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3,676,055

**PRESERVING CELLULOSIC MATERIALS
THROUGH TREATMENT WITH ALKYLENE
OXIDES**Richard Daniel Smith, 1369 E. Hyde Park Blvd.,
Chicago, Ill. 60615No Drawing. Continuation-in-part of application Ser. No.
661,190, Aug. 15, 1968. This application Aug. 31, 1970,
Ser. No. 68,472

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12 Claims

ABSTRACT OF THE DISCLOSURE

An improvement in nonaqueous processes for deacidification and preservation of cellulosic materials is disclosed, comprising reacting the deacidified cellulosic material with alkylene oxide such as ethylene oxide. Particularly effective is contacting cellulosic material, such as books, which are deacidified by a nonaqueous deacidification process, with ethylene oxide for 15 minutes or less at ambient temperature and atmospheric pressure, and equivalent reaction conditions at other pressures and temperatures.

This application is a continuation-in-part of copending application Ser. No. 661,190, filed Aug. 15, 1968, entitled "Process for Improving the Durability and the Permanence of Books, Papers, and Other Cellulosic Materials" and now abandoned.

The present invention relates generally to the treatment of cellulosic materials, and, more particularly, relates to

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earth deacidification agent as disclosed in the above identified copending application Ser. No. 68,499, Aug. 31, 1970. This treatment is preferable after the nonaqueous deacidification solution is removed, but it may be conducted while the nonaqueous deacidification solution is present. Preferably, the deacidification cellulosic material is reacted in an atmosphere of alkylene oxide for a period of less than about one hour at ambient temperature and atmospheric pressure, or for an equivalent reaction time for different pressures and temperatures.

The following examples illustrate the practice of the invention. In these examples, relative degrees of preservation are measured by accelerated aging tests which are employed over experimental laboratory time spans to predict changes in cellulosic materials which would occur over extended periods during natural aging. The physical properties of the samples are measured by a folding endurance test which measures the ability to withstand repeated folding under a specified tension. Such folding endurance tests are a measure of the durability of cellulosic materials, and when combined with accelerated aging tests accordingly provide a measure of the preservational effects of various treatments.

EXAMPLE 1

Four types of book papers are selected to provide an assortment of papers for testing. These types of papers are identified by the letters A, B, C, and D, respectively, and a description of their properties appears in Table I. Each type of book paper is tested with respect to the pH of cold and hot water extracts according to TAPPI Standard Methods, T 509, su-68 and T 435, su-68, respectively, and this data also appears in Table I.

TABLE I

Paper Identification	Type of paper	Type of Fiber	Percent	pH		Comments
				Cold extract	Hot extract	
A.....	Letterpress...	Bleached softwood kraft..... Bleached hardwood kraft.....	34 66	6.60	4.60	Filler—25% clay; English finish.
B.....	Offset.....	Bleached softwood sulfite..... Bleached softwood kraft..... Bleached hardwood kraft.....	60 10 30	5.90	4.40	Ash, 10%, contains substantial portion deinked fiber.
C.....	do.....	Softwood bleached kraft..... Hardwood bleached kraft..... Groundwood.....	20 10 70	6.00	4.98	
D.....	do.....	Softwood bleached sulfite..... Softwood bleached kraft..... Hardwood bleached kraft.....	5 20 75	5.85	4.80	

an improvement of nonaqueous processes for the deacidification and preservation of cellulosic materials.

The deterioration of cellulosic materials, particularly printed cellulosic materials such as books, manuscripts and other documents, is a serious problem. As disclosed in copending application Ser. No. 68,499, Aug. 31, 1970, filed contemporaneously herewith and herein incorporated by reference, cellulosic materials may be deacidified by contacting the cellulosic materials with a substantially nonaqueous solution of an alkali or alkaline earth deacidification agent and an organic solvent for the agent. It has now been found that under certain conditions, treatment of cellulosic materials with alkylene oxides subsequent to such a deacidification treatment will result in an improvement in some properties relating to the permanence and endurance of the cellulosic materials.

This invention is generally directed to a process for reacting alkylene oxides with cellulosic materials, subsequent to their deacidification by means of a nonaqueous deacidification process employing an alkali or alkaline

A quantity of each type of paper is dried in a chamber at 11 percent relative humidity at a temperature of 73° F. for 24 hours, and this dried paper is used in the subsequent testing.

Separate samples of each type of bookpaper are subjected to four different types of treatment procedures. Dried sheets of paper treated according to procedure number 1 are deacidified by a five minute immersion in a solution of 75 parts by weight methylene chloride and 25 parts of a 7 percent by weight solution of magnesium methoxide in methanol. Following removal from the deacidification solution, the samples are quickly dried by means of infrared lamps.

Dried sheets of paper treated according to procedure number 2 are treated exactly like those of procedure number 1 except that following removal from the deacidification solution, the sheets are transferred immediately to a vacuum desiccator, which is flushed with nitrogen, sealed, and its contents vacuum dried for 45–60 minutes at a reduced pressure of less than 5 mm. of mercury, with

the concurrent application of heat by infrared lamps. After drying the desiccator is flushed again with nitrogen and evacuated again for a period of 5 to 10 minutes. Ethylene oxide gas is then introduced at ambient temperature into the desiccator until the sliding seal between the lid and the base of the desiccator is broken, thus providing an essentially pure atmosphere of ethylene oxide in the desiccator at approximately atmospheric pressure. The samples are kept in this ethylene oxide atmosphere for 15 minutes and then removed.

Dried sheets of paper treated according to procedure number 3 are treated exactly like those of procedure number 2 except that rather than being removed after 15 minutes in the ethylene oxide atmosphere of the desiccator, the ethylene oxide atmosphere of the des-

ment can tolerate before it breaks during the first M.I.T. double fold.

Untreated sheets of each type of paper, as control comparisons, are conditioned, heat-aged, and tested in exactly the same manner to provide the same data for the untreated papers. A value of treatment index is then computed for each type of treatment of each type of paper by dividing the life of paper estimate for the untreated type of paper, respectively, into the life of paper estimates for that type of paper treated according to each type of treatment procedures. These values of treatment indices are dimensionless values which compare the effect of each treatment on ultimate paper life. These data appear in Table II, under columns headed by the type of paper designations of Table I.

TABLE II

Treatment procedure Number	Type of treatment	Identification of book papers tested, and value of treatment indices for each according to each type of treatment				
		A	B	C	D	Average
1.....	Deacidified by 25:75 mixture of 7% $Mg(OCH_3)_2$ in methanol, and methylene chloride.....	2.19	3.63	1.98	2.91	2.68
2.....	Deacidified as in Treatment I followed by 15 minute exposure to C_2H_4O	5.70	4.08	2.98	3.89	4.18
3.....	Deacidified as in Treatment I followed by 30 minute exposure to C_2H_4O	3.13	3.46	2.26	3.19	3.01
4.....	Deacidified as in Treatment I followed by 60 minute exposure to C_2H_4O	3.41	4.28	1.69	2.14	2.88
5.....	Untreated control.....	1.00	1.00	1.00	1.00	1.00

iccator is replenished by again breaking the seal, and the samples are kept in the ethylene oxide atmosphere for an additional 15 minutes to provide a total ethylene oxide treatment time of 30 minutes, after which they are removed.

Dried sheets of paper treated according to procedure number 4 are exactly like those of treatment number 3 except that after 30 minutes and 45 minutes of ethylene oxide treatment, ethylene oxide is again introduced into the desiccator to break the seal, and the samples are accordingly kept in the desiccator for an additional 30 minutes, for a total time of 60 minutes in the ethylene oxide atmosphere, after which they are removed.

All of the samples treated according to procedures number 1, 2, 3 and 4 are conditioned according to TAPPI Standard Method T 402 m-49: "Conditioning Paper and Paperboard For Testing," and then M.I.T. folding endurance samples are cut, according to TAPPI Standard Method T 423 m-50: "Folding Endurance of Paper." The cut test specimens are then conditioned for 24 hours at 73° F. in air having a relative humidity of 95 percent, and subsequently dried in air with 50 percent relative humidity at 73° F. prior to dry-heat aging.

The folding endurance samples are then dry-heat aged at 100° C. according to TAPPI Standard Method T 453, ts-63: "Relative Stability of Paper (By Effect of Heat on Folding Endurance)" and the number of double folds to failure in M.I.T. folding endurance of each type of paper for each type of treatment is determined in accordance with this standard test as a function of the duration of heat aging. The change in folding endurance versus time (of accelerated aging) is determined by measuring the number of double folds of each sample required for sample failure. Ten samples of each type of paper for each treatment are evaluated at heat-aging durations of 0, 3, 6, 9, 12, and 15 days. Linear folding endurance regression lines are computed by regressing the log of the number of double folds (plus one double fold) on the respective heat-aging times. A standard least squares analysis of variance procedure is used to prepare folding endurance regression lines for each treatment on each type of paper. The slopes of these regression lines of folding endurance loss versus heat-aging time are divided into their respective initial values at zero days heat aging to obtain a life of paper estimate based on these accelerated aging tests. Such life of paper values are predictions giving the number of days of heat-aging at 100° C. a particular type of paper having a given treat-

This data reveals that permanence and endurance (the ability, for example, of library books to withstand patron use as a function of natural aging) may be improved by treating the cellulosic materials subsequent to a non-aqueous deacidification treatment, with ethylene oxide for periods of about an hour or less. The benefits are strikingly and uniformly apparent for the 15 minute treatment of this example, for all papers tested, the predicted average lifetime of the papers tested being almost twice that of the same papers which are only deacidified, and more than four times greater than the untreated control samples.

EXAMPLE 2

Three books are placed head down, with a wrapping cord inserted between the fly and text leaves, into a pressure vessel and the vessel is sealed. The pressure vessel is then placed into a bath of hot water, maximum temperature 200° F., the vessel evacuated, and the contents dried under a vacuum of about 5 millimeters of mercury, for a period of about 4 hours. The pressure vessel is then removed from the hot water bath and allowed to cool overnight at room temperature.

A nonaqueous deacidification solution for treating comprises 1000 cc. of 7 percent magnesium of oxide in methanol, and, in addition, 20 pounds of dichlorodifluoromethane (Freon 22). The solution is introduced to the vessel under pressure sufficient to liquify the Freon 22, and the solution is warmed to provide heat energy so the solvent will evaporate rapidly on reducing the pressure. The pressure vessel is 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 books are permitted to return to room temperature (if they are not) and the reaction vessel is evacuated. A one to one by volume mixture of ethylene oxide gas and nitrogen is then introduced into the reaction chamber until the pressure in the chamber is atmospheric, and the deacidified books are retained to react in this atmosphere for one half an hour. The chamber is then evacuated to remove the remaining ethylene oxide. The treated books, on opening the vessel, are found to be dry, and ready to use or reshelve, in a preserved state. The books have suffered no apparent damage from the treatment.

EXAMPLE 3

A number of books are placed in a pressurizable reaction vessel, and the vessel is then sealed and cooled to a temperature below -25°F . by packing in Dry Ice to deactivate the water present in the books undergoing treatment. A solution composed of 1000 cc. of 7 percent magnesium methoxide in methanol and 24 pounds of dichlorofluoromethane (Freon 12) is introduced into the pressure vessel and the pressure vessel is warmed to a temperature of about 100°F . The pressure vessel was then relieved of solution after about one hour of such warming. The chamber is evacuated, heated to 40°C ., and ethylene oxide is introduced to provide a pressure of about atmospheric pressure. The deacidified books are reacted in the ethylene oxide atmosphere for about 5 minutes, the vessel is again evacuated to remove ethylene oxide. The vessel is then opened to provide the preserved books, which have suffered no apparent adverse effects with respect to general physical appearance or fidelity of printed material.

EXAMPLE 4

A nonaqueous deacidification solution is prepared by reacting sodium in isopropyl alcohol to provide a solution of isopropoxide at a level of about $\frac{1}{2}$ percent by weight. Enough aluminum isopropoxide prepared by reacting aluminum in isopropyl 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 methyl alcohol at a level of about 11 percent and trichlorofluoromethane is added to reduce the concentration to about 2 percent by weight.

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 loose sheets of paper, and whole books, in order to deacidify and preserve them. Books and papers having an initial acidity of pH 4.0 as determined by TAPPI Standard Method T 435, m-52 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 Standard Method. This change is effected by immersion in the respective solutions for approximately 30 minutes, and the papers and books are dried under ambient conditions.

The books and loose sheets of paper are then placed in a drybox which encloses an almost pure atmosphere of ethylene oxide at ambient temperature, for 10 minutes. The pages of the books are ruffled to expose the interior surfaces to the ethylene oxide gas, and the books and loose sheets of paper are removed from the drybox, after 10 minutes exposure to the ethylene oxide.

EXAMPLE 5

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

	Parts
Barium methoxide -----	0.1
Magnesium methoxide -----	3
Anhydrous methyl alcohol -----	50
1,1,2 - trichloro - 1,2,2-trifluoroethane (Freon-114, B.P. about 118°F .) -----	50
CCl_3F (Freon-11, B.P. about 75°F .) -----	500
CCl_2F_2 (Freon-12, B.P. about -22°F .) -----	400

A quantity of old books and documents which require deacidification and preservation are removed from library shelves and 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 deacidified 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 deacidified books and documents are placed for 20 minutes at room temperature in a drybox containing an atmosphere of 50 percent air and 50 percent ethylene oxide, by volume. Upon removal from the drybox, the preserved books and documents are replaced on the library shelves in ready-to-use condition.

The preservation reaction employing alkylene oxides may be carried out over a wide range of temperatures and pressures. Temperatures in the range of from about 65°F . (i.e., in the lower range of room temperature) to 200°F . would ordinarily be selected. It should be noted that an upper limit in reaction temperature is determined by the potential injurious effect of elevated temperatures on cellulosic materials and the lower limit is determined as a practical matter by the slowness of the reaction at lower temperatures. For many types of cellulosic materials, particularly those which are already badly deteriorated, it is particularly desirable to employ low reaction temperatures, and in general, lower temperatures in the range of ambient temperatures are preferred for all types of cellulosic materials.

The preservation reaction is carried out by contacting the deacidified cellulosic material with an alkylene oxide atmosphere for a period of time of about an hour or less at about ambient temperature and about atmospheric pressure. For other reaction conditions of temperature and pressure, the reaction is carried out for an equivalent time period which is increased or decreased, respectively, depending upon whether the alternate reaction conditions involve increased or decreased temperature and/or alkylene oxide pressure.

If desired, the effective pressure (in this case, the partial pressure) of the alkylene oxide may be decreased for an atmospheric pressure process by dilution with another gas such as air or nitrogen, and/or, the alkylene oxide pressure may be decreased by conducting the process at a reduced pressure. A moist gas may be a desirable diluent. Conducting the process at decreased alkylene oxide pressures results in increasing the reaction time at a given reaction temperature, while increasing the alkylene oxide pressure by operating at a superatmospheric pressure results in decreasing the reaction time.

It has been found that reaction periods of about 15 minutes or less, for a condition of about ambient temperature and an alkylene oxide pressure of about one atmosphere, are particularly desirable and have a particularly pronounced long term preservational effect on the cellulosic materials.

It is preferred that the deacidified cellulosic materials have a pH of from about 6 to about 11, and more preferably from about 8 to about 11. It is also preferred that the nonaqueous deacidification process, used to deacidify the cellulosic materials prior to treatment with an alkylene oxide, employ a nonaqueous solution of an alkali or an alkaline earth alkoxide as a deacidification agent. Magnesium alkoxides are particularly preferred, especially magnesium methoxide.

The process is particularly effective when employed in conjunction with a nonaqueous deacidification process which employ a liquified gas solvent in a pressurized system. Following the deacidification treatment, a vacuum can be drawn on the system, followed by the introduction of an alkylene oxide, particularly ethylene oxide, into the system. Such a procedure permits the alkylene oxide to thoroughly penetrate throughout the deacidified cellulosic materials, to result in uniform treatment. Such a process

ture is particularly effective for treating cellulosic aggregates such as books, pamphlets, tied or stacked agglomerations of documents, and whole file drawers of documents.

It is effective, particularly for the mass treatment of cellulosic aggregates to subject the cellulosic materials to a vacuum treatment after a nonaqueous deacidification treatment followed by introduction of alkylene oxide to break the vacuum. By employing such a procedure, the alkylene oxide may be caused to penetrate throughout the deacidified cellulosic material, thus resulting in relatively uniform treatment. However, the preservation reaction may alternately be carried out by introducing the alkylene oxide with, or into, the nonaqueous solution during the nonaqueous deacidification process. For example, sheets of paper which are dipped in a nonaqueous deacidification solution may be removed and, without evaporation to remove all of the solvent, transferred into an alkylene oxide atmosphere to effect final preservation.

Ethylene oxide is the preferred alkylene oxide, having a boiling point of about 11° C. at atmospheric pressure. Other alkylene oxides, such as propylene oxide which has a boiling point of about 35° C. at atmospheric pressure, may be used also. Such higher alkylene oxides may be used at temperatures at which they are in the gaseous state at atmospheric pressure, or may be used at reduced pressures. In addition, they may have sufficient vapor pressure even below their boiling points so that their vapors may be used in a diluent atmosphere, or mixed with ethylene oxide to provide an alkylene oxide mixture for the treatment of the deacidified cellulosic materials.

It can be seen from the foregoing that an improvement in nonaqueous processes for the treatment of cellulosic materials has been provided which permits preservation of such materials for greatly extended periods of time and which can be used to treat papers before or after deterioration 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.

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

What is claimed is:

1. In a nonaqueous deacidification process for the preservation of cellulosic material wherein the cellulosic material is contacted with a deacidification solution comprising an alkali or alkaline earth deacidification agent and an organic solvent therefor, and the solvent is removed, the improvement comprising contacting the cellulosic material with an alkylene oxide or a mixture of alkylene oxides concomitantly with the deacidification solution or subsequent to removal of the solvent.

2. A process according to claim 1 wherein the cellulosic material is contacted with the alkylene oxide or mixture of alkylene oxides concomitantly with the deacidification solution.

3. A process according to claim 1, wherein the alkylene oxide or mixture of alkylene oxides is diluted with moist gas.

4. A process according to claim 1 wherein the cellulosic material is contacted with the alkylene oxide or mixture of alkylene oxides subsequent to removal of the solvent.

5. A process according to claim 4 wherein the cellulosic material is contacted with an alkylene oxide atmosphere for a period of time of about hour or less at about ambient temperature and about atmospheric pressure, or for an equivalent time period for other conditions of temperature and pressure which is increased or decreased, respectively, depending upon whether such other reaction conditions involve increased temperature and/or alkylene oxide pressure, or, decreased temperature and/or alkylene oxide pressure.

6. A process according to claim 5 wherein the period of time of contacting the cellulosic material with an alkylene oxide atmosphere is about 15 minutes or less at ambient temperature and atmospheric pressure, or an equivalent period of time for other conditions of temperature and pressure.

7. A process according to claim 5 wherein the alkylene oxide pressure is decreased by conducting the process at a reduced pressure, or by dilution with another gas.

8. A process according to claim 5 wherein the alkylene oxide pressure is increased by conducting the process at superatmospheric pressure.

9. A process according to claim 5 wherein the alkylene oxide is ethylene oxide.

10. A process according to claim 9 wherein the cellulosic material is one or more cellulosic aggregates such as books, pamphlets, tied or stacked agglomerations of documents or whole file drawers of documents, and wherein a vacuum is drawn on the cellulosic aggregates prior to contacting the aggregates with ethylene oxide, and the vacuum is then broken by introducing ethylene oxide into contact with the cellulosic aggregates.

11. A process according to claim 10 wherein the deacidification agent is a magnesium alkoxide.

12. A process according to claim 11, wherein said solvent is a liquified gas solvent.

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