United States Patent [19]

Walker et al.

[11] **3,837,804**

[45] **Sept. 24, 1974**

[54] **PROCESS FOR DEACIDIFYING A BOOK WHICH HAS A PYROXYLIN-CONTAINING COVER**

[75] Inventors: **Bernard F. Walker,** Richmond; **James E. Kusterer, Jr.,** Montpelier, both of Va.

[73] Assignee: **Council on Library Resources, Inc.,** Washington, D.C.

[22] Filed: **Aug. 15, 1973**

[21] Appl. No.: **388,472**

[52] **U.S. Cl.** **21/58,** 21/7, 21/76, 117/154, 252/401

[51] **Int. Cl.** **A61l 13/00**

[58] **Field of Search** 21/58, 76, 7; 117/154; 252/401; 162/160

[56] **References Cited**

UNITED STATES PATENTS

3,135,627 6/1964 Sadler ..... 117/154 X

Primary Examiner—Joseph Scovronek
Assistant Examiner—Barry I. Hollander
Attorney, Agent, or Firm—Morton, Bernard, Brown, Roberts & Sutherland

[57] **ABSTRACT**

Books having pyroxylin-containing covers can be deacidified by impregnation with morpholine vapors without substantially damaging the covers, if the impregnation is conducted for about 5 to 15 minutes with a gaseous atmosphere consisting essentially of about 30 to 55 weight percent morpholine and a balance of water vapor at a temperature of about 90° to 115° F.

11 Claims, No Drawings

PROCESS FOR DEACIDIFYING A BOOK WHICH HAS A PYROXYLIN-CONTAINING COVER

This invention relates to a process for deacidifying books covered in pyroxylin-containing bookbinding material without causing substantial damage to the books.

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 alumrosin sized papers, whether made from wood or rags, or both. 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.

Some of the paper deacidification processes which have heretofore been developed in an attempt to solve this problem 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 and U.S. Pat. No. 3,703,353 to Kusterer and Hind. All of these processes share at least one common objective: to effect a long lasting elevation of the pH of the paper. If this is accomplished the deterioration of the paper that is induced by acidic conditions therein will be substantially alleviated.

In Kusterer and Sproull's U.S. Pat. application Ser. No. 214,217, filed Dec. 30, 1971, now U.S. Pat. No. 3,771,958, issued Nov. 13, 1973, is described a method of deacidifying paper which involves impregnating the paper with gaseous morpholine. Using the gaseous morpholine impregnation method, the deacidification is rapid, non-injurious to the physical strength of the paper, and relatively permanent; however, as discussed in application Ser. No. 214,217, such treatment can discolor, and/or render tacky, book covers that contain pyroxylin, making it necessary to practically encapsulate such covers with a protective wrap prior to subjecting the books to such treatment.

Pyroxylin, sometimes called soluble guncotton, is a cellulose nitrate consisting chiefly of cellulose trinitrate. It is used extensively in coating cloth, such as book covers and window shades. Pyroxylin-containing book covers have been in use for several decades, usually in the preparation of relatively inexpensive books. A large percentage of these books have been printed on paper that is acidic or becomes so in time, and thus susceptible to the physical deterioration that is mentioned above. It may be desired to deacidify some of these books by the gaseous morpholine impregnation method, but the expense of encapsulating their pyroxylin-containing covers so as to protect them from damage can be prohibitive.

It has now been found that effective deacidification of books having pyroxylin-containing covers can be achieved by the gaseous morpholine impregnation method without causing substantial damage to the covers, if the book is impregnated for about 5 – 15 minutes, preferably about 7 to 12 minutes, with a gaseous atmosphere consisting essentially of about 30 to 55 weight percent, preferably about 35 to 50 weight percent, morpholine and a balance of water vapor at a temperature of about 90° to 115° F., preferably about 95° to 110° F.

The impregnation method of the present invention can best be performed by first placing the book or books to be treated in an air-tight chamber surrounded by a constant temperature bath, evacuating the chamber, and then introducing a liquid solution of morpholine in water (containing about 30 to 55 weight percent morpholine) into the chamber. The solution will vaporize immediately and the mixed morpholine and water vapors will rapidly and thoroughly impregnate the pages of the book or books. When the designated treatment time has elapsed, the chamber can be vented to the atmosphere and then purged with air so as to sweep the unabsorbed morpholine vapors away from the books.

The amount of the aqueous solution of morpholine that is desirably introduced to the evacuated treatment chamber depends upon many factors: the volume of the chamber, the number of books therein to be treated, the pre-treatment pH of the pages of the books, the after-treatment pH that is sought, the concentration of the solution etc. Generally, however, the amount of solution introduced to the evacuated chamber will be sufficient to provide the pages of the book 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 6.5, but most preferably at least about 7.0. 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 1 hour in 70 ml. of distilled, deionized 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.

Another preference with regard to the extent of the morpholine-water vapor impregnation is that the books be allowed to absorb no more than about 2 percent morpholine, based on the weight of the books. This can be achieved by controlling the amount of morpholine-in-water solution that is introduced to the evacuated treatment chamber. It has been observed that the most morpholine that is relatively permanently, or chemically, absorbed by the books is generally about 0.5 weight percent. While the initial absorption level may reach as high as 3 percent or more if sufficient morpholine is present, that amount of morpholine above about 0.5 percent will evaporate slowly from the book in the days or weeks following treatment. If much more than 1 percent morpholine has been absorbed in the treatment chamber, e.g. about 2–3 percent, then the odor of the evaporating excess morpholine will be quite pronounced in the vicinity of the books for a few weeks. If desired, chemicals which mask the odor of morpholine can be included in the aqueous morpholine treatment solution so as to protect against an odor problem after the treatment. Examples of such odor masking chemicals are Reodorant R-474-Ma a product of Reynaud, Ltd. of Union City, New Jersey, and Odamask

1410 B, a product of S. B. Penick & Co. of New York, New York.

To enhance the completeness of the deacidification, it is generally preferred that the differential between the evacuated treatment chamber pressure and the pressure within the chamber during treatment be maintained as large as possible, while still adhering to a treatment temperature of about 90° to 115° F. One manner of providing a high pressure differential is to evacuate the book-containing chamber prior to treatment to a very low pressure, e.g. about 0.7 mm. Hg or less, most preferably about 0.5, or even about 0.20, mm. Hg or less. The vapor pressure within the chamber during treatment may then preferably range, for example, between about 10 and about 100 mm. Hg.

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

EXAMPLES

In each of the following examples the book which was treated was a 1st Edition of The Pope Speaks, by Jean Guitton, published by Meredith Press. The paper pages of the books had a pH range prior to treatment of about 4.7–5.2.

The cover of the book is made of a bookbinding material that is devoid of pyroxylin. Therefore, in order to simulate a book which is covered with a pyroxylin-containing material, samples of a conventional pyroxylin-containing bookbinding material were appended to each book's cover. Each sample was a rectangular strip measuring about 1 inch by 6 inches of a pyroxylin-impregnated buckram: either Interlacken Art's "buckram sunbeam" or "Group 'F' pyroxylin-impregnated buckram" by Special Fabrics Inc., Saylesville, Rhode Island. To each book there were appended 11 such samples, in each of the following colors: orange, red, black, grey, blue, yellow, purple, brown, green, tan, and salmon.

Treatment of the books and their appended samples of bookbinding materials was effected by placing them in a 89.95 liter volume air-tight chamber, evacuating the chamber to a pressure of about 0.5 mm. Hg, and then introducing about 25 ml. of the aqueous solution of morpholine into the chamber. The desired treatment temperature within the chamber was maintained by circulating heated water through a jacket surrounding the chamber. At the end of the designated treatment time the chamber was vented to the atmosphere and swept with air. The conditions and the results of the treatments were as indicated in the following table:

Ex. No.	Wt. % Morpholine In Solution	Temperature	Time	Resultant pH of Pages After 24 Hours of Aeration	Effect on the Pyroxylin-Containing Bookbinding Materials
32973	70%	100°F.	15 min.	6.2	Discoloration and loss of glossy surface.
4573A	60%	110°F	15 min.	7.6	Discoloration and some dissolution of surface pyroxylin.*
4573	60%	100°F.	15 min.	6.8	Slight discoloration and slight dissolution of surface pyroxylin.
51573	55%	115°F.	15 min.	8.0	Slight dissolution of surface pyroxylin.
4973	50%	120°F.	15 min.	8.0	Dissolution of surface pyroxylin.
4173	50%	100°F.	5 min.	6.3	No damage to physical appearance.
5173	50%	100°F.	10 min.	7.4	No damage to physical appearance.
5373	50%	110°F.	10 min.	7.6	No damage to physical appearance.
5273	50%	100°F.	15 min.	7.6	No damage to physical appearance.
5373A	50%	110°F.	15 min.	7.0	Slight dissolution of surface pyroxylin.
41773	50%	100°F.	5 min.	5.7	No damage to physical appearance.
5273B	30%	100°F.	10 min.	6.9	No damage to physical appearance.
5373B	30%	110°F.	10 min.	6.0	No damage to physical appearance.
41773A	30%	100°F.	15 min.	7.1	No damage to physical appearance.
5373C	30%	110°F.	15 min.	6.0	Slight dissolution of surface pyroxylin.
71673	100%	110°F.	10 min.	8.0	Discoloration and extreme dissolution of surface pyroxylin.
71673A	20%	110°F.	10 min.	4.8	No damage to physical appearance.
71773	50%	110°F.	20 min.	8.3	Slight discoloration and slight dissolution of surface pyroxylin.

* Dissolution of surface pyroxylin was observed as a "slickness" on the surface, the wiping dry of which also served to remove some dye or pigment.

As illustrated in the table, although the pH of the pages of the book is elevated, extensive damage to the pyroxylin-containing cover material often occurs when using morpholine-water atmospheres containing 60 percent or more morpholine (Examples 32973, 4573A, 4573, and 71673), and/or when using treatment temperatures of 120° F. or more (Example 4973), and/or when using treatment times of 20 minutes or more (Example 71773). Conversely, although the cover material escapes damage when using a morpholine-water atmosphere containing only 20 percent or less morpholine (Example 71673A) the pH of the pages so treated is often not apparently elevated. When the conditions of the present invention are employed, however, as in Examples 51573, 4173, 5173, 5373, 5273, 5373A, 41773, 5273B, 5373B, 41773A, and 5373C, the pH of the paper pages is elevated (to an aerated pH of about 5.7 or more) without damage to the pyroxylin-containing cover material.

It has also been found that the wet morpholine impregnation process of the present invention is safer for treating very old books having colored pages or covers than is impregnation with dry morpholine. Some of the pigments and dyes used in colored inks of yesteryear have been found to be susceptible to color change damage from morpholine, whereas the more modern inks

are generally unaffected by dry morpholine vapors. As stated, though, the process of the present invention is generally safe for these old books as well as those of more recent vintage. Also, the process of the present invention has been found to provide a greater degree of deacidification in very old, dried out books than is provided by treatment with dry morpholine vapors.

We claim:

1. A process for treating a book that has paper pages and a pyroxylin-containing cover so as to render the paper pages resistant to the deterioration that is promoted by acidic conditions in paper without effecting substantial damage to the pyroxylin-containing cover, which process comprises impregnating the book for about 5 to 15 minutes with a gaseous atmosphere consisting essentially of about 30 to 55 weight percent morpholine and a balance of water vapor at a temperature of about 90° to 115° F.

2. The process of claim **1** wherein the book is impregnated for about 7 to 12 minutes.

3. The process of claim **1** wherein the gaseous atmosphere consists essentially of about 35 to 50 weight percent morpholine and a balance of water vapor.

4. The process of claim **1** wherein the impregnation is conducted at a temperature of about 95° to 110° F.

5. The process of claim **1** wherein the paper pages prior to treatment have a pH of about 5.0 or lower, as determined by soaking 1 gram of one-eighth inch squares of the paper for 1 hour in 70 ml. of distilled, deionized water at room temperature and then measuring the pH of the resultant aqueous solution.

6. The process of claim **5** wherein the book is impregnated for about 7 to 12 minutes.

7. The process of claim **6** wherein the gaseous atmosphere consists essentially of about 35 to 50 weight percent morpholine and a balance of water vapor.

8. The process of claim **7** wherein the impregnation is conducted at a temperature of about 95° to 110° F.

9. A process for treating a book that has paper pages and a pyroxylin-containing cover so as to render the paper pages resistant to the deterioration that is promoted by acidic conditions in paper without effecting substantial damage to the pyroxylin-containing cover, which process comprises placing the book in an air tight treatment chamber, evacuating the treatment chamber to a pressure of about 0.7 mm. Hg or less, introducing a sufficient amount of a solution of morpholine-in-water containing about 30 to 55 weight percent morpholine into the chamber to provide a pressure within the chamber of about 10 to 100 mm. Hg, maintaining the temperature within the chamber at about 90° to 115° F., and purging the morpholine and water vapor atmosphere out of the chamber after about 5 to 15 minutes of residence time.

10. The process of claim **9** wherein the treatment chamber is evacuated to a pressure of about 0.5 mm. Hg or less prior to introducing the aqueous morpholine solution.

11. The process of claim **9** wherein the treatment chamber is evacuated to a pressure of about 0.20 mm. Hg or less prior to introducing the aqueous morpholine solution.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,837,804 Dated September 24, 1974

Inventor(s) Bernard F. Walker, James E. Kusterer, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Cover page, item 73, after "Assignee:" should read --Research Corporation, New York, N. Y.--.

Signed and sealed this 3rd day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
☆ U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,837,804 Dated September 24, 1974

Inventor(s) Bernard F. Walker, James E. Kusterer, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Cover page, item 73, after "Assignee:" should read --Research Corporation, New York, N. Y.--.

Signed and sealed this 3rd day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
☆ U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334