ABSTRACT OF THE DISCLOSURE

A non-aqueous process for deacidifying and preserving cellulosic materials by means of a solution of an alkali or alkaline earth oxide, or mixtures thereof, in an organic solvent therefor. Also disclosed are nonaqueous deacidification processes employing other alkali and alkaline earth compounds, and processes which employ a liquefied gas and/or halogenated hydrocarbon solvent. Also disclosed are processes for deacidifying and preserving cellulosic aggregates such as whole books, and cellulosic plastics.

This application is a continuation-in-part of now abandoned applications Ser. No. 850,991 filed Aug. 18, 1969, Ser. No. 695,631 filed Jan. 4, 1968, and Ser. No. 559,415 filed June 22, 1966. The present invention relates generally to the treatment of cellulosic materials and, more particularly, the invention relates to the treatment of cellulosic materials which may deteriorate or which may have become deteriorated through aging. Still more particularly, the invention is directed to the preservation of printed cellulosic materials, such as books and manuscripts, which through aging, have lost or may lose some of their initial properties.

A serious problem throughout the world is the preservation of cellulosic materials and particularly the preservation of printed cellulosic materials such as books, manuscripts and documents. Large quantities of these materials have deteriorated to such an extent that only a very few people can use them under restricted conditions. The problem is not limited to isolated instances of the deterioration of individual examples of known ancient documents, but alarmingly threatens substantial portions of library collections. Libraries and others are greatly concerned about the deterioration of these valuable cellulosic materials, and their losses of virtually irreparable records are already very large.

The deterioration of cellulosic materials is a more or less continuous phenomenon, the rate of which depends on such factors as the nature of the cellulosic material, its storage conditions, and the degree to which it has already deteriorated. As cellulosic materials deteriorate, they become embrittled so that their ability to withstand the flexure, abrasion and wear associated with their normal use is greatly reduced. Deteriorating cellulosic materials such as books, documents and manuscripts will eventually disintegrate or be damaged beyond repair by patron use or handling in libraries.

It has been recognized that the cellulose in cellulosic materials deteriorates on aging as a consequence of hydrolytic, oxidative, and photochemical reactions. These effects occur in cellulosic materials in the normal course of events when the materials are kept for extended periods of time. Acid-catalyzed hydrolysis of the cellose during aging is considered, and has been known, as one of the most significant causes of deterioration of cellulosic materials. Hydrolytic attack causes degradation of cellulose by random scission of the hemi-acetal links between the glucose residues of cellulose molecules, thus shortening the molecules and weakening and embrittling the cellulosic material. Acids catalyze this reaction and the presence of the relatively large numbers of hydrogen ions associated with an acidic condition can greatly accelerate the rate of deterioration. An acidic condition may result from the manner in which the cellulosic materials are manufactured or it can result from storage conditions. The acidity may come from the use of papermakers' alum in the manufacture of cellulose derivatives, air pollutants, or the degradation products of the cellulosic material and printing ink mediums. Oxidative and photochemical degradation, and other aging mechanisms, have a similarly deleterious effect on cellulosic materials.

The great bulk of present day library collections dates from the development of the Fourdrinier paper making machine in the early nineteenth century, the development and use of wood pulp as a source of cellulose fibers for paper, and the general acceptance of alum and rosin in the sizing step for the mass production of paper. Not only does the use of alum contribute to the acidity of paper and its subsequently accelerated deterioration, but conventional wood pulping processes may also degrade and/or oxidize the cellulose fibers or may not remove all unstable non-cellulosic materials from the wood. Accordingly, much of these library collections are printed on acidic paper with poor aging characteristics, and in terms of their permanency lifetimes, have reached old age or are rapidly approaching it. For example, my studies indicate that almost all books published between 1900 and 1960 cannot be effectively rebound after they are 60 years old, and will be unable to resist even mild use when they are 100 years old. The urgency of the situation is compounded by the more recent problem of significant atmospheric concentrations of acidic and oxidizing air pollutants such as sulfur and nitrogen oxides. The absorption of such atmospheric contaminants can accelerate the deterioration of ordinary paper and even cause otherwise permanent paper to become nonpermanent.

A known technology has developed in respect to deacidification of cellulosic materials. In this connection, organic deacidification agents have been employed as well as inorganic deacidification agents. Deacidification has also been practiced under nonaqueous conditions. However, this previously known technology has failed to effectively preserve cellulosic materials.

It has been recognized that organic bases such as amines may be used to deacidify cellulosic materials. Low molecular weight amines can be used in gaseous form and heavier amines may be used as liquids or dissolved in organic solvents. However, such use of organic bases such as amines has not effectively solved the problem. Some of the organic bases may slowly vaporize into a library atmosphere from the treated cellulosic materials, and are poisonous or have other physiological effects upon human beings. Furthermore, organic bases usually have the effect of forming compounds which result in browning of paper and blackening of cellulosic plastic materials. In any event, the use of organic bases for effecting deacidification of cellulosic materials has not provided an adequate solution to the problem of preserving such materials over extended periods of time.

Insofar as concerns the use of inorganic deacidification agents, it has been known to sprinkle dry inorganic powders, such as calcium carbonate, on papers. This provides a surface effect and does not result in effective preservation of cellulosic materials.

This use of barium and magnesium carbonates as stabilizing agents in cellulosic materials has also been recognized. These materials have been widely used as extenders, fillers and whiteners in paper. The Egyptians, thousands of years ago, used a form of sodium bicarbonate...
in mummification. Some of this material came into contact with the mummy wrappings with resultant long term preservation of the wrapping. In more recent times, paper has been immersed in or sprayed with aqueous solutions of barium, calcium, or strontium bicarbonate or hydroxide. Subsequently, the paper is dried and the carbonate is produced in the paper. Successive immersion of paper in calcium hydroxide and then in calcium bicarbonate aqueous solutions is known and it has been claimed to improve or spray paper in magnesium bicarbonate for preservation purposes. It is also known to use buffered aqueous solutions of borates and phosphates for paper preservation.

However, these aqueous solutions cause problems because it is often difficult to wet sized paper and wetted paper is relatively slow and/or expensive to dry, particularly without cockling or distortion. Furthermore, paper takes up about twice its weight in water and, when wetted, this absorption causes the paper to expand substantially. Because of this expansion, paper and books may be seriously damaged on wetting. Since wetted paper is weak and easy to damage in handling, it requires great skill to effect deacidification of paper with aqueous treatments. Furthermore, such conventional, aqueous techniques are generally applicable only to individual sheets. If the restoration of aggregates of sheets such as books is desired, the book must be unbound, its pages separated and individually treated, and then re-assembled and re-bound. Such restoration techniques are not only expensive and time consuming, but also destroy the integrity of the book and require the individual attention of highly skilled personnel. Because of the expense of such restorative techniques, they may be limited to only the most important documents, and cannot be economically applied to the increasingly large quantities of standard reference and other materials which, due to steady deterioration, require preservation to extend their usefulness and accessibility. Accordingly, the use of aqueous solutions or dried powders for traditional deacidification has not solved the problem of preservation of cellulosic materials.

A committee of the International Institute for Conservation of Historic and Artistic Works reported, less than two years ago, as follows:

"A non-aqueous means of deacidification that would not be harmful to paper, pigments and the various media must be developed."

As above indicated, deacidification of paper under non-aqueous conditions is known. In this connection, it has been known to treat paper with diglycolamine but the use of this compound has been small because the paper did not become alkaline on aging. The diglycolamine apparently volatilized out of the paper or entered into a reaction resulting in an acidic condition. It has also been taught that barium hydroxide, a toxic chemical, in methanol, could be used for paper preservation. However, this treatment is limited to the deacidification of single documents in cases where aqueous solutions cannot be used, e.g., for water-labile inks and vellum, and consequently is not effective for substantial use.

Magnesium acetate has been used as a stabilizer for cellulosic materials such as cellulose acetate films. In addition, as taught in British Pat. No. 1,002,981, various alkaline earth acetates and carbonates have been dissolved or suspended in industrial alcohol along with a thermoplastic polymer, and used to impregnate a fibrous sheet such as lens tissue which is subsequently laminated to printed cellulosic materials to deacidify them. Not only is such a process tedious and time consuming, but it also may not involve uniform deacidification of the printed cellulosic material. In addition, such a process may release acetic acid which may itself have a deleterious effect on both the lens tissue and the printed cellulose material. In addition, although such as alkaline earth acetates may be capable of raising or neutralizing the pH, the elimination of an acidic condition is not the sole criterion for a process for preserving cellulosic materials. In addition, such acetate salts may slowly release acetic acid into the atmosphere, having an adverse effect on the esthetic qualities of a library collection. Furthermore, such materials may darken or discolor the cellulosic material, thereby more than offsetting any other preservational benefit.

Accordingly, despite the seriousness of the problem, and the extensive effort toward solving it, a satisfactory solution to the problem of deacidification and long term preservation of cellulosic materials, and particularly a solution which is not harmful to the paper, pigments or media of printed materials, has not been found.

Accordingly, there is a present and serious need for a proper method to effect preservation of cellulosic materials so that old books, manuscripts, works of art, and valuable papers may be preserved. Such a process which would be capable of mass as well as individual treatment of cellulosic materials, including treatment of whole books, is not only desirable, but necessary for the economical preservation of the large quantities of cellulosic materials which are presently deteriorating.

Accordingly, it is a principal object of this invention to provide improved means for preserving cellulosic materials.

It is an additional object of this invention to preserve cellulosic materials which are printed without destroying or impairing the fidelity of the printed material.

It is a still further object of this invention to provide means for preserving cellulosic materials for extended periods of time.

Another object of the invention is to provide a means for preserving cellulosic materials which includes depositing benign chemicals compatible with the cellulosic materials over long periods of time.

It is an additional object of this invention to provide a solution for effecting deacidification of cellulosic materials, which solution comprises a benign chemical dissolved in a solvent which should be harmless to books during the treatment, while at the same time being capable of drying from the books under mild conditions.

A further object of the invention is to provide an improved means for preserving cellulosic materials which also effects plasticizing and strengthening of the materials.

An additional object of this invention is to provide an improved method of preserving books and paper which affects improving the durability and strength retention of such materials.

In general, a non-aqueous solution is used for treating the cellulosic materials in accordance with the present invention, and it comprises a deacidification agent which preserves and is compatible with the cellulosic material over long periods of time. The solution further comprises a low boiling solvent for the deacidification agent which solvent is harmless to books during treatment. The solvent is readily removed from the cellulosic materials and does not result in significant swelling or weakening of the cellulosic material. Several solvents may be combined together to produce a solution with properties especially designed for particular applications or decalcification agents. The function of some solvents may be to produce specific working properties while other solvents may act to solubilize the deacidification agent or to provide a medium in which to handle the agent. Water may be a solubilizing agent for certain deacidification agents but the lower alcohols and others may be more generally satisfactory. The water naturally present in paper may restrict the workability of certain deacidification solutions particularly when the solution or solvent are to be reclaimed or recycled. It may be important for best results from the solution when treating large quantities of cellulosic materials that the cellulosic material, the solvent and/ or solution or solvent mixture be in an essentially dry or otherwise inactivated with respect to adverse effects of excess water which may be present therein. The water can be removed by drying or may be made inactive as by freezing. This control of water is particularly important when treating books en masse as contrasted with
treatment of paper. The solution may further include a plasticizing agent which softens the cellulotic materials. The plasticizing agent should be soluble in or miscible with the solvent. The solution may also include a resin strengthening agent which strengthens the cellulotic materials and makes them more durable in subsequent use. The resin strengthening agent should also be soluble in or miscible with the solvent.

The deacidification agent must meet two criteria to be satisfactory in the practice of the present invention. First, the deacidification agent must provide permanence for the cellulotic materials over long periods of time. This can be evaluated by accelerated aging tests which may be used to evaluate the change in cellulotic materials over long periods. Such an aging test is the Technical Association of the Pulp and Paper Institute (TAPPI) Standard Method known as “Relative Stability of Paper, T 453, ts–63.” The second criteria for the deacidification agent is to provide a pH in a water extract of the treated cellulotic materials which is substantially above that of the untreated materials and which is sufficient to provide long term preservation of the cellulotic materials. In this connection, the treated cellulotic materials should provide a water extract having a pH between 6.0 and 11.0, and preferably between a pH of 7.5 and 10.0. Ideally a pH between 8.5 and 9.5 should be established. The pH can be determined by the TAPPI Standard Method known as “Hydrogen Ion Concentration (pH) of Paper Extracts—Cold Extraction, T 509, su–68.”

It has been found that particularly suitable deacidification agents in accordance with this invention, are alkali and alkaline earth alkoxides and mixtures thereof. Examples using the Group Ia and Iib metals of the Periodic Table are the methoxides and ethoxides of lithium, sodium, potassium, calcium and barium. Although higher alcohols may be used, it is preferred that the alkyl chain of the alkoxide have a chain length of from 1 to 5 carbon atoms to facilitate removal of the alcohol moiety from the cellulotic material incident or subsequent to the deacidification treatment. The alkyl chain of the alkoxide will most preferably have a chain length of from 1 to 3 carbon atoms. Mixtures of various alkoxides may also be employed.

The use of alkali alkoxides, like sodium or potassium methoxide, requires special care to prevent the development of alkali over a pH of 11; such excess basicity may catalyze alkaline degradation processes. This care includes introducing only the quantity of agent necessary to effect stabilization. For example, the degree of acidity in the cellulotic material may be eliminated by prior treatment and the strength of the treatment solution adjusted accordingly to produce the pH desired after treatment. However, it is preferred to neutralize any excessive basicity of the alkali agent itself prior to treatment of the cellulotic material, so that aqueous extracts of treated cellulotic materials will necessarily have a pH of 11 or less. This neutralization can be achieved by adjusting the basicity of the deacidification agent such as by formation of a double alkoxide through the addition of an alkoxide of an amphoteric or weakly acidic element such as aluminum, tin, boron, titanium, zirconium, zinc, or the like, for example, aluminum isopropanoxide. It may be desirable to employ such a technique with alkaline earth alkoxides as well, particularly alkoxides of calcium, which also may tend to produce pH values over 11.

In addition, the cellulotic material may be treated with carbon dioxide gas after deacidification treatment with an agent having high basicity, in order to provide a more mildly alkaline preservative. Magnesium alkoxides are particularly preferred as deacidification agents, and have been found to have exceptional attributes with regard to the deacidification and long term preservation of cellulotic materials. Treatment of cellulotic materials with magnesium alkoxides, for example, is capable of providing a protective residue of magnesium hydroxides which under ordinary atmospheric conditions will provide, in paper, a complex mixture of carbonates and hydroxides, called basic magnesium carbonate. The residue is white, insoluble, non-toxic, and provides exceptional preservation protection. Furthermore, reaction of any acidic cellulotic carboxyl groups with magnesium alkoxides provides a stable, white magnesium salt of the carboxyl group. Reaction of a magnesium alkoxide with other acidic materials present in a cellulotic material will also provide reaction products which are relatively benign. For example, reaction with sulfuric acid, which may be present in much cellulotic material, will provide a colorless magnesium salt which is present in the presence of which may be accepted in cellulotic materials.

Since magnesium sulfate is moderately soluble in water, and since it may sometimes be preferred that salts which may hydrate or migrate not be present in cellulotic materials, it may be desirable to employ a mixture of a magnesium alkoxide with another alkoxide which forms an insoluble sulfate. Thus, although the presence of a magnesium sulfate reaction product may be acceptable, it may be preferred that a mixture of magnesium alkoxide and another alkoxide, such as calcium or barium alkoxide, be used which will provide colorless and insoluble reaction products with which should be employed acidic constituents of the cellulotic material to be treated. For example, a deacidification agent comprising a major proportion of a magnesium alkoxide, and a minor proportion of a calcium alkoxide just sufficient to react with the soluble sulfate ions present in the cellulotic materials, will provide insoluble calcium sulfate, in addition to the protective residue from the magnesium alkoxide.

The amount of deacidification agent dissolved in the solvent should be sufficient at the level of impregnation of solution into the cellulotic material to leave a residue which effects preservation of the cellulotic materials when tested by TAPPI Standards Method T 509, su–68. In general, the deacidification agent will comprise from 0.1 percent to about 10 percent of the weight of the solvent. The residue deposited in the cellulotic material, on a dry basis, should be between about 0.2 percent and about 20 percent by weight, based on the weight of the dry cellulotic material. The deposition of less than 0.2 percent may be satisfactory in some cases where the added protection provided by a more substantial residue of alkaline material is not desired. It is unusual for the acidity, measured in sulfuric acid equivalents, to exceed 0.1 percent by weight and consequently, the deposition of deacidification agent in the deposited range of 0.2 to 20 percent may produce a useful improvement. The range of 0.2 to 20 percent is suggested to provide protection during an unforeseeable future as well as for current uses in particularly corrosive atmospheres such as may occur in industrial practice. In some instances, for example, cellulotic molding plastics where clarity of product is detrimentally affected with increasing concentration, it may be desirable to introduce only a small fraction of the quantities proposed above.

The solvent, as before pointed out, is non-aqueous and must dissolve the deacidification agent to the cellulotic material or printing during treatment, and be readily removed therefrom. For books and other printed matter, a solvent should be selected which does not dissolve the dye stuffs, ink, adhesive components, etc., of these cellulotic materials. A number of solvents or solvent mixtures can meet these tests. The solvent components include short chain aliphatic hydrocarbons, aromatic hydrocarbons having low boiling points, volatile ethers and the lower alcohols. These solvents should have boiling points below about 250° F., preferably below about 175° F., to effect drying in commercially feasible times. Mixtures can be used to provide drying rates of the solvent selected, so that a drying rate is obtained which is sufficient to prevent warpage of the paper during drying and subsequent use.
vide an alcoholic solution of magnesium methoxide, into which individual sheets or aggregates of cellulosic materials may be dipped, removed from the solution, drained, and dried. The deacidification treatment is performed at a boiling point of about 65°C, has sufficient vapor pressure at ambient temperature to dry from cellulosic sheets, and heat and/or reduced pressure may be employed to aid drying. Non-aqueous solvents, such as various hydrocarbons or alcoholics, may, however, have certain disadvantages in solvents. For example, they may be flammable, and without proper precautions may tend to dry unevenly from cellulosic aggregates such as books with the attendant possibility of uneven residue formation and migration of materials from the center of the book to the edge. In this regard, it has been found that the halogenated hydrocarbon solvents provide some usual advantages, particularly when combined with the lower alcohols, or ethers. In this connection, the halogenated hydrocarbon solvents have high flame points, particularly when related to other solvents, and have low boiling points, which facilitates drying, and they convey these properties to solvents of which they form a part. In addition, they can convey hydrophobic properties to deacidification solutions of polar solvents such as alcohols, and provide some solubility for the deacidification agents hereinafter set forth. Particularly preferred are the Freon polyhalogenated ethanes, diethyl ether, ethyl methylene, fluorinated ethanes, and chlorofluoromethane, because they are generally the organic, non-aqueous solvents with a boiling point of about 65°C. Dichlorofluoromethane, dichlorodifluoromethane, dichlorodifluoromethane, and trichlorofluoromethane. Of course, various mixtures of the solvents can be employed to this end. The solvents are particularly benign with respect to the futility of printed cellulosic materials, are hydrophobic, have properties of inflammability, low heat of vaporization, low surface tension, high dielectric constants, and low viscosity, and tend to impart these properties to solvent mixtures of which they form a part. The solubility of alkoxide deacidification agent may be enhanced by adding to the halogenated hydrocarbon solvent a lower alcohol or ether. The halogenated hydrocarbon solutions of deacidification agents readily and thoroughly inorganic groups and have been found to have exceptionally desirable properties with regard to their ability to transport a deacidification agent throughout the cellulose material. Another class of solvents has been found to be particularly useful for deacidification and preservation of cellulosic materials; these are the liquefied gas solvents which have boiling points below ambient temperature at atmospheric pressure, and which are used as solvents at elevated pressures. The lower aliphatic hydrocarbons such as n-butane, iso-butane, n-propane, and cyclopropane are examples of such solvents. The solubility of deacidification agents in such solvents may be increased by employing a quantity of a lower ether or lower aliphatic alcohol as a solvent component. The solutions may be conveniently produced by dissolving the alkoxide in a small quantity of ether or alcohol and mixing this alkoxide solution with another solvent component. It should be noted that certain of the halogenated hydrocarbon solvents, such as chlorodifluoromethane and dichlorodifluoromethane, are also liquefied gas solvents, and provide the cumulative advantages of both classes of solvents. The liquefied gas mixtures or solvent mixtures containing minor quantities of lower alcohols and/or ethers, penetrate the deacidification agent throughout the cellulosic materials including cellulosic aggregates such as whole books. Subsequently, the excess deacidification solution may be drained from the pressure-treat-
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or inactivated so as to prevent premature formation of alkaline or alkaline earth oxides or hydroxides. Such premature formation impairs the effectiveness of the decalcification agent throughout the cellulose materials, particularly cellulose aggregates such as books. In addition to promoting uniform penetration of the decalcification agent, and uniform distribution of the preservative residue, control of the water content provides a protective alkaline residue which is firmly incorporated throughout the cellulose materials. After impregnation of the cellulose materials, the presence of water is not particularly deleterious to the system.

Prior to treatment, the cellulose material may be dried by storage in an atmosphere of low humidity, and drying may be facilitated by reduced pressure and/or application of heat; however, the use of temperatures above about 150°C, to 200°C, is generally to be avoided in processing cellulose materials, particularly for cellulose materials which are highly acidic. Storage at ambient temperature in a relative humidity of less than 20% has proven to be an effective drying procedure. Although dry or otherwise water-inactivated cellulose materials are preferably employed, such materials, including paper and books, may be, however, effectively stabilized without special precautions as to their water content.

In practicing the process under conditions which inactivate water by freezing is in situ in the cellulose materials, certain advantages may result including possible reduction in treatment costs resulting from elimination of initial drying operations, improved appearance for cellulose materials resulting from reduced solubility of colored components in the printing material and consequently reduced migration of these components during the decay process, and a stronger finished product due to reduction in the deleterious effects which may result from heating of materials in the course of treatment. These advantages may best be obtained by the use of the halogenated hydrocarbon solvents which have boiling points well below the freezing point of water so that there is a relatively wide range of temperatures below the freezing point of water and above the freezing point of the solvent materials within which the treatment may be conducted. This range is extended in the case of liquefied gas solvents through the use of a pressurized treatment to liquefy a material which is a gas at atmospheric pressure above a given temperature. In this connection, for treatments involving the deactivation of water, the temperature for impregnation of the treatment solution into the cellulose material should be below 32°F, and will normally be about —40°F, for typical halogenated hydrocarbon solvents and liquefied gas solvents.

The treating solution may contain a plasticizing agent for softening deteriorated and embrittled cellulose material. The plasticizing agents should be soluble in or miscible with solvents at the levels used. The plasticizing agents which may be used include ethylene and polyethylene glycols such as diethylene glycol, and may be selected to also promote solubilization of the decalcification agent. Such plasticizing agents may also convey some protection against acid attack. The amount of plasticizing agent can vary from 0 to 10 percent of the solution and will usually be used at a level of less than 5 percent.

The treating solution may also contain a resin strengthening agent for improving the durability of new or deteriorated and embrittled cellulose materials. The resin strengthening agent should be soluble in or miscible with the plasticizing agent. The resin strengthening agents which may be used include acrylic and methacrylate ester resins, as well as cellulose ester resins. Such resins can be made more plastic (flexible) by incorporating other polymeric or plasticizing materials like ethyl hydroxyethyl cellulose if desired. The amount of resin strengthening agent can vary from about 0 to 10 percent and will be used for strengthening purposes at levels usually between 3 and 5 percent. The resin strengthening agent may be beneficial for other reasons, such as to make bibliographic data on the binding more legible after treatment and to tack down any powdery deposits of the decalcification agent residue. The strengthening treatment may occur in conjunction with the decalcification treatment or it may follow or precede the decalcification treatment. In this regard it should be noted that both the incorporation of a decalcification agent, and the use of a liquefied gas solvent with subsequent flash drying incident to venting of the pressure employed, tends to keep the components of cellulose aggregates from sticking together when a resin strengthening agent is employed.

It is important for the solution to impregnate the cellulose materials. Mere coating of cellulose materials with a decalcification agent will not provide the desired resistance to aging. The solution should distribute itself uniformly throughout the cellulose material in order to achieve the most desired results of the invention. It is recognized that there are disclosures of coatings for cellulose material of varying kinds and degrees but such coating does not provide extended preservation of the cellulose materials. The decalcification agent must be distributed throughout the cellulose material to provide enduring preservation of cellulose material. This distribution can be obtained by selection of solvent for preformed cellulose materials like paper and books or it can be aided with solvents or mixing devices prior to final fabrication in the case of cellulose plastic materials, such as by film-casting cellulose acetate and magnesium ethoxide from solution, or melt-blending cellulose ethers with magnesium methoxide and cellulose.
or above the ambient temperature to avoid the possibility of moisture condensation from the atmosphere on chilled books. The central condition, regardless of mode of treatment, is to thoroughly impregnate the cellulosic materials with the solution and to remove the solvent, leaving the alkali or alkaline earth preservative deposited throughout the treated cellulosic material.

After treatment has occurred for a sufficient amount of time, the solvent and any volatile reaction products of the deacidification agent with the cellulosic material, such as the alcoholic moiety of the original alkoxide, are removed from the cellulosic material. For example, the cellulosic materials may be drained of the treating solution and the solvent evaporated. The cellulosic materials may be dried at ambient conditions, under conditions of heat and/or reduced pressure to remove the solvent and other volatiles, so as to cause dissolved alkali or alkaline earth deacidification agent, in addition to that which has already reacted, to be distributed throughout the cellulosic material as the solvent is removed. Various methods of drying may be employed, including the use of reduced pressures or pressure fluctuation and vacuum, external heat or induced heat through the use of high frequency electromagnetic radiation, and flushing with dry or moisturized gas.

The cellulosic materials are then ready for extended storage with greatly reduced deterioration of the material over long periods of time. If plasticizing agents are used in the solution, the cellulosic materials have improved plasticity. If resin strengthening agents are used in the solution, the cellulosic materials will have increased strength.

Another method involves spraying the cellulosic materials with a deacidification agent dissolved in a non-aqueous solvent. For example, individual sheets of paper or manuscripts may be sprayed with a solution of magnesium methoxide dissolved in methanol and subsequently dried; such operations may range from operator application of solution to individual documents by means of a hand atomizer, to large-scale continuous production operations involving integrated spraying, document handling, and drying equipment. In addition to other benefits of using the preferred fluorocarbon solvents, their nonflammable and nontoxic nature is particularly valuable for spray applications of deacidification solutions to cellulosic materials. In one particularly efficient and effective embodiment of the present invention, a mixture of a fluorinated hydrocarbon, which is a gas at ambient conditions; and a fluorinated hydrocarbon, which has a boiling point at or above the ambient temperature at atmospheric pressure, are employed under pressure as the solvent (which may also include a lower alcohol or ether) for a deacidification agent. This deacidification solution is placed in an aerosol can, and may be used to quickly and effectively spray-treat cellulosic materials by hand; this lower boiling fluorocarbon acts as an aerosol propellant for the remaining components of the deacidification solution, which upon spray contact tends to wet and penetrate, and transport the deacidification agent throughout the cellulosic materials without excessive swelling. It is preferred that the cellulosic materials be relatively dry, or otherwise inactivated with respect to the presence of water, in order to achieve uniform treatment.

The following examples illustrate various deacidification processes of the present invention, and the benefits to be obtained thereby.

**EXAMPLE 1**

A first solution is prepared by dissolving magnesium acetate in anhydrous methyl alcohol at a level of 5 percent by weight/volume. A second solution is prepared which is a saturated solution of magnesium acetate in anhydrous methyl alcohol.

A third solution is prepared by dissolving potassium acetate in anhydrous methyl alcohol at a level of 5 percent by weight/volume.

A fourth solution is prepared which is a saturated solution of potassium acetate in anhydrous methyl alcohol.

A fifth solution is prepared by dissolving magnesium methoxide in anhydrous methyl alcohol at a level of 5 percent by weight/volume.

A sixth solution is prepared by saturating anhydrous methyl alcohol with aluminum isopropoxide and adding sufficient sodium methoxide to raise the solution pH to between 10.0 and 10.5 (as measured by pH indicator paper dipped into the solution and withdrawn into the atmosphere).

Sheets 5 1/2" x 8 1/2" of an offset book paper having a fiber composition of 34 percent bleached softwood kraft and 66 percent bleached hardwood kraft, which contains 25 percent by weight clay and have cold and hot water extraction pH values of 6.6 and 4.6 respectively, were immersed individually in these solutions for approximately 5 seconds, held vertically to drain off excess solution, and dried on mosquito netting by means of infrared lamps. Samples of sheets of paper treated with solutions one, two, three, five and six were then cut parallel to the machine direction of the book paper to provide samples for the M.I.T. folding endurance test, according to TAPPI standard test T 423 M-50: "Folding Endurance of Paper." Paper treated with solution number four, a saturated methanolic solution of potassium acetate, would not dry and was so limp that folding endurance samples were impractical to cut. This paper appeared to remain damp for months.

The folding endurance samples were then dry-heat aged at 100°C. According to TAPPI standard test T 453, ts–63 and the change in M.I.T. folding endurance observed with respect to time (up to and including 9 days heat-aging) at 1.0 kg. tension in accordance with the above-identified TAPPI standard folding endurance test. Untreated testing samples of the same paper were also dry-heat aged and tested under the same conditions. The results of this aging study were evaluated by linearly reexpressing the common logarithms of the folding endurance measurements against their respective days of aging. The slopes of the regression lines thus computed were divided into the log value of the respective regression line at zero days of aging to obtain a life of paper estimate based on these accelerated aging tests. The life values thus obtained for each solution treatment were then each divided by the life value obtained for the control samples to provide a comparative value of treatment index for each of the solution treatments. These values appear in Table 1. In addition, the initial folding endurance value of each of the solution treatments (logarithm of the folding endurance at zero days heat aging) was divided by the value for the untreated control to provide percent comparison figures for the initial effect of the various treatments. These values also appear in Table 1, labeled as the Retention of Initial Endurance.

**TABLE 1**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Value of treatment index</th>
<th>Retention of initial endurance, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 6% MgO</td>
<td>1.80</td>
<td>96</td>
</tr>
<tr>
<td>2. Saturated MgO</td>
<td>6.47</td>
<td>72</td>
</tr>
<tr>
<td>3. 4% K2O</td>
<td>3.76</td>
<td>89</td>
</tr>
<tr>
<td>4. Saturated K2O</td>
<td>3.76</td>
<td>89</td>
</tr>
<tr>
<td>5. 8% Mg (OCH3)</td>
<td>2.78</td>
<td>101</td>
</tr>
<tr>
<td>6. Saturated Al (OCH3) plus NaOCH3</td>
<td>2.10</td>
<td>103</td>
</tr>
</tbody>
</table>

A comparison of the data shows alkoxide treatment solutions numbers 5 and 6 were clearly superior to either magnesium acetate solution with respect to both the value of treatment index, and the retention of initial folding endurance following deacidification treatment. Although
The quantity of solution charged into the pressure vessel was selected to fill the vessel to about half the height of the books undergoing treatment. The fact that sufficient solution traveled vertically up the leaves of the books to reduce the paper acidity to pH values of 7.80 and 7.20 must be strongly emphasized. This ability of such treatment to produce solution travel through the sheets and to transport deacidification agent throughout the books under the specified conditions is an important feature of the process. The books themselves were found to be ready for use upon removal from the pressure vessel, and the books appeared to have suffered no apparent damage from the treatment. Also, the impregnated magnesium compounds appeared to be tightly held within the components of the treated books. In addition to the paper pages of the books, the binding and other cellulose components are also preserved.

**EXAMPLE 2**

Three copies of the book entitled "Cooking the Greek Way" by Maro Duncan (about 256 pages in each book) were placed head down, with a wrapping cord inserted between the fly and text leaves, into a pressure vessel and the vessel was sealed. The book paper comprised uncoated sheets of approximately 50 percent softwood groundwood and 50 percent softwood sulfite fibers. The pressure vessel was then placed into a bath of hot water with maximum temperature 200°F, the vessel was evacuated, and the contents were dried under a vacuum of about 5 millimeters of mercury, for a period of about 4 hours. The pressure vessel was then removed from the hot water bath and allowed to cool overnight at room temperature. The following day the pressure vessel and its contents were cooled to sub-zero temperature by packing the vessel in Dry Ice (solid CO₂). One function of this cooling operation was to facilitate the introduction of treatment solution into the pressure vessel because a suitable pump was not available.

The solution for treating comprised 500 cc. of 7 percent magnesium methoxide in methanol, and, in addition, 10 pounds of dichlorodifluoromethane (Freon 22). The solution was introduced to the pressure vessel and the vessel was warmed by hot water until its pressure gauge read in excess of 300 p.s.i. gauge. It was subsequently cooled until the gauge read 200 p.s.i. (about 100°F). This warming served two purposes: (1) The increase in temperature caused an increase in pressure which assured a uniform impregnation of the solution into the cellulose material and (2) introduced enough heat energy so the solvent would evaporate rapidly on reducing the pressure and deposit the deacidification agent throughout the books. The pressure vessel was discharged, after about one hour of warming, by allowing the internal pressure to force the solution out from the bottom of the vessel: through a piping arrangement. When only gases were exhausting, the valve at the base of the pressure vessel was left open and the valve at the top of the vessel was then opened to facilitate the free exit of the gases which remained in the vessel.

The treated books, on opening the pressure vessel, when it had returned to ambient pressure, were found to be substantially dry. The mid-page (page 128) of each book thus treated, and the mid-page of an untreated copy of such book were tested for pH by a non-destructive method, using a contact pH electrode. This procedure has been found to give pH values related to the pH values of the beforementioned TAPPI method T 509 m–68. The pH values found are presented in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>pH value of—</th>
<th>Untreated copy</th>
<th>Treated copy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position at head of leaf</td>
<td>4.4</td>
<td>9.15</td>
</tr>
<tr>
<td>Near margin half way down leaf</td>
<td>4.3</td>
<td>9.90</td>
</tr>
<tr>
<td>Near spine half way down leaf</td>
<td>4.3</td>
<td>9.05</td>
</tr>
<tr>
<td>Near margin, at tail of leaf</td>
<td>4.3</td>
<td>7.80</td>
</tr>
<tr>
<td>Near spine, at tail of leaf</td>
<td>4.3</td>
<td>7.20</td>
</tr>
</tbody>
</table>

As in the case of Example 2, a quantity of deacidification solution charged into the vessel was only sufficient to fill the vessel to about one half the height of the books undergoing treatment. The solution demonstrated its stability and transitory power of the treatment by transporting itself vertically up the leaves of the treated books, and thereby depositing a beneficial agent in the book materials being treated.

FIG. 1 presents the results of an accelerated aging test measuring the improvement in performance of the leaves of the books treated in Examples 2 and 3. The same leaves from three copies of "Cooking the Greek Way" were aged according to TAPPI standard test T 453, ts–63, and changed in M.I.T. folding endurance observed at 0.5 kg. tension. The regression lines of folding endurance loss versus time show that both deacidification treatments improved the permanence of the treated book papers as contrasted with the untreated control.

**EXAMPLE 4**

Copies of "Cooking the Greek Way" are deacidified as described in Examples 2 and 3 above, except that the books are entirely immersed in a liquefied n-butane sol-
vent in place of the Freon, and both ether and methanol are used as solubilizing agents. After treatment, the books are cut in half and treated in an analogous manner with a resin strengthening solution containing a 75:25 ratio of low-molecular-weight acrylic resin and ethyl hydroxyethyl cellulose dissolved initially in dichloromethane with n-butane added subsequently. The concentration of the resin strengthening solution is established to deposit from about 3 to 5 parts resin strengthening solution throughout the books. After impregnation and solution and solvent removal the dried books are found to be in excellent condition with very legible lettering on the bindings. The leaves in the strengthened books are not bonded together because the escaping gases keep them apart as the book dries to deposit the resin. The strengthened paper is waterproofed by the treatment and has a characteristic somewhat similar to a paper heavily sized with gelatin. The strengthened paper may be expected to have improved resistance to the effects of atmospheric contaminants. The M.I.T. folding endurance at 1 kg. tension is increased from 7.9 folds to 32.3 folds in the machine direction and from 2.8 to 9.1 folds in the cross machine direction. After dry-heat aging at 105° C. for five days, the untreated leaves have a folding endurance (machine direction) of 5.6 folds while the treated leaves have a cross machine value of 2.2 and 5.0 respectively. Further improvement may be expected if the quantity of ethyl hydroxyethyl cellulose is reduced or when nonwoven wood fiber papers are strengthened.

**EXAMPLE 5**

A solution is prepared by reacting magnesium shavings with methyl alcohol to give a 5 percent by weight magnesium methoxide solution in methanol.

A second solution is prepared by taking 50 parts of this solution and adding to it 50 parts of anhydrous ethyl ether, by weight.

A third, but aqueous, solution is prepared by bubbling carbon dioxide for one hour through a water suspension of magnesium and calcium carbonates. The clear aqueous solution is decanted for use in stabilizing paper.

A testing procedure similar to that of Example 1 is followed. However, three commercial book papers were treated but they were not dried nor other special precautions taken prior to treatment. The treatment consisted of five minute immersions in the non-aqueous solutions and twenty minute immersions in the aqueous solution. There were no problems in handling or manipulating the sample papers wetted with the non-aqueous solutions and the treated samples dried rapidly hanging suspended in air.

The aqueous solution weakened the papers and great care was required to prevent damage during handling. Moreover, drying took many times longer.

**EXAMPLE 6**

A solution is prepared by reacting sodium in isopropyl alcohol to provide a solution of sodium isopropoxide at a level of about 1/2 percent by weight. Enough aluminum isopropoxide, prepared by reacting aluminum in isopro pyl alcohol, is added to give a pH of about 11.0 (as measured by indicator paper in moist air).

Another solution is provided by dissolving magnesium methoxide in methanol at a level of about 11 percent and trichlorofluoromethane is added to reduce the concentration to about 2 percent.

A further solution is prepared with sodium ethoxide dissolved in ethyl alcohol at a level of about 1 percent, and also containing enough aluminum n-butoxide to give a pH of about 10.0.

Another solution is prepared with sodium methoxide at a level of about 0.1 percent in methyl alcohol and dichloromethane.

These solutions are used to immerse sheets of paper in order to deacidify and preserve them. Books having an initial acidity of pH 4.0 as determined by TAPPI test T 509, su-68, after treatment with the above solutions, will have a pH in the range of about 7.0 to 11.0 when determined by the TAPPI test. This change is effected by immersion of the books in the respective solutions for approximately 30 minutes, and the books are dried under ambient conditions.

It is found that the covers and leaves of books do not warp or cockle on drying.

During the treatment, the leaves of the book are splayed to produce slight spaces between them and to facilitate the entry of the solution to all faces of the leaves. It is found that the leaves, after treatment, do not stick together.

Following treatment, drying is done by splaying the leaves and permitting them to dry under ambient conditions, although accelerated drying conditions can be employed by using heated air or by passing the books through alternating di-electric fields.

**EXAMPLE 7**

A variety of books are split down the spine and one-half immersed in a solution consisting of magnesium ethoxide at a level of 6 percent and diethylene glycol at a level of 2.2 percent in ethyl alcohol. The book halves are immersed for 30 minutes, the leaves being splayed to facilitate impregnation of the solution into the leaves of the book.

The book halves were removed from the solution and, after the excess solution was squeezed out, allowed to air-dry overnight with the leaves again splayed. After drying the book halves are tested and the tests disclose a pH shift from a pH of 4 for the untreated book halves to a pH of 6 or above after treatment.

**EXAMPLE 8**

A solution is prepared by reacting magnesium in methanol to produce a solution containing magnesium methoxide at a level of about 11 percent by weight. This solution is then impregnated into sheets of paper through contacting them with it by roller coating, or brushing, etc., to minimize the quantity of solution handled or to be recovered and recycled. Heavy deposits of alkaline preservative exceeding 20 percent may be produced. The solution may be diluted with, for example, trichloroethane or trichlorofluoromethane, to obtain different working properties and lighter deposits. The treated papers are found to be alkaline, having pH values between 6.0 and 11.0, and more stable than acidic untreated papers with respect to the passage of time.

**EXAMPLE 9**

A solution is prepared having the following composition in parts by weight, and placed in a pressurized aerosol spray can:

<table>
<thead>
<tr>
<th>Parts</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium methoxide</td>
<td>0.1</td>
</tr>
<tr>
<td>Magnesium methoxide</td>
<td>3</td>
</tr>
<tr>
<td>1,1,2-trichloro-1,2,2-trifluoroethane (Freon-114, B.P. about 118° F.)</td>
<td>50</td>
</tr>
<tr>
<td>CCl₃F (Freon-11, B.P. about 75° F.)</td>
<td>500</td>
</tr>
<tr>
<td>CCl₂F₂ (Freon-12, B.P. about -22° F.)</td>
<td>400</td>
</tr>
</tbody>
</table>

A quantity of old books and documents which require deacidification and preservation are stored overnight at room temperature in an enclosure in which the relative humidity is maintained at about 10 percent or less. The edges of the books are more acidic and have deteriorated to a greater extent than the central portions.

The documents and books are treated and preserved by spraying by means of the aerosol spray can. The Freon-12 acts as the propellant, and the remaining components of the solution penetrate and transport the alkaline earth methoxide deacidification agents throughout the cellulosic material, evaporate quickly, and deposit the protective
alkaline residue therein. The treatment is not only rapid and efficient, but is also effective for extending the remaining useful lifetimes of the books and documents. It is not necessary to unbind the books; spraying each leaf and down the spine effectually desiccates the whole book. Additional spraying passes along the margins of edges will leave a somewhat larger concentration of protective alkaline residue along the edges of the book in which protection is most necessary. A treatment with carbon dioxide gas may be desirable to produce barium carbonate if sufficient carbon dioxide is not naturally available from the atmosphere, or alternatively, the barium methoxide may be deleted. The use of one of the above mentioned solutions in a hypodermic syringe may be useful to impregnate the backbones of tightly bound books.

Additional examples are provided in my article "New Approaches to Preservation," Library Quarterly, 40 (January 1970), 139-71. Although the preceding description has specifically described alkali and alkaline earth alkoxides as the deacidification agents, other alkali and alkaline earth materials which are soluble in liquefied gas and halogenated hydrocarbon solvents useful herein might also be employed in a non-aqueous deacidification process specifically employing such solvents. Examples of such materials are organometallic alkali and alkaline earth compounds such as alkyl, aryl, and alkylaryl compounds. Additional deacidification agents are alkali and alkaline earth carbonates, carbonates, and hydroxides which are normally insoluble in such solvents employed herein, but which are solubilized in such solvents by forming complexes with a complexing agent of the alkali or alkaline earth cation, wherein the complexing agent is either removable such as by volatilization or not deleterious to cellulosic materials.

It should be noted that the alkali and alkaline earth alkoxides, and particularly magnesium alkoxides, are generally preferred over alkali and alkaline earth organometallic compounds. However, although such compounds have some serious disadvantages, these disadvantages may be overcome to some degree through proper care in handling and selection of materials, and selective use of such materials may be rewarded through unique advantages.

Examples of organometallic alkali and alkaline earth compounds include alkyls as butyl lithium and diethyl magnesium. The development of excessive basicity can be controlled through titration with suitable amphoteric materials such as triethyl aluminum. The major disadvantages of such organometallics are their extreme reactivity; they may react with some of the halogenated hydrocarbon solvents and may be spontaneously flammable in air. They will react with protonic solvents such as methyl alcohol to form alkoxides, which reaction may be undesirable if the benefits of the specific use of organometallics are desired. Furthermore, control of water in the cellulosic materials which are treated is exceptionally important because of the extreme reactivity of such materials with water; generally, the water content should be as low as possible. Furthermore, some organometallic alkali and alkaline earth compounds may be insoluble or difficulty soluble in non-aqueous solvents with which they do not react. In addition, compounds like Grignard reagents or their alkoxylithide reaction products may be used provided sufficient solubility exists. Grignard reagents are, however, only about 25 percent as efficient as equivalent alkoxides because they have only half the neutralizing potential and cost twice as much, and in addition, provide chlorine gas which might not be desired.

However, selection of suitable solvents such as hydrocarbons, particularly the liquefied gas solvents, or mixtures of hydrocarbons and lower ethers such as diethyl ether, tetrahydrofuran or dioxane as a solubilizing agent, specific advantages in addition to deacidification are achieved. For example, the alkyl or aryl group of the organometallic compound may be more volatile than an alcohol group of the corresponding alkoxide, and hence, more readily removed. In addition, such organometallics may achieve reduction of carbonyl groups, which are thought to be points of weakness for degradation of cellulosic material. Of the organometallic compounds, organomagnesium compounds are preferred. Mixtures of alkali and alkaline earth alkoxides, and organometallic compounds may be employed in a suitable solvent.

Alkali and alkaline earth aluminum hydrides, which are soluble in non-aqueous solvents, such as sodium aluminum hydride, have properties and advantages similar to the organometallic compounds, and in fact are considered herein to be the first of the series of such compounds, subsequent members of which replace hydride groups which hydrocarbon groups, and are accordingly considered to be within the scope of the term "alkali and alkaline earth organometallic compounds."

Examples of suitable complexes of alkali and alkaline earth compounds are the complexes of lithium, sodium, potassium, calcium and barium carbonates and bicarbonates with macro cyclic polyethers, which complexes are soluble in solvents such as n-heptane and dichloromethane.

Such complexes are described by C. J. Pedersen in articles entitled "Cyclic Polyethers and Their Complexes With Metal Salts," Journal of the American Chemical Society, vol. 89, pp. 2695-96, 701-7 (1967). Such cyclic polyether complexing agents are regarded as not deleterious to cellulosic materials.

Where appropriate, in addition to deacidification agents, plasticizers, and resin strengthening agents, other materials such as dyes, antioxidants, brighteners, release agents, biostats, biocides and the like may be conveniently incorporated in the solution.

Furthermore, the feature of the invention including a liquefied gas may be employed to introduce into cellulosic materials, in addition to the above-described deacidification agents, known paper-treating materials such as sodium borohydride, and other soluble alkali and alkaline earth organonitros, including borohydrides as the first in the series or organonitros. The insolubility of some such materials in nonpolar solvents can be circumvented by adding small quantities of a polar solvent on as low as one to one molar basis with the compound. Such alkali and alkaline earth organonitros may be employed with liquefied gas solvents either alone, or in combination with other deacidification agents such as alkali and alkaline earth alkoxides. The borohydrides not only form buffering deacidification agents (e.g., sodium borate), but are also useful for reducing carboxyl groups in cellulosic materials. A particular advantageous embodiment is an aerosol spray employing fluorinated hydrocarbon solvents and including an alkali or alkaline earth borohydride alone or in combination with an alkali or alkaline earth alkoxide such as magnesium methoxide.

It can be seen from the foregoing that an improved process for the treatment of cellulosic materials has been provided. The process permits preservation of these materials for greatly extended periods of time and can be used to treat papers before or after deterioration of the cellulosic materials has occurred. Furthermore, the process may be employed to treat a paper sheet or web, such as that from the drying section of a papermaking machine, in order to provide a preserved and deacidified paper as it is produced. The practice of this invention makes possible the saving of many library materials, including valuable manuscripts and rare books, which heretofore has been impractical.

Various of the features of the invention are set forth in the following claims.

What is claimed is:

1. A process for treating cellulosic material to preserve the cellulosic material against deterioration through aging, comprising contacting said cellulosic material with a substantially non-aqueous deacidification solution to impregnate the cellulosic material with said deacidification solu-
tion, said deacidification solution comprising a deacidification agent and an organic solvent for said agent, said deacidification agent being an alkali or alkaline earth alkoxide or mixtures thereof, and removing the solvent to deposit up to about 20 percent by weight of an alkali or alkaline earth material throughout the cellulosic material.

2. A process in accordance with claim 1 wherein the deacidification agent is a magnesium alkoxide.

3. A process in accordance with claim 1 wherein the alkoxide has a carbon chain length of from 1 to 5 carbon atoms.

4. A process in accordance with claim 1 wherein the alkoxide has a carbon chain length of from 1 to 3 carbon atoms.

5. A process in accordance with claim 1 wherein the deacidification agent is selected from the group consisting of magnesium methoxide, magnesium ethoxide and magnesium propoxide.

6. A process in accordance with claim 1 wherein the deacidification agent is magnesium methoxide.

7. A process in accordance with claim 1 wherein a water extract from the treated cellulosic material after removal of said solvent has a pH between 6.0 and 11.0.

8. A process in accordance with claim 1 wherein a water extract from the treated cellulosic material after removal of said solvent has a pH between about 8.5 and about 9.5.

9. A process in accordance with claim 1 wherein the solution further includes a resin strengthening agent.

10. A process in accordance with claim 1 wherein the solution further includes a plasticizing agent.

11. A process in accordance with claim 1 wherein the treated cellulosic material is also treated with a resin strengthening agent dissolved in a non-aqueous organic solvent either prior to or subsequent to being contacted with the solution containing the deacidifying agent.

12. A process in accordance with claim 1 wherein the solution contains a solvent which permits or increases solubilization of the deacidification agent.

13. A process in accordance with claim 12 wherein the solution contains a lower alcohol or ether.

14. A process in accordance with claim 1 wherein the deacidification agent comprises between 0.1 percent and 10 percent of the weight of the solvent.

15. A process in accordance with claim 1 wherein the deacidification agent deposits alkaline or alkaline earth material throughout the cellulosic material in an amount of between 0.2 percent and 20 percent of the weight of the cellulosic material.

16. A process in accordance with claim 1 wherein the solvent consists of a solvent selected from the group comprising short chain aliphatic hydrocarbons, aromatic hydrocarbons having low boiling points, volatile ethers and lower alcohols.

17. A process in accordance with claim 1 wherein the solvent comprises a fluorinated, polyhalogenated hydrocarbon.

18. A process in accordance with claim 1 wherein the solvent comprises a fluorinated, polyhalogenated methane or ethane.

19. A process in accordance with claim 1 in which the solvent is selected from the group including dichloromethane, dichlorodifluoromethane, dichlorodifluoromethane, chlorodifluoromethane, and trichlorotrifluoroethane.

20. A process in accordance with claim 1 in which the cellulosic material is dried prior to being contacted with the solution of deacidification agent.

21. A process in accordance with claim 1 wherein the cellulosic material is contacted with the solution of the deacidifying agent and organic solvent at a temperature below about 32°F, and above the freezing point of the solution.

22. A process in accordance with claim 1 wherein the treated cellulosic material is dried to remove the solvent and cause the deacidification agent to be deposited throughout the cellulosic material.

23. A process in accordance with claim 22 wherein the solution of deacidification agent is drained from the cellulosic material prior to drying to remove the solvent.

24. A process in accordance with claim 19 wherein the cellulosic material is contacted with the deacidification agent at an elevated pressure.

25. A process in accordance with claim 1 wherein the cellulosic material is a cellulose ether.

26. A process in accordance with claim 1 wherein the cellulosic material is in the form of a printed cellulosic aggregate.

27. A process in accordance with claim 1 wherein the cellulosic material is a book.

28. A process in accordance with claim 1 wherein the cellulosic material is a paper sheet or web.

29. A process according to claim 1 wherein the solution also contains an amphoteric or weakly acidic alkoxide selected from the group consisting essentially of alkoxydes of aluminum, tin, boron, titanium, zirconium, and zinc to prevent the development of excess basicity.

30. A process according to claim 1 wherein the process comprises the additional step of reacting the cellulosic material with carbon dioxide subsequent to removing the solvent.

31. A process for treating cellulosic material to preserve the cellulosic material against deterioration through aging comprising contacting said cellulosic material with a substantially non-aqueous deacidification solution to impregnate the cellulosic material with the deacidification solution, said deacidification solution comprising a deacidification agent and an organic solvent for said agent, said deacidification agent being selected from the group consisting of alkali and alkaline earth alkoxydes, alkali and alkaline earth organometallic compounds, alkali and alkaline earth organoboron compounds and macrocyclic ether complexes of alkali and alkaline earth hydroxides, carbonates and bicarbonates, or mixtures thereof, and wherein the solvent comprises a liquified gas solvent or a halogenated hydrocarbon solvent, and removing the solvent.

32. A process according to claim 31 wherein the solvent comprises a lower aliphatic hydrocarbon.

33. A process according to claim 31 wherein the solvent comprises a fluorinated, polyhalogenated methane or ethane.

34. A process according to claim 31 wherein the solvent also comprises a lower ether or alcohol as a solubilizing agent for the deacidification agent.

35. A process according to claim 31 wherein the solvent comprises a material which is both a liquified gas solvent and a fluorinated, polyhalogenated methane or ethane.

36. A process according to claim 31 wherein said contacting of the cellulosic material with the solution is accomplished by spraying the solution onto the cellulosic material from an aerosol container, wherein the aerosol container contains a fluorinated, polyhalogenated methane or ethane which is a liquified gas solvent, as a propellant, and wherein the solvent comprises a solvent component which is a liquid at ambient temperature.

37. A process according to claim 36 wherein the deacidification agent is selected from the group consisting of an alkali or alkaline earth alkoxide, and an alkali or alkaline earth borohydride, and mixtures thereof.

38. A process for the preservation of printed cellulosic aggregates comprising, at least partially immersing one or more cellulosic aggregates to be preserved in a substantially non-aqueous deacidification solution comprising a deacidification agent and an organic solvent for said agent, said deacidification agent being an alkali or alkaline earth alkoxide or mixture thereof, maintaining the aggregates in contact with the deacidification solution for a sufficient period of time to uniformly impregnate the cellulosic aggregates.
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lulosic aggregates with the solution, and volatizing
the solvent from the cellulosic aggregates to deposit up to
about 20 percent by weight of an alkali or alkaline earth
material throughout the cellulosic aggregates.

39. A process in accordance with claim 38 wherein the
decidification agent comprises a magnesium alkoxide
having a carbon chain length of from 1 to 5 carbon atoms,
and wherein the solvent includes a halogenated hydrocarbon
that is gaseous at ambient conditions.

40. A process in accordance with claim 39 wherein the
cellulosic aggregates are dried prior to immersion in the
solution.

41. A process in accordance with claim 39 wherein the
cellulosic aggregates are cooled to a temperature below
32° F. and above the freezing point of the solution prior
to immersion in the solution.

42. A process in accordance with claim 39 wherein the
impregnation of the treating solution in the cellulosic ag-
gregates is at least partially carried out at elevated pres-
ures sufficient to liquify the halogenated hydrocarbon.

43. A process according to claim 42 wherein the cel-
lulosic aggregates are books.

44. A process for preserving a cellulosic plastic comprising
mixing said plastic with an alkali or alkaline earth
alkoxide.

45. A process according to claim 44 wherein the mixing
is carried out in a solvent for both the alkoxide and the
plastic.

46. A process according to claim 44 wherein the plastic
and the alkoxide are melt-blended.

47. A process according to claim 44 wherein the alkoxide is selected from the group consisting of mag-
nesium methoxide, magnesium ethoxide and magnesium
propoxide.

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