

A method for the deacidification of papers and books

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IT HAS BEEN SHOWN THAT THE deterioration of the mechanical properties of paper with aging is caused by acid in the sheet (1–3). Many papers have been produced under acidic conditions and further acidity may have arisen from contact with atmospheric pollutants after manufacture (4,5). Under these conditions, some of the acid groups attached to the lignin-cellulose matrix of the fiber wall will be ion-exchanged to the hydrogen form and provide a significant reservoir of chemically bound acidity (6–8). Over time, the cellulose is degraded by acid hydrolysis, weakening the fibers in the sheet (9,10). This results in a loss of sheet strength which manifests itself as sheet brittleness. Within time, even the gentle mechanical action of handling an acidic sheet can cause it to fall apart.

In an attempt to overcome the problem of embrittlement, processes have been developed to neutralize the acidity of paper sheets and books. Reviews of these methods can be found in the literature (11,12). The simplest method consists of the treatment of the paper with an aqueous solution of alkali followed by drying (13–15), but there is a risk of damage to the paper caused by handling in the wet state. It can also cause curl and cockle as a result of uneven wetting and drying. To overcome these problems, various non-aqueous treatments have been suggested. The first to be proposed was a treatment with a solution of barium hydroxide in methanol (16). Other methods have employed mag-

nesium alkoxide in alcohol or fluorocarbons (17), methyl magnesium carbonate in methanol or halogenated hydrocarbon (18), magnesium or zinc hydroxide in hydrocarbon or halogenated hydrocarbon solvents (19) and diethyl zinc in various organic solvents (20). Yet another approach has been the use of particles of inorganic alkaline hydroxides or carbonates dispersed in air or freon (21). Gaseous methods have also included the use of ammonia (15), morpholine (22), and cyclohexamine (23). Although some of these methods are in use, none has been widely accepted as many of the treatments are expensive, require specialized equipment, use hazardous chemicals, and need trained operators.

In this report we present a simple alternative method of deacidification which avoids many of the above problems. The method simply involves bringing the acidic sheet into intimate contact with an alkaline sheet containing calcium carbonate and then facilitating ion exchange between the two sheets. It is already known that migration of materials can occur between sheets of paper in contact over long periods of time (24,25), and in particular the migration of free acid has been observed (24). It has also been suggested that calcium carbonate may be useful to act as a barrier material to neutralize any migrating acid (21). However, in a sheet of paper, deacidification cannot be achieved merely by the migration of the free acid from the sheet. As already stated, the

ABSTRACT

A simple method for the deacidification of paper sheets has been developed and tested on a variety of papers. The method consists of placing the sheet to be deacidified in intimate contact with an alkaline sheet of paper containing calcium carbonate. With time, ions migrate between the sheets resulting in the neutralization of the hydrogen ions of the acidic sheet by ions derived from the calcium carbonate of the alkaline sheet. However, deacidification only proceeds at a useful rate if the sheets are initially conditioned at a high relative humidity and this humidity is maintained while the sheets are held together under an applied pressure. At 97% RH and 350 kPa (50 psi), deacidification can often be completed in less than a day. Other factors such as the roughness and the electrolyte content of the sheets in contact are also important in determining the treatment time. The method has advantages over other deacidification procedures in that it uses benign, inexpensive, readily available materials and equipment. The method can be applied to acidic books by interleaving the pages with alkaline sheets.

Application:

The mechanical properties of many papers deteriorate rapidly with time due to attack by acid incorporated in the sheet at the time of manufacture. The authors describe a new and simple method for the deacidification of archival papers and books to improve their permanence.

fibers in the sheet also contain acid groups bound within the cell walls of the fibers. For complete deacidification to occur, any hydrogen counter-ions of these groups must be neutralized and replaced by other ions such as calcium, magnesium, or sodium. Thus, the objectives of this work were to demonstrate the

occurrence of such ion-exchanges and find the conditions necessary to promote them. As will be shown, this led to a process by which a sheet of paper can be deacidified in the presence of only the moisture picked up by exposure to high relative humidity. The simplicity of the method makes it suitable and safe even for small libraries or private collections. However, it may well be that its advantages are such that it can be used for the mass deacidification programs of major libraries.

EXPERIMENTAL

Acidic sheets

All experiments reported in this text (except where otherwise stated) were carried out using acidic hand-sheets made from unbleached kraft pulp. Such a pulp, of course, is not used in printing papers; but, nevertheless, we felt that it was very suitable for experimentation. With its high content of bound acid groups (81 meq/kg), it represents a more challenging material to deacidify than the bleached kraft pulp used in fine papers (bound acid group content circa 25 meq/kg). The acid group content in fact is similar to that of the mechanical pulps used in the manufacture of newsprint and paperback books. The use of hand-sheets was also considered valuable because of our ability to control composition, ion content, and acidity.

For the preparation of hand-sheets, the pulp was ion-exchanged so that the counter-ions of the acid groups were in the hydrogen form (7). Handsheets were then made at a basis weight of 60 g/m² after adding hydrochloric acid to the deckle to ensure a "salt pH" of 4.0 in the finished sheet. ("Salt pH" will be defined later.) Sheets had an acid content of about 40 meq/kg by titration since only about half the original hydrogen ions survived paper-making due to ion exchange with

the blotters. The replacement counter-ions of the bound acid groups were found to be about 20 meq/kg each of calcium and sodium.

Alkaline sheets

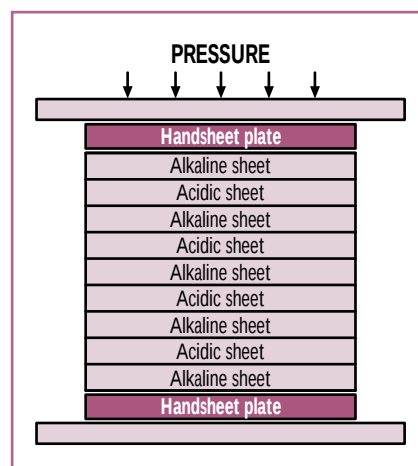
We define "the alkaline sheets" as those paper sheets which carry the calcium carbonate, alkali, or any other deacidification agent. For all experiments reported in this text (except those in Table I), the alkaline sheets were a commercial reprography paper. The paper had a basis weight of 83 g/m² and a calcium carbonate content of 22%. The salt pH was 9.8.

In some cases, the alkaline sheets were modified by the addition of electrolytes (NaCl, CaCl₂, or NaHCO₃). To modify a sheet, it was soaked in a solution of known concentration of electrolyte for 24 h and was then removed from the solution and blotted quickly to remove excess liquid. The sheet was weighed to give the amount of liquid absorbed and so permit the calculation of the amount of electrolyte added. Before use for deacidification, the treated sheets were conditioned at the same relative humidity as were the untreated sheets.

Deacidification procedure

Sheets were either circular hand-sheets or paper sheets cut to the size and shape of a handsheet. All sheets were conditioned at the appropriate humidity (50–97% RH) for 48 h, before assembly into piles for deacidification. In all experiments reported (except those given in Fig. 9), a pile consisted of alternate alkaline and acidic sheets held between hand-sheet "mirror plates" as shown in Fig. 1. Pressures were applied to the piles by adding metal weights or by use of a platen press.

Sheets were conditioned and assembled in a glove box conditioned to the correct humidity using a saturated salt solution (NaCl 75% RH, KCl 85% RH, KNO₃ 92% RH, K₂SO₄ 97% RH). Some assembled



1. Diagram of the experimental assembly

piles of sheets were maintained at the correct humidity in a glove box or similar device. Other piles were put into conditioned plastic bags for pressure treatment in the normal laboratory atmosphere; these piles were returned to the humidified glove box for the removal of samples.

Timing of an experiment commenced at the first application of pressure. At intervals, the pressure was released and some sheets removed from the pile for analysis. The weights of the sheets were determined immediately on removal from the pile and the weights used to calculate the moisture contents of the sheets. For the most part, one-half of each acidic sheet was used for acidity determination and one-half for cation analysis. Following these analyses, the dry weight of fiber was determined.

Acid content of sheets

The progress of deacidification was evaluated in various ways by the following sequence of measurements. The paper to be examined was dispersed in 70 mL deionized water per gram of sample and the pH determined according to the TAPPI Method (26). Solid sodium chloride was then added so as to raise the average concentration of the liquor to 0.1M and the pH was again deter-

mined (hereafter referred to as the "salt pH"). The pulp suspension was then titrated with 0.01M sodium hydroxide, and the amount of alkali required to reach pH 7.0 was used to calculate the acid content of the paper in the units of meq/kg of dry paper. No correction was made for the negligible amount of alkali needed to bring a 0.1M salt blank (no fiber) to pH 7. All pH measurements and titrations were carried out under an atmosphere of nitrogen.

The presence of a neutral salt, such as sodium chloride, is essential for accurate evaluation of the acidity of cellulose fibers. In aqueous suspensions of low ionic strength, the hydrogen ions are much more concentrated inside the fiber walls than in the external liquor and the pH of the suspension as measured in the external liquor is erroneously high as a measure of the total acid present (6). The addition of sufficient salt makes the hydrogen ions more evenly distributed between the fiber walls and the external solution and leads to a realistic evaluation of acid content as determined by pH measurement or by titration. These important aspects of salt addition were described as early as 1937 (27), but they do not seem to have been fully appreciated by the conservation community.

Cation contents of sheets

The paper sample (weight 0.5-1.2 g) was cut into small pieces and added to a bottle containing 50 mL of 0.1M HCl to displace the cations from the acid groups. After 2 h of periodic shaking, the fiber fraction was removed by filtration and the filtrate was analyzed by induced coupled plasma emission or atomic absorption spectroscopy for calcium, sodium, magnesium, iron, manganese, aluminum, and potassium concentrations. From these concentrations, the cation contents of the paper sample were calculated in meq/kg dry fiber.

RESULTS AND DISCUSSION

The phenomenon of ion migration can be demonstrated in simple experiments using acidic sheets, alkaline sheets, and pH indicator papers, all previously conditioned at a high relative humidity. Thus, if a piece of blue litmus paper is placed next to a sheet of acidic paper under an applied pressure and protected from humidity loss, the litmus will turn red over a day or so, indicating the acidity in the adjacent acid sheet. If now a second sheet containing calcium carbonate is placed on the opposite side of the acidic sheet to the litmus paper then, after a day or two, the litmus will regain its blue color indicating neutralization of the acidity in the litmus sheet and in the interleaving sheet. Such demonstrations show how we might deacidify an acidic sheet and indicate a useful, nondestructive method of monitoring the progress of deacidification.

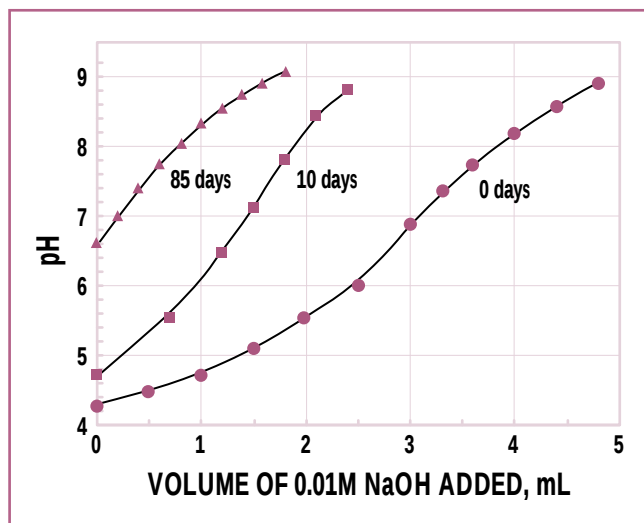
Although the experiments with indicator papers illustrate the migration phenomenon, more quantitative measures are required to obtain actual rates and to optimize conditions for deacidification. Our procedures involved the measurement of both deacidification (loss of hydrogen ions in the acidic paper) and the gain of replacement cations such as calcium. A typical arrangement for an experiment is shown in Fig. 1 where each acidic sheet is sandwiched between two sheets containing calcium carbonate. This arrangement gives the greatest area of contact between the two types of sheet. Deacidification is envisioned as proceeding by a multi-step process. At a given humidity, there will be a certain amount of water in the sheets. This water will be partially absorbed within the fibers and partially condensed in small capillaries between fibers and between the calcium carbonate particles. A limited amount of the calcium carbonate from the alkaline sheet will then dissolve into this

water, and the resultant ions will migrate along the aqueous pathways within the sheet and into the adjacent acidic sheet. Similarly, hydrogen ions from the acidic sheet are able to migrate in the opposite direction. The exact sequence of ion movements may be quite complex; however, the end result is the neutralization of the acidic sheet with the replacement of the hydrogen ions by other cations such as calcium. In the following sections, we will show that the main physical factors affecting the extent of deacidification are time, humidity, and the pressure applied to create intimate contact between the sheets.

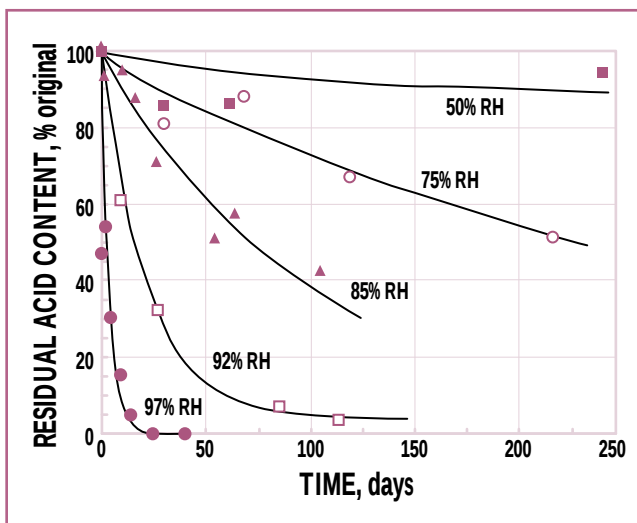
Effect of time

A pile of sheets was assembled as shown in Fig. 1 using acidic sheets composed of unbleached kraft hand-sheets and alkaline sheets made from a commercial paper containing calcium carbonate. At various times after assembly, a pair of alkaline and acidic sheets was removed and analyzed. In Fig. 2, we show the titration curves of the acidic sheets. The amount of NaOH needed to titrate the suspension of fibers to a given pH reduces with time indicating the progress of deacidification. In Fig. 3, the results of the experiments are expressed in different ways. The decreasing acidity of the sheet with time as measured by titration is also reflected by increases in the TAPPI pH, in the salt pH, and in the number of metal cations in the sheet.

From Fig. 3, it is noted that the acid content of the sheet decreases with time until almost no acid remains, i.e., complete deacidification. The acid content of the sheet is calculated from the amount of alkali required to bring the fiber suspension to pH 7. The value of pH 7 was selected because, apart from being neutrality, it is very close to the measured inflection point on the titration curve and is a value beyond which few carboxyl groups in the



2. Titrations of the acidic handsheets taken at various times from an assembly at 92% RH and 7 kPa (1 psi)



4. The effect of relative humidity on the rate of deacidification at a pressure of 7 kPa

fiber wall remain in the hydrogen form.

Figure 3 also shows the change in ion content of the acidic sheet. Only the major ions (calcium and sodium) are shown, and it is readily seen that the increase in concentration of these ions in the acidic sheet is equal to the reduction in acid content. Both the calcium and the sodium ions originate from the commercial reprographic paper. The transfer of the sodium ion appears to reach an equilibrium quickly and is probably associated with the migration of free electrolyte. On the other hand, the migration of calcium appears to take place over a longer time, and this probably reflects the process of dissolution of the calcium carbonate and a slow process of migration due to the low concentration of the dissolved calcium carbonate. To illustrate this, if the sheet contains 10% water and it is assumed that the calcium carbonate has dissolved to its maximum solubility, 0.015 g/L, then the free calcium in solution is only 0.003 meq/kg pulp. This value is very much less than the acid content of the acidic sheet at the start of an experiment (40 meq/kg) and indicates that the con-

Alkaline sheet	Contact with acidic sheet	Deacidification
UBK + CaCO ₃	Smooth - smooth	99%
UBK + CaCO ₃	Rough - smooth	73%
UBK + Dolomite	Smooth - smooth	88%
UBK + Dolomite	Rough - smooth	52%

1. Two-sidedness of deacidification with handsheets. Conditions: 7 kPa. 97% RH. 5 days.

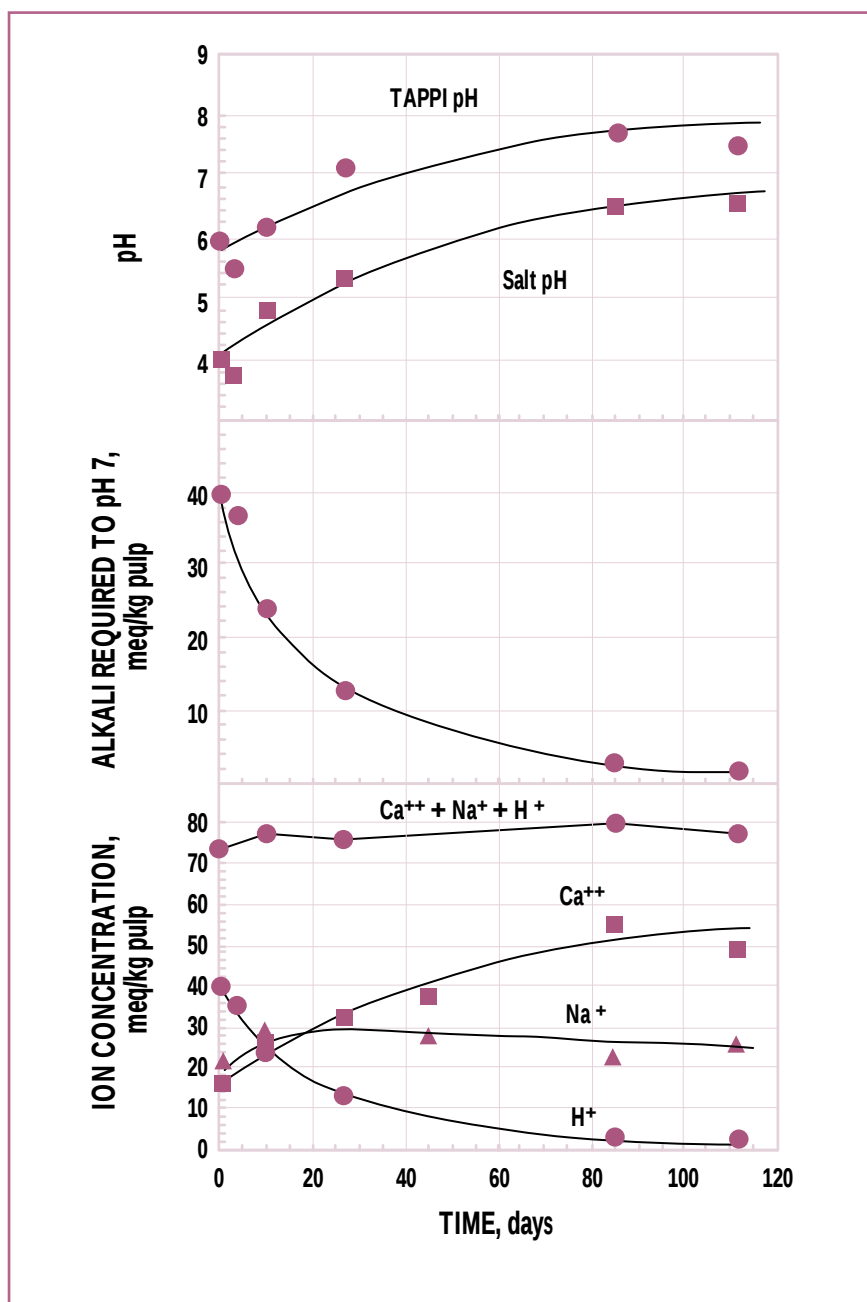
stant dissolution of solid calcium carbonate and transport of the resultant ions is necessary for the deacidification process to be maintained.

Effect of humidity

In the previous section, the rate of deacidification was measured for sheets at 92% RH. In Fig. 4, we show the effects of changing the relative humidity while maintaining all other conditions constant. It is clear that the rate of deacidification is strongly influenced by the relative humidity, and it is probable that this is because the relative humidity controls the water content of the sheets. The relationship between the water content of the sheet and the relative humidity of the atmosphere is given in Fig. 5 for the sheets used most frequently in this work. The different water contents are a reflection of the composition of the sheets. Thus,

for example, the commercial reprography paper has a low water content at a given humidity partly due to the low water absorbency of the filler that it contains.

The role of water is no doubt that of providing pathways for ion migration. Evidence for increasing ion mobility with water content is seen in the electrical conductivity of paper as a function of relative humidity. The conductivity of paper increases by many orders of magnitude as a sheet is changed from the bone dry condition through the range of moisture contents that may be achieved by conditioning samples to different relative humidities (28, 29). Indeed, it was this knowledge that led the authors to explore this line of research.



3. Different measures of deacidification of the acidic handsheets following treatment at 92% RH and 7 kPa (1 psi)

Effects of pressure and sheet roughness

Figure 6 shows that the rate of deacidification is dramatically increased as the pressure applied to an assembly of sheets is increased. It is believed that the major role of pressure at a given relative humidity is to increase the area of intimate contact

between sheets and hence provide larger pathways for ion migration.

The importance of intimate contact on the rate of deacidification is readily observed when using standard handsheets, the preparation of which leaves each with a rough and a smooth side. Simple demonstrations are given in Table I. In the first

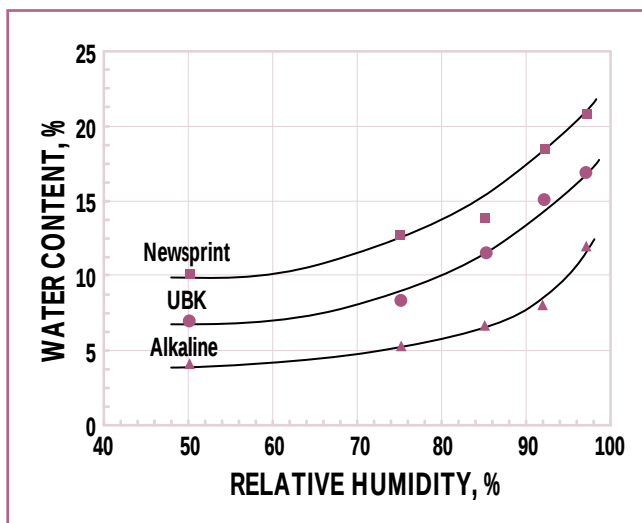
case, an alkaline handsheet was prepared by adding 5% calcium carbonate filler to unbleached kraft pulp. This alkaline sheet was then placed between two acidic sheets. These sheets were the acidic unbleached kraft handsheets and therefore also had pronounced two-sidedness, but only the smooth sides were placed in contact with the alkaline sheet. After 5 days, the acid sheets were removed and analyzed. It was found that the acidic sheet in "smooth-smooth" contact deacidified appreciably faster than that in "rough-smooth" contact. As shown in Table I, this result was confirmed in a second experiment in which the alkaline sheet was prepared using a filler prepared from dolomite (dolomite is $\text{CaCO}_3 \cdot \text{MgCO}_3$).

Manufacturers strive to minimize any tendency to two-sidedness in papers designed for printing and, in keeping with this, we have not observed any significant side dependency on the rate of deacidification of commercial papers. However, a practical implication of the effect of roughness is that the alkaline sheets should be as smooth as possible for the highest efficiency of deacidification at a given applied pressure.

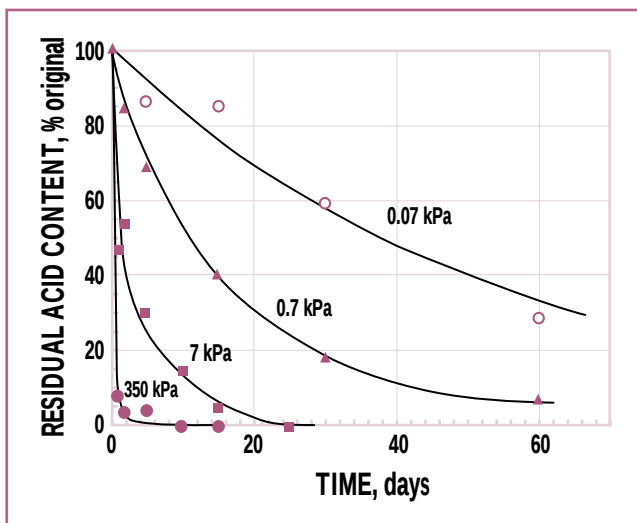
Composition of the alkaline sheet

In addition to physical effects (water content, sheet roughness), the presence of chemicals in addition to calcium carbonate can also play a role in determining the efficiency of the alkaline sheet in producing deacidification. These effects are illustrated in experiments where specific chemicals were added to the alkaline sheet before use. As seen in Fig. 7, these can appreciably accelerate deacidification. There are a number of possible mechanisms for this type of behavior.

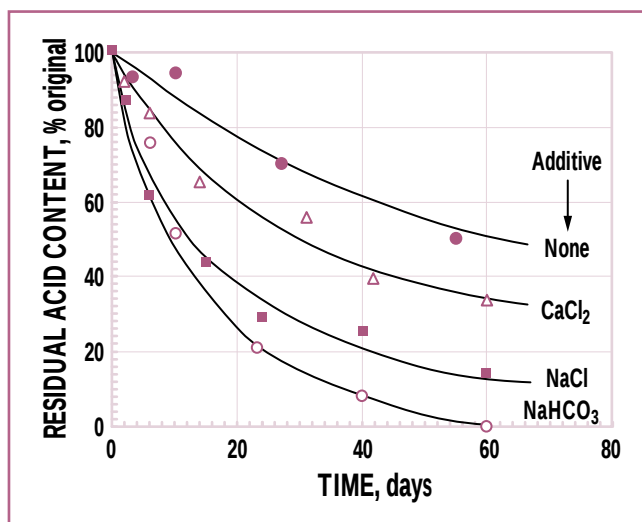
The first mechanism is that the presence of an electrolyte provides a concentration of mobile ions in excess of those originating from the



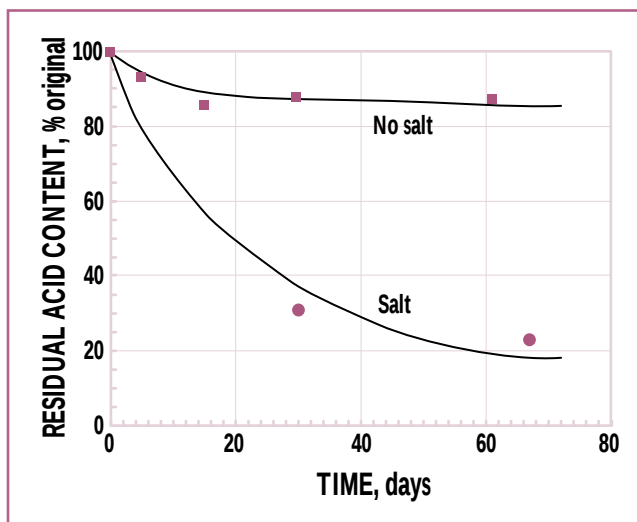
5. The moisture contents of three different sheets as a function of relative humidity. The sheets include two acidic ones and the commercial alkaline paper.



6. The effect of pressure on the rate of deacidification at 97% RH. Note: 350 kPa = 50 psi, 7 kPa = 1 psi, etc.



7. The deacidification of the acidic handsheets using the commercial alkaline sheets to which small amounts of various salts have been added. Conditions: 85% RH and 350 kPa.



8. The effect of 1000 meq/kg sodium chloride added to the alkaline sheet on the deacidification of the unbleached kraft handsheets. Conditions: 50% RH and 350 kPa.

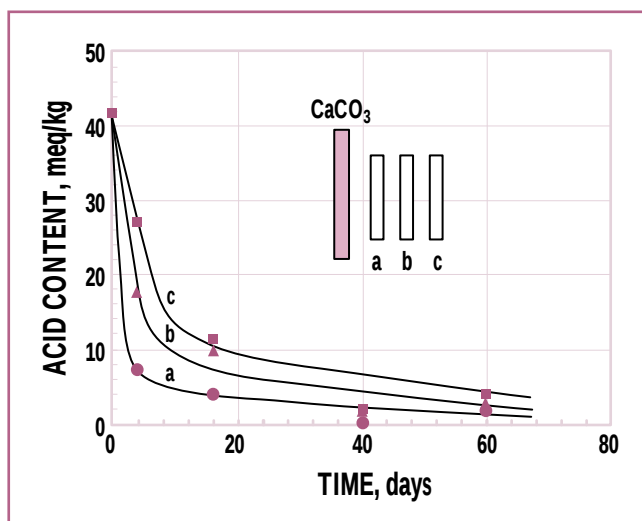
calcium carbonate. A high electrolyte concentration could act to reduce the uneven distribution of ions between the interior of the fiber walls and the inter-fiber solution caused by the Donnan equilibrium (8). Most particularly the tendency for the hydrogen ions to be confined within the fiber walls would be reduced; thus, their migration toward

the alkaline sheet would be facilitated.

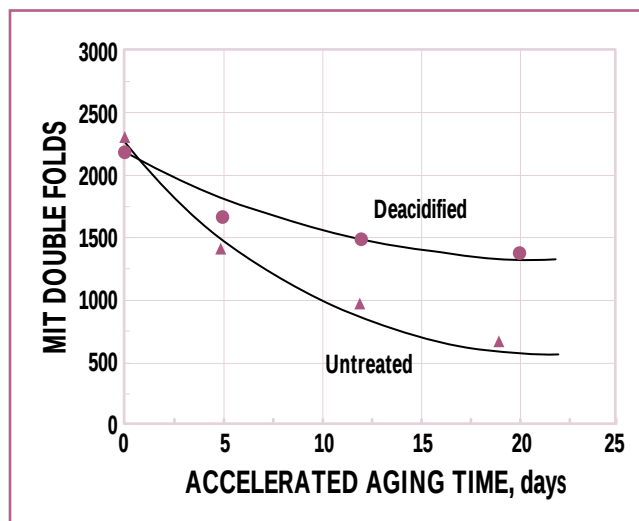
A second mechanism is where the chemical supplies an alternative source of alkali to calcium carbonate. Thus sodium bicarbonate with its much greater solubility than calcium carbonate is the most effective of the three salts used in Fig. 7. However, a drawback to the use of such alkalis is the risk of going beyond

neutralization of the acidic paper and causing damage by rendering the paper too alkaline.

A third effect is that the presence of a large quantity of a salt can accelerate deacidification by increasing the water content of a sheet at a given humidity. For the experiment described by Fig. 7, in which the salt was added at 100 meq/kg, this effect is not a large one. However, if the



9. The deacidification of sets of three acidic handsheets coupled with one commercial alkaline sheet. Conditions: 97% RH and 350 kPa.



10. The loss of folding strength under accelerated aging conditions of samples of newsprint before and after deacidification.

concentration of salt is high, then the increase in water content of the sheet can become very significant. This is illustrated in Fig. 8, in which the addition of 1000 meq/kg sodium chloride to the alkaline sheet produces a marked increase in the deacidification at a relative humidity of 50%. Without salt addition, the rate at this relative humidity is virtually zero; thus, this could be a useful approach to deacidification when high humidities are not practical.

Deacidification through a number of sheets

In the experiments already described, piles of sheets were used consisting of alternate acidic and alkaline ones. However, it is envisioned that, in practice, it would often be convenient to use one alkaline sheet to deacidify several acidic sheets. For example, to deacidify a book, it might only be necessary to insert alkaline sheets after every few pages. Figure 9 shows the result of one experiment to test this possibility using piles consisting of three acidic sheets adjacent to just one alkaline sheet. As expected, the sheet closest to the alkaline sheet deacidified most rapidly; but, with time, all

the sheets deacidified to the same level.

In theory, the number of sheets that it is possible to deacidify by one alkaline sheet is limited only by the amount of calcium carbonate in the sheet. With one sheet containing 10% calcium carbonate, it should be possible to deacidify 40 acidic sheets of 50 meq/kg acid content and similar basis weight. Of course, the process would be extremely slow if the acidic sheets were placed as a pile against a single alkaline sheet.

Deacidification of different types of paper

For comparison of the magnitude of different effects, the results reported in this text largely refer to handsheets of unbleached kraft pulp deacidified by one particular alkaline paper. However, most of the experiments have been repeated on other acidic papers. All papers examined proved responsive to deacidification in a similar manner and papers differed only in the rate of response. In Table II, we list the results of the treatment of a variety of acidic papers with one set of conditions (two-sided contact with the commercial alkaline sheet, 97% RH, and 350

kPa). The list includes commercial samples of book paper, magazine paper, and newsprint. Similarly, all sheets containing calcium carbonate that have been tried have been found suitable for use as the "alkaline" sheet.

Properties of deacidified paper

A study has not been made of the changes that occur to the paper structure and properties as a result of the treatment. The conditions are extremely mild and it is expected that changes would be minimal. A pressure of 350 kPa (50 psi) is low compared with pressures experienced during manufacture. A relative humidity of 97% does not raise the moisture content of a sheet to such a level that causes important changes.

Tests were made to confirm that deacidification by our procedure did indeed improve the aging properties of paper in terms of mechanical strength. Figure 10 shows the effect of deacidification on the folding endurance of the newsprint sample as evaluated by exposure to accelerated aging conditions of 80°C and 75% RH. As is seen, the loss in fold of the newsprint was much reduced by deacidification.

KEYWORDS

Acid groups, acidolysis, aging, bibliographies, books, calcium carbonate, cellulose degradation, deacidification, durability, ion exchange, ions, migration, neutralization, paper humidity, paper sheets, pH.

CONCLUDING REMARKS

A simple process for the deacidification of paper sheets and books has been outlined and the factors controlling the deacidification rate discussed. Pressure and elevated humidity are the major requirements to reduce the treatment time. If the alkaline sheets contain little else other than calcium carbonate and perhaps "neutral" electrolyte, side effects and risks of over-treatment to the acidic paper are minimal. In practice, the completion of deacidification could be determined by the use of indicator papers placed between the sheets. Alkaline sheets are inexpensive, readily available, and may be used many times. The benign nature of calcium carbonate compared to other chemicals proposed for deacidification poses little hazard to operating personnel or the environment.

Finally, some question may arise as to the novelty of this process in view of the widespread use of alkaline paper products in the form of archival envelopes and storage boxes, alkaline mounts for paper prints, and even "permanent" stamp albums. These devices protect their contents against atmospheric pollutants and volatile acids. However, it is clear from the present work, the pressure and usually the humidity involved in the usage of these devices are so low that the acidity arising from bound acid groups would not be significantly reduced even over many years. The proposed close contact between acidic and

Type of paper	Contact time, days	Acid content, meq/kg	Salt pH
High-yield sulfite	0	181	2.8
60 g/m ²	1	13	6.1
0.5% ash	16	3	6.8
Paperback	0	98	4.0
60 g/m ²	1	25	6.1
11% ash	15	0	7.1
Hardback book	0	81	4.3
90 g/m ²	1	57	5.2
17% ash	15	3	6.8
Newsprint	0	57	4.3
40 g/m ²	1	2	6.4
0.5% ash	15	0	6.8
Unbleached kraft	0	42	3.9
60 g/m ²	1	3	6.3
0.5% ash	15	0	6.8
Bleached kraft	0	11	4.5
60 g/m ²	1	0	7.3
0.5% ash			
Magazine	0	2	7.0
60 g/m ²	1	0	7.5
25% ash			

Paperback: "Hallowe'en Party," Fontana Books, London (1971).
 Hardback: "Wetting and Detergency," A. Harvey, London (1937).
 Magazine: *Pulp and Paper Magazine of Canada* (1965).
 Handsheets: High-yield sulfite, unbleached kraft, bleached kraft.

II. Deacidification of different types of paper at 350 kPa and 97% RH.

alkaline sheets coupled with the simultaneous application of high humidity and high pressure are the novel aspects of our process. Deacidification by this combination of conditions appears not to have been proposed before, perhaps because ion transfer is not expected under "dry" conditions. TJ

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H9R 3J9. Page, formerly a director of research at Paprican is now Distinguished Professor of Physics at the Institute of Paper Science and Technology, 500 10th St., Atlanta, GA 30318.

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APPENDIX

A patent has been issued on this process (Page, Scallan, Middleton and Zou, U.S. pat. 5,433,827, July 18, 1995). It is, however, the intention of Paprican to offer all libraries a royalty-free license to use this technology on receipt of a written request.

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Anyone with a personal computer, a modem and access to the Internet World Wide Web can access TAPPI's web site. The URL (internet address) is: <http://www.tappi.org>. Users can locate and access material in such broad topical areas as membership, publications, conferences, and education – all with a click of a mouse button. The TAPPI page features links to other pulp and paper industry sites as well as e-mail access to key TAPPI staff members. Information provided on the site is updated regularly.