United States Patent [19]

Kusterer, Jr. et al.

[11] **3,771,958**

[45] **Nov. 13, 1973**

[54] **GASEOUS DIFFUSION PAPER DEACIDIFICATION**

[75] Inventors: **James E. Kusterer, Jr.; Reavis C. Sproull,** both of Richmond, Va.

[73] Assignee: **Research Corporation,** New York, N.Y.

[22] Filed: **Dec. 30, 1971**

[21] Appl. No.: **214,217**

[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, 7, 76; 162/160; 117/154; 252/401

[56] **References Cited**

UNITED STATES PATENTS

3,472,611	10/1969	Langwell	21/58
2,185,954	1/1940	Ryner	21/58 UX
3,135,627	6/1964	Sadler	117/143
3,419,498	12/1968	Palumbo et al.	162/160 X

Primary Examiner—Morris O. Wolk
Assistant Examiner—D. G. Millman
Attorney—John W. Behringer et al.

[57] **ABSTRACT**

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 morpholine.

10 Claims, 2 Drawing Figures

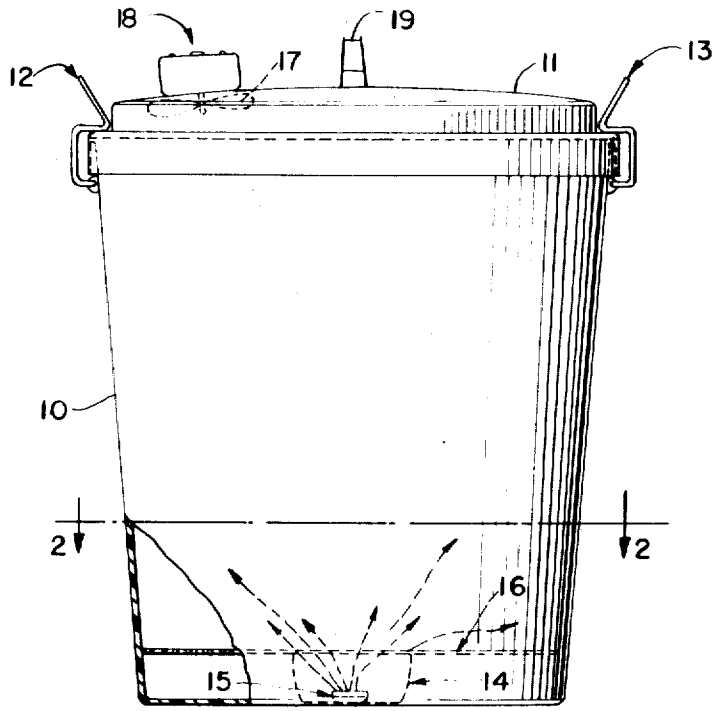


FIG. 1.

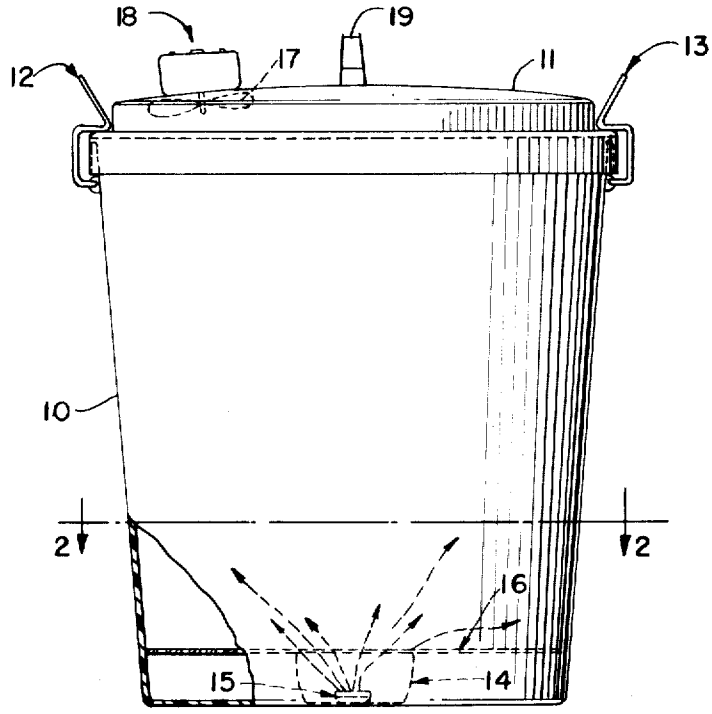
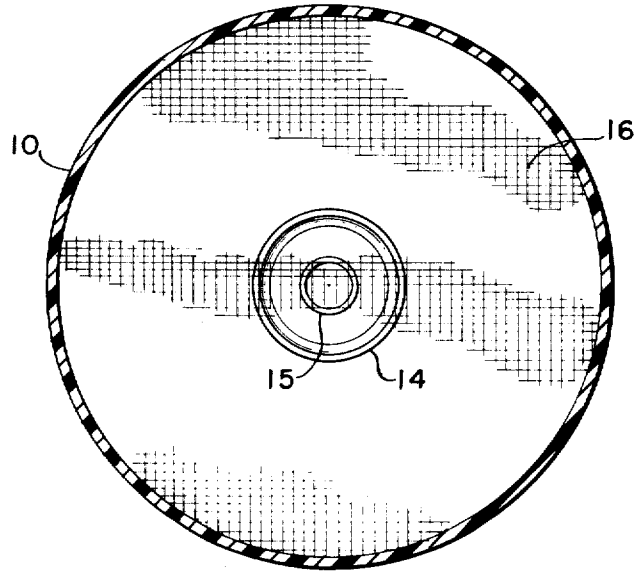


FIG. 2.



GASEOUS DIFFUSION PAPER DEACIDIFICATION

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 morpholine.

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 of the deacidification processes which have heretofore 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 these 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, often 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 strongly toxic chemicals (e.g., cyclohexylamine), thereby requiring relatively elaborate equipment to conduct the treatment safely. There is, then, an urgent need for effective, safe and relatively inexpensive methods of treating paper so as to render it resistant to acid-catalyzed 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.

The invention will be understood from the following description, made with reference to the accompanying drawings. In the drawings:

FIG. 1 is a view, partly broken away, of an apparatus suited for the practice of the process of the invention; and

FIG. 2 is a horizontal section, taken along line 2—2 of FIG. 1.

It has now been discovered that paper which is susceptible to acid-catalyzed deterioration can be effectively, safely, and relatively inexpensively deacidified, and thereby made resistant to such deterioration, if it is impregnated with gaseous morpholine. Moreover, it has been found that such treatment can be effected even with tightly closed books, so well will 7.6, penetrate them, and the resultant deacidification is extremely long lasting, maybe even permanent.

The extent of morpholine impregnation of paper that is to be deacidified by the process of the present invention is preferably 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 7.6, preferably at least about 8.5. 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.

The time period required to complete such an impregnation process will of course vary, depending upon the amount and type of paper being treated, the amount of morpholine employed, the treatment temperature, the pH level desired for the paper, etc. As an example, however, a book having an initial pH of, for instance, about 4.3 can be made to have a pH of 8.3 in as little as 8 hours when immersed in an approximately 100 percent morpholine atmoshpere at room temperature. No harm to the paper has been observed to occur through prolonged treatments, but it is generally unnecessary to continue the treatment for more than about 4 days.

No special treatment temperature is required for the present process; however, preferred operating temperatures are in the range of about −5°C. to 128°C., most especially about 25°C. to 75°C.

The gaseous morpholine used in the present process can, if desired, be in admixture with one or more other gases, such as air, that are non-interfering with the deacidification process. Preferably, though, the morpholine accounts for at least about one-third, and most preferably a major amount, e.g. about 90 to 100 percent, or even 98 to 100 percent, of the volume of the atmosphere surrounding the paper during treatment.

Impregnation of the paper with the gaseous morpholine can be effected by simply contacting the aper with morpholine vapors. The vapors may be under atmospheric, sub-atmosphierc or superatmospheric pressure. At room temperature the pressure exerted by a 100 percent morpholine atmosphere is about 7 to 10 mm. Hg, which is entirely adequate to penetrate the paper.

It may be desirable after treating paper according to the present process to pass air over the paper under subatmospheric pressure so as to permit the escape of any excess morpholine present and thereby lessen the residual morpholine odor of the paper.

It has been observed that the treatment of this invention can discolor and/or render tacky any book covers that contain pyroxylin. Such covers should therefore preferably either be removed or tightly encased in a protective covering such as polyethylene film prior to treatment of the book.

It has also been observed that paper treated according to the present process retains its high pH slightly better, and therefore better maintains its resistance to deterioration, if it is kept in a dry atmosphere. The

more humid the storage atmosphere, the somewhat poorer will be the pH retention. Nevertheless, the present process is useful even if not followed by storage in a dry atmosphere, as evidenced by the fact that even 6 months storage under 100 percent relative humidity at 23°C. will cause only a modest drop in pH, e.g., from about 8.5 to 7.4 or 7.7.

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

EXAMPLE I

Four sets of experiments were run using the apparatus shown in FIG. I of the attached drawings. Referring now to FIG. I, there is shown a rigid, round containment vessel **10** fitted with a lid **11** that is clamped in place during use by clamps **12** and **13**. In the bottom of vessel **10** is an open bowl **14** which contains a much smaller, open dish **15**. Resting on the top of bowl **14** is a horizontal screen **16** which substantially fills the cross-sectional area of vessel **10**. Mounted to the underside of lid **11** is fan blade **17**, driven by motor **18**. Mounted on top of lid **11** is handle **19**. The diameter of vessel **10** is about 15 inches at its base and about 20 inches at its top. The height of the vessel is about 26 inches.

The above apparatus is used in practicing the present process by placing liquid morpholine in dish **15**, then putting screen **16** in place on top of bowl **14**, and then placing the paper to be treated on top of screen **16**. The lid **11** is then clamped into place and fan motor **18** is turned on. The morpholine then vaporizes and mixes with the air in the vessel and impregnates the paper.

In each experiment samples of 100 percent chemical wood paper were treated in the apparatus of FIG. I with gaseous morpholine at room temperature. The paper is composed of 49 percent Puget sulphite pulp, 24 percent bleached soda pulp, and 27 percent Astracel hardwood pulp, is filled with bag clay, and is sized with alumrosin. Control samples of the paper (untreated) were tested for pH, tear resistance, and fold endurance.

The treatment time in the morpholine-containing vessel was shortened with each succeeding set of experiments, as reported hereinafter in Tables I, II and III. After treatment, some of the paper samples were immediately evaluated for pH, fold endurance, and tear resistance, while the remainder were first heat-aged in a dry oven for varying periods at 100°C. The pH levels of the treated samples (reported in Table I) were measured after each aging period, and the fold endurance and tear resistance values (reported in Tables II and III) were obtained after the 12 day aging period. From the fold endurance and tear resistance values were calculated the useful half-lives of the treated and untreated paper at the dry oven accelerated aging temperature, 100°C. These too are reported in Tables II and III.

Fold endurance testing was performed 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 fold endurance (M.D.) and cross directional fold endurance (C.D.) were determined in this manner.

Tear resistance testing was performed with the Elmendorf Tear Tester.

TABLE I

Set	pH before treatment	Length of morpholine treatment, hours	pH after treatment, before aging	pH after treatment and aging at 100° C. for the following number of days— 2 days	4 days	6 days	8 days	10 days	12 days
1	4.3	96	8.4	8.4	8.3	7.9	7.8	7.6	7.5
2	4.3	48	8.6	8.4	8.1	7.7	7.5	6.4	6.0
3	4.3	24	8.7	7.8	7.9	7.2	6.1	6.9	6.6
4	4.3	8	8.6	7.7	6.8	7.0	5.6	5.8	6.0

TABLE II

Set	Average fold endurance before treatment or aging, bends per strip M.D.	C.D.	Length of morpholine treatment, hours	Average fold endurance after treatment, bends per strip: After treatment, before aging M.D.	C.D.	After treatment, after 12 days aging M.D.	C.D.	Half-life (days) at 100° C. M.D.	C.D.
1	397	88	96	347	81	52	36	4.6	10.7
2	397	88	48	360	81	21	25	3	7
3	397	88	24	418	98	24	26	3	6.4
4	397	88	8	352	91	11	17	2.4	4.6
Control	397	88	None	*397	*88	*10	*12	2.3	4

*Aged but not treated with morpholine.

TABLE III

Set	Average tear resistance before treatment or aging, grams tear M.D.	C.D.	Length of morpholine treatment, hours	Average tear resistance after treatment, grams tear: After treatment, before aging M.D.	C.D.	After treatment, after 12 days aging M.D.	C.D.	Half-life (days) at 100° C. M.D.	C.D.
1	52.0	57.2	96	55.2	60.1	41.1	43.8	30.2	30
2	52.0	57.2	48	53.2	62.0	33.7	40.0	20.4	21
3	52.0	57.2	24	53.0	65.0	39.9	48.9	27	27
4	52.0	57.2	8	54.1	59.8	34.9	38.5	18.7	17.3
Control	52.0	57.2	None	*52.0	*57.2	*17.9	*21.4	8.7	9.3

*Aged but not treated with morpholine.

The test data in Table I illustrate quite clearly the long-lasting quality of the deacidification that is effected by the process of the present invention.

The test data in Tables II and III demonstrate that the deacidification treatment of the present invention provides resistance to strength loss and a much longer useful life than that to be expected for the untreated paper. Thus, for example, the paper that had been treated with morpholine for 96 hours (i.e., that of set 1), had a fold endurance half-life at 100°C. of 4.6 days in the machine direction and 10.7 days in the cross direction, whereas the untreated paper had a half-life under those conditions of only 2.3 days M.D. and 4 days C.D. Similarly, the tear resistance half-life at 100°C. of the paper that was treated with morpholine for 96 hours was about 30 hours in both directions, while the untreated paper's half-life was only about 9 hours in both directions.

EXAMPLE II

Four more sets of experiments were run, but using a different apparatus than that depicted in FIG. I of the attached drawings. The essential difference was that the apparatus used for this set of experiments was air-tight and attached to a vacuum pump. In each of the present experiments, then, the impregnation chamber was placed under a partial vacuum, measuring about 30 inches of mercury. Thus, as compared to the experiments of Example I, the morpholine concentration in the gaseous atmosphere around the paper treated in this example was considerably greater, due to the removal of air by the vacuum pump. To prevent morpholine from contacting and possibly harming the pump, a condenser was placed in the line between the treatment chamber and the vacuum pump.

In this apparatus and manner, then, samples of the same type of chemical wood paper used in Example I were treated with gaseous morpholine, and untreated control samples were tested for tear resistance as well as pH.

Again the treatment time was shortened with each succeeding set of experiments, as reported hereinafter in Tables IV, V, and VI. After treatment, some of the paper samples were immediately evaluated for pH, folding endurance, and tear resistance, while the remainder were first heat-aged in a dry oven for varying periods at 100°C. The pH levels of the treated samples (reported in Table IV) were measured after each aging period, and the fold endurance and tear resistance values were obtained after the 12 day aging period. From the folding endurance and tear resistance values there was calculated for each sample the half-lives (both M.D. and C.D.) after the 12 day accelerated aging process. These percentages are reported in Tables V & VI.

TABLE IV

1V**----------	4.3	96	9.1	8.9	8.8	8.7	8.5	8.5	8.5
2V**----------	4.3	48	9.1	8.5	8.8	8.3	8.4	8.5	8.4
3V**----------	4.3	24	8.9	8.5	8.1	8.4	8.4	8.3	8.2
4V**----------	4.3	8	9.0	8.6	8.5	8.3	7.4	7.8	8.0

**V=Treated in vacuum chamber.

TABLE V

	Average fold endurance before treatment or aging, bends per strip		Length of morpholine treatment, hours	Average fold endurance after treatment, bends per strip				Half-life (days) at 100° C.	
				After treatment before aging		After treatment, after 12 days aging			
Set	M.D.	C.D.		M.D.	C.D.	M.D.	C.D.	M.D.	C.D.
1V**----------	397	88	96	136	40	19	16	4.5	10
2V**----------	397	88	48	143	44	20	16	4.7	9
3V**----------	397	88	24	171	49	28	20	5	10.3
4V**----------	397	88	8	154	54	23	20	4.3	8.7
Control----------	397	88	None	*397	*88	*10	*12	2.3	4

*Aged but not treated with morpholine.
**V=Treated in vacuum chamber.

TABLE VI

	Average tear resistance before treatment or aging, grams tear		Length of morpholine treatment, hours	Average tear resistance after treatment, grams tear				Half-life (days) at 100° C.	
				After treatment, before aging		After treatment, after 12 days aging			
Set	M.D.	C.D.		M.D.	C.D.	M.D.	C.D.	M.D.	C.D.
1V**----------	52.0	57.2	96	56.8	64.0	37.9	43.6	23.4	27
2V**----------	52.0	57.2	48	56.0	60.4	41.8	47.2	33.7	35
3V**----------	52.0	57.2	24	53.3	60.0	40.1	47.0	32	34.3
4V**----------	52.0	57.2	8	54.7	62.5	40.8	47.4	25.7	28
Control----------	52.0	57.2	None	*52.0	*57.2	*17.9	*21.4	8.7	9.3

*Aged but not treated with morpholine.
**V=Treated in vaccum chamber.

The test data in Table IV again illustrate quite clearly the long-lasting quality of the deacidification that is effected by the process of the present invention. Also, the values indicate that higher pH values are obtained by using a more concentrated morpholine atmosphere in treating the paper than that used in Example I.

It was also noted, but not reported in Table IV, that a decrease in the pH of the treated paper is generally effected by extensive handling of the paper, as, for example, in testing it for tear resistance. This pH depression is generally slight, however. In the case of the samples reported on in Table IV, for instance, the pH of the paper after aging and testing was usually at least 8.0 and was always at least 7.5.

The test data reported in Tables V and VI again show quite clearly that the morpholine treatment of the present invention enables the paper to withstand much better the accelerated aging process, insofar as the paper's tear resistance and folding endurance properties are concerned, than if the paper were not so treated.

As indicated above, the process of this invention is applicable to any paper that is subject to deterioration due to acidic conditions in the paper. Thus, the paper can be manufactured from, for instance, sisal, jute, flax, wood, cotton, or any combination of the foregoing. Other experiments have been run, for instance, with a paper composed of 50 percent cotton linter and 50 percent chemical wood furnish which had a pH of about 4.7. Impregnation with gaseous morpholine raised that pH to about 8.6, and the paper retained its basicity and physical properties as in the case of the 100 percent chemical wood paper.

We claim:

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 a gaseous atmosphere consisting essentially of morpholine, the said morpholine being present in at least about one-third the volume of the said gaseous atmosphere.

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

3. The process of claim 1 wherein the morpholine accounts for about 90 to 100 volume percent of the atmosphere surrounding the paper during the impregnation.

4. The process of claim 3 wherein the paper is in the form of a book.

5. The process of claim 1 wherein the amount of morpholine 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 7.6, as determined by soaking one gram of one-eighth inch squares of the paper for one 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 paper is in the form of a book.

7. The process of claim 5 wherein the paper prior to treatment has a pH of about 5.0 or lower.

8. The process of claim 7 wherein the paper is in the form of a book.

9. 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 impregnating the book with a gaseous atmosphere consisting essentially of morpholine, the said morpholine being present in at least about one-third the volume of said gaseous atmosphere, at about 25° to 75°C. in an amount sufficient to raise the pH of the paper to at least about 8.5, said pH values being as determined by soaking one gram of one-eighth inch squares of the paper for one hour in 70 ml. of distilled, deionized water at room temperature and then measuring the pH of the resultant aqueous solution.

10. The process of claim 9 wherein the morpholine accounts for about 90 to 100 volume percent of the atmosphere surrounding the book during the impregnation.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,771,958 Dated November 13, 1973

Inventor(s) James E. Kusterer, Jr., and Reavis C. Sproull

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

Column 2, line 2, "7.6," should read --the morpholine--:
line 46, "aper" should read --paper--;
line 48, "sub-atmosphierc" should read --sub-atmospheric--.

Columns 3 and 4, Table III, fifth column, "53.0" should read --54.0--.

Columns 5 and 6, Table IV should have column headings so as to read as follows:

Table IV

Set	pH Before Treatment	Length of Morpholine Treatment	pH After Treatment, Before Aging	pH After Treatment and Aging @ 100° C. for the following number of days					
				2 days	4 days	6 days	8 days	10 days	12 days
1 V**	4.3	96 hours	9.1	8.9	8.8	8.7	8.5	8.5	8.5
2 V**	4.3	48 hours	9.1	8.5	8.8	8.3	8.4	8.5	8.4
3 V**	4.3	24 hours	8.9	8.5	8.1	8.4	8.4	8.3	8.2
4 V**	4.3	8 hours	9.0	8.6	8.5	8.3	7.4	7.8	8.0

**V = Treated in vacuum chamber

Signed and sealed this 2nd day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,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. 3,771,958 Dated November 13, 1973

Inventor(s) James E. Kusterer, Jr., and Reavis C. Sproull

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

Column 2, line 2, "7.6," should read --the morpholine--:
line 46, "aper" should read --paper--;
line 48, "sub-atmosphierc" should read --sub-atmospheric--.

Columns 3 and 4, Table III, fifth column, "53.0" should read --54.0--.

Columns 5 and 6, Table IV should have column headings so as to read as follows:

Table IV

Set	pH Before Treatment	Length of Morpholine Treatment	pH After Treatment, Before Aging	pH After Treatment and Aging @ 100° C. for the following number of days					
				2 days	4 days	6 days	8 days	10 days	12 days
1 V**	4.3	96 hours	9.1	8.9	8.8	8.7	8.5	8.5	8.5
2 V**	4.3	48 hours	9.1	8.5	8.8	8.3	8.4	8.5	8.4
3 V**	4.3	24 hours	8.9	8.5	8.1	8.4	8.4	8.3	8.2
4 V**	4.3	8 hours	9.0	8.6	8.5	8.3	7.4	7.8	8.0

**V = Treated in vacuum chamber

Signed and sealed this 2nd day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,771,958 Dated November 13, 1973

Inventor(s) James E. Kusterer, Jr., and Reavis C. Sproull

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

Column 2, line 2, "7.6," should read --the morpholine--:
line 46, "aper" should read --paper--;
line 48, "sub-atmosphierc" should read --sub-atmospheric--.

Columns 3 and 4, Table III, fifth column, "53.0" should read --54.0--.

Columns 5 and 6, Table IV should have column headings so as to read as follows:

Table IV

Set	pH Before Treatment	Length of Morpholine Treatment	pH After Treatment, Before Aging	pH After Treatment and Aging @ 100° C. for the following number of days					
				2 days	4 days	6 days	8 days	10 days	12 days
1 V**	4.3	96 hours	9.1	8.9	8.8	8.7	8.5	8.5	8.5
2 V**	4.3	48 hours	9.1	8.5	8.8	8.3	8.4	8.5	8.4
3 V**	4.3	24 hours	8.9	8.5	8.1	8.4	8.4	8.3	8.2
4 V**	4.3	8 hours	9.0	8.6	8.5	8.3	7.4	7.8	8.0

**V = Treated in vacuum chamber

Signed and sealed this 2nd day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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