United States Patent [19]

Williams et al.

[11] **3,898,356**

[45] **Aug. 5, 1975**

[54] **METHOD OF DEACIDIFYING PAPER**

[75] Inventors: **John C. Williams**, Alexandria, Va.; **George B. Kelly, Jr.**, Gaithersburg, Md.; **Richard L. Best**, Arlington, Va.

[73] Assignee: **The United States of America as represented by Librarian of Congress**, Washington, D.C.

[22] Filed: **Feb. 28, 1974**

[21] Appl. No.: **447,120**

[52] **U.S. Cl.** **427/343**; 8/118; 21/58; 21/76; 427/354

[51] **Int. Cl.**[2] **A61L 13/00**

[58] **Field of Search** .... 8/119; 117/152, 153, 169 R; 21/58, 76

[56] **References Cited**

UNITED STATES PATENTS

2,033,452	3/1936	Schierholtz	117/152
2,864,723	12/1958	Fluck et al.	117/76 T
3,676,182	7/1972	Smith	117/60

OTHER PUBLICATIONS

Barrow, W. J., Deterioration of Book Stock – Causes and Remedies – Virginia State Library, Richmond, Va. 1959.

Barrow, W. J., Permanence/Durability of the Book, Book III, W. J. Barrow Research Lab., 1964, TS1109B37.

Primary Examiner—Michael R. Lusignan

Attorney, Agent, or Firm—Joseph A. Hill; A. David Spevack

[57] **ABSTRACT**

A method of deacidifying paper wherein paper in serial order is contacted with a saturated aqueous solution of a group II metal salt and another aqueous solution capable of forming a substantially insoluble buffer material in situ with the group II metal and subsequently washing out soluble reaction products in a controlled wash.

10 Claims, 1 Drawing Figure

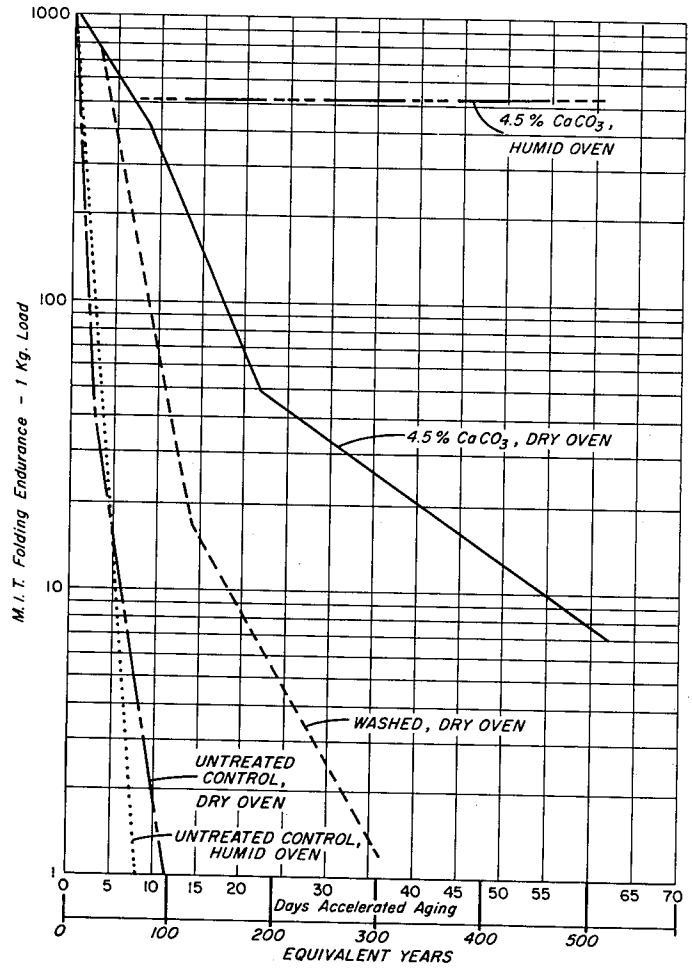
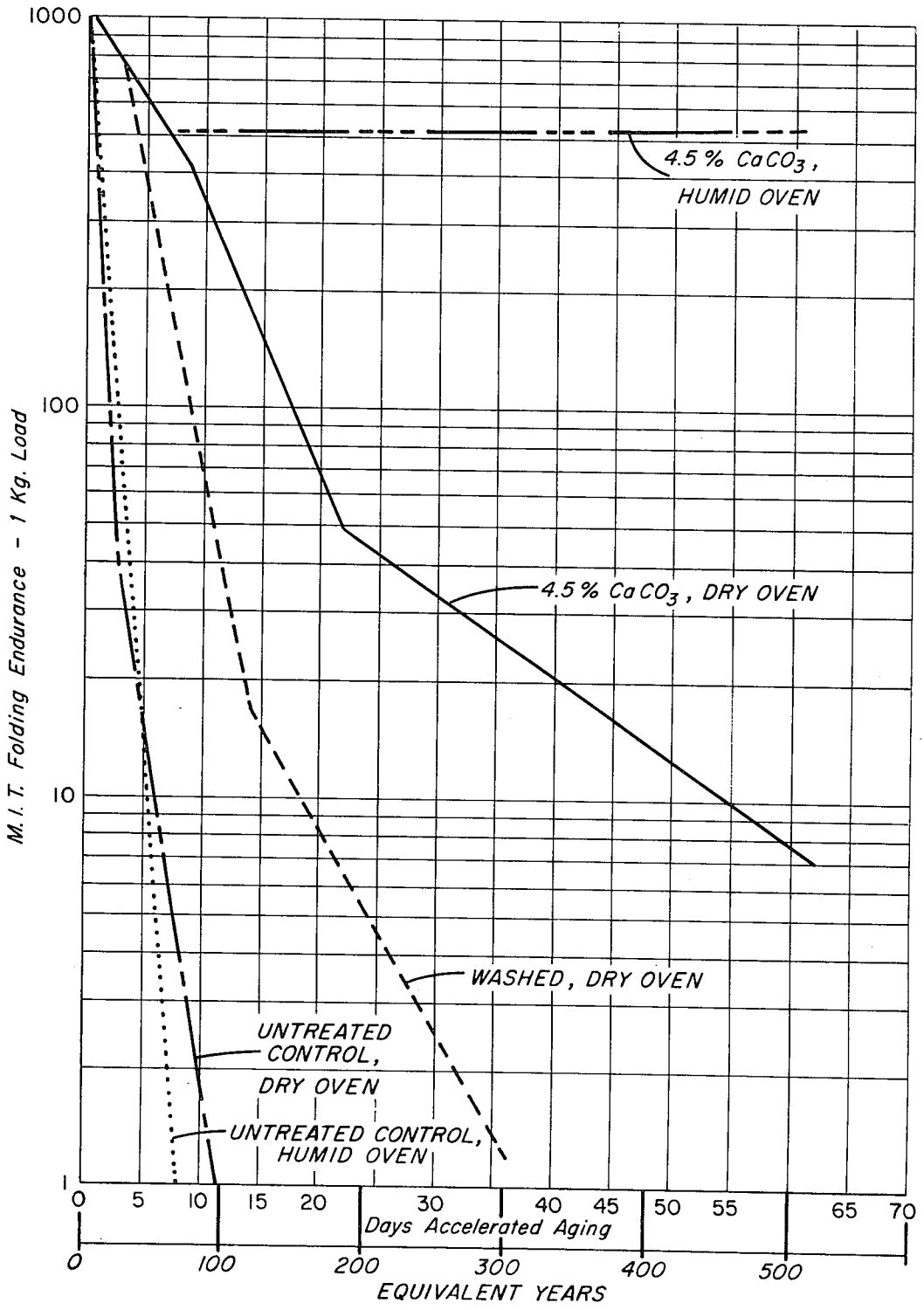


Fig. 1


1000
100
10
1
M.I.T. Folding Endurance - 1 Kg. Load
4.5 % CaCO3, HUMID OVEN
4.5 % CaCO3, DRY OVEN
WASHED, DRY OVEN
UNTREATED CONTROL, DRY OVEN
UNTREATED CONTROL, HUMID OVEN
0 5 10 15 20 30 40 45 50 55 65 70
Days Accelerated Aging
0 100 200 300 400 500
EQUIVALENT YEARS

METHOD OF DEACIDIFYING PAPER

GOVERNMENT LICENSE

The invention described herein may be manufactured and used by or for the Government of the United States of America for Governmental purposes without the payment of any royalties thereon or therefor.

This invention pertains to a method of preserving paper and more particularly to a method for neutralizing the acidity of paper and buffering it on the alkaline side to improve its permanence.

BACKGROUND OF THE INVENTION

Certain early papers have lasted for over 1,000 years and many papers made during the Middle Ages are still in excellent condition. The quality of most paper made in the last 150 years has dropped drastically. Many valuable volumes printed today will be brittle and useless within 25 to 50 years.

This phenomenon is apparent to any person searching in the patent copies in the Patent Office search files. The older patents issued since about 1860 are so yellow and brittle that they fall apart. Deterioration with age can be graphically seen by leafing through a sub-class which begins before the turn of the century.

A number of investigators have established the problem as the use of rosin alum size which leaves the paper acid causing lowered endurance. Jarrel, Hankins and Veitch, in the Technical Bulletin No. 334, U.S. Department of Agriculture, Washington, D.C., September 1932, show that paper is quite stable at a pH value of 7 and will last for hundreds of years. However, the same paper at pH value of 4.2 will be brittle and crumbling after 25 years of storage. Rosin alum sizing may leave paper anywhere between pH values of 4.2 and 7, but usually it is in the range of 4.5 to 5.5. In addition, paper tends to go slightly more acid during aging. When it is exposed to acid atmospheres the pH can also drop rapidly. Today's polluted city atmosphere causes an increase in acidity because of oxides of sulfur and other acid pollutants.

W. J. Barrow in Permanence/Durability of the Book I, II, III, IV, V and VI, W. J. Barrow Research Laboratory, Richmond, Virginia, 1963–1969, and others have demonstrated that by neutralizing the acidity of modern paper which is in reasonably good condition and buffering it slightly on the alkaline side, the paper can be restored to its archival character and the paper will last for 500 years or more. Barrow utilized a method of Schierholz described in U.S. Pat. No. 2,033,452 in his work. In the Barrow procedure, the paper is first dipped into a solution of saturated calcium hydroxide and then into a solution of calcium bicarbonate. This neutralizes the acidity in the paper and precipitates the buffer calcium carbonate in place.

Kelly, a co-inventor herein, in a speech given to the Washington Region Conservation Guild, Mar. 1, 1973, at the Library of Congress, has estimated that approximately 3% calcium carbonate, based on the weight of the paper, is required to protect paper for 500 years. However, as the energy shortage develops, high sulfur coals are again being burned; the sulfur dioxide content of the atmosphere is starting to rise. The figure of 3% will probably have to be revised upward.

One of the difficulties with the Barrow method lies in the insolubility of calcium bicarbonate and the consequent low concentration of the solutions which can be

prepared. The saturated solution of calcium hydroxide is only 0.11%. That of calcium carbonate solubilized by carbon dioxide under one atmosphere pressure is the same. The average paper takes up about 0.3% calcium carbonate in a single Barrow treatment. Barrow, therefore, went to magnesium carbonate as giving a more soluble bicarbonate solution, 1.1%, under carbon dioxide at one atmosphere. With a bibulous paper this single treatment with magnesium carbonate will occasionally leave the equivalent of 3% calcium carbonate in the paper but this is not achieved with either consistency or reliability. The two methods are not equivalent since, in the two step Barrow treatment, non-migrating calcium carbonate is precipitated in the paper, while with the magnesium bicarbonate a soluble material is applied which may migrate to the drying surface.

The preparations and use of bicarbonate solutions is difficult for those engaged in repairing and restoring paper, particularly for those working without chemical equipment or chemical training. Carbon dioxide cylinders are heavy and are dangerous unless strapped to the wall or to a bench. The solutions must be prepared as needed and must be monitored by titrations which often require the services of a chemist. As carbon dioxide escapes from the solutions, the bicarbonate decomposes to the carbonate and precipitates. When the solutions are sprayed, as in the Barrow method using magnesium bicarbonate, the carbon dioxide escapes rapidly and much of the material may reach the paper as insoluble magnesium carbonate which remains at the surface of the dried sheet as a powder and is removed by ordinary surface manipulation of the paper such as rubbing.

These difficulties and defects have led to developments of solvent-based deacidification techniques such as Baynes-Cope's use of barium hydroxide dissolved in methanol described in "The Non-Aqueous Deacidification of Documents", Restaurator, Volume 1, No. 1, 1969, pp. 2–9, and Smith's method of soaking the paper in magnesium methoxide dissolved in methanol-fluorocarbon solutions described in U.S. Pat. No. 3,767,182. These materials and solvents are poisonous and must be used in hood-equipped laboratories. Also, the solvents used in these methods often attack inks and colors and spread them through the book, thus ruining the work. Magnesium methoxide, barium hydroxide and calcium hydroxide give the paper high pH values which change color tones in art on paper and often bring out undesirable changes in paper containing groundwood, or dyed paper.

Neutralization of acid in cellulose materials is also applied in the textile art (U.S. Pat. No. 2,864,723) although the textile chemist is not faced with the same ultimate problems.

OBJECTS OF THE INVENTION AND GENERAL DESCRIPTION

The method of deacidifying and buffering paper which is our invention is intended to remove the difficulties from the Schierholz/Barrow methods and to extend the usefulness of aqueous treatments. The new methods are simple and can be operated with a minimum of equipment. The solutions are stable and their concentration and effectiveness can be readily checked using simple and even improvised equipment by an operator untrained in chemistry. In our new method, neutralization and buffering are combined with modified

procedures similar to those employed by most conservators, such as washing paper after treatment.

It is therefore an object of this invention to avoid the insolubility problems of the lime and calcium bicarbonate procedure.

It is an object of this invention to provide deacidification and buffering treatments for paper which operate without taking the paper to high pH values which change or generate colors.

It is an object of this invention to avoid poisonous solvents and to avoid leaving poisonous soluble material in the treated paper.

It is also an object of this invention to simplify the treatment techniques so they may be conducted by persons who do not necessarily have chemical skills.

It is further an object of this invention to eliminate the use of cumbersome or dangerous equipment.

Yet another object of the invention is to provide a method utilizing the skills presently used by most conservators.

Other objects of this invention will become apparent in the following description.

SUMMARY OF THE INVENTION

This invention contemplates a process of neutralizing the acidity of paper and buffering it on the alkaline side to improve its permanence. The method contemplates in serial order contacting paper with a solution of an aqueous soluble salt of a group II metal and a salt capable of forming a relatively aqueous insoluble buffering compound in situ with the group II metal. Preferred group II metals within the meaning of the present invention are magnesium, barium, calcium, strontium and zinc. The salts are preferably the water-soluble halides and acetates. The chlorides are the most preferred of the halides. The water-soluble alkaline earth salts are most preferred of all the group II metal salts. When necessary the buffering agent is 'set' into the paper by drying the paper prior to washing as in the case of partially soluble buffer salt. The paper is then washed in a controlled manner to remove excess reactants and the soluble reaction products and finally dried as a neutralized and buffered paper.

While either of the two solutions used may contact the paper first, it is preferred to use the suitable group II metal salt solution first in most cases to allow the metal ion to react with cellulosic carboxyl groups which may be present. It is within the ordinary skill in the art for one to determine which salts should be added first in view of the criteria set forth below. The reactant salt is an aqueous soluble material capable of interacting with the Group II metal salt to form a water-insoluble basic salt. Such reactant salt is preferably a carbonate. Obviously any material whose end product of reaction with the Group II metal salt will form an insoluble buffering agent and a soluble side product can be used without differing from the intent of this invention.

Washing is an important element of this procedure. The wash step should be of such a nature so that it does not dissolve deposited buffering material while physically removing gross surface deposits of excess materials and the soluble reaction products. It is necessary that the wash water be at least neutral and it is preferred the wash be slightly alkaline in pH. It is also preferred that the wash water be saturated with the same salts as the buffering agent when the buffer is not very insoluble.

In general two solutions are prepared from readily available common salts. In the most preferred embodiment the Group II metal salt solution is 10% calcium chloride and the reactant solution is 10% ammonium carbonate. The sheet of paper to be deacidified and buffered is dipped in the Group II metal salt solution and then in the reactant salt solution. Any number of methods of contacting the paper and solution are available. Besides dipping the paper in the solution, the solution may be sprayed or sponged onto either the obverse or reverse side of the paper. One solution can be applied to one surface and the other solution applied to the reverse side of the paper causing the interaction to take place deep within the fiber structure of the paper. This produces the insoluble buffer such as calcium carbonate in situ in a desired amount from 0.3 to 10% dependent upon the concentration of the starting solutions and absorptive ability of the paper. The reaction also produces ammonium chloride or like soluble salt which is subsequently removed. The treated sheet is next washed in running water until the wash water tests at a normal chloride content for the wash water. Such a test may be made by known methods such as by conductivity apparatus or by a drop or two of dilute silver nitrate in the wash water effluent.

Any gross amounts of calcium carbonate or other insoluble buffer (dependent on starting materials) formed on the surface of the paper are removed in the washing step.

The use of wetting agents or alcohols is appropriate to make the sheets wet rapidly and expedite the work. Thickeners known to the art may also be incorporated in the solutions to make them adhere to the side of a vertical sheet during spraying.

The solutions may be purchased from chemical supply houses in the proper concentration or easily prepared by simply weighing the ingredients out and dissolving in water. The concentrations of the two starting solutions are preferred to be approximately stoichiometrically equal although this is not critical since the starting materials are water soluble and will be removed in the washing step. The solutions may be tested for strength and usability at any time by pouring small portions together and observing the amount of calcium carbonate product nephelometrically and comparing to a standard. Because of the reasonable price of materials, they may be discarded after one use.

The wash water must be alkaline or it will dissolve the deposited alkaline earth compound. It is preferred that the wash water be saturated with the deposited alkaline earth compound. For example, when the deposited compound is calcium carbonate, the wash water is first flowed through a bed of calcium carbonate, such as marble chips or like material to saturate the water. A final rinse with distilled water is used before testing the effluent from the paper.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now, having generally described the method of this invention in general terms, the following examples are set forth to more particularly illustrate the invention.

EXAMPLE 1

Three pounds of prepared rag and two pounds of

bleached northern kraft were beaten to a Williams freeness of eight minutes. 1% Hercules Neuphor, a modified rosin and 3% dissolved papermakers alum were added, based on 100 dry fiber. The stock was formed into handsheets, the slurry receiving further alum solution as required to give the dry sheet a pH of from 4.6 to 4.8. The basis weight of the sheets was 75 grams per square meter, the brightness was 64 (according to TAPPI 452-OS58, Standards and Suggested Methods, Technical Association of the Pulp and Paper Industry) and titration of 2.5 grams of paper opened in 250 grams of water showed 91 milliequivalents of acidity per kilogram. Such an acid paper shows a rapid drop in MIT folding endurance (TAPPI T511-su69) on accelerated aging in the oven.

Sheets to be deacidified and buffered were wet out by being immersed in an aqueous 50% methanol solution. The sheets were then soaked 15 minutes in 6% aqueous calcium chloride solution and drained. The sheets were next immersed for 15 minutes in 6% ammonium carbonate solution and drained.

As a washing procedure, the sheets were rinsed separately in a shallow pan three times with deionized water, draining between each wash. Next, the sheets were soaked together in fresh deionized water for 15 minutes. Finally, each sheet was rinsed separately in fresh water. Drippings from the sheets were tested with 0.3% silver nitrate solution and turbidity was found. Washing was therefore resumed. The sheets were soaked another 15 minutes in deionized water with agitation and then each sheet was washed with running deionized water in a pan tilted at 45°. After two minutes of continuous washing, the sheets were drained. Drippings now showed a negligible content of chloride ion when tested with the silver nitrate test.

The sheets were air dried and prepared for oven aging along with the untreated controls. Dry oven aging was carried out according to TAPPI T453 ts-63 except that 100°C was used. Generally 72 hours at this temperature is considered to be equivalent to 25 years at ambient conditions. The paper was also aged in an oven held at 90°C and 50% R.H. The aged and unaged sheets were analyzed with the results shown in Table 1. The treatments can be seen to be very effective.

Electron microscope pictures were taken of the paper. Calcium carbonate particles could not be seen at a magnification of 100X but were visible at 1000X in the treated sheet as well distributed round particles. The washings with deionized water had evidently partially solubilized the crystals and removed the corners.

Table 1

	pH	Titration Meq/Kg	% $CaCO_3$ (Alk. Reserve)	Fold End.	Brightness
Start					
Control	4.8	96	—	1072	77.1
Treated	9.0	—	4.75	1110	77.1
3 Days Aging (25 Years Equivalent) Dry Oven					
Control	5.0	56	—	38	73.8
Treated	8.9	—	3.21	980	74.7
Humid Oven					
Control	4.8	86	—	33	68.0
Treated	9.2	—	6.48	787	74.2
6 Days Aging (50 Years)					
Dry Oven					
Control	5.5	45	—	9.6	—
Treated	9.2	—	3.50	524	—
Humid Oven					
Control	5.2	80	—	9.2	—
Treated	9.2	—	5.60	475	—
9 Days Aging (75 Years) Dry Oven					
Control	5.4	67	—	1.8	—
Treated	9.0	—	2.66	434	—
Humid Oven					
Control	5.3	111	—	0.6	—
Treated	—	—	—	459	—
14 Days Aging (116 Years) Dry Oven					
Control	5.0	48	—	0.4	55.0
Treated	8.7	—	3.58	158	65.0
Humid Oven					
Control	4.5	150	—	0	30.0
Treated	8.9	—	5.48	53.5	65.0

EXAMPLE 2

The handsheets of Example 1 were remade except the formulation was 50% prepared rag to 50% bleached northern kraft. The sheets were made to a pH of 4.7 as before with alum.

Sheets were first immersed in the following solution for five minutes.

100 grams calcium chloride
200 grams isopropyl alcohol 70%
700 grams water

The isopropyl alcohol functioned to make the sheets wet rapidly. The sheets were drained and dipped in 10% aqueous ammonium carbonate for five minutes. Washing was carried out using Washington, D.C., tap water which had a pH of 8.65. The sheets were separated by plastic screens, to allow the water to flow past each sheet, and washed for 20 minutes. At this time drippings from the sheets gave no more of a chloride test with the 0.3% silver nitrate solution than with the city water. The calcium carbonate content of the treated sheets averaged 4.5%.

The sheets were oven aged to the equivalent of 500 years. One set of sheets was aged after nothing more than washing in the alkaline Washington tap water. This gave some improvement in permanence. The results are shown in FIG. 1. The treatment greatly improved the acid paper as can be seen from the curves.

The humid oven aging is generally considered to be more severe than the dry oven aging and the curve shows this on the acid controls. Remarkably, the treatment improved the paper (the upper curve) to the point where it no longer lost folding endurance when aged in the humid oven. This interesting result indicates that with properly buffered paper and an adequate level of humidity, paper can be kept in humidity-controlled libraries indefinitely without loss in folding endurance.

EXAMPLE 3

A commercial book paper was selected for treatment which had a composition of 30% bleached hardwood sulfate and 70% bleached softwood sulfate. The paper was sized with rosin and alum and had a pH of 5.7. MIT folding endurance at one-half kilogram load was 350.

The paper was soaked in a 10% solution of sodium carbonate for 20 minutes, drained and immersed for ten minutes in a 10% solution of magnesium chloride. The paper was then washed in tap water, which in this area has a pH of 8.5, for one half hour until the drainings of the sheet showed a pH of less than 8.9. The paper was dried and analyzed and found to contain 4.5% magnesium carbonate and pH of 9.0.

Aging studies showed that after nine days in the 90°C, 50% R.H. oven the folding endurance of the untreated paper had dropped to 240 folds, while the treated paper tested at 320 folds.

Aqueous magnesium chloride when added to aqueous ammonium carbonate does not give the desired precipitate of magnesium carbonate due to the formation of a soluble double salt. In such a case, ammonium salts are excluded and sodium carbonate is used as the precipitant in preparing the buffer. Of course, other soluble alkali salts may also be used. This procedure produces relatively high pH values in the paper for the brief soaking period until the washing step lowers the pH. Accordingly, a small portion of the material to be treated is tested to see whether damage will occur. Sodium carbonate solution enhances the solubility of magnesium carbonate therefore the paper is first dipped in the sodium carbonate solution and next in the magnesium salt solution.

EXAMPLE 4

Treatment with zinc chloride and ammonium carbonate

Zinc carbonate is somewhat like magnesium carbonate in its tendency to dissolve in excess ammonium carbonate solution, particularly at higher pH levels. For this reason, the order of addition with the zinc carbonate impregnation is also reversed, dipping the paper first in the ammonium carbonate solution and then in the zinc chloride solution. Since it is known that high concentrations of zinc chloride can damage paper or even dissolve it completely, the concentration of the zinc chloride should be limited to not more than 10–15% by weight, at which level no damage has been observed even with soaking for several hours.

A solution of ammonium carbonate was made up with

10% ammonium carbonate by weight
20% isopropyl alcohol by weight
70% water by weight

The paper to be treated, a sheet of newsprint with an initial pH of 5.8, was soaked in the ammonium carbonate solution for 20 minutes and drained of excess solution. It was next immersed in a solution of zinc chloride of the following composition:

10% zinc chloride by weight
90% water by weight

The paper was allowed to remain in this solution for 20 minutes and then removed and washed for approximately 30 minutes in tap water which had a pH of 8.5. At the end of 30 minutes the chloride content of the washings had been reduced to that of tap water as measured by conductivity. Specific conductance of the wash water was 0.00018 mhos per centimeter. During the washing period, conductivity rose as high as 0.0018 mhos per centimeter and then fell to the original value after 30 minutes.

The paper was aged 14 days, equivalent to 115 years under ambient conditions, in the 100°C dry oven, and for the same time in the oven at 50% R.H. and 90°C.

The pH of the untreated newsprint dropped to 4.5 in the dry oven and 4.2 in the humid oven. The treated paper dropped from a pH of 8 to 7.3 in the dry oven and to 7.0 in the humid oven. Folding endurance of the untreated newsprint dropped from 40 to 2 in the dry oven and to 1 in the humid oven. Folding endurance of the treated paper dropped to 5 in the dry oven and to 38 in the humid oven.

EXAMPLE 5

A printing paper at a pH of 5.5 was selected for treatment. In this test, the insoluble buffering salt was formed centrally in the sheet thickness. Blotters were cut to the same size as the paper being treated. One set of blotters was saturated with 15% aqueous calcium acetate solution and one set with 15% aqueous ammonium carbonate solution. Paper and wet blotters were assembled into a stack in the following order: calcium acetate-impregnated blotter, paper to be treated, ammonium carbonate-impregnated blotter, paper, calcium acetate-impregnated blotter, etc. A stack of 30 sheets was placed under light pressure in a book press. As a test of penetration, sheet aluminum electrodes were placed at the top and bottom of the stack. An electric current source was placed in series with an ammeter and the electrodes. As the solutions penetrated the papers the ammeter current rose to a maximum. This took approximately three minutes. The sheets were left under pressure for 15 minutes. The press was then opened and the stack separated. The treated sheets were washed in tap water which had a pH of 8.5 until the specific conductivity of the used wash water had dropped to that of the water being employed. This required approximately 30 minutes of washing time. The treated sheets were dried, analyzed and found to contain 4% calcium carbonate, at a pH of 8.5. On dry oven aging at 90°C and 50% R.H. for nine days, the folding endurance of the untreated paper dropped from 80 to 30. The folding endurance of the treated paper dropped from 80 to 60.

EXAMPLE 6

A white bond paper, 30% bleached hardwood sulfate and 70% bleached softwood sulfate sized with rosin and alum and at a pH of 5.7 was deacidified using 10% barium chloride at 40°C in the first dip and 5% ammonium carbonate in the second dip, allowing the sheets to remain in each solution until thoroughly saturated and draining between the first and second solutions. The sheet was washed until the conductivity measurement showed the soluble salts, principally ammonium chloride, to be removed. The paper had a folding endurance of 600 at one-half kilogram load. In three days in the 100°C dry oven, the fold dropped to 520. In six days the fold dropped to 460. The treated paper showed 610 folds after three days aging and 550 folds after six days aging.

The barium carbonate buffer has a particularly advantageous use when collections are to be protected against vermin. However, the extremely poisonous nature of the compound militates against its use in library materials that are to be handled. It is ideal for protecting drawings, sketches, etc., that are displayed under glass. To avoid dusting of buffer in this use or in other high buffer content treatments, paper sheets may be resized before drying. Dipping in a 5% solution of Hubin-

ger company Keogum 3800 cooked starch has been found to be a satisfactory method of resizing.

EXAMPLE 7

An early newspaper, The National Intelligencer of 1822, was neutralized and buffered by the new method. Sample sheets 12 inches square were dipped in 6% calcium chloride solution one at a time, interleaved with a porous plastic sheet to carry the fragile paper. After 35 minutes soaking, with frequent agitation of the bath, the sheets were removed, drained and transferred one at a time, with fresh interleaving sheets of plastic into a 6% ammonium carbonate solution. They were allowed to soak 20 minutes, with frequent agitation. The sheets were removed and drained singly. They were then placed in two piles of six sheets each, interleaved with plastic and allowed to soak for one and one half hours with running tap water at pH 8.5 overflowing to sink. Sheets were then removed from time to time, dried and analyzed, with the following results:

Control	No treatment	pH 4.8	Titration: 50 milliequivalents alkali per kilogram to reach pH 7.0
Top sheets	Washed	pH 9.2	4.6% calcium carbonate
Center sheets	Washed	pH 9.3	4.0% calcium carbonate
Control	No treatment Washed	pH 6.7	9 milliequivalents alkali per kilogram to reach pH 7.0

This ancient paper was quite weak and folding endurance could only be run at a 200 gram load. Strips were cut from top to bottom of the paper, parallel to the center fold. Folding endurance of the control was 580. Treated and untreated paper was aged for six days in the dry oven, reconditioned and the folding endurance run again. The untreated paper showed a folding endurance of 72, the treated paper a folding endurance of 135.

What we claim is:

1. A method of neutralizing the acidity of paper and buffering it on the alkaline side wherein the paper to be treated in serial order is contacted with an aqueous solution of a group II metal salt and an aqueous solution of a reactant material capable of interacting with the Group II metal to form a relatively water-insoluble buffering material, permitting interaction of said solutions to form said buffering material, washing the treated paper with a controlled wash to remove excess treating agents and soluble reaction products and drying said treated paper.

2. The method of claim **1** wherein the controlled wash has a pH of 7 or above.

3. The method of claim **2** wherein the controlled wash is saturated with the buffering material.

4. The method of claim **1** wherein the group II metal salt is selected from the group of an alkaline earth halide and alkaline earth acetate.

5. The method of claim **4** wherein the halide is the chloride.

6. The method of claim **4** wherein the alkaline earth halide is calcium chloride.

7. The method of claim **1** wherein the reactant solution is a soluble carbonate.

8. The method of claim **7** wherein the carbonate is ammonium carbonate.

9. The method of claim **2** wherein the first solution is calcium chloride and the second solution is ammonium carbonate.

10. The method of claim **3** wherein the first solution is calcium chloride and the second solution is ammonium carbonate.

* * * * *