Vapor Phase Deacidification: A New Preservation Method

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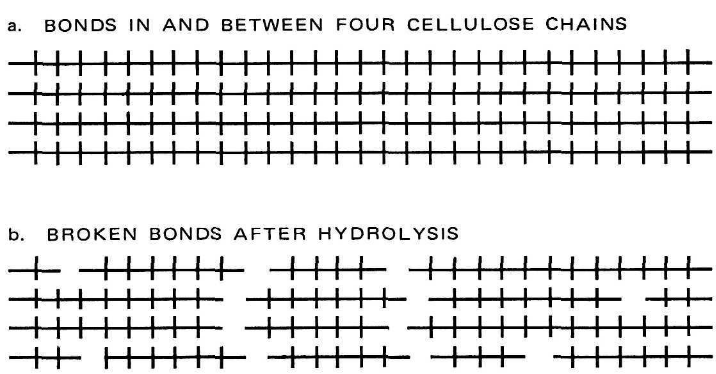
IN DISCUSSING the Vapor Phase Deacidification (VPD) process, we are exploring a relatively new development in the effort to protect and preserve manuscript material through deacidification. As many researchers have noted, "A major cause of paper deterioration over prolonged periods is identified as the acid-catalyzed hydrolysis of the cellulose in paper fibers."[1] Acid in paper, regardless of its source, destroys cellulose fibers by accelerating a chemical reaction that ruptures the long chains of sugar residues. As the hydrolysis continues and cellulose fibers are broken, the paper becomes weaker and more brittle until it is dangerously impaired. "The physical properties of

EFFECT OF ACID HYDROLYSIS ON CELLULOSE CHAINS[2]



a paper change relatively little during the greater part of the cellulose degradation . . ." until it reaches a critical range below which "the paper rapidly loses strength and becomes embrittled if the degradation continues."[3]

The author, University Archivist and Curator of Manuscripts, read this paper on Sept. 30, 1968, at the annual meeting of the Society of American Archivists in Ottawa, Canada.

[1] Richard D. Smith, "Paper Deacidification: a Preliminary Report," in *Library Quarterly,* 36:273 (Oct. 1966).
[2] Figure from *ibid.,* p. 276.
[3] *Ibid.*

So far the most effective deacidification process developed by the Barrow Laboratory uses a wet process to neutralize acids in paper. In spite of the demonstrated effectiveness of this wet process it does have severe limitations in treating the voluminous records in the modern manuscript repository.

In the effort to simplify the deacidification process, to eliminate the difficulty associated with the use of alkaline solutions in aqueous or non-aqueous solvents and to make the deacidification process easily usable by librarians and archivists, preliminary experiments were conducted in England to exploit the obvious convenience of gaseous processes of de-acidification. Early tests eliminated the most common volatile alkali, ammonia, because it could not keep the treated document alkaline when exposed to air. The Barrow report no. 3, *Spray Deacidification,* published in 1964, evaluated (p. 14) the effect of gaseous deacidification. The Barrow Laboratory eliminated the use of ammonia when test materials that had been neutralized by exposure to ammonia fumes returned to what was deemed an undesirable acid condition within 24 hours.

Table 1.
EFFECT OF GASEOUS DEACIDIFICATION[4]

The pH of 7 book papers suspended in ammonia fumes for 18 hours and after suspending them in the laboratory atmosphere (72°–78° F.) for the following length of time:

Sample Number	Year Made	Untreated	3 hrs.	3 days	6 days	12 days	18 days	24 days	54 days
1	1958	4.8	6.9	5.8	5.5	5.4	5.4	5.4	5.3
2	"	4.6	6.9	5.8	5.5	5.5	5.4	5.4	5.1
5	"	4.8	6.7	5.8	5.5	5.5	5.5	5.5	5.0
1B	1908	4.3	7.1	5.7	5.4	5.4	5.4	5.4	—
102B	1914	4.1	7.3	5.9	5.5	5.5	5.4	5.5	—
103B	1925	4.2	7.3	6.1	5.8	5.6	5.8	5.5	—
303B	1931	4.2	6.8	5.5	5.2	5.1	5.0	5.0	—
Three of the above papers were suspended in an oven maintained at 122° F.									
1	1958	4.8	6.8	5.7	5.4	5.2	5.0	5.0	—
2	"	4.6	6.8	5.8	5.4	5.2	5.0	5.0	—
5	"	4.8	6.7	5.8	5.5	5.1	5.0	5.0	—

Within 54 days the treated materials had reverted to nearly the same pH that they had when originally tested. "Other related organic alkaline compounds were considered but abandoned because possible improvements over the use of ammonia were believed to be small."[5]

[4] "Table 2" in William J. Barrow, *Permanence/Durability of the Book—III: Spray Deacidification* (Richmond, Va., 1964).
[5] Barrow, *Spray Deacidification,* p. 14.

In both cases ammonia was dismissed from consideration because of its inability to insure that treated materials would remain alkaline when exposed to air. The British investigations, however, directed by W. H. Langwell, began studying the amines, which are organic derivations of ammonia but more alkaline than ammonia. After examining a large number of amines the chemical cyclohexylamine carbonate (CHC) was investigated in depth when it showed a great deal of promise. The chemical CHC was then utilized by Langwell in his gaseous deacidification process, which is commonly called Vapor Phase Deacidification, or VPD, for short.

The VPD process as developed by Langwell is designed to offer archivists and manuscript curators a simple, nontechnical method of treating manuscript material to a gaseous alkali compound for the purpose of neutralizing the sulfuric acid commonly found in paper.

CHC is available from the U.S. distributor, Process Materials Corp., in two forms. One, the CHC-impregnated paper, can be used in loose papers or with bound papers and books without removing the binding. The CHC-impregnated sheet should be interleaved with the papers at approximately 25- to 50-page intervals depending on the porosity of the paper involved. CHC-impregnated paper can also be used with boxed manuscripts. In either case the sheets should be slightly larger than the materials to be treated. The documents should then be placed in an airtight container, such as a tightly closed plastic bag. The deacidification process using the sheets should normally take about 2 weeks, but a pH determination should be made before the CHC paper is removed.

A second and more economical way to treat boxed manuscript material is through the use of the Vapor Phase Deacidification sachets. The deacidification sachets, distributed in 10-gram high-porosity sachets, are meant to be placed under the boxed manuscripts and then placed in an airtight container. Heavy plastic bags can be used, or special aluminum foil lined bags are available from the U.S. distributor for this purpose. Langwell estimates that one 10-gram sachet will treat approximately two pounds of paper. Since the contents of the typical archival box weigh about 6 to 8 pounds, each box would require probably 3 to 4 VPD sachets to treat the contents safely. Normally 6 to 8 weeks is required for the process to be completed. Because there is practically no residue left after the sachets are exhausted, there is no need to take the time or effort to remove them.

At the end of each of the two deacidification processes described, a pH determination should be made to check the effectiveness of the treatment. This can be accomplished through two methods. A test paper with a known pH that is equal to the lowest pH of the papers to be treated can be inserted into the manuscripts before treatment by VPD. After the CHC treatment has been concluded a pH test can be run, using the cold extraction on the test paper and a pH meter. An easier pH determination can be made by colorimetry, using a Harlco "Wide Neutral Range Indicator," which permits pH readings to the half units from 4.0 to 10.0.

Process Materials Corp. suggests that two precautions should be taken when using CHC:

1. The Vapor Phase Deacidification papers and sachets are composed of a volatile alkali and will vaporize when in contact with air. All papers and sachets should be stored in airtight containers to avoid slow wastage.

2. Since cyclohexylamine is a strong alkali it may cause irritations of the respiratory system as well as skin irritations. Prolonged breathing of these vapors should be avoided, and the use of rubber gloves in handling the chemical is recommended.

In judging the effectiveness of the Vapor Phase Deacidification process both its initial deacidification effect and its long term deacidification effect should be tested and evaluated.

The initial deacidification effect can be evaluated by recording the difference between the original pH and the pH or hydrogen-ion concentration of the documents after they have been through the deacidification process. The pH of an extract is a measure of the hydrogen-ion concentration of the extracted acids expressed in logarithms. The Barrow report no. 2, *Test Data of Naturally Aged Papers,* contains a table indicating pH values and the amount of acidity that they represent and relating this to an arithmetical equivalent so that the average lay person may have a better understanding of the amount of acidity a pH value represents. pH measures the concentration of free hydrogen ions, the unique characteristic of acids in solution; pH from 7 through 1 indicates progressively greater levels of acidity.

Table 2.
pH VALUES AND ACTIVE ACIDITY AND ALKALINITY[6]

pH	*Active Acidity*	*pH*	*Active Alkalinity*
4.0	1000	7.0	1
4.2	630	7.2	1.6
4.4	400	7.4	2.5
4.6	250	7.6	4
4.8	160	7.8	6
5.0	100	8.0	10
5.2	63	8.2	16
5.4	40	8.4	25
5.6	25	8.6	40
5.8	16	8.8	63
6.0	10	9.0	100
6.2	6	9.2	160
6.4	4	9.4	250
6.6	2.5	9.6	400
6.8	1.6	9.8	630
7.0	1	10.0	1000

[6] William J. Barrow, *Permanance/Durability of the Book—II: Test Data of Naturally Aged Papers,* p. 18 (Richmond, Va., 1964).

As can be seen from the table, a decrease in acidity from pH 4 to pH 5 really represents a 10-fold decrease; a decrease to pH 6 represents a 100-fold decrease in hydrogen-ion concentration.

The experimental data available on the Vapor Phase Deacidification process are somewhat limited so far. Capt. G. M. Cunha of the Boston Athenæum probably has undertaken the most detailed testing program of VPD in the United States. In the October 1967 *American Archivist,* Captain Cunha published the first results of his initial test of Vapor Phase Deacidification.

Table 3.
RESULTS OF CUNHA'S FIRST TEST[7]

Results of evaluation of VPD impregnated paper for book deacidification. Book* interleaved at pages 12, 150, 250, and 350 and put aside for 120 days.

Page	*pH*	*Page*	*pH*	*Page*	*pH*
1	5.0	225	5.5	475	4.0
12	5.0	250	6.0	500	4.5
25	5.0	275	5.5	525	4.5
50	5.5	300	5.0	550	4.0
75	5.5	325	5.5	575	4.0
100	5.0	350	6.0	600	4.0
125	5.5	375	5.5	625	4.5
150	6.0	400	4.0	650	4.0
175	5.5	425	5.5	675	4.0
200	5.0	450	4.5	700	4.0

* Washington Irving, *Life of Washington* (Putnam & Sons, New York, 1870). 715 pages of unfoxed, unstained, but brittle rag paper. Probably alum-rosin sized. pH before testing, 4.0.

In this test Cunha inserted CHC-impregnated sheets at pages 12, 150, 250, and 350 of the book, *Life of Washington,* by Washington Irving, published in 1870. The original pH of the book before treating with CHC was 4.0. As the results in this initial test show, the CHC-impregnated paper was successful in effecting a reduction in acidity of the treated pages ranging from a 10-fold to a 100-fold decrease. The effects of the CHC-impregnated paper drops off rather dramatically within 50 pages of the last treated sheet, which was inserted at page 350.

A short while later, in January 1968, Captain Cunha published the results of some more extensive trials of the VPD process. In this test CHC-impregnated paper was interleaved in the text to be treated at 25-page intervals, in contrast to the 100-page intervals used in his first test of VPD. The text used for the test was *King Noanett,* by F. J. Stimson, printed in 1896. The pH of all the pages was 4.0 before the test.

[7] Table from George M. Cunha, "Technical Notes," in *American Archivist,* 30:615 (Oct. 1967).

Table 4.
CUNHA'S SECOND TEST RESULTS[8]

Page	*pH*	*Page*	*pH*
1	7.0	Pages 162 on were not interleaved:	
13	6.5	162	6.0
24	7.0	175	6.0
38	6.5	188	6.0
50	7.0	200	5.0
62	6.5	225	5.0
75	7.5	250	5.0
88	7.5	275	4.5
100	7.0	300	4.0
112	7.0	325	4.0
125	7.5		
138	6.5		
150	7.5		

After 24 hours in a Boekel laboratory oven at 100° C., the pH of the interleaved pages (*i.e.*, 1–150) was reduced to 5.0 and the pH of the noninterleaved pages (*i.e.*, 160–325) was reduced to 4.0. All of the paper became dark and more brittle.

The test results were taken 15 days after the text was interleaved with VPD paper.

As the results show, the use of CHC-impregnated paper substantially decreased the acidity of the paper and, in fact, turned some of the test papers slightly alkaline, with pH values of 7.5 on pages 75, 88, 125, and 150. All the treated pages were well above the pH value of 6.2, which the Barrow Laboratory has found is a critical point in paper preservation. Papers above the pH 6.2 were found generally to have a slow rate of deterioration, while paper below pH 6.1 deteriorated more rapidly.[9] The last half of the text was not interleaved and the test results show a lessening of the effect of the CHC-impregnated paper the farther the pages were from the last CHC-treated sheet.

The next test, which was similar in technique to this one, had one modification: the text treated was wrapped in a plastic bag to entrap the CHC vapors during the testing program. This text was *Cities of Northern and Central Italy*, by A. J. C. Hare, printed in 1876. Before the test the pH of all the pages was 4.5.

As the results show, a rather dramatic change took place in which pages that were decidedly acidic before the test became mildly alkaline after the treatment; pH values ranged from 7.5 to 8.0. As in the first test, there is general lessening effect of CHC in the untreated pages the farther removed they are from page 200, the last page at which a CHC-impregnated sheet was interleaved.

[8] Table from George M Cunha, "Technical Notes," in *American Archivist*, 31:85 (Jan. 1968).

[9] William J. Barrow, *Permanence/Durability of the Book: a Two-Year Research Program*, p. 12 (Richmond, Va., 1963).

Table 5.
CUNHA'S THIRD TEST RESULTS[10]

Page	*pH*	*Page*	*pH*
1	8.0	Pages 213 on were not interleaved:	
12	7.5	213	8.0
25	8.0	225	7.5
38	8.0	238	6.5
50	8.0	250	6.5
62	8.0	262	6.5
75	8.0	275	5.5
88	8.0	288	5.0
100	8.0	300	5.0
113	8.0	313	5.0
125	8.0	325	5.0
138	8.0	350	4.5
150	8.0	375	4.5
162	8.0		
175	8.0		
188	8.0		
200	8.0		

After 24 hours in a Boekel laboratory oven at 100° C., the pH of the pages that had been interleaved averaged to 5.0. The pH of the noninterleaved pages had dropped to 4.0 or less. All of the pages became dark and more brittle.

Cunha also conducted tests on the effect of CHC-impregnated sheets on boxed papers. Two sachets were placed in a manuscript box containing 32 ounces of 19th-century letters on rag paper. The original pH of the letters was between 4.5 and 5.0. At the conclusion of the test, 6 weeks later, the pH of the letters had risen to 7.0. In another test four sheets of CHC-impregnated paper was interleaved for 14 days with 32 ounces of 19th-century manuscripts and broadsides in a manuscript box. The original pH of the paper, which varied between 4.5 and 5.0, was raised to 7.0 with some as high as 8.0 at the end of the 2-week test period.

Our own tests, although incomplete at this time, seem to confirm that CHC will neutralize the acids in paper at the time of treatment. Langwell has stated that his own tests of VPD process have consistently shown that the use of CHC-impregnated sheets and CHC sachets can substantially reduce acidity in books and manuscripts. He has written that tests in Caracas, Venezuela, confirm the "surprisingly" good results obtained by Cunha. He also states that a large number of institutions are currently testing VPD, with the most extensive tests being undertaken by the National Coal Board of Great Britain. In his own words, "So far as these tests have gone, the results have been satisfactory and promise well for future larger scale tests."[11]

[10] Table from George M. Cunha, "Technical Notes," in *American Archivist,* 31:86 (Jan. 1968).
[11] W. H. Langwell to Paul McCarthy, Sept. 5, 1968.

In summary, based on the results and experimental data available so far, it can be said that the use of CHC-impregnated sheets and CHC sachets in the VPD process has been very effective in initially reducing the acidity in books and manuscripts at the time of treatment.

This original reduction of the level of acidity in paper, however, is only half of a successful deacidification program. The second half of the problem is the maintenance of the alkalinity or reduced acidity in paper over a long period of time. The ability of a deacidification process to maintain this reduced level of acidity can be checked during the document's natural aging process or by checking the document during an accelerated heat aging process. The American use of a deacidification process has been too short lived to yield any results on the effectiveness of VPD during the natural aging process. Langwell maintains that books he had treated with CHC 7 years ago have remained neutral. He adds, however, that since CHC leaves no reserve of base in the paper, the paper, once treated, should be stored away from a polluted atmosphere. This, he states, is owing to the fact that a neutral paper absorbs sulfur dioxide more quickly than an acid paper.

There is more experimental data on the long term effectiveness of Vapor Phase Deacidification through the use of the accelerated aging process. The accelerated aging test takes advantage of the fact that, in general, chemical activity proceeds faster at elevated temperatures than at lower temperatures. A number of scientific studies have explored the problem of accelerated aging vs. natural aging, and it had been concluded that paper stability can be predicted with some accuracy by using accelerated aging tests under specified conditions. Barrow and a number of laboratories state that the subjection of a paper sample to an atmosphere of 100° C. for 3 days gives a similar amount of loss in strength to what naturally occurs if the sample were stored for a period of 22–28 years at 20–25° C. (68–77° F.). Both Langwell and Cunha have used the technique of accelerated aging to evaluate the long term effect of CHC in the Vapor Phase Deacidification process. Each is using different conditions, however, to accelerate the aging. This probably explains why they get conflicting results regarding the long term effectiveness of the VPD process.

Langwell states that he has subjected deacidified paper samples to accelerated aging tests in temperatures of 150° C. (300° F.) and at a temperature of 40° C. (104° F.), 100 percent r.h., without noting any increases in acidity.

In the test undertaken by Captain Cunha the results were somewhat different. Cunha used test conditions similar, if not identical, to those recommended by the Barrow Laboratory reports except that the time period was shortened. The results of his second test reveal that the initial pH of the page—4.0—was raised by CHC treatment to between 6.5 to 7.5. When the CHC-treated pages were subjected to an accelerated aging test for 24 hours at 100° C. in a laboratory oven, however, the pH of the treated pages was reduced to 5.0.

The results of Captain Cunha's third published test are quite similar. The pages of Hare's *Cities of Northern and Central Italy* had a tested pH of 4.5 before treatment. After exposure to CHC-impregnated sheets for 15 days the acidity dropped dramatically as the pH of the treated pages rose to between 7.5 and 8.0. Again, however, after 24 hours in a laboratory oven at 100° C. the pH of the treated pages was reduced to 5.0. The boxed manuscript material that Cunha had treated had an original pH of between 4.5 and 5.0 that was raised to 7.0 through exposure to CHC vapors. As had happened in the other two tests the pH of the material was reduced to 5.0 when treated at 100° C. for 25 hours.

This reduction of the pH of CHC-treated material from an alkaline or near alkaline condition to an acidic condition after accelerated aging is in sharp contrast to the effect of heat aging upon documents treated by a spray solution of concentrated magnesium bicarbonate with 25 percent ethyl alcohol as developed by the Barrow Laboratory. The Barrow report no. 3, *Spray Deacidification,* makes data available concerning the effect of heat aging on the laboratory's spray deacidification process. In his table (reproduced below), sample no. 41, the control material had a pH of 7.0. After 6 days of accelerated aging at 100° C. ±2° the pH had dropped 4/10 of a unit to 6.6. After 24 days—the equivalent of approximately 156 years of natural aging—the pH had dropped another 1/10 of a unit to 6.5. Sample no. 42 had a treated pH of 8.7, which declined to 8.6 after 6 days of aging and then declined to 8.4 after 24 days of accelerated aging. Thus the rather significant decline in pH during accelerated aging for samples treated with CHC is in sharp contrast with the rather minor decline in pH of the Barrow spray method during similar accelerated aging.

Table 6.
EFFECT OF HEAT AGING[12]

The pH of the sprayed text book-papers before and after heat-aging at 100° C. ±2° for the following number of days.

Sample No.	*Control*	*6 days*	*12 days*	*18 days*	*24 days*
1	6.2	6.1	6.1	5.9	6.0
6	6.1	5.9	6.0	5.9	5.9
15	7.2	6.9	6.8	6.8	6.8
17	7.0	6.8	6.9	6.5	6.7
40	6.7	6.6	6.2	6.1	6.1
41	7.0	6.6	6.7	6.6	6.5
42	8.7	8.6	8.4	8.4	8.4

[12] "Table 10" in Barrow, *Spray Deacidification.*

This significant difference in the response of CHC-treated paper as contrasted with the response of materials sprayed or immersed in magnesium bicarbonate would lead one to believe that the difference in response might be owing to one of two factors. The difference, as measured by pH, might be because of the different techniques used by the two methods to arrive at a pH value of their respective treated papers. Barrow used the cold extraction method with a Beckman pH meter. Cunha made his tests by colorimetry using a pH sensitive dye. Langwell maintains that under normal conditions of use, in paper in equilibrium with the carbon dioxide of the normal atmosphere, a pH of 5.0 should be considered neutral when testing for pH using standardized acid/base indicator dyes. Though the use of different methods for obtaining pH values from treated papers may produce different results, the data available on the long term effectiveness of CHC in the VPD process seem to be in conflict. Papers sprayed or immersed in magnesium bicarbonate have maintained the approximate pH they had after treatment even when subjected to lengthy accelerated aging tests. Cunha, however, noted a significant increase in acidity of CHC-treated materials when they were subjected to similar accelerated aging tests. The same method was employed by Cunha to measure pH before and after CHC treatment as well as after accelerated aging. The second possible factor and probably the more significant is the volatile nature of CHC. The VPD process depends on this nature of CHC to vaporize and neutralize the acid already formed in the paper. CHC, however, does not affect the latent acids in the paper. Gradually, when exposed to the general atmosphere, the excess CHC vaporizes off the treated materials. The sulfite in the papers gradually oxidizes to sulfuric acid in the presence of water and air. The paper should slowly increase in acidity since the CHC leaves no buffer in the paper to neutralize the sulfuric acid as it is formed.

In summary, although it has been demonstrated that CHC in treated sheets or sachets will effectively decrease acidity in paper initially, there must be serious concern for its long term effectiveness. The difficulty in evaluating the aging tests is due in part to the different conditions prevailing during these aging tests. Further tests would probably be informative if CHC treated papers were compared with papers treated with solutions, such as magnesium bicarbonate, that have already been demonstrated as being effective. Future tests of CHC could employ similar test methods and similar conditions so that these results would be easily comparable to the test data already available on spray and wet process deacidification.