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THE EVALUATION OF THE EFFICACY OF TWO MAGNESIUM BASED DEACIDIFICATION METHODS ON THE STABILITY OF THREE DIFFERENT TYPES OF PAPERS

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Abstract

The degradation and embrittlement of paper is due to the depolymerization of cellulose fibers; this is induced by acidity and oxidation. An important part of dealing with these chemically unstable materials is the neutralization of acid and deposition of a buffer reservoir to protect the fibers from introduction of acid in future. Paper deacidification is a fundamental process for achieving this goal. Any deacidification method chosen must be able to treat large numbers of items, safely, quickly and cheaply. The main goal of this paper was to investigate the effect of two deacidification solutions, which have never been used in Egypt, on the chemical and physical properties of different types of paper in order to find an alternative to Calcium hydroxide the most common deacidification method used in Egypt. Magnesium salts have been chosen to produce two deacidification methods, one of them in aqueous media, and the other in nonaqueous media; however, the magnesium has excellent deacidification properties and never have been applied in Egypt before. This paper is concerned with the Evaluation of Magnesium Bicarbonate (MBC) and Methyl Magnesium Carbonate (MMC), as neutralization agents, on the stability of paper substrate before and after accelerated ageing. Deacidification of acid paper samples (old book and newspaper) coming from wood pulp (20 century) and whatman paper samples, has been carried out with elaborate findings. Examinations and scientific analyses have been used in the assessment of treated samples, to figure out the efficacy of the two methods on the paper stability. Both methods have adequate deacidification properties; the pH value of paper has increased after deacidification. Mechanical testing and Fourier-transform infrared spectroscopy (FTIR) have proven considerable stability of mechanical and chemical properties of deacidified paper after accelerated ageing.

Keywords*: Acidity; Hydrolysis; Methyl Magnesium Carbonate; Magnesium Bicarbonate; Neutralization; FT-IR; pH; Tensile strength*

Introduction

The ageing process of paper is a result of chemical reactions, whose intensity count on several factors that influence the degradation of books and papers. There are two main degradation processes take place in paper-based materials: acid hydrolysis of cellulose and photo-oxidation of cellulose and lignin [1, 2].

In the middle of the 19th century, paper industry witness's industrial revolution; handmade paper sheet was replaced by machine made sheet; Cotton-based raw materials were

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replaced by wood based raw materials; producing chemically unstable paper sheets, subjected to Hydrolysis and oxidation [3]. the amount of moisture exists in the paper, which depends on the relative humidity; pH value; and the temperature, control the rate of the hydrolytic degradation of cellulose molecules [4, 5].

The acidic-catalyzed degradation of paper is started by several factors, including acidic components added to the cellulose fibers during papermaking; for example, using natural alum in sizing procedures [6-8]; absorption of sulphur dioxide and nitrogen oxides. As a result of this, the main components of paper, cellulose, lignin, and hemicellulose, oxidize and produce acidic degradation products that break down the fibers, which lead to dramatically loss of paper strength [9]. These processes can be slowed by a deacidification treatment which is nowadays the first-rate option for the rescue of our cultural heritage of paper and book [10].

Deacidification is a chemical process, including neutralizing of the acids present in the paper, and produces into treated paper an alkaline reservoir to retard further acidification [11, 12].

At the end of the nineteenth century, the concept of deacidification as a step-in paper conservation field sees the light. Various deacidification techniques and products have been developed and tested to reduce the degradation rate of paper [13-16]. Several methods were disused, and others developed to mass deacidification systems. The efficiency of the deacidification method should be evaluated by [17] :

- Ability of removing and neutralizing acidic content of paper
- Depositing alkaline reserve should be at least 1%, to encounter future acidity, besides keeping the pH around 8-9 [11].
- No negative effects on the deacidified paper; no visibly change of the object appearance by leaving residues on the surface; or leaving remaining odors.
- The treatment solution should be Easy to prepare, with the possibility of application in more than one method (immersion – spray) according to the condition of the object.
- Contribute to the maintenance of mechanical properties of paper after ageing compared to untreated paper.

the most common deacidification method has been used in Egypt is the aqueous solution of calcium hydroxide, $Ca(OH)_2$, which is an effective deacidifying agent; it works very well as an alkaline reservoir, the easiest to apply, the cheapest [18]; but since this solution is from a chemical point of view, too aggressive because of its high alkalinity(pH = 12−13) ; that it may cause notable yellowing to treated paper [18], turn the colour of iron gall ink from black to brown [19]; what is considered as the most serious drawback of this method; also significantly loss of tensile strength has been reported by Sistach [20]. As a consequence, other alternatives have been considered to use as an effective deacidification agent; can avoid the significant drawbacks of Calcium hydroxide method and can be readily prepared in the laboratory without any complicated procedures.

This paper reports an approach for paper deacidification, As the Magnesium salts are characterized by high solubility properties, which give excellent features for deacidified papers [21], so two methods based on using magnesium salts in both aqueous and nonaqueous solvents were selected as an adequate alternative to calcium hydroxide method. The two methods are the aqueous solution of magnesium dicarbonate, $Mg\ (HCO_3)_2$, and non-aqueous solution of methyl magnesium carbonate, $MeMgCO_3$.

Magnesium Bicarbonate is a recommended deacidification agent. It reports sufficient results, estimated by physical properties after ageing [19, 22]. However, one drawback is reported by *H. Hey* [18], concerning the deposition of magnesium bicarbonate crystals on the surface of paper [23]. Remarkable decrease of the catalytic role of metal ions on the autoxidation of cellulose after deacidification with magnesium bicarbonate is mentioned by *C.J. Shahani and F. H. Hengemihle* [24]. Preparation of magnesium bicarbonate using magnesium

hydroxide is described by *H. Hey* [18]; however other researchers suggest the use of basic magnesium carbonate or magnesium carbonate.

Methyl magnesium carbonate (MMC) is deacidification method based on organic solvents. This method was evolved by *G.B. Kelly et al.* in 1977 [25]. Adequate result in retention of mechanical strength after accelerated ageing, increase of pH values and sufficient alkaline reserve is reported by *A. Lienardy and P.; Van Damme* [19] after treatment with (MMC) method. A mixture of 5% MMC and 4% MMMC in methanol (Wei T'o product) has been evaluated by *J. Hanus* [26], *V. Bukovsky and I. Kuka* [27], *K. Bredereck* [28] and reported significantly reduce of degradation rate of treated paper samples after accelerated ageing. Nevertheless, decrease of mechanical strength has been reported.

The two methods mentioned above have been applied with success to different types of paper samples, whatman filter paper, naturally acidic newsprint paper and naturally Book paper dating from the 20th century. In these papers the efficiency of the two deacidification solutions on chemical and mechanical properties of treated samples before and after ageing have been reported.

Materials

Deacidification solutions

Chemicals involved

- Magnesium Hydroxide, $Mg(OH)_2$ (reagent grade, 95%; mp: 350°C(lit.); Molecular Weight 58.32 (Sigma- Aldrich).
- Methyl alcohol (methanol), CH_3OH, (reagent, ≥ 99.8%); Molecular Weight 32.04 (Sigma- Aldrich).
- Magnesium turnings, Mg, (reagent grade, 98%); Molecular Weight 24.31 (Algomhuria company-Egypt).

Preparation of Magnesium Bicarbonate solution

To prepare a 0.05 M of aqueous solution of magnesium bicarbonate $Mg(HCO_3)_2$; approximately, 2.916 g/L of magnesium hydroxide powder were dispersed in distilled water, and carbon dioxide gas CO_2 was bubbled through the solution with Constant stirring , according to W.K. *Wilson et al.* [21]. The hydroxide dissolves easily in water through several stages until there is no precipitation and the milky white color solution became clear (Fig. 1). The pH value of 8.9 was obtained in the prepared solution.

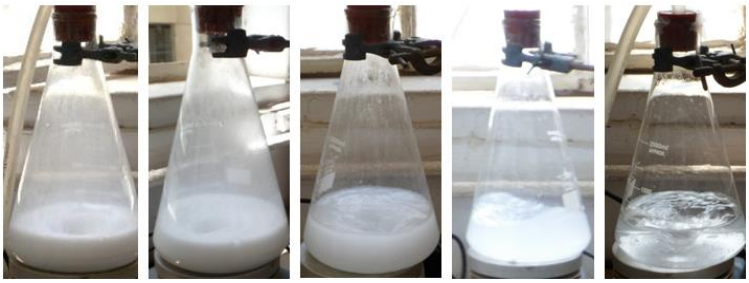

Fig.1. Stages of the preparation of aqueous solution of magnesium Bicarbonate in laboratory

Preparation of methyl magnesium carbonate solution

According to *N.A. North* [29] a non-aqueous solution of methyl magnesium carbonate, $MeMgCO_3$, was prepared in the laboratory using two steps procedure. (Fig. 2), Firstly, 12 grams of magnesium turnings were reacted with 200mL of methanol, the mixture was electrically heated until reaction initiated and proceed till all the magnesium was consumed to form white crystals of magnesium methoxide; the reaction had to be controlled by a water

cooled condenser. Secondly, Carbon dioxide was bubbled through the solution for approximately 30 minutes until the entire solid was dissolved and methyl magnesium carbonate $MeMgCO_3$ was formed. This solution was then diluted with Methanol to form a 1.3% w/v solution. The pH value of the prepared solution was 9.1

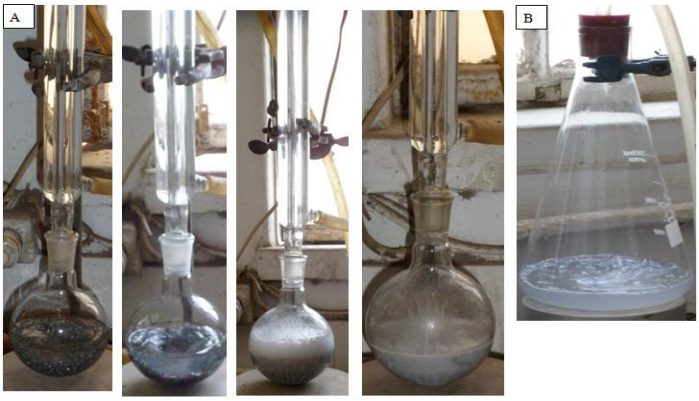

Fig. 2. Preparation of Non aqueous solution of methyl magnesium carbonate in laboratory in two stages procedure

Paper samples

Paper tested

Three paper types have been selected to evaluate the effect of the two deacidification methods:

- Whatman® paper qualitative filter paper (a pure cellulose paper), Grade 1 cat No. 1001, circles, diam. 150mm, made in china; was supplied by Algomhuria Company, Egypt.
- Acidic newsprint papers printed in 2001, made of mechanical wood pulp, pH = 5.
- Acidic Book papers printed in 1929, made of mechanical pulp, pH = 4.

Preparation of samples

- 12 Samples with a size of 15×20cm were cut out of sheets of the selected paper, newsprint paper (NP), Book paper (BP) and Whatman paper (WP). 4 sheets of each type stay untreated as a control; 4 sheets were immersed for 20 minutes in a 0.05M solution of magnesium bicarbonate. On the other hand, spraying technique was used to treat 4 samples of each type of the selected paper by the non-aqueous solution of methyl magnesium carbonate.

Tested Papers were divided into 3 groups:

- ❖ Control: untreated papers
- ❖ MMC: The papers were deacidified by solution of methyl magnesium carbonate
- ❖ MBC: The papers were deacidified by aqueous solution of magnesium Bicarbonate.

After complete drying of excess solution, the samples conditioned for 48 hours at laboratory temperature 22 ± 2°C and 45% RH.

Fig. 3. (A) Acid Newspaper samples (B) Acid Book paper samples, after deacidification Using MMC, Illustrative for color changes to yellowness after artificial ageing

• To evaluate the effect of the two deacidification methods on the stability of paper on the long term, samples of the three types of paper were subjected to an accelerated ageing using heat (6 days at 105°C) in a drying oven according to TAPPI test T 453ts-63, considering that every 3 days of accelerated ageing stand for 25 years of natural ageing. (Fig. 3)

Methods

To evaluate the efficacy of the two deacidification methods on the treated paper samples, the following examination and analysis were carried out

PH measurements

PH measurements have been performed according to the TAPPI standard, using the cold-water extraction method at room temperature using HI 2211 bench top pH meters (Hanna instruments). Sample of paper 1 gm. was extracted in 70mL of distilled water (pH = 7).

Environmental Scanning Electron Microscope (SEM/EDX)

The morphological analysis of the untreated and treated paper sheets surfaces has been performed with The SEM model FEI Quanta 200 FEG, to examine the changes in surface morphology, and analyses on the paper samples have been performed using an energy-dispersive X-ray (EDX) spectrometer for The comparison of the amount of magnesium within the fibers for the untreated and treated samples.

Atomic absorption Spectroscopy

To determine the amount of magnesium present as an alkaline reservoir in the treated paper, atomic absorption spectroscopy using a Unicam AAS Model 939 spectrophotometer, in flam mode, burning by Acetylene air was performed following TAPPI test methods T266 om-94.

Optical properties

Whiteness and Yellowness Index Determination

The Whiteness and yellowness index for whatman paper samples treated with the two deacidification methods, were performed and evaluated according to ASTM, D 1925 using (Optimatch 3100 SDL) Spectrophotometer. For each colorimetric value an average of five measurements was calculated.

Mechanical testing measurements

To evaluate the mechanical properties of the papers treated with magnesium bicarbonate and methyl magnesium carbonate, the following parameters were measured:

-Tensile strength and elongation for the paper samples before and after treatment was tested using testing machine model H5KT/130 -500, according to standard ISO 1421, strip method.

- Number of double folds was recorded using MIT Folding Endurance Tester, model 427 according to ASTM D 2176.

Fourier Transform Infra-Red Spectroscopy

FTIR - ATR spectra were measured on paper samples with a Bruker – Model Vertex 70 spectrophotometer by the absorbance method using ATR accessory with diamond crystal, in the wavelength range 400- 4000cm^{-1}; mid infrared source. The FTIR absorbance frequencies for the treated samples were recorded using a resolution of 4cm^{-1}, Range to 0.16.

X- Ray Diffraction Analysis

X- Ray diffraction data were obtained using Philips analytical X-ray B.V.– Diffractometer – PW 1480- Netherland. The instrument equipped with copper anode producing Cu K X-rays using an accelerating voltage of 45kV with a tube current of 30mA. The goniometer scanned a 2Θ range between 10° and 58° with scan rate of 0.026°/18.8 sec. Paper samples were fixed using holders into Flat sample stage, Diffractometer system: EMPYREAN; Measurement program: Aisha. Wavelength K-Alpha1 [Å]:1.54060-K-Alpha2 [Å]: 1.54443.

Results and Discussions

The notations for the deacidification treatments and the paper samples are as follows:

- MMC: deacidification treatment by non-aqueous methyl magnesium carbonate ($MeMgCO_3$)
- MBC: deacidification treatment by aqueous dispersion of magnesium bicarbonate $Mg(HCO_3)_2$
- Control: untreated samples
- WP: what man filter paper samples
- NP: newspaper samples
- BP: book paper samples;

pH variation

After deacidification

The examined samples were acidic before the treatments (book paper samples, pH = 4.0); (newspaper samples, pH = 5.0); with the exception of the whatman sample, whose pH was neutral (7.0). Both MMC (non- aqueous solution of methyl magnesium carbonate) and MB (aqueous dispersion of magnesium bicarbonate) treatments caused an increase in the pH of all the samples examined; the deacidification produces an evident pH increase (up to 3-4 pH units).

The nonaqueous MMC treatment causing higher pH values than the aqueous one (MB); Because there will be a long-term consume of the alkaline compound the pH should be above neutral after treatment but not too high to avoid alkaline depolymerization, so the optimal value would be in the 8.5 range

The final pH values achieved after the MMC treatment were Ranges between (8.0 – 10.0) (Fig. 4), and after the aqueous MB treatment were ranges between 7.9–8.7 (Table 1), dependent on the initial pH paper.

Fig. 4. Measuring of treated samples using the cold water extraction and strips

Table 1. pH values of paper samples (WP), (NP), (BP): Before and after deacidification

Samples	Whatman (WP)		Newspaper (NP)		Book paper(BP)	
	BA	AA	BA	AA	BA	AA
Untreated samples (WT)	7.0	7.1	5.0	4.6	4	3.8
MMC treatment	10.0	10.1	9	8.1	8	7.2
MBC treatment	8.53	8.7	8.4	8.2	7.9	7.4

After the ageing

After the ageing tests period, the initially acid samples (NP and BP) show a higher decrease in the pH with Non aqueous treatment, suggesting a continuous consumption of the alkaline reserve after the non-aqueous deacidification treatment. The neutralization of the acid groups will probably occur in a long-term process, in contrast to the aqueous treatment where the neutralization takes place during its immersion operation. For the samples with an initial nearly neutral pH (WP), the variation of pH is very similar in both kinds of treatments (Fig. 5), since the neutralization reaction with the subsequent alkaline consumption is negligible.

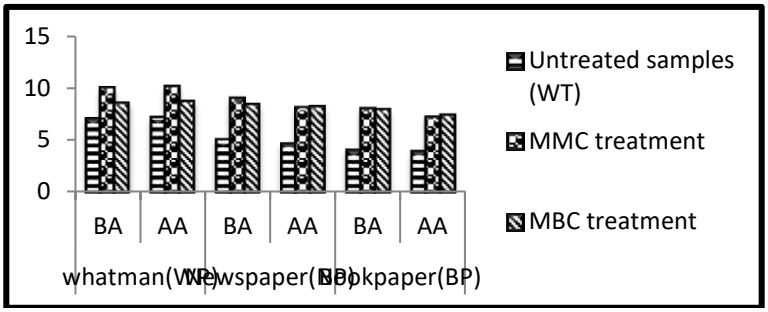

Fig. 5. pH value of the tested Paper before and after deacidification treatments

Environmental Scanning Electron Microscope (SEM/EDX)

Examination performed using SEM showed a homogeneous distribution of magnesium particles inside the paper texture for the aqueous treatment (MB) using the immersion methods. (Fig. 6) shows a paper samples treated with suspension of $Mg(HCO_3)_2$ particles adhere to the paper fibers with a homogeneous distribution. The figure demonstrates that no morphological changes of cellulose fibers have done. However, the non-aqueous treatment MMC by spraying caused uneven deposition on the paper surface, showed a chalky white precipitate, due to the difficulty to have a homogeneous treatment with spraying, in contrast of the immersion treatment. The untreated control of paper sample showed no peak in the SEM/EDX spectrum for magnesium in whatman paper (WP), and weak peak for magnesium in untreated samples of NB and BP it was most likely not in the form of the alkaline reserve. However, after deacidification treatments a strong peak of magnesium comes from Magnesium bicarbonate or methyl magnesium carbonate has been detected by EDX microanalysis (Fig. 6-11).

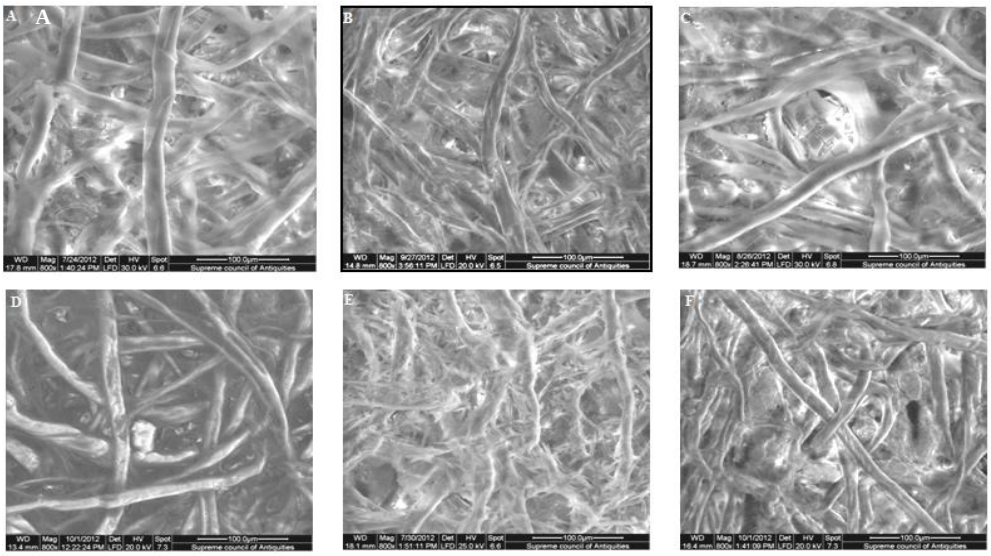

Fig. 6. SEM photomicrograph of whatman paper WP 800× magnification:
(A) control (no treatment), (B) control after ageing, (C) MMC treatment,
(D) MMC after ageing, (E) MBC treatment (F) MBC after ageing

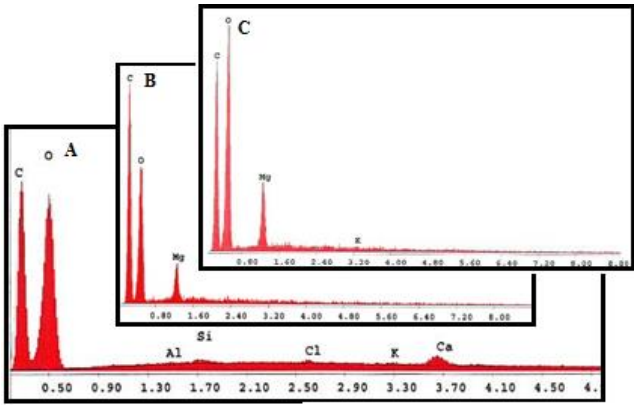

Fig. 7. EDX Spectra of whatman paper WP (A) untreated control show no Mg^+ peak (B) MMC treatment (C) MBC treatment. Both treatments show strong magnesium peak after treatment

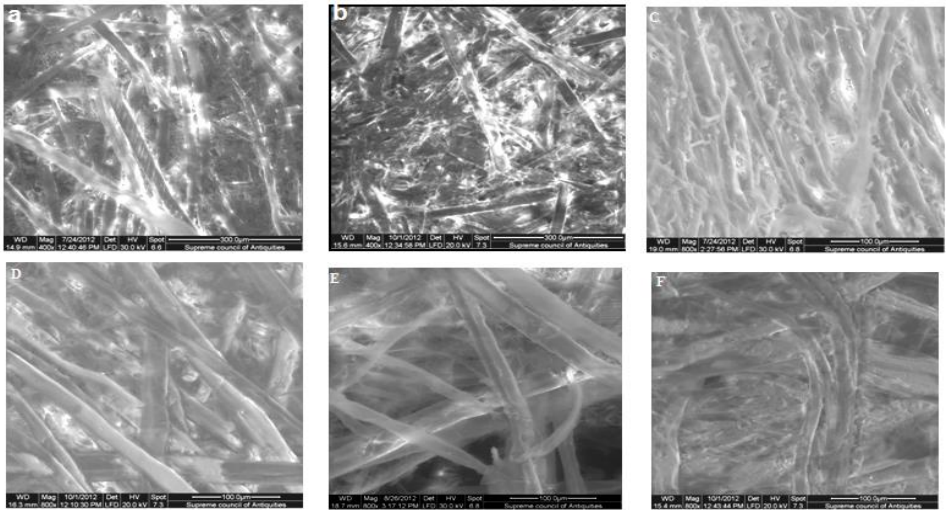

Fig. 8. SEM photomicrograph 400-800× of Newspaper NP: (A) control (no treatment), (B) control after ageing, (C) MMC treatment, (D) MMC after ageing, (E) MBC treatment (F) MBC after ageing

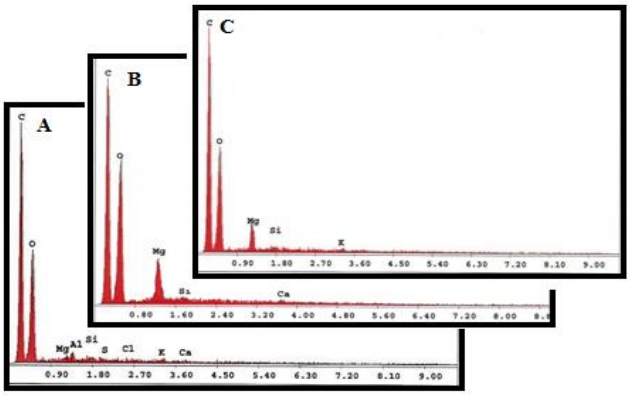

Fig. 9. EDX Spectra of Newspaper paper NP (A) untreated control showed very weak Mg^+ peak (B) MMC treatment (C) MBC treatment. Both treatments indicate strong magnesium peak after treatments

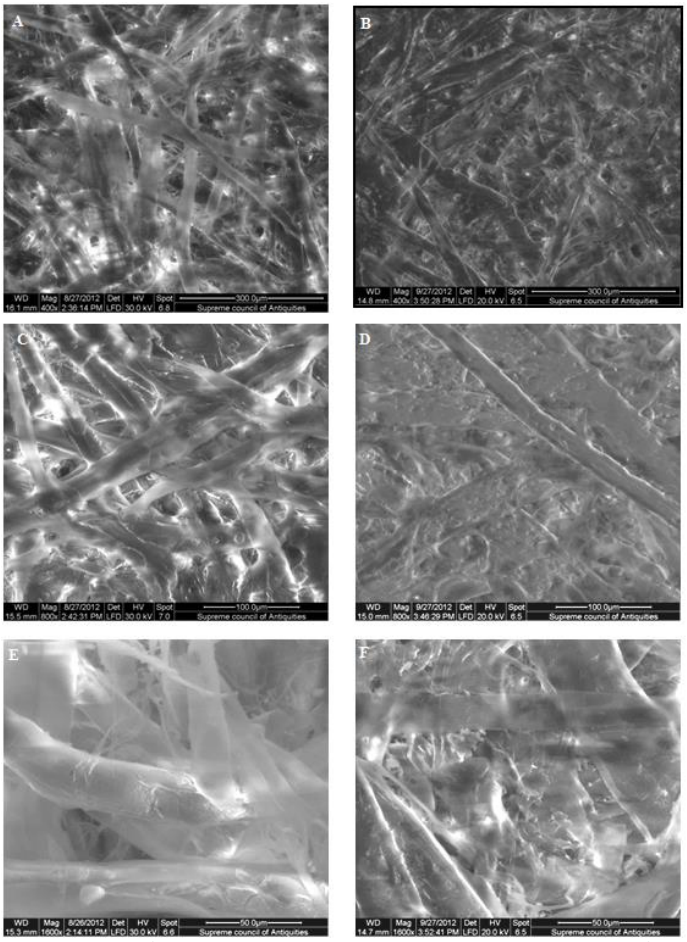

Fig. 10. SEM photomicrograph of Book paper BP: (A) control (no treatment), (B) control after ageing, (C) MMC treatment, (D) MMC after ageing, (E) MBC treatment (F) MBC after ageing.
Indicates the serious damage of fibers as a result of acid hydrolysis

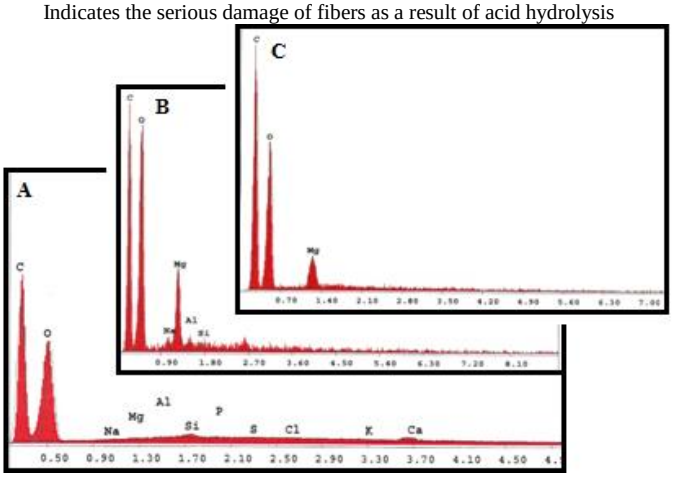

Fig. 11. EDX Spectra of Book paper BP (A) untreated control, very weak Mg^{+} peak (B) MMC treatment (C) MBC treatment. Both treatments indicate strong magnesium peak after treatments

Amount of Magnesium Deposited

The optimum amount of Mg^{2+} according to TAPPI test is 3.6 milligrams for 1 gram of paper [22]. The untreated control of book paper and newspaper samples recorded minor magnesium content; however, it should be noted that these papers were brittle and discolored, and had a pH of 5.0 and 4.0; this magnesium content most likely not in the form of alkaline reserve and it was less than required as alkaline reserve.

Figure 12 show the amount of magnesium deposited. The average amount of magnesium was three to seven times more than considered necessary for alkaline reserve (3.6mg Mg^{2+}), the amounts deposited varying considerably from application to application. For instance, immersion in aqueous solution of magnesium bicarbonate on paper samples deposited from 9.1 to 13.1mg Mg^{2+}/g paper. The spray of non-aqueous methyl magnesium carbonate on paper samples ranged from 19 to 23mg Mg^{2+}/g paper. Obviously, it is difficult, to apply deacidification solution consistently with a hand-held sprayer. On the other hand, the amount of Mg^{2+} dependent on the pH of the tested paper, and consuming alkaline reserve in the reaction with acidic content in paper samples during treatment and continuously after treatment while drying in air. So, the amount of Mg^{2+} recorded stable values at the neutral whatman paper samples (WP).

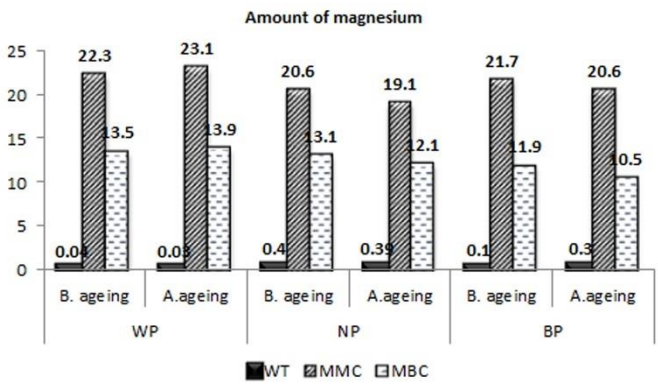

Fig. 12. result of atomic absorption spectroscopy shows variation of Magnesium by milligram on paper samples before and after treatments

Colorimetric change of papers

Yellowness and whiteness index were obtained as an indication of color change for the whatman paper samples (WP) after deacidification treatments. Table 2 shows the effects of the two deacidification methods on the color component **L*** (Lightness/darkness), the difference in **L*** value (**ΔL***), the yellowness (**Y***) and whiteness (**W***) index of untreated and treated paper whatman samples. The result listed in table 2 shows the deacidification by **MMC** cause a remarkable increase in **L*** and Y* values, while the whiteness index **W*** decreased. The **Y*** value show higher increase after accelerated ageing. On the other hand, the **L*** value show a very slight increase with the **MBC** deacidification treatment, while the **Y*** yellowness show significant increase, and higher increase after ageing. The whiteness **W*** index value decrease after **MBC** treatment, then recorded dramatically decrease after ageing. This means that the artificial ageing revealed an overall greater decrease in whiteness and increase in yellowing. The **L*** increasing is probably caused by the deposition of the alkaline reserve on the paper surface, while the yellowing could be caused by oxidation reactions, which are increased at higher pH values [23]. The yellowing of cellulose is a characteristic sign of its oxidation and takes place in the hydroxyl groups available. The darkening of cellulose should be related to the

polymer degradation. Previous experiments have demonstrated that after deacidification of paper with Mg^{2+} solution, particularly with MMC, yellowing of paper takes place [14].

Table 2. The color parameters of the untreated and treated whatman paper samples (WP) Before and after ageing

samples	*L**	*ΔL*	*W*	*Y*
Control (WT)	90.44	----	85.38	0.72
Control (AA)	90.03	- 0.31	78.18	3.02
MMC	91.36	0.92	81.62	1.92
MMC(AA)	91.34	0.9	77.29	3.49
MBC	90.67	0.23	83.15	1.31
MBC(AA)	90.49	0.05	74.38	3.43

Mechanical properties of the deacidified samples

Tensile strength

In order to test the effect of the deacidification methods on the mechanical properties of the treated paper samples, ten sequent strips (110×20mm) were cut from each sample in machine direction (treated and untreated, aged and unaged). Prior to tensile strength measurements, the papers were conditioned in a chamber with 55±5% RH (relative humidity) and 22±2°C. mechanical properties of paper samples treated with MMC and MBC were measured. Table 3 shows the results, as the ten strips in a given set were contiguous; it was assumed that they would be similar to one another in strength. But significant variations were observed; in some instances, these appeared to be caused by the presence or absence of printing in **NP** and **BP** samples, but not for whatman paper samples **WP**. The median was therefore chosen as the indicator of tensile strength for the three types of papers.

The data listed in table 3 demonstrate the effect of the two deacidification methods on the mechanical properties of the treated paper samples before and after artificial ageing; including tensile strength, elongation, double folds.

Analysis of variance was performed to summarize the effect of deacidification treatments on the different type of paper samples, and the effect of aging. In this case, the analysis of variance indicated that any differences greater than 10% are significant and are improbable to have appeared by incident. Another finding of the analysis of variance was a significant increase in tensile strength for the samples treated with MMC, suggesting that treatment effects appear in change differentially on artificial aging. And differences between each treatment were clearer and more significant for the filter paper results than the printed book paper and newspaper samples because what we have mentioned above about the effect of the present or absence of printing.

The values of the untreated control samples represent the complete 100% value to measure the variation of the treated samples value of mechanical properties. An increase in tensile strength of 21% was measured after the whatman paper **WP** samples were treated with nonaqueous solution of methyl magnesium carbonate (MMC). A greater loss of 11% in tensile strength after immersion in Magnesium bicarbonate (MB), has been reported for the **WP** samples. However, newspaper **NP** and printed book paper **BP** show significant increase in tensile strength of between 37- 74% for the non aqueous treatments **MMC**, and similar increase approximatly 23% were observed for **BP** after treated with aqueous solution of magnesium bicarbonate **MBC**, but very slight increase in tensile strength for the **NP** treated samples with the aqueous treatment.

After artificial ageing we noticed that almost all the untreated samples showed a significant decrease in the tensile strength; however the **MMC** treatments caused an increase in tensile strength of the treated samples **WP, NP, BP**; while the **MBC** treatment showed slight increase of the book paper samples **BP** and a decrease in **WP** and **NP** samples. Although unexpected, this increase is statistically significant. As ageing was undertaken in dry conditions, the paper may have lost water from between fibers, which may not have been completely replaced by standing in 55 ± 5% RH. This water may act as a lubricant during tensile strength measurements, allowing the fibers to slide over each other more easily. Therefore, reduction of the amount of water in the paper may cause an increase in the force necessary to break the strip of paper, and thus the tensile strength of the paper may appear greater, though a different measure of strength, such as double folds, possibly would clarify if the increasing of tensile strength would be as a result of the deacidification treatment.

Double fold

Double fold measurements recorded improve after treatment with the two deacidification methods in whatman paper **WP** and newspaper **NP** samples; On the other hand, the book paper samples were unmodified; the sample **BP** has very low double fold, which is a characteristic feature of a low-pH-ground-wood paper from the end of the 19th century. In the samples after deacidification the folds has been decreased, which is caused by the increased paper fragility.

On the other hand, the decrease of double fold in control samples of acidic papers is very precipitous right to samples NP and BP. The loss of mechanical qualities is very big and papers after AA are in very bad condition. Compared to controls the loss of strength of deacidified samples is considerably slower. The result is that the treatments modify significantly the initial mechanical characteristics.

Table 3. Tensile strength, Elongation and Double fold values of the untreated and treated samples Before and after ageing

Paper samples	Deacidification Treatment	Tensile strength (N)	Elongation (%)	Double fold
Whatman paper (WP)	Control	48.16	0.843	39
	MMC	58.40	1.430	68
	MBC	42.73	0.915	54
Newspaper (NP)	Control	55.10	0.645	34
	MMC	75.50	0.793	52
	MBC	56.00	0.718	57
Book paper (BP)	Control	27.32	0.379	5
	MMC	47.81	0.542	4
	MBC	33.64	1.264	5
Whatman paper (WP)	Control	44.98	1.180	34
	MMC	68.60	1.660	41
	MBC	44.69	1.200	40
Newspaper (NP)	Control	44.92	0.645	22
	MMC	63.96	0.572	38
	MBC	48.23	0.687	63
Book paper (BP)	Control	16.94	0.328	1
	MMC	35.24	0.431	3
	MBC	29.62	0.491	3

Identification of chemical changes by Fourier Transform Infra-Red Spectroscopy

Analysis of the deacidification process has been performed by Fourier transform infrared spectrometry (FT-IR). Although FT-IR spectra of paper are complex, some absorption frequencies are illustrative of the deacidification process and of the formation of magnesium carbonate particles (Fig. 13).

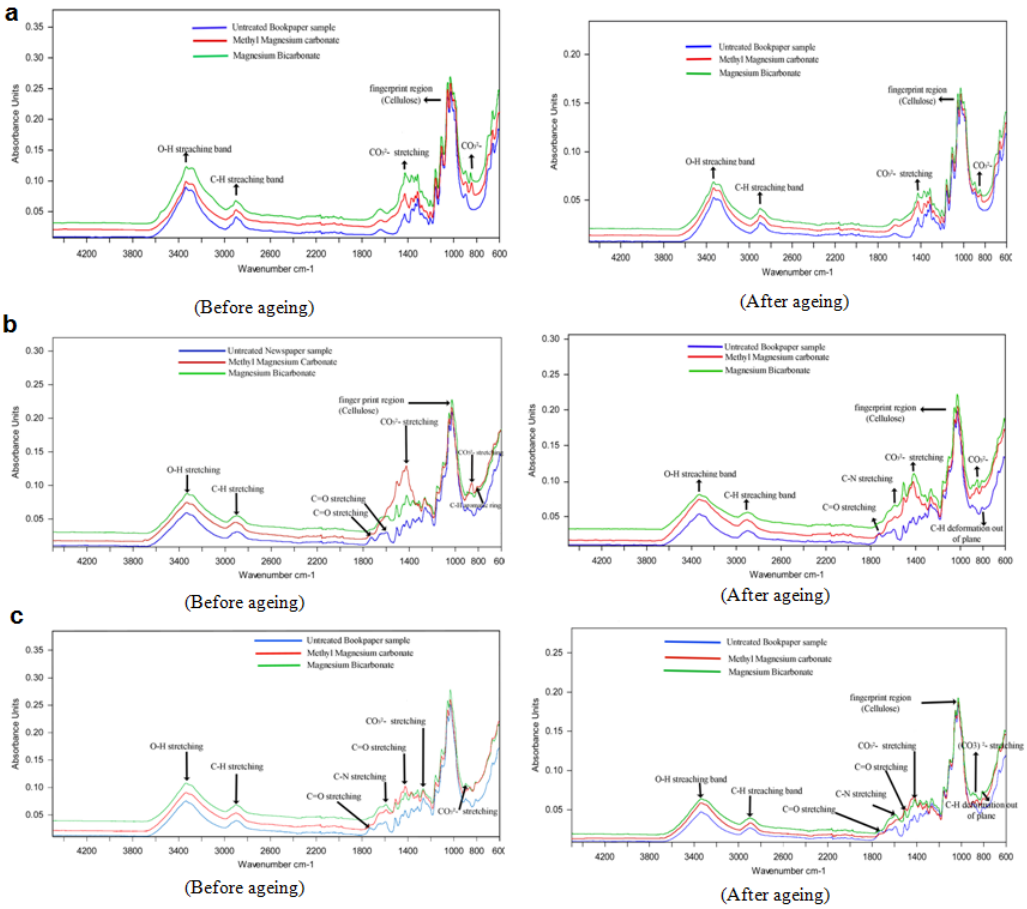

Fig. 13. FTIR spectra of untreated and treated paper: a - whatman paper samples; b - old newspaper samples; c - old book paper samples; blue – untreated, red – MMC treatment, green – MBC treatment: a -

Figure 13 a illustrates a comparison of the FTIR spectrum of unaged whatman paper with the spectrum of unaged treated sample of WP. Treatment of the WP with MMC non aqueous solution led to increase the intensity of the peak in the 1428cm^{-1} region, corresponding to the vibrations of magnesium carbonate. Figure 13b depicts a comparison of the FTIR spectrum of unaged WP with the spectrum of unaged treated sample of WP with MBC (magnesium bicarbonate) aqueous dispersion; The FTIR spectrum show that the aqueous treatment reduced the intensity of the absorbance peak 3335cm^{-1} which refer to the hydrogen bond H-OH , which indicates cellulose hydrolysis. the aqueous treatment led to increase the intensity of the peak in the 1428cm^{-1} region, corresponding to the vibrations of magnesium carbonate.

Figure 13b depicts a comparison of the FTIR spectrum of acidify newspaper (pH = 5.5) with the spectrum of unaged treated sample of newspaper with MMC non aqueous and MBC aqueous treatments.

Since oxidation evokes the production of carbonyls that absorb at the 1720-1735cm^{-1} region, the recording of this area of the IR spectrum of paper facilitates the estimation of the extent of oxidation. The spectrum exhibits a peak of strong absorption at 1727cm^{-1}, which indicates extensive oxidation. Non aqueous deacidification reduced the intensity of this peak; however, the aqueous deacidification eliminated it. It has been shown that this peak corresponds

to the carbonyl of the protonated carboxyl (-COOH), which only exists at low pH = 15- 17. Deacidification increases the pH of paper and converts the carboxyl to the carboxylate form (-COO-), which absorbs at 1630cm^{-1}. It can be seen that there was no discernible change in the absorption at this region of the spectrum of the deacidified paper (NP, fig. 13b).

Therefore, the most sensible explanation for the disappearance of the 1727cm^{-1} peak from the spectrum of the deacidified paper (NP) is that it must be associated to the water-soluble, low molecular mass degradation products of paper components (cellulose, lignin, hemicelluloses and various additives), which were dissolved by the deacidification bath and removed from the paper. Magnesium carbonate forms an alkaline reserve in the deacidified paper and, because the alkaline reserve is important for stabilization of the paper substrate, the band of magnesium carbonate was investigated after the deacidification. It can be seen in Figure 11 that the band responsible for the vibrations of magnesium carbonate (1424cm^{-1}) is already increasing after both treatments. As well, the 875cm^{-1} adsorptions could be safely used for Magnesium carbonate detection.

Figure 13c depicts a comparison of the FTIR spectrum of acidify printed book paper BP (pH = 4) with the spectrum of unaged treated sample of book paper BP with MMC non aqueous and MB aqueous treatments. The spectrum exhibits a peak of strong absorption at 1727cm^{-1}, which indicates extensive oxidation. Non aqueous and aqueous deacidification eliminated the intensity of this peak. The intensity of magnesium carbonate band (1424cm^{-1}) increased after the deacidification treatments.

Determination of crystallinity changes

As seen in **Table 4** there was a slight reduction in the crystallinity Index (CI) values after deacidification treatment by methyl magnesium carbonate (MMC) for the whatman paper samples and book paper samples; while the newspaper samples show improvement after deacidification with MMC. On the other hand, the the crystallinity index of whatman paper samples didn't change after deacidification using Magnesium Bicarbonate, however the book paper samples and newspaper samples show improvement of crystallinty index after deacidification with aqueous treatment of MBC. This mean that he deacidification treatment with MMC didn't change the crystalline structure of the newspaper samples. The treatment with MMC for the whatman and book paper samples produced a reduced level of crystallinity as compared to those treated with MBC which yielded a higher value of crystallinity. This supports the previous finding that aqueous deacidification treatment imparts wet recovery to cellulose.

Table 4. the amount of crystalline Cellulose I for the untreated and treated samples Before and after ageing

Paper samples	Deacidification Treatment	Cr (%)
Whatman paper (WP)	Control	80.31
	MMC	77.20
	MMC(AA)	79.06
	MBC	79.84
	MBC (AA)	80.46
Newspaper (NP)	Control	45.54
	MMC	47.42
	MMC(AA)	45.83
	MBC	44.32
	MBC (AA)	48.27
Book paper (BP)	Control	47
	MMC	43.15
	MMC(AA)	43.11
	MBC	47.41
	MBC (AA)	49.09

Conclusion

This work focused on the working characteristics and deacidification benefits of magnesium bicarbonate and methyl magnesium carbonate used in individual immersion and spray applications to be used as alternative to calcium hydroxide the most common method in Egypt. The study shows that $Mg(HCO_3)_2$ and methyl magnesium carbonate can be prepared readily in laboratory. The application of both deacidification solutions to acidic paper samples from newspaper, book paper and whatman paper provided excellent results. These methods have interesting features that could make it competitive to others. One of the advantages of this deacidification methods is the carbonation of $Mg(HCO_3)_2$ and $MeMgCO_3$, which is fast enough to avoid damaging of cellulose fibers from a long contact with the very basic $Ca(OH)_2$. Reaction with CO_2 produces an alkaline reservoir of $MgCO_3$ that efficiently works as an alkaline reservoir, maintains constant pH and allows a long-term protection of paper

On the other hand, papers treated with both methods showed observable color changes after ageing and some changes in the paper character. An excess of methyl magnesium carbonate is easily deposited with hand-held sprayers; thus, an even deposition is difficult to achieve. The magnesium-containing particles leave a noticeable whitish haze on some samples that can be visually distracting. Color shifts during artificial aging indicate that at least some types of paper treated with MMC experience a whiteness reduction greater than that occurring in papers treated with MBC.

In conclusion, the two methods are very efficient for the deacidification of paper and can be applied to paper using several and simple methods commonly at hand. Preliminary results using spraying and emersion applications were acceptable .

Both deacidification treatments increase the longevity of paper by imparting stability of paper by enhancing the mechanical properties of the treated paper than the untreated paper after ageing.

It was proven in this paper that treatments with MMC and MBC are sufficient methods for deacidification.

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