium carbonate on gel		Barium hydroxide carbonate by brush		Barium hydroxide carbonate on gel		Nano magnesium hydroxide by brush	
	Wave length	intensity	Wave length	intensity	Wave length	Intensity	Wave length	intensity	Wave length	intensity	Wave length	intensity
OH stretching	3431	35.7	3414	38.8	3427	50.2	3431	43.4	3427	46.3	3441	57.7
Amide I Amid II	1641 1429	47.1 48.2	1655 1512	47.3 48.8	1651 1510	57.7 58.6	1643 1633	54.3 54.4	1647 <i>1516</i>	56.2 57.4	1647 1647	66.1 63.1



Fig. 30. The comparison between the standard sample and samples treated with calcium carbonate applied by brush and loaded on gellan gum gel on the photographic samples



Fig. 31. The comparison between the standard sample and samples treated with barium hydroxide applied by brush and loaded on gellan gum gel on the photographic samples



Fig. 32. The comparison between the standard sample and sample treated with nano magnesium hydroxide applied by brush on the photographic samples

Conclusions

The USB microscopic examination of the photograph samples showed that calcium carbonate applied on gellan gum gel yielded the best results in terms of acidity neutralization; as for the secondary support samples, calcium carbonate loaded on gel did decrease the acidity to a good level. Nevertheless, fungal growth was observed on the samples. On the other hand, barium hydroxide loaded on gel gave satisfactory results as it removed the acidity and didn't cause fungal growth.

The SEM images showed that the most efficient treatment method for photograph samples was nano magnesium hydroxide, and it also enhanced the surface of the samples. In the case of the secondary support samples, barium hydroxide loaded on gel gave the best results since the substance's particles covered the fibers of the cardboard and filled some of the gaps between them.

The pH measurement results showed that the methods which efficiently decreased the pH level in both the photograph and secondary support samples are: calcium carbonate loaded on gel followed by barium hydroxide loaded on gel.

The FTIR analysis showed that barium hydroxide loaded on gel didn't affect the properties of the photograph samples or make any changes to their functional groups unlike other treatment methods. For the secondary support samples, calcium carbonate and barium hydroxide applied by brush caused oxidation and reduction in the water content while using gel loaded with these substances didn't make noticeable changes to the functional groups.

By combining and comparing the results of all testing methods, it turns out that the method which has efficiently decreased the acidity without having a noticeable negative effect on the samples whether the photographs or supports is gellan gum gel loaded with barium hydroxide.

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