Nov. 21, 1972 J. E. KUSTERER, JR., ET AL 3,703,353

GASEOUS DIFFUSION PAPER DEACIDIFICATION

Filed April 15, 1971 3 Sheets-Sheet 1

FIG. 1.

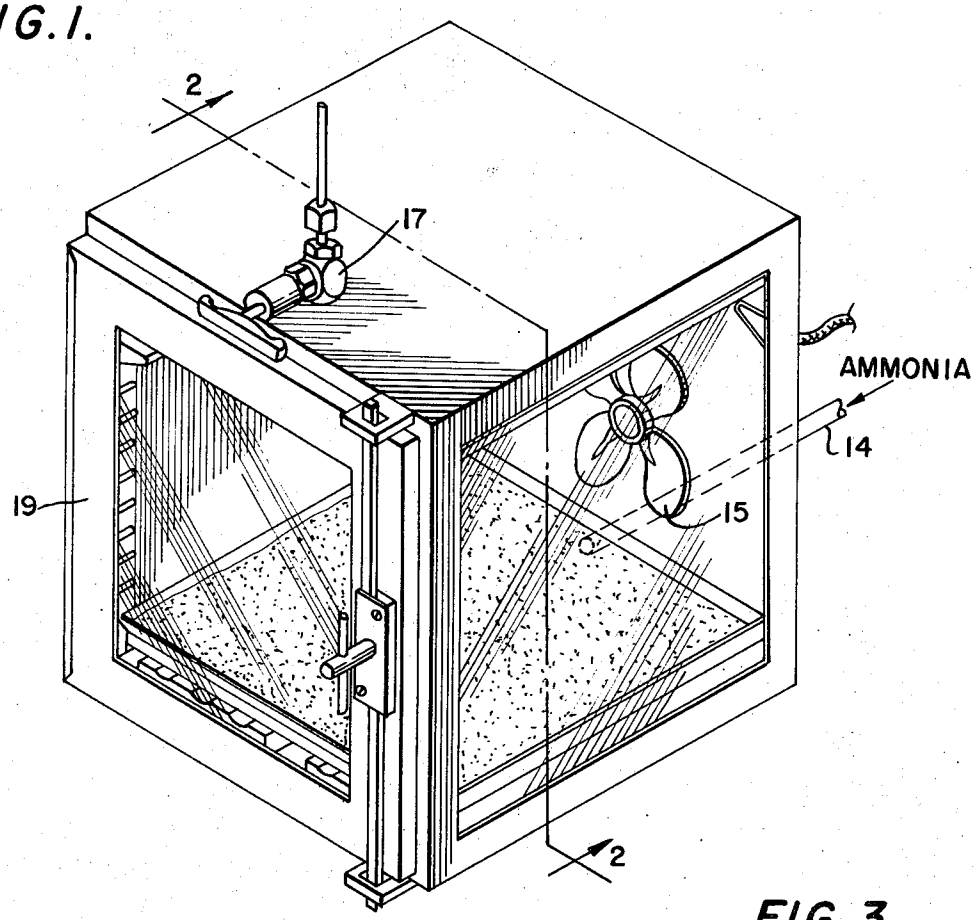


FIG. 2.

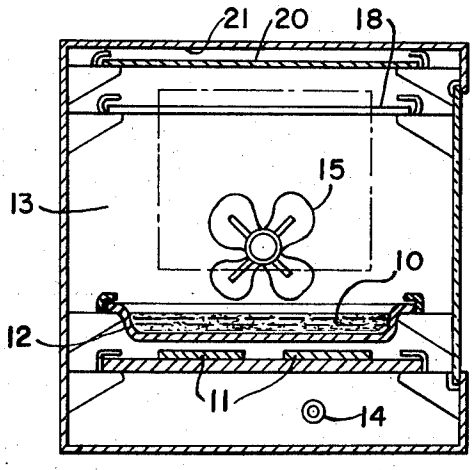
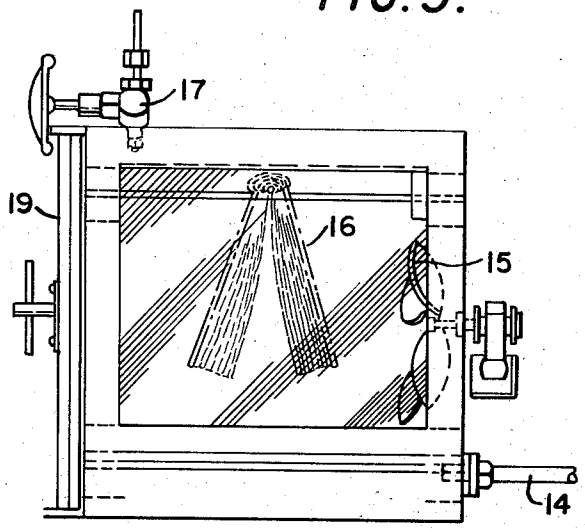


FIG. 3.



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GASEOUS DIFFUSION PAPER DEACIDIFICATION

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FIG. 5.

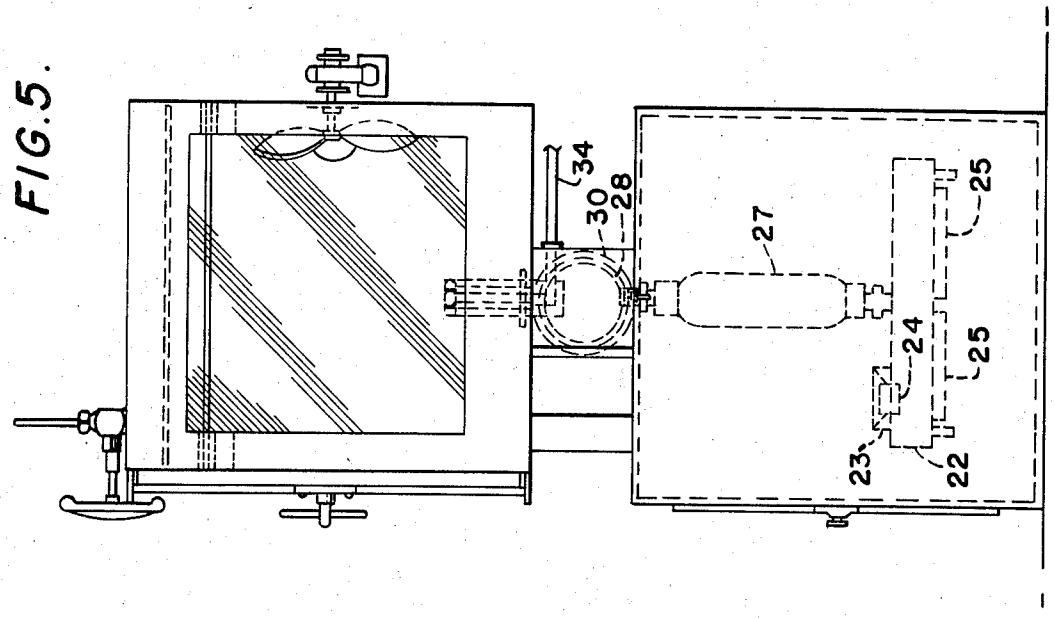

FIG. 4.

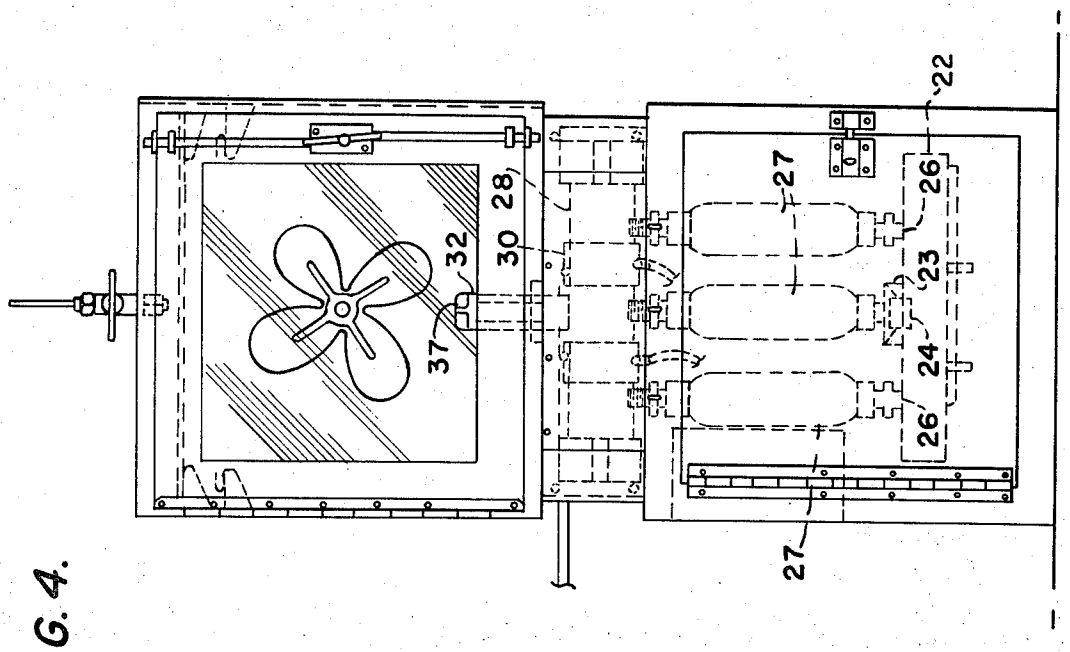

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FIG. 6.

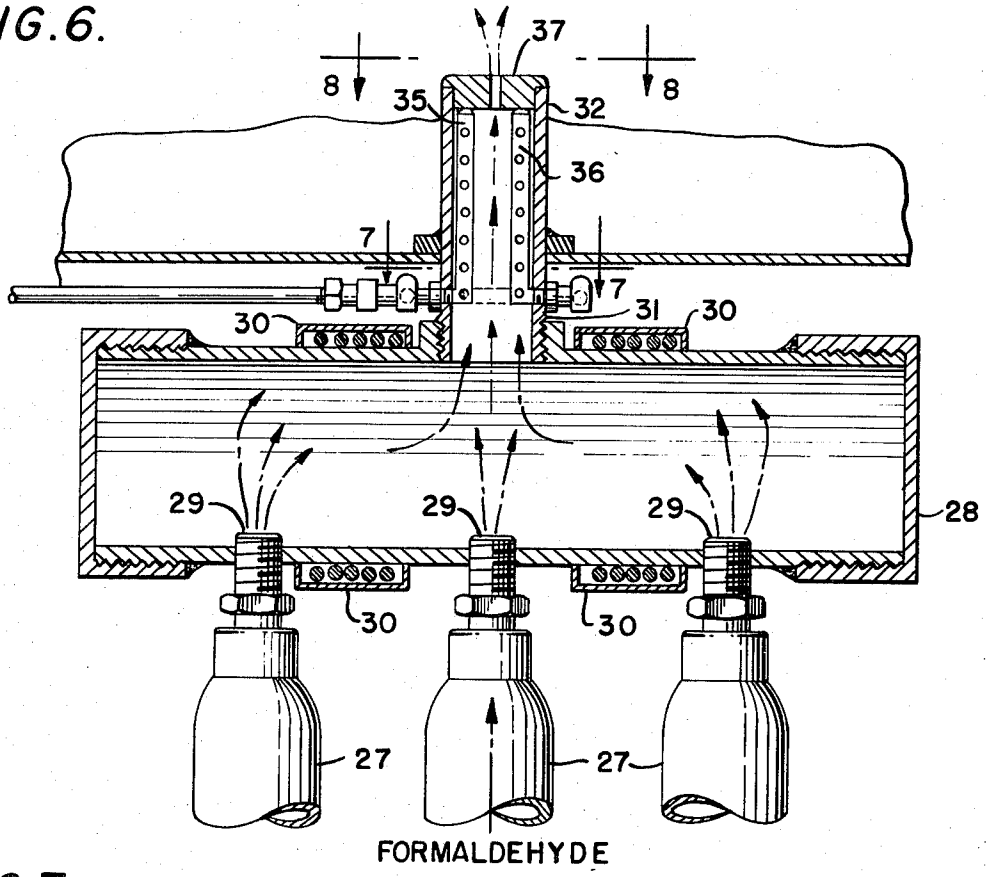


FIG. 7.

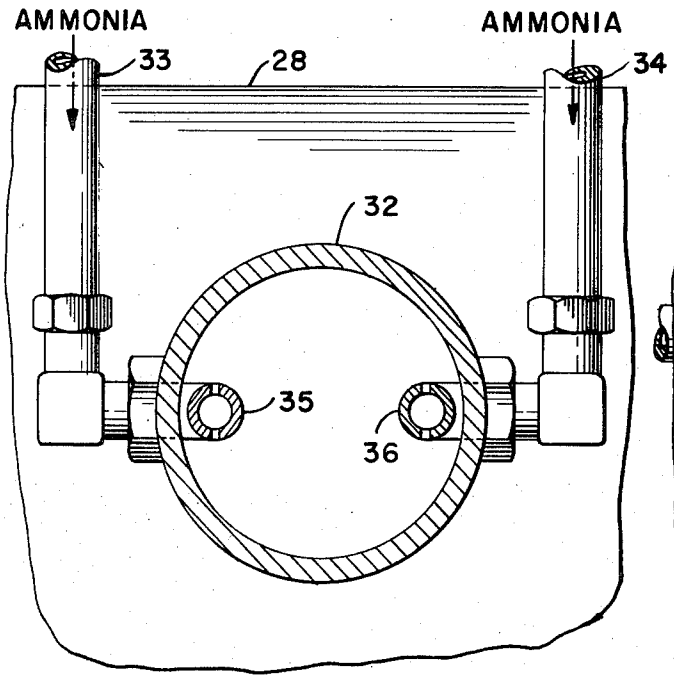
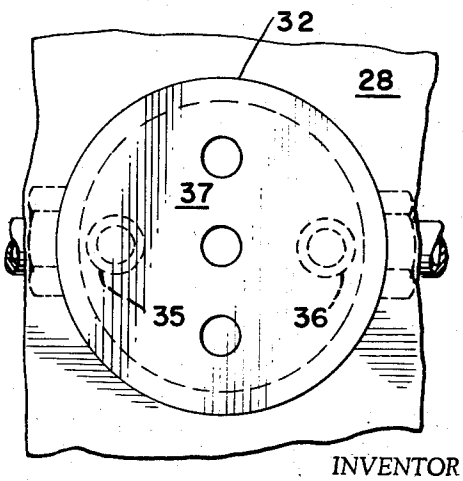


FIG. 8.



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GASEOUS DIFFUSION PAPER DEACIDIFICATION

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Int. Cl. A61l 13/00
U.S. Cl. 21—58 17 Claims

ABSTRACT OF THE DISCLOSURE

Paper, for example having a pH of about 5.0 or lower, is rendered resistant to the deterioration that is promoted by acidic conditions in paper by impregnating the paper, for example in the form of a book, with gaseous hexamethylenetetramine. Preferably, the hexamethylenetetramine is formed by reacting gaseous ammonia with gaseous formaldehyde, and such reacting can either be effected while the reactants are in contact with the paper or be carried out in a zone apart from the impregnation zone and the hexamethylenetetramine product vapors then conducted to the impregnation zone.

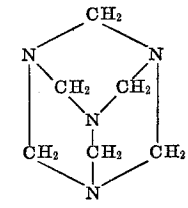
This invention relates to a process for treating paper to render it resistant to the deterioration that is promoted by acidic conditions in paper. More particularly, it concerns such a process wherein the treatment constitutes impregnating the paper with gaseous hexamethylenetetramine.

The recognition of the severe problem of deterioration of documents printed on paper that is or becomes acidic has prompted the development of several different processes for deacidifying such paper so as to halt or slow its deterioration. Prime examples of acidic papers which are susceptible to such deterioration (caused by hydrolysis of acidic ions which impregnate the cellulose during manufacture) are groundwood (as opposed to chemical-wood) papers and alum-rosin sized papers, whether made of wood or rags. Some other deacidification processes which have been developed are disclosed in "Restoration Methods," by W. J. Barrow, The American Archivist, 6: 151–154, July 1943; "Permanence/Durability of the Book—III: Spray Deacidification," published by W. J. Barrow Research Laboratory, 1964; "Vapor Phase Deacidification: A New Preservation Method," by Paul McCarthy, The American Archivist, 32: 333–342, October 1969; and U.S. Pat. No. 3,472,611 to Langwell. Each of the processes shares at least one common objective: to effect a long lasting elevation of the pH of the paper. If this is accomplished, then the deterioration of the paper that is induced by acidic conditions therein will be substantially alleviated.

The paper deacidification processes heretofore developed, however, possess significant drawbacks. Some, for example those involving a leaf-by-leaf treatment, while perhaps technically effective are prohibitively expensive. Others, such as ammoniation, may provide only a short-lived resistance to deterioration. Still other processes may be longer lasting in their intended effect but have one or more undesirable side effects such as causing discoloration, e.g., yellowing, of the paper, diminution of the paper's fold endurance, cockling of the paper, and leaving the paper with a lingering, unpleasant odor. Still other methods of treatment may require the use of particularly noxious and/or toxic chemicals (e.g., cyclohexylamine), thereby requiring relatively elaborate equipment to conduct the treatment safely. There is, then, an urgent need for some effective, safe, and relatively inexpensive method of treating paper so as to render it resistant to acid-induced deterioration. The magnitude of the problem is revealed, for example, in "The Case of the Vanishing Records," by David G. Lowe, American Heritage, volume XX, No. 5 (1969), page 34.

It has now been discovered that paper which is susceptible to acid-induced deterioration can be effectively, safely, and relatively inexpensively deacidified, and thereby made resistant to such deterioration, if it is impregnated with gaseous hexamethylenetetramine. A surprising discovery regarding this process is that the gaseous hexamethylenetetramine penetrates even tightly closed books extremely thoroughly and very rapidly.

Hexamethylenetetramine, also known as hexamine, formin, aminoform, and urotropin and having the chemical formula $(CH_2)_6N_4$, is a colorless, substantially odorless, normally solid, organic alkaline compound that can be structurally represented as follows:



When the paper is sufficiently impregnated with the gaseous hexamethylenetetramine according to the process of the present invention, its resistance to the deterioration that is induced by acidic conditions in paper is substantially increased. Preferably, the extent of impregnation will be sufficient to provide the paper with a pH (measured after the paper has been allowed to stand at room temperature and atmospheric pressure for 24 hours) of at least about 7.5, preferably at least about 8.3. The pH values referred to are those of the resultant aqueous solution when one gram of one-eighth inch square pieces of the treated paper is soaked for one hour in 70 ml. of distilled water at room temperature. As determined by this method, the initial pH value of paper which is susceptible to the deterioration that is alleviated by the present invention is usually about 5.0 or lower, and frequently about 4.3 or lower.

The temperature in the immediate vicinity of the paper, i.e., the impregnation zone, during the treatment is sufficiently high, e.g., at least about 35° C., that the hexamethylenetetramine can exist in the gaseous state long enough to diffuse through and/or condense on the paper. Preferably, though, the impregnation zone temperature is not raised above about 42° C., most preferably not above about 40° C., because the higher the temperature to which paper is exposed, the greater it will be degraded by the heating.

One suitable manner of impregnating the paper with the gaseous hexamethylenetetramine is by reacting gaseous ammonia with gaseous formaldehyde while the reactants are in contact with the paper to be treated to yield the gaseous hexamethylenetetramine and H_2O, the reaction equation for which is as follows:

$$4NH_3+6CH_2O\rightarrow(CH_2)_6N_4+6H_2O$$

In this manner the gas generation zone and paper impregnation zone are not separated. Alternatively, however, this reaction can be effected in a separate zone from, e.g., an anteroom to, that in which the impregnation of the paper is to be effected, and the hexamethylenetetramine-containing product vapors then conducted into the impregnation zone. The use of separate generation and impregnation zones has the advantage of permitting the use of lower temperatures in the impregnation zone due to cooling of the product vapors in the course of their transit

from the generation zone to the paper to be treated in the impregnation zone.

The preferred temperature range for effecting the hexamethylenetetramine-yielding reaction is about 96 to 135° C. It is also preferred that the mixture of gases in the generation zone contain at least that amount of ammonia which is stoichiometrically required to convert all of the gaseous formaldehyde in the zone to hexamethylenetetramine. One purpose of this is to avoid as much as possible the situation in which formaldehyde polymerizes in, on, or near the paper being treated and leaves deposits of paraformaldehyde on or in the paper. Most preferably, then, the amount of gaseous ammonia in the generation zone will be maintained at about 101 to 103 percent of that which is stoichiometrically required to convert all of the gaseous formaldehyde in the zone to hexamethylenetetramine.

Amounts of ammonia which exceed the preferred excess of 1% to 3% of that which is stoichiometrically required for the reaction have been determined to be detrimental to the paper being treated, possibly causing losses in physical properties as great as 55%, and not less than 29%.

A suitable source of gaseous formaldehyde which can be employed for producing the gaseous hexamethylenetetramine is that obtained by the decomposition of paraformaldehyde, which latter material decomposes to gaseous formaldehyde at about 90° C. to 135° C. This decomposition can be effected right in the generation zone, for example by heating a slurry of paraformaldehyde in an inert, heat-transfer liquid such as mineral oil. The aforementioned preference for reacting the ammonia and formaldehyde in an anteroom to the impregnation zone holds especially true where formaldehyde vapors are generated from an oil bath in the generation zone, for if the oil bath is right in the impregnation zone there is a greater propensity for an oily film to be deposited on the paper being treated.

Advantageously, a decomposition catalyst such as phosphorous pentoxide is admixed with the paraformaldehyde, for example in an amount in the range of about 1 to 5 percent, preferably about 2 to 3 percent, based on the weight of the paraformaldehyde. Another suitable decomposition catalyst is concentrated phosphoric acid, which can be used, for example, in an amount of about 5 to 7 percent, preferably about 5 to 6 percent, based on the weight of the paraformaldehyde. Preferably, the mixture of paraformaldehyde and catalyst, when employed, is heated to about 115° C. to 125° C. to effect release of gaseous formaldehyde.

When generating gaseous formaldehyde right in the generation zone by this method, it will usually be preferred to regulate the amount of paraformaldehyde used and the temperature at which it is heated so that it decomposes at the rate of about 0.015 to 0.018 milligram per minute per cubic centimeter of combined volume of the generation and impregnation zones. As indicated above, the preferred flow rate of gaseous ammonia into the generation zone in such circumstances is that which is sufficient to maintain at least that amount of ammonia which is stoichiometrically required to convert all of the gaseous formaldehyde in the zone to hexamethylenetetramine. Often suitable ammonia flow rates are those in the range of about 1.0×10^{-5} to 1.05×10^{-5} cubic centimeter of ammonia (measured at standard temperature and pressure) per minute per cubic centimeter of combined volume of the generation and impregnation zones. The foregoing preferences are especially pertinent where the generation and impregnation zones are not separate. Above this flow rate, wood pulp manufactured using standard chemical wood techniques may begin to yellow and lose brightness and strength.

It is preferred when operating according to those embodiments of the present invention in which water-containing hexamethylenetetramine product vapors are contacted with the paper being treated that the paper be suspended in the impregnation zone substantially out of contact with any condensed water which might collect on the internal surfaces of the zone. The reason for this precaution is to avoid, as much as possible, the circumstance in which the water is absorbed by capillary attraction onto the paper and causes the final treated paper to be cockled (i.e., to have a wavy texture). Thus it is preferred that the impregnation zone be equipped with a shield to protect the paper being treated from droplets of water which may form on the roof of the zone.

The presence of vaporous water in the impregnation zone in amounts sufficient to slightly moisten the paper being treated has been found desirable in that it aids the diffusion of the gases into the paper. An advantage in producing the hexamethylenetetramine by reacting ammonia with formaldehyde and then impregnating the paper with the vaporous product mixture from the reaction is that the amount of vaporous water of condensation that is liberated by the reaction is usually ideal for slightly moistening the paper and promoting such diffusion. Optimum conditions are thus achieved without either adding to or extracting from the water of condensation produced in the reaction.

It has been observed when practicing the process of the present invention in treating certain types of bound books, that unless the cover of the book is somehow shielded, for instance with paper toweling, a deposit can sometimes form thereon of white, powdery hexamethylenetetramine.

The hexamethylenetetramine-yielding condensation reaction is facilitated if the reactant gases are agitated, for example by a fan rotating at about 1400 r.p.m. Use of a fan can also facilitate dispersal of the gaseous hexamethylenetetramine throughout the impregnation zone.

There are illustrated in the attached drawings two different types of paper deacidification apparatus which can be used to practice the present invention. Referring now to the drawings, FIG. 1 is an isometric view of a single chamber apparatus; FIG. 2 is a front sectional view of the same apparatus taken along line **2—2** of FIG. 1; and FIG. 3 is a side view of the same apparatus.

FIG. 4 is a front view of a dual chamber paper deacidification apparatus of the present invention; FIG. 5 is a side view of the same apparatus; and FIG. 6 is an enlarged view of the reaction chamber portion of the same apparatus. FIG. 7 is an enlarged sectional view of the ammonia delivery system portion of FIG. 6 and is taken along line **7—7** of FIG. 6. FIG. 8, finally, is an enlarged sectional view of the gas delivery tube nozzle portion of FIG. 6 and is taken along line **8—8** of FIG. 6.

In using the single chamber apparatus depicted in FIGS. 1–3 to perform the deacidification process of the present invention, a book **16** to be deacidified is hung over rod **18** in chamber **13** and the access door **19** to the chamber is closed and secured. Chamber venting valve **17** is closed and a slurry **10** of paraformaldehyde in mineral oil is heated by electrically powered heating elements **11** while contained in pan **12** to release gaseous formaldehyde into the reaction-impregnation chamber **13**. Gaseous ammonia is simultaneously introduced to chamber **13** via line **14**. The gases are thoroughly admixed by fan **15** while they react to form hexamethylenetetramine which impregnates book **16**. Condensation drip shield **20** prevents whatever water drops that form on chamber ceiling **21** from falling on book **16**. After conclusion of the treatment, heating of the paraformaldehyde-oil slurry **10** is ceased, as is the introduction of ammonia via line **14**, and unreacted gases are vented from chamber **13** by opening chamber venting valve **17**.

The dual chamber impregnation apparatus of FIGS. 4–8 differs from the single chamber apparatus discussed above in the means provided for gas introduction to the impregnation chamber. Referring to FIGS. 4–8, a slurry of paraformaldehyde in mineral oil is charged to cov-

ered pan **22** via charging station **23**, after which plug **24** is put in place. Electrically powered heating elements **25** raise the temperature of the slurry, causing decomposition of the paraformaldehyde and generation of gaseous formaldehyde. The gaseous formaldehyde exits pan **22** via ports **26** and is collected in the three accumulator tanks **27**. From tanks **27** the formaldehyde gas enters manifold **28** via ports **29** wherein it is heated to reaction temperature by electrically powered manifold heater **30**.

The heated formaldehyde gas exits manifold **28** via neck **31** and enters gas delivery tube **32** wherein it is mixed and reacted with gaseous ammonia. The ammonia is supplied to delivery tube **32** via feed lines **33** and **34** and distribution nozzles **35** and **36**. The resultant hexamethylenetetramine-containing mixtures of gases exits the delivery tube via nozzle **37** and passes into the impregnation chamber where the paper to be treated is suspended.

The invention will be better understood by reference to the following non-limiting examples.

EXAMPLE I

A cloth bound book entitled "You and Your Eyes," by L. Lewison, the pages of which were composed of chemical-wood paper (50% hardwood and 50% softwood) having a pH of 4.2, was suspended in the impregnation zone of the deacidification apparatus depicted in FIGS. 1–3 of the attached drawings. The volume of the chamber of the apparatus was 22.157 liters.

Ammonia gas was passed through the chamber for 30 minutes at a flow rate of 0.12 mole per minute, while 40 grams of paraformaldehyde was slurried in a 135° C. mineral oil bath in the bottom of the chamber. The chamber temperature in the vicinity of the book reaches about 42° C. After two hours in the chamber, the paraformaldehyde having been substantially completely decomposed as evidenced by no appearance of white solid in the mineral oil bath, the book was removed and observed to have a strong smell of ammonia, most, if not all, of which left the book after it was allowed to sit open in a room overnight. The pH of the pages of the book was then determined to be 8.3. The pages of the book were observed to be no more discolored than they were before the treatment. Portions of the book had a very slight amount of an oily film on them. The pH of the pages was measured again 4 days later, during which period the book was only subjected to ambient conditions, and was found to be 8.2, indicating the lasting effect of the deacidificataion process of the present invention.

EXAMPLE II

Using the same conditions as in Example I, samples of both chrome-tanned and untanned leather hides were treated in the deacidification apparatus used in Example I in order to ascertain the effect which such treatment would have on books bound in leather or similar materials. The treated hides showed absolutely no signs of physical degradation. Their odor had changed, however, and resembled that of the paper which had been so treated in Example I. The pH's of the hides before and after treatment were substantially unchanged, being acidic in every instance.

EXAMPLE III

Another copy of the book used in Example I, "You and Your Eyes," was clamped tightly closed with four "C"-clamps, suspended in the impregnation chamber of the apparatus used in Example I, and then treated in the same manner as in Example I. The treated book was then allowed to stand open in the room for 24 hours and the pH of portions of pages selected at random from the book was measured. All of the portions, even those which were directly beneath the head of a clamp, had a pH greater than 8.0, thus evidencing the surprising facility with which the gaseous hexamethylenetetramine can penetrate and impregnate even densely stacked sheets or books of paper.

Pages of another copy of the book used in this example, both before and after being subjected to a 2½ hour deacidification treatment such as above, were subjected to fold endurance testing to determine the effect of the treatment on the strnegth of the paper. Testing was with The Massachusetts Institute of Technology folding endurance tester which repeatedly bends a 15 mm. wide strip of the paper to be tested across a line in a 270° arc, under ½ kilogram tension, until failure. The endurance was recorded as the average number of bends endured per strip, after testing 50 strips.

Both machine directional (M.D.) fold endurance and cross directional (C.D.) fold endurance were determined in this manner. The results were that the deacidification treatment caused an average 26.2% reduction in the C.D. fold endurance and 44.2% reduction in the M.D. fold endurance of the paper.

The treated (deacidified) and untreated paper were then both subjected to an accelerated aging test, consisting of maintaining the paper at 68° C. for 30 days, and the fold endurances of the thus aged papers determined. The fold endurance of the treated paper was substantially unaffected by the accelerated aging, exhibiting 102% of the C.D. fold endurance it possessed before aging, and 96% of the M.D. fold endurance it had before aging. The results with the untreated paper were quite different, however. Aging of those samples caused a drop in their C.D. fold endurance to 64% of the pre-aging value, and a drop in their M.D. fold endurance to 61% of the pre-aging value.

These test data demonstrate that the deacidification treatment of the present invention, while effecting an initial strength loss for the paper, provides resistance to further loss of strength and, overall, a much longer useful life than that to be expected for the untreated paper. Specifically, under the above-mentioned aging conditions the treated paper had a half-life of greater than 150 days for both M.D. and C.D. fold endurance, while the untreated paper had only a 49 day half-life for C.D. fold endurance and a 42.5 day half-life for the M.D. fold endurance.

EXAMPLE IV

Example I was repeated using the apparatus depicted in FIGS. 4–8 of the attached drawings. The results were substantially the same, except that the treated book from this example had no apparent oily film.

It is claimed:

1. A process for treating paper to render it resistant to the deterioration that is promoted by acidic conditions in paper, which process comprises impregnating the paper with gaseous hexamethylenetetramine.

2. The process of claim **1** wherein the paper is in the form of a book.

3. The process of claim **1** wherein the amount of hexamethylenetetramine impregnated into the paper is sufficient to provide the paper with a pH (measured after the paper has been allowed to stand at room temperature and atmospheric pressure for 24 hours) of at least about 7.5, as determined by soaking one gram of one-eighth inch squares of the paper for one hour in 70 ml. of distilled water at room temperature and then measuring the pH of the resultant aqueous solution.

4. The process of claim **3** wherein the paper prior to treatment has a pH of about 5.0 or lower.

5. The process of claim **1** wherein the gaseous hexamethylenetetramine is prepared by reacting gaseous ammonia with gaseous formaldehyde in a reaction chamber at a temperature of about 35° C. to 42° C. to yield a gaseous product mixture of hexamethylenetetramine and H_2O, and the paper is then impregnated in an impregnation chamber with said gaseous product mixture.

6. The process of claim **5** wherein the ammonia is employed in at least the amount stoichiometrically required to convert all of the formaldehyde present in the reaction chamber to hexamethylenetetramine.

7. The process of claim 6 wherein the amount of ammonia employed is about 101 to 103 percent of that stoichiometrically required to convert all of the formaldehyde present in the reaction chamber to hexamethylenetetramine.

8. The process of claim 6 wherein the gaseous ammonia is introduced to the reaction chamber at a flow rate of about 1.0×10^{-5} to 1.05×10^{-5} cubic centimeter (measured at standard temperature and pressure) per minute per cubic centimeter of volume of the reaction chamber.

9. The process of claim 6 wherein the paper is suspended in the impregnation chamber substantially out of contact with any condensed H_2O that collects on the internal surfaces of the impregnation chamber.

10. The process of claim 5 wherein the gaseous formaldehyde is produced in situ in the reaction chamber by decomposing paraformaldehyde therein.

11. The process of claim 10 wherein the decomposition of the paraformaldehyde is effected with the latter being in admixture with a catalytic amount of phosphorus pentoxide.

12. The process of claim 11 wherein the amount of phosphorus pentoxide employed is about 1 to 5 percent, based on the weight of the paraformaldehyde.

13. The process of claim 11 wherein the paraformaldehyde is decomposed in the reaction chamber at a rate of about 0.015 to 0.018 milligram per minute per cubic centimeter of volume of the reaction chamber.

14. The process of claim 11 wherein the mixture of paraformaldehyde and catalyst is heated to a temperature of about 90° C. to 135° C. to effect the decomposition.

15. The process of claim 14 wherein the mixture of paraformaldehyde and catalyst is slurried in mineral oil while being heated.

16. A process of treating a book made of paper having a pH of about 5.0 or lower so as to render the paper resistant to the deterioration that is promoted by acidic conditions, which process comprises suspending the book in a reaction-impregnation chamber substantially out of contact with any condensed H_2O that collects on the internal surfaces of the chamber, introducing gaseous ammonia into the chamber at a flow rate of about 1.0×10^{-5} to 1.05×10^{-5} cubic centimeter (measured at standard temperature and pressure) per minute per cubic centimeter of volume of the chamber, and simultaneously heating a mineral oil slurry of paraformaldehyde mixed with about 2 to 3 percent phosphorus pentoxide, based on the weight of the paraformaldehyde, at a temperature of about 115° C. to 125° C. in the chamber so as to decompose the paraformaldehyde into gaseous formaldehyde at a rate of about 0.015 to 0.018 milligram of paraformaldehyde per minute per cubic centimeter of volume of the chamber and to effect a condensation reaction between the gaseous ammonia and the gaseous formaldehyde, while those reactants are in contact with the book, to yield gaseous hexamethylenetetramine and H_2O, said gaseous hexamethylenetetramine impregnating the paper of the book sufficiently to provide the paper with a pH (measured after the book has been allowed to stand at room temperature and atmospheric pressure for 24 hours) of at least about 7.5, said pH's being as determined by soaking one gram of one-eighth inch squares of the paper in 70 ml. of distilled water at room temperature for one hour and then measuring the pH of the resultant aqueous solution, and said flow rate of ammonia being sufficient to provide about 101 to 103 percent of the amount of gaseous ammonia that is stoichiometrically required to convert all of the gaseous formaldehyde present in the chamber to hexamethylenetetramine.

17. A process of treating a book made of paper having a pH of about 5.0 or lower so as to render the paper resistant to the deterioration that is promoted by acidic conditions, which process comprises suspending the book in an impregnation chamber substantially out of contact with any condensed H_2O that collects on the internal surfaces of the impregnation chamber, introducing gaseous ammonia into a reaction chamber separate and distinct from said impregnation chamber at a flow rate of about 1.0×10^{-5} to 1.05×10^{-5} cubic centimeter (measured at standard temperature and pressure) per minute per cubic centimeter of volume of the reaction chamber, and simultaneously heating a mineral oil slurry of paraformaldehyde mixed with about 2 to 3 percent phosphorus pentoxide, based on the weight of the paraformaldehyde, at a temperature of about 115° C. to 125° C. in the reaction chamber so as to decompose the paraformaldehyde into gaseous formaldehyde at a rate of about 0.015 to 0.018 milligram of paraformaldehyde per minute per cubic centimeter of volume of the reaction chamber and to effect a reaction between the gaseous ammonia and the gaseous formaldehyde to yield a gaseous product mixture of hexamethylenetetramine and H_2O, conducting said gaseous product mixture to the impregnation zone and impregnating the mixture into the paper of the book sufficiently to provide the paper with a pH (measured after the book has been allowed to stand at room temperature and atmospheric pressure for 24 hours) of at least about 7.5, said pH's being as determined by soaking one gram of one-eighth inch squares of the paper in 70 ml. of distilled water at room temperature for one hour and then measuring the pH of the resultant aqueous solution, and said flow rate of ammonia being sufficient to provide about 101 to 103 percent of the amount of gaseous ammonia that is stoichiometrically required to convert all of the gaseous formaldehyde present in the reaction chamber to hexamethylenetetramine.

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MORRIS O. WOLK, Primary Examiner

D. G. MILLMAN, Assistant Examiner

U.S. Cl. X.R.

21—7, 76, 110; 117—154; 162—160