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Richard D. Smith

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The laboratory portion of this investigation was conducted at the Chicago Paper Testing Laboratory from October, 1967, to January, 1968. The final report on this investigation, dated June 24, 1969, was completely revised and corrected during the preparation of this report.

This revised report was accepted by the State Board of Registration for Professional Engineers and Surveyors on March 23, 1971, as the engineering report which fulfilled the final requirements for my registration as a Professional Engineer in the State of Ohio.

CHAPTER 1

Introduction

The purpose of this investigation was to establish the condition of paper in identical copies of books, published between 1899 and 1964, selected from the Samuel Appleton-Carnegie Library of the Lawrence University in Appleton, Wisconsin, The Newberry Library in Chicago, Illinois, and The Research Libraries of The New York Public Library, New York. This investigation grew out of a larger study* designed to determine the condition of paper in a sample of books drawn from the general collections of The Newberry Library. In this larger study, approximately fifty per cent of the contact pH values fell below a pH** of 4.0 for the first test group of Newberry Library books. The general objectives of this smaller investigation were (1) to confirm the extraordinarily acidic contact pH values found for the first lot of Newberry Library books tested in the original study, and (2) to determine whether this highly acidic condition had accelerated the rate at which these books were deteriorating.

The potential significance of this acidity is illustrated by Figure 1 which compares the pH values of the 25 Newberry Library books with the pH values determined by Barrow[3,8] for the paper in books discarded from libraries located in the vicinity of Richmond, Virginia. Figure 1 uses line-bar graphs to compare the number of pH values within certain pH ranges against the number of hydrogen ions present at the pH mid-point values of these ranges.

The pH values along the base line below the bars of Figures 1a–1f are positioned in the middle of the distance along the base line these pH values represent. The relative numbers of hydrogen ions that occur from a pH

* The objectives of this larger study were to estimate the current condition of paper in the general book collections of The Newberry Library and the cost of a conservation program for the Library. Three hundred and ninety books were selected by a statistical method and tested at the Chicago Paper Testing Laboratory. The findings on pH were in accord with those reported in this article. They will be reported in a future publication.

** pH is a logarithmic expression of the degree of acidity or alkalinity and it is derived from the number of hydrogen ions present. pH values range from 0 to 14. A pH value of 7 is neutral; lower values indicate acidity and higher ones alkalinity.

value of 3 to a pH value of 7 are indicated by the factors along the lowest base line.*

Thus, Figure 1 is based upon the actual number of hydrogen ions present at the different pH values. Figure 1 illustrates the importance of this study because the probable rate of paper deterioration in libraries is largely determined by the number of hydrogen ions that are available to catalyze the hydrolysis of cellulose in paper fibers.

Figure 1a presents the frequency of the one minute extraction pH values in the 25 Newberry Library books listed in Table 8 of this study. Figures 1b, 1c, 1d, 1e, and 1f present the frequency of five sets of cold water extraction[30] pH values reported by Barrow[3] and Church.[8] A comparison of Figure 1a with Figures 1b, 1c, 1d, 1e, and 1f indicates that *the average Newberry Library book probably contains about ten times more hydrogen ions than the average book from libraries located in the Richmond, Virginia, area.* The comparison implies that the hydrolysis of cellulose in The Newberry Library collection may be proceeding about ten times faster than it is in the collections studied by Barrow.

Two possibilities may explain these differences in pH value. The first possibility is that the contact pH procedure used in this investigation gives pH values that are not directly comparable with the pH values obtained by the Technical Association of the Pulp and Paper Association (TAPPI) cold extraction procedure[30] followed by Barrow. The second possibility is that one of the investigations studied a sample of books that suggests an erroneous picture of the acidity of paper in research library collections located in major urban areas. The article *»Paper Impermanence as a Consequence of pH and Storage Conditions«*[24] provides background on this second possibility. In an attempt to test the first possibility, the testing method was checked experimentally and verified for the exploratory purposes of this study. The low contact pH values for the paper of the initial lot of books were determined to be acceptable estimates of the TAPPI cold extraction procedure pH values. However, no explanation was obtained for these unexpectedly low pH values because the destructive nature of the TAPPI cold water extraction procedure necessitated the use of books with an unknown history that had been discarded from The Newberry Library.

* These factors were obtained by dividing the number of hydrogen ions present in a liter of water at the various pH values and 25° C. by the number of hydrogen ions (3.35×10^{18}) in a liter of water at a pH of 7 and 25° C. and moving the decimal point two places to the left.

The purpose of this study, therefore, was to expand this preliminary work on pH and investigate the second possibility by comparing the condition of the paper in identical copies of books with established histories. The Newberry Library made arrangements with the Lawrence University Library to borrow their duplicate copies of the titles tested in the larger Newberry Library study. The Lawrence University Library, Appleton, Wisconsin, was selected because it is located in a cooler and less polluted area than The Newberry Library is, just north of downtown Chicago. The higher contact pH values for the paper in the Lawrence University Library books implied that the less acidic paper in the Lawrence books would be more durable than the more acidic paper in the books of The Newberry Library. The Research Libraries of The New York Public Library were asked to send their duplicate copies to match the copies already tested from The Newberry and Lawrence University Libraries. This was done to see how books from a heavily used collection in a severely polluted area compare with the books from Chicago and Appleton. Twenty-one volumes were supplied by the Research Libraries.

The stepwise expansion of this investigation did affect the laboratory work. Some sampling and certain tests were performed on duplicate copies at different times and under slightly different conditions of humidity and temperature. The variations from specified procedures are noted in the following section, *2. Experimental Procedures and Laboratory Results.* However, these variations are considered unlikely to change the broad relationship between the condition of paper in the books of these libraries as based upon measurements of basis weight, contact pH, sonic modulus of elasticity, folding endurance, groundwood fiber content, and paper thickness.

The findings of this study suggest that, if present day storage practices are continued, it is very optimistic to believe that libraries, in the year 2000, will be able to circulate very many of the books published between 1900 and 1960. The findings also suggest that the makeup of the original paper, the location of the library, and its storage practices are more important factors than use by patrons is in determining the useful life of research library collections.

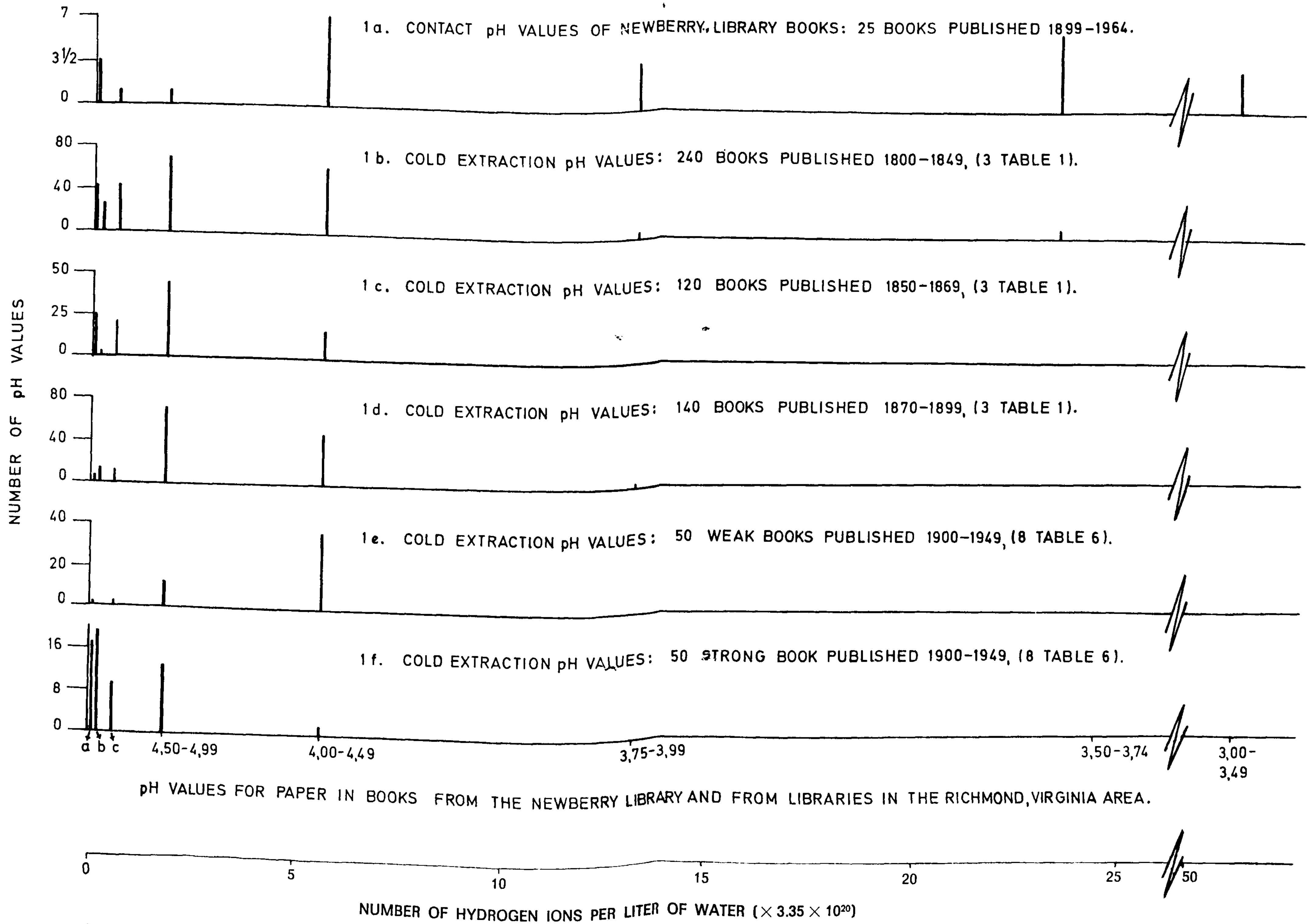


FIG. 1. A comparison of pH values for paper in books from The Newberry Library and from Libraries in the Richmond, Virginia, area. a=pH of 6.00 or higher; b=pH of 5.50–5.59; c=pH of 5.00–5.49.

CHAPTER 2

Experimental Procedures and Laboratory Results

2.1 Introduction

The primary objectives of the experimental procedures were to validate the data collection methods of The Newberry Library study and to provide an estimate of the relative condition of paper today in the collections of the three participating libraries. The secondary objectives were to contribute towards an improvement in the methods for estimating the condition of library collections and for extending the useful life of such holdings.

This investigation differs from most previous examinations of library materials in its use of non-destructive test methods. Earlier investigators typically studied the condition of paper in library discards or in second-hand books. The books used in this study came from and were returned to active collections. This emphasis on real life conditions made the use of non-destructive test methods essential.

This study was not oriented towards fundamental research, but rather towards obtaining data which can be used to estimate the magnitude of difference between papers. This investigation was both an exploratory study for testing methodology and a study of the differences between the condition of identical books in three libraries. These aims made it possible to use less costly, non-destructive testing procedures.

2.2 Sample Selection

The 25 titles examined in this study came from a sample of 527 books drawn by a cluster sampling plan from the general collections of The Newberry Library. The details of how these books (and the sub-sample of 390 books actually tested) were selected may be obtained from the author and will be presented in a future report.

The selection of the 25 titles considered in this study began by comparing the 390 Newberry Library catalog entries with the entries in the Lawrence University Library catalog. 40 books represented in both catalogs were

TABLE 1: Bibliographic data

Title no.	Year published	Author	Short title	Publisher	Place of publication
1	1964	Hansen, L.	Prokofiev	Random House	New York, N. Y.
2	1960	Nest'ev, I. V.	Prokofiev	Stanford Univ. Press	Stanford, Calif.
3	1959	Conkin, P. K.	Tomorrow a new world	Cornell Univ. Press	Ithaca, N. Y.
4	1958	Chapman, H. W.	Last Tudor king...	Jonathan Cape	London, England
5	1953	Rossiter, C. L.	Seedtime and the Republic	Harcourt, Brace, & Co.	New York, N. Y.
6	1953	Fowlie, W.	Mallarmé	Chicago Univ. Press	Chicago, Ill.
7	1951	Robert, O. J.	Court of the Constitution	Harvard Univ. Press	Cambridge, Mass.
8	1951	Marek, G. R.	Puccini, a biography	Simon & Schuster	New York, N. Y.
9	1949	Weinstock, H.	Chopin...	Alfred A. Knopf	New York, N. Y.
10	1948	Smith, H. M.	Henry VIII...	Macmillan Co.	London, England
11	1946	Nest'ev, I. V.	Sergie Prokofiev...	Alfred A. Knopf	New York, N. Y.
12	1941	U. S. War Ind. Board	American industry...	Prentice-Hall, Inc.	New York, N. Y.
13	1938	Reed, C. (ed.)	Constitution reconsidered	Columbia Univ. Press	New York, N. Y.
14	1938	Howells, W. D.	Life of Abraham Lincoln	Abraham Lincoln Assoc.	Springfield, Ill.
15	1934	Wallace, H. A.	America must choose	Foreign Policy Assoc.	New York, N. Y.
16	1934	Pickthorn, K. W. M.	Early Tudor govern.: Henry VIII	Cambridge Univ. Press	Cambridge, England
17	1931	Hertz, E.	Abraham Lincoln, Vol. I	H. Liveright, Inc.	New York, N. Y.
18	1931	Hertz, E.	Abraham Lincoln, Vol. II	H. Liveright, Inc.	New York, N. Y.
19	1931	Puccini, G.	Letters...	Lippincott Co.	Philadelphia, Pa.
20	1930	Van Hise, C. R.	Conservation...	Macmillan Co.	New York, N. Y.
21	1926	Randall, J. G.	Constitutional problems	Appleton & Co.	New York, N. Y.
22	1923	Veblen, T.	Absentee ownership	B. W. Huebsch, Inc.	New York, N. Y.
23	1921	– –	Engineers of price system	B. W. Huebsch, Inc.	New York, N. Y.
24	1906	Dry, W.	Giacomo Puccini	J. Lane Co.	New York, N. Y.
25	1899	Montaigne, M.	Education of children	Appleton & Co.	New York, N. Y.

TABLE 2: Pages tested and special comments

Title no.	Year published	Pages tested			Special comments		
		First (F)	Center (C)	Third (T)	Lawrence	Newberry	New York
1	1964	121	181	381			Not available in this edition
2	1960	188	265	525			
3	1959	117	175	349			
4	1958	100	150	280			
5	1953	180	275	550			
6	1953	100	149	299			Not available in this edition
7	1951	33	50	100			
8	1951	133	200	400			
9	1949	111	166	333			
10	1948	160	240	470	F = 140* C = 215 T = 420	F = 160 C = 240 T = 470	F = 159 C = 239 T = 469
11	1946	66	100	190			
12	1941	166	255	495			
13	1938	140	210	420			F = 141
14	1938	31	45	91			
15	1934	–	11	–			
16	1934	180	280	550			
17	1931	161	247	493			
18	1931	665	750	1006	F = 669		
19	1931	110	165	320			Cropped – die cut sample slightly short
20	1930	187	275	551			
21	1926	190	285	570			Cropped – die cut sample slightly short
22	1923	145	223	445			Cropped – die cut sample slightly short
23	1921	56	85	169			Not available in this edition
24	1906	34	57	110			F = 33
25	1899	63	95	189			Not available in this edition

* These leaves were tested for sonic modulus only

submitted by the Lawrence University Library to the Chicago Paper Testing Laboratory for possible testing. These copies were compared with the same books from The Newberry Library. 25 of the 40 were established as identical copies of books from The Newberry Library. The same 25 catalog entries were sent to The Research Libraries of The New York Public Library where 21 identical copies were located and sent to Chicago. The identical nature of these copies of 21 titles from Appleton, Chicago, and New York was established on the basis of paper appearance and texture, copyright, printing and publication dates, edition, imprint, and type face images. Abridged entries for the original 25 titles are given in Table 1 and additional information is provided in Appendix 1.

Three leaves from each book were sampled and tested with the exception of title 11 which contained only nineteen numbered leaves. Normally, the first test leaf was selected at about the end of the first third of the total numbered leaves, the second at the half way point, and the third from the last signature of the book. The exact page numbers that were tested in each of the individual copies from the three libraries are listed in Table 2. The pH tests were conducted on the pages listed under the column »Pages tested«. In a few cases for Lawrence University and The Newberry Libraries, the die cut samples were inadvertently removed from the pages on which the sonic modulus tests were conducted. These exceptions are noted under the column »Special comments«.

2.3 Testing Procedure and Experimental Data

The function of the testing procedures was to provide the data necessary to compare the paper in the books of the three libraries. A large number of testing procedures were considered, but only six were selected to obtain data for evaluating the condition of the paper. The criteria for the selection of these six tests were the amount of information obtained, the damage to the book, and the cost of testing. The contact pH and sonic modulus test were developed for this study. The other four tests were modifications of *TAPPI Standards and Suggested Methods.* Each book was examined and compared with identical copies from the other two libraries.

2.31 Book Evaluation

Patron use, as well as other kinds of wear and tear, affects the rate at which books deteriorate. The effect of storage conditions is interrelated with the

TABLE 3: Book usage and condition of binding

Title no.	Year pub-lished	Book usage: Based upon observed wear and tear	Condition of binding: Rebound L	Rebound N	Rebound Y	Needs repair L	Needs repair N	Needs repair Y
1	1964	N ≈ L						
2	1960	L > Y ≈ N						
3	1959	Y > L ≈ N						
4	1958	Y ≫ N ≈ L						
5	1953	Y ≫ L > N						
6	1953	L > N						
7	1951	Y > N > L						
8	1951	Y > L > N			×			
9	1949	Y > L > N			×			
10	1948	Y ≫ N > L			×			
11	1946	Y > L > N						
12	1941	Y > L > N						
13	1938	N > Y > L						×
14	1938	Y > L > N						
15	1934	Y ≫ L > N		×*	×*			×
16	1934	Y > N > L			×		×	
17	1931	Y > N ≈ L			×			
18	1931	Y > N ≈ L			×			
19	1931	Y > L > N			×			
20	1930	Y > L > N			×	×	×	
21	1926	Y > N > L		×	×			
22	1923	Y ≫ N >L			×			×
23	1921	L > N		×				
24	1906	Y ≫ N > L			×		×	
25	1899	N > L				×	×	
			–	8 %	52 %	8 %	16 %	11 %

* Bound paperback pamphlet
\> Greater than
≫ Very much greater than
≈ Approximately equal

effects of wear and tear. There is no information available on the level of patron use other than the information given by the appearance of the various copies. No effort was made to separate the deterioration caused by the storage history of the book from that caused by wear and tear.

The bindings and the overall condition of the different copies were examined to determine whether the visual degree of deterioration varied from library to library. The bindings were checked to determine if binding repairs were needed and if rebinding had occurred. It was assumed that a cropped and rebound copy had experienced more wear and tear than a book which had not been rebound. The copies of each title were then ranked for wear and tear on the basis of the condition of the marginal areas of the leaves. The degree of use and condition of the binding estimates are listed in Table 3.

2.32 PAPER EVALUATION

The six tests used in this study to obtain data are listed in Table 4. They can be classified by their measurement of a chemical or physical (dimensional or strength) property and by their destructive or non-destructive nature.

The groundwood test can be defined as a non-destructive test because a test specimen can be snipped from an unobtrusive location at the edge of a leaf. A description of these six tests along with the experimental results obtained is given following the details of specimen preparation for the destructive tests.

Two test specimens were die cut from the margins of each of the three test pages with a steel mallet die. These specimens were used in the basis weight, folding endurance, groundwood, and thickness tests. The sampling and the testing for the books from the Lawrence University (L) and Newberry (N) Libraries occurred under standard conditions (73° F. ± 2° F., 50% R. H. ± 2%) as specified by TAPPI method »Conditioning Paper and Paperboard for Testing«.[27] The copies from The New York Public Library (Y) were also tested according to the TAPPI methods, but the test specimens were die cut in the main room of the Chicago Paper Testing

TABLE 4: Classification of tests

Identification	Description
1. Basis weight	Dimensional test – destructive
2. Thickness (caliper)	Dimensional test – nondestructive
3. Presence of groundwood fibers	Chemical test – destructive
4. Contact pH	Chemical test – nondestructive
5. M. I. T. folding endurance	Strength test – destructive
6. Sonic modulus of elasticity	Strength test – nondestructive

Laboratory under winter indoor conditions rather than according to the TAPPI method. The die cut test specimens (and books for the sonic dynamic modulus of elasticity test) were brought to TAPPI standard humidity conditions from a lower relative humidity for all tests. The dimensions of the die cut specimens were 15 mm. (0.59 in.) wide by 23 mm. (0.91 in.) long with 1/8 in. radius corners and an area of 0.525 sq. in. The specimens were die cut at the center points of the fore edge and the tail margins. The long dimension of the tail margin shecimens was perpendicular to the lines of text and the long dimension of the fore edge margin specimens was parallel to the lines of print.

2.321 Basis weight

The basis weight of book paper has been traditionally expressed in pounds per ream of 500 sheets measuring 25 × 38 inches. The testing concepts expressed by TAPPI method, »Basis Weight of Paper and Paperboard« were followed in this study.[26] The six die cut samples were conditioned and weighed in grams to four decimal places on a Mettler analytical balance. Then the basis weight was computed with an appropriate scaling-up factor and reported as basis weight in pounds for 500 sheets measuring 25 × 38 inches. The results are tabulated in Table 5.

2.322 Thickness (caliper)

»The thickness of paper or paperboard is the thickness (in thousands of an inch) of a single sheet when placed under a steady pressure of 7 to 9 pounds per square inch, between two circular and parallel plane surfaces, the smaller of which has an area of approximately 0.25 square inches (160 sq. mm.)«.[32] One of the test specimens *was chosen at random* and its thickness was measured in inches to four decimal places per TAPPI Method »Thickness and Density of Paper«.[32] The data obtained are given in Table 5.

2.323 Presence of groundwood fibers

Papers containing significant quantities of groundwood fibers have an infamous reputation for impermanence. One of the broken die cut test samples *was selected at random* after the M. I. T. folding endurance test and used in checking for the presence of groundwood fibers. A drop of phloroglucinol stain solution, prepared according to TAPPI method »Fiber Analysis of Paper and Paperboard«,[28] was applied to the specimen and the quantity of ground wood fibers present was estimated microscopically if a

TABLE 5: Basis weight and thickness (caliper)

Title no.	Year published	Basis weight in pounds for 500 sheets of paper 25 × 38 in.			Thickness in 0.001 in.		
		L	N	Y	L	N	Y
1	1964	58	58	–	6.3	6.2	–
2	1960	52	51	51	4.5	4.5	4.6
3	1959	60	59	57	4.9	4.7	4.8
4	1958	62	63	60	5.6	5.7	5.5
5	1953	50	50	48	4.9	4.6	4.8
6	1953	51	52	–	6.0	6.4	–
7	1951	59	60	60	5.5	5.7	5.6
8	1951	56	55	55	5.2	5.2	5.4
9	1949	54	57	57	4.5	4.5	4.8
10	1948	47	49	48	5.0	5.2	5.3
11	1946	52	55	53	5.1	5.2	4.9
12	1941	61	61	59	5.5	5.7	5.4
13	1938	59	59	59	4.9	4.7	4.9
14	1938	83	81	81	6.7	6.8	7.0
15	1934	62	53	62	5.7	5.7	5.7
16	1934	48	47	48	4.8	4.7	4.6
17	1931	64	65	63	5.5	5.5	5.4
18	1931	64	64	65	5.5	5.5	5.4
19	1931	73	74	69	7.5	7.7	7.2
20	1930	67	66	67	4.1	3.8	4.1
21	1926	44	46	44	4.3	4.4	4.3
22	1923	61	46	45	4.9	4.8	4.5
23	1921	60	61	–	6.1	6.0	–
24	1906	80	77	74	8.9	8.8	8.4
25	1899	83	87	–	6.0	6.1	–

magenta stain resulted from application of the phloroglucinol solution. The quantities of groundwood fibers are reported as none, less than 1 %, or as less than 5 %, in Table 6.

2.324 CONTACT pH

2.3241 Introduction

The pH of a paper, as conventionally expressed, is not a measurement of the paper's pH *per se*, but rather it is a measurement of the pH of a water

TABLE 6: Presence of groundwood fibers

Title no.	Year published	Groundwood fiber content		
		Lawrence	Newberry	New York
1	1964	None	None	–
2	1960	»	»	None
3	1959	»	»	»
4	1958	»	»	»
5	1953	»	»	»
6	1953	»	»	–
7	1951	< 1 %	< 1 %	< 1 %
8	1951	None	None	»
9	1949	»	»	None
10	1948	»	»	< 5 %
11	1946	»	»	None
12	1941	»	»	»
13	1938	»	»	»
14	1938	< 5 %	< 5 %	< 5 %
15	1934	None	None	None
16	1934	»	»	»
17	1931	»	»	»
18	1931	»	»	»
19	1931	< 1 %	»	»
20	1930	None	»	»
21	1926	< 1 %	»	»
22	1923	None	»	»
23	1921	< 5 %	< 5 %	–
24	1906	None	None	None
25	1899	< 1 %	»	–

extract of the paper. This means that the acidity or alkalinity of paper is defined as the pH value of a water extract of the paper. The pH value of such a water extract is accepted as a useful indicator of the potential permanence of a paper. Moderately alkaline papers normally have greater properties of permanence than otherwise equivalent acidic papers do. The rate of paper deterioration, caused by the acid-catalyzed hydrolysis of cellulose, usually increases rapidly with a decrease in the paper's pH value, particularly below a pH of about 6.0.

Background on the meaning and use of pH will be provided now preceding a discussion of the literature and presentation of the experimental data on contact pH. Aqueous solutions and materials which contain water also contain hydrogen and hydroxide ions. A small quantity of the water (H_2O) naturally ionizes to produce equal numbers of positively charged hydrogen ions (H^+) and negatively charged hydroxide ions (OH^-). Acids and bases also ionize to produce hydrogen and hydroxide ions. Some of the hydrogen and hydroxide ions encounter one another and combine into water molecules during the course of their movements. At equilibrium, the number of water molecules ionizing equals the number of water molecules being formed. An analagous pattern of reassociation occurs with acids and bases. It follows that water and aqueous solutions at equilibrium contain a well defined average concentration of hydrogen and hydroxide ions at all levels of acidity and alkalinity. Hence, the Law of Mass Action applies to the ionization equilibrium precisely as it does to other chemical equilibria. Water ionizes as:

$$H_2O \rightleftarrows H^+ + OH^- \qquad (1)$$

and the ion product constant of water, k_w, is a constant at a specified temperature. For example, at 25° C., k_w is defined by the equation:

$$k_w = [H^+]\,[OH^-] = 1 \times 10^{-14} \qquad (2)$$

where H^+ and OH^- represent the concentration of the hydrogen and hydroxide ions in moles per liter. At 100° C., the ion product constant of water is larger and has a value about 1×10^{-12}

The conventional practice is to express the concentration of hydrogen and hydroxide ions in terms of pH values. pH is defined by equation (3) as the negative logarithm of the hydrogen ion concentration:

$$pH = -\log\,[H^+] \qquad (3)$$

and similarly, the pOH is:

$$pOH = -\log\,[OH^-] \qquad (4)$$

The pH and pOH are not independent expressions of hydrogen and hydroxide ion concentrations. The equilibrium between the numbers of hydrogen and hydroxide ions must be satisfied. The ion product constant for water defines the relationship between pH and pOH. Equation (2) can be written in logarithm form as:

$$\log\,[H^+] + \log\,[OH^-] = -14 \qquad (5)$$

and in other words:

$$pH + pOH = 14 \qquad (6)$$

Accordingly, since the pH value is defined to equal the pOH value when the concentration of hydrogen ions equals the concentration of hydroxyl ions, equation (6) indicates that a neutral point occurs at a pH of 7 in water at 25° C. At 100° C., the neutral point would occur at a pH of 6 because the k_w at 100° C. is 1×10^{-12}.

The above equations indicate that the relationship between hydrogen and hydroxide ions varies greatly with change in pH value. The probability of acid-catalyzed hydrolysis increases tremendously with decrease in pH. For example, since there are one thousand times more hydrogen ions present at a pH of 4 than at a pH of 7, the theoretical rate of acid attack (i. e., rate of deterioration) can be one thousand times more rapid at a pH of 4 than at a pH of 7.

The pH of an aqueous extract of paper is usually acidic when a sample of alum-rosin sized paper is extracted (soaked) in distilled or deionized water. All of the pH values previously reported for paper in the literature were determined by one or another extraction procedure. Unless the paper has substantial buffering capacity, the extract pH may be affected to a significant degree by the amount and the quality of the distilled or deionized water. (The pH of distilled water can vary from between 5 and 6 to between 7 and 8 depending upon such factors as the quantity of alkali and carbon dioxide dissolved from glass containers and air).

The pH values obtained by aqueous extraction methods give values related to the hydrogen ion concentrations which exist within paper components. The details of this relationship are not yet known. These pH values are extremely useful but they should not be viewed as equivalent to the pH values which actually exist within the paper. At the present state of the art, it is not believed possible to determine the pH value within a paper fiber. However, present day pH test methods do offer a means to control manufacturing operations and do suggest the possible permanence of a paper. The method of pH measurement must be identified and all pH data must be interpreted with care because the best data are only crude suggestions of the average acidic or alkaline condition which exists within a paper substrate.

2.3242 Literature and preliminary work

The contact method of measuring pH, as applied in this study, was introduced by Hudson and Milne.[14] It was subsequently considered by Boustead,[4] Flynn and Smith,[11] Huber,[12] Illukowicz,[15] Palenius, Ålander, and Joselius,[21] and Stamm.[25] The findings of these authors indicate that comparatively good agreement can be obtained between the cold water extraction pH and contact pH values and that the contact pH method has particular merit as a non-destructive test. The quantity and quality of water, interference of carbon dioxide from the atmosphere, period of extraction (exposure to wetting), buffering capacity of paper, variation in experimental results between laboratories, as well as the techniques of measurement were considered by these authors in evaluating the contact pH method.

Cambell and Bryant[6] demonstrated a method in 1941 which overcomes the errors in measuring pH which are caused primarily by the reaction of paper components with extraction water. They carefully extracted a variety of different woods in a series of unbuffered aqueous solutions representing a range of pH values. The solution which did not change its pH value was taken to represent the true pH of the wood. The procedure followed by Cambell and Bryant is certainly sound, but it is impractical because of the time-consuming series of extractions necessary to establish an estimate of the true pH.

Stamm[25] simplified the method of Cambell and Bryant[6] and applied their approach on wood to estimating the true pH of paper. Stamm used fewer solutions and graphed the equilibrium pH values of the treated unbuffered solutions against their initial values before the paper sample was introduced. He took the point at which the resulting S-shaped curve crossed the 45° line as the true pH value of the paper. Stamm compared this theoretically true pH value to pH values obtained by a cold extraction procedure and by a contact pH procedure. A number of Stamm's experimental values for the three methods are given in Table 7.

Stamm concluded that the contact pH method gives just as good estimates of the true pH value as those obtained by the TAPPI cold extraction procedure for the papers which he tested.

Flynn and Smith[11] challenged Hudson and Milne's contention that the contact pH value is an accurate predictor of the cold water extraction pH value as measured by the TAPPI method »Hydrogen Ion Concentration (pH) of Paper Extracts«.[30] Flynn and Smith base their criticism on contact pH measurements taken within 5–10 sec. after wetting the paper, that is, on extraction times of 5–10 sec. Hudson and Milne took their readings 120 sec. after wetting the paper. In Table II of their publication, Flynn and Smith[11] (p. 225) list contact pH values for five book papers at wetting times ranging from 5 to 240 sec. At 120 sec., Flynn and Smith's contact pH values are excellent estimators of the cold extraction pH values which

Table 7: pH of paper determined by different methods

Paper	Extraction time	pH values: True	pH values: Cold extraction	pH values: Contact	Buffering capacity
Filter paper	15 min.	6.5	6.8	6.5	Low
	60 min.	6.4	6.4	6.3	Low
Alpha dissolving pulp sheets	15 min.	5.0	5.7	5.1	Medium
	60 min.	5.0	5.4	5.0	Medium
Paper toweling	15 min.	5.8	6.1	5.6	High
	60 min.	5.7	5.8	5.4	High
Kraft liner board	15 min.	7.5	7.5	–	High
	60 min.	7.5	7.4	7.5	High

they report for these same five papers in Table I[11] (pp. 224–25). Two of these book papers had the same pH values for both methods, two book papers differed by 0.1 pH unit, and one book paper (the only coated paper) differed by 0.4 pH units. It was found, in working out the contact pH procedure followed at The Chicago Paper Testing Laboratory, that the differences between contact pH and cold extraction pH values for book papers decreased with the increase in wetting time. It seems, therefore, that the 5 to 10 sec. extraction time used by Flynn and Smith was insufficient to justify their reservations about the use of the contact pH technique for recently produced book papers. In addition, their data provides no basis on which to evaluate the applicability of contact pH measurement to older book papers.

Both Huber[12] and Stamm[25] considered buffering capacity when comparing contact pH techniques with other methods of estimating the pH of paper. Their results indicate that the contact pH and cold water extraction pH values are most closely related when the papers have high buffering capacities.

The contact and TAPPI cold extraction pH values for paper in fifteen books published between 1748 and 1964 were determined at the Chicago Paper Testing Laboratory in an effort to establish the validity of the contact pH technique for older papers. Piper[22] at The Institute of Paper Chemistry, Appleton, Wisconsin, verified these pH data and determined the buffering capacity for the paper in six of these fifteen books after

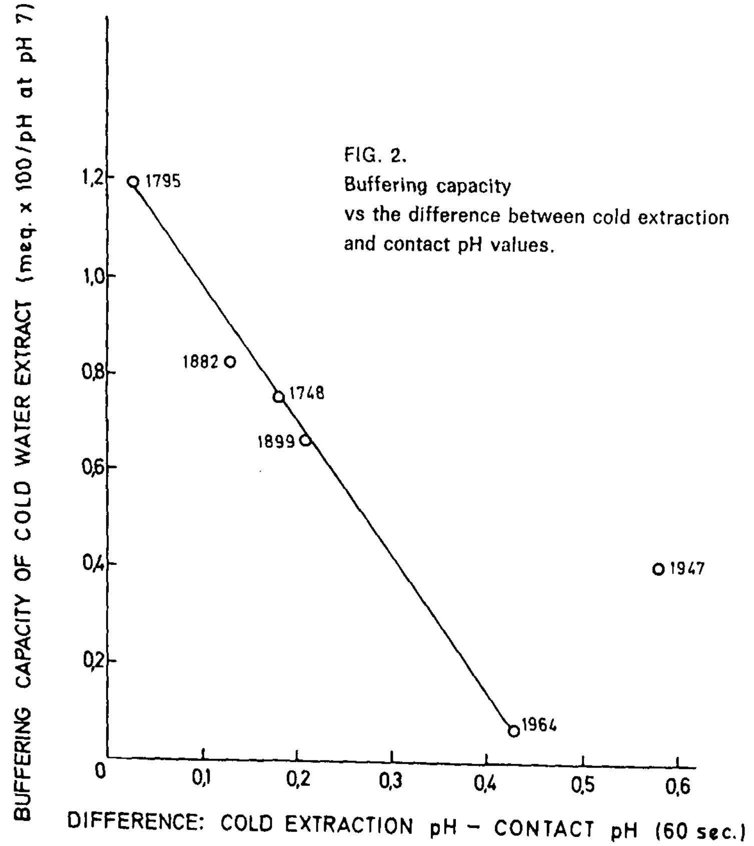


FIG. 2.
Buffering capacity
vs the difference between cold extraction
and contact pH values.

trimming off the margins from the leaves tested. He noted the differences between the contact and the TAPPI cold extraction pH values were greatest when the buffering capacities were least, thereby confirming the work of Huber[12] and Stamm.[25] As shown in Figure 2, the differences between the contact pH and the TAPPI cold extraction pH values plotted against buffering capacity were linear with respect to age for five of the six books. The buffering capacity increased with increasing age of the papers. Figure 3 indicates that the difference between the contact pH and the cold water extraction pH values decreases with an increase in age of the paper, that is, with the date of book publication. The implication of Figures 2 and 3, insofar as this study and the larger Newberry Library study are concerned, is that the contact pH and TAPPI cold extraction pH values become more accurate estimators of the true pH as the age of the paper being tested increases. The TAPPI hot and cold extraction pH

values[30] of a paper likewise tend towards the same value with an increase in the paper's buffering capacity. It seems reasonable, therefore, to assume that Flynn and Smith's reservations[11] may be discounted and the contact pH method may be applied to the measurement of pH for all library paper materials.

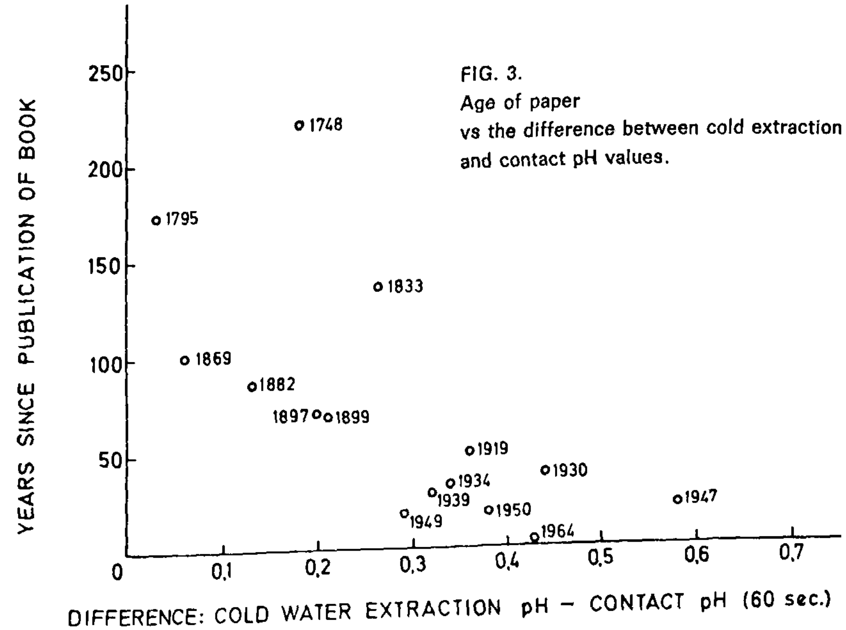


FIG. 3.
Age of paper
vs the difference between cold extraction
and contact pH values.

Wetting time, the period of exposure or extraction time which begins when the paper is wetted and extends until the contact pH is read, has been related to the differences between the contact pH and cold extraction pH values. In the preliminary work for this study, the extraction time required to obtain a steady contact pH reading was found to be related to the rate of water take-up, that is, to the degree or quality of sizing in the paper. This preliminary work also demonstrated that contact pH value varies more across a leaf of a book, probably an effect caused by acidic gas pick-up from polluted atmospheres, than this same contact pH value varies with extraction time, from twelve up to 300 seconds. Today book papers are not normally heavily sized because different practices by papermakers, printers, and readers (for example, the introduction of the ball point pen in the late 1940's) have resulted in a change of requirements. It has been noted that the quality of sizing in book papers has deteriorated with time.

Rare books, which probably tend to be older, were not investigated in this study and it is possible that the degree of sizing deterioration may be different in this class of books, particularly because early papermakers applied large quantities of gelatin size.

2.3243 Experimental procedure and data

An E. H. Sargent Chemical Company Model LS pH meter equipped with their flat-headed glass electrodes, Numbers S-30050-19 and S-30080-15c, was used in this study to make the contact pH measurements.* The electrodes were mounted in a holder, supplied by Sargent, designed to slide up and down a pole adjacent to the pH meter. The paper being tested was placed upon a one half inch thick polyurethane sponge covered with a sheet of polyethylene. The pH meter was standardized with pH 4, 7, and 9 buffer solutions at the beginning of and at intervals during each series of pH measurements. Deionized, freshly boiled water (cooled to room temperature) was used to rinse the electrodes and wet the paper. The electrodes were rinsed, wiped dry with tissue paper, neutralized in a pH 7 buffer solution, and rinsed again between pH measurements. The quantity of wetting water was minimized to reduce the brown line effect and controlled by picking the drop off one electrode and observing that the drop on the other electrode remained the same from measurement to measurement. The electrodes were slid gently down the pole into contact with the paper, moved in a small arc to spread the drop of water, and then allowed to rest by their own weight on the paper. The extraction time was standardized with a stop watch with the time beginning when the electrodes came to a rest on the paper. A stream of nitrogen gas was directed downwards between the electrodes to sweep over the paper during the contact pH measuring procedure. The purpose of this nitrogen gas flush was to maintain a neutral atmosphere and minimize interference from carbon dioxide in the atmosphere.

For the experimental work of this investigation, contact pH extraction time of 10–15 sec. (normally about 12 sec.) was selected as a realistic compromise between the quality of data desired and funds available. That is, the 12 sec. extraction time was chosen because the accuracy of this pH estimate was considered sufficient to meet the purposes of this study; this

* Recently, Beckman Instruments, Inc., Fullerton, California, introduced their »flat bulb combination pH electrode No. 39182.« This Beckman combination electrode is considered more convenient for measuring contact pH than the two electrode system used in this study.

TABLE 8: Contact pH values for the middle of the center page

Title no.	Year published	Page no.	Lawrence L			Newberry N			New York Y		
			12 sec.	30 sec.	60 sec.	12 sec.	30 sec.	60 sec.	12 sec.	30 sec.	60 sec.
1	1964	181	6.30	6.35	6.55	6.35	6.55	6.75	–	–	–
2	1960	265	6.30	6.40	6.45	6.40	6.45	6.60	6.25	6.40	6.50
3	1959	175	6.80	6.85	6.95	6.80	6.90	7.05	6.70	6.85	7.00
4	1958	150	3.90	3.85	–	3.85	3.90	3.90			
			3.85	*3.95*	*3.95*				*3.85*	*4.00*	*4.10*
5	1953	275	3.80	3.65	3.60	3.50	3.50	3.55	*3.35*	*3.50*	*3.55*
6	1953	149	3.40	3.50	3.50	3.45	3.45	3.45	–	–	–
7	1951	50	4.20	4.20	4.20	3.95	4.00	4.00	4.00	4.05	4.10
8	1951	200	3.30	3.30	3.30	3.30	3.25	3.25	*3.10*	*3.25*	*3.30*
9	1949	166	5.75	5.50	5.45	5.35	5.35	5.40	*4.75*	*4.85*	*4.95*
10	1948	215	3.70	3.75	3.75	3.55	3.60	3.60			
						(3.95)	*(3.90)*	*(3.90)*	*3.80*	*3.75*	*3.70*
11	1946	100	3.95	3.90	3.90	4.00	3.95	3.90	3.80	3.90	3.90
12	1941	250	3.75	3.70	3.65	3.80	3.75	3.75	3.80	3.85	3.90
13	1938	210	3.60	3.55	3.55	3.50	3.50	3.55	*3.20*	*3.40*	*3.50*
14	1938	45	3.90	3.85	3.80	3.80	3.80	3.80	*3.65*	*3.75*	*3.95*
15	1934	15	3.80	3.80	3.80	3.60	3.60	3.60	*(3.75)*	*(3.70)*	*(3.70)*
16	1934	280	4.70	4.65	4.60	4.50	4.45	4.40	*4.25*	*4.30*	*4.45*
17	1931	750	4.40	4.30	4.20	4.45	4.30	4.30	4.20	4.25	4.25
18	1931	247	*3.95*	*4.10*	*4.30*	*4.10*	*4.15*	4.20	4.00	4.10	4.10
19	1931	165	3.60	3.60	3.60	3.60	3.60	3.60	*3.45*	*3.50*	*3.60*
20	1930	275	4.30	4.20	4.20	4.35	4.35	4.35	*3.65*	*3.85*	*3.90*
21	1926	285	4.30	4.25	4.25	4.10	4.15	4.20	3.90	4.05	4.10
22	1923	223	4.10	4.10	4.10	4.30	4.20	4.10	*3.40*	*3.55*	*3.60*
23	1921	85	3.75	3.85	3.85	3.70	3.70	3.65	–	–	–
			(3.95)	*(4.00)*	*(4.10)*						
24	1906	57	4.60	4.50	4.45	*4.40*	*4.50*	*4.55*	*(4.40)*	*(4.40)*	*(4.35)*
25	1899	95	3.45	3.55	3.65	3.30	3.35	3.40	–	–	–

estimate could be obtained at a reasonable cost and the error introduced was considered less important than the value of a large number of readings. This 12 sec. extraction time is not recommended for work where a highly reproducible estimate of the pH value is desired. An extraction time of at least one, preferably two or five minutes, would improve reproducibility, particularly for tests with recently produced or well-sized papers.

The results of the contact pH measurements are given in Tables 8, 9,

TABLE 9: Contact pH values for the margins of the center page

Title no.	Year pub-lished	Page no.	Top margin L 12 sec.	Top margin N 12 sec.	Top margin Y 12 sec.	Side margin L 12 sec.	Side margin N 12 sec.	Side margin Y 12 sec.
1	1964	181	6.40	6.05	–	6.50	6.45	–
2	1960	265	6.80	6.40	6.15	6.60	6.65	6.10
3	1959	175	6.80	6.65	6.05	6.70	6.60	6.10
4	1958	150	4.00	3.85	3.80	4.05	3.85	3.75
5	1953	275	3.95	3.65	3.65	3.85	3.50	3.40
6	1953	149	4.10	4.10	–	3.90	3.75	–
7	1951	50	4.20	4.05	3.95	4.25	4.00	3.85
8	1951	200	3.50	3.35	3.30	3.65	3.40	3.30
9	1949	166	5.15	4.95	4.25	5.35	5.15	4.30
10	1948	215	3.90	3.35 *(3.70)*	*(3.80)*	3.85	3.35 *(3.85)*	*(3.75)*
11	1946	100	4.00	3.70	3.80	4.00	3.95	3.75
12	1941	250	3.85	3.55	3.50	3.90	3.60	3.50
13	1938	210	3.75	3.30	3.30	4.30	3.45	3.45
14	1938	45	4.20	3.90	3.45	4.45	3.60	3.70
15	1934	15	4.20	3.95	*(3.45)*	3.85	3.55	*(3.50)*
16	1934	280	4.65	3.90	3.55	4.60	4.00	3.60
17	1931	750	4.90	4.00	3.60	4.65	4.00	3.85
18	1931	247	4.30	3.85	3.60	4.35	3.95	3.90
19	1931	165	4.20	3.75	3.70	3.95	3.65	3.65
20	1930	275	4.45	4.10	3.80	4.50	3.70	3.45
21	1926	285	4.45	4.20	3.60	4.30	3.90	3.65
22	1923	223	4.25	4.10	3.60	4.20	3.90	3.35
23	1921	85	4.00	3.50	–	3.95	3.40	–
24	1906	57	4.90	4.50	*(4.20)*	4.75	4.55	*(4.20)*
25	1899	95	3.55	3.20	–	3.70	3.20	–

and 10. Table 8 lists the results on the center page for 12, 30, and 60 sec. wetting times. Table 9 lists the results on the center page for 12 sec. wetting times at the middle of the top (head) margin about 0.5 inch in from the edge of the leaf and at the middle of the fore edge (side) margin about 1 inch below its center. Table 10 lists the results for 12 sec. wetting times on the other two leaves tested.

The composition the pH data in Tables 8, 9, and 10 represents a code to indicate different testing times. The body type ciphers represent pH values

TABLE 10: Contact pH values for the middle of the first and third pages

Title no.	Year published	First page Page no.	First page L 12 sec.	First page N 12 sec.	First page Y 12 sec.	Third page Page no.	Third page L 12 sec.	Third page N 12 sec.	Third page Y 12 sec.
1	1964	121	6.75	6.45	–	365	6.35	6.60	–
2	1960	188	6.55	6.50	*6.25*	525	6.35	6.30	*6.10*
3	1959	117	6.15	6.25	*6.00*	349	6.10	6.25	*5.85*
4	1958	100	3.75	3.80	*3.70*	280	3.75	3.90	*3.70*
5	1953	180	3.70	3.70	*3.40*	550	3.70	*3.65*	*3.85*
6	1953	100	3.60	3.45	–	299	3.65	3.55	–
7	1951	33	4.95	3.95	*4.25*	100	4.30	4.30	*4.10*
8	1951	133	3.50	3.45	*3.20*	400	3.40	3.30	*3.20*
9	1949	111	4.85	5.10	*4.60*	333	4.90	4.80	*4.50*
10	1948	140	3.70	3.65	*(3.75)*	420	3.55	3.70	*(3.80)*
11	1946	66	4.05	4.00	*3.70*	190	4.00	3.90	*3.75*
12	1941	166	3.80	3.85	*3.80*	495	3.95	3.95	*3.80*
13	1938	141	3.60	3.40	*3.45*	420	3.65	3.60	*3.35*
14	1938	31	3.70	3.80	*3.35*	91	3.90	4.00	*3.55*
15	1934	–	–	–	–	–	–	–	–
16	1934	180	4.60	4.60	*4.15*	550	4.60	4.60	*4.45*
17	1931	161	5.10	4.90	*4.45*	493	4.20	4.20	*4.05*
18	1931	665	*3.90*	*4.05*	*3.95*	1006	*3.95*	*4.05*	*4.10*
19	1931	110	3.85	3.80	*3.70*	320	4.05	4.05	*3.80*
20	1930	187	4.60	4.10	*3.90*	551	4.20	4.60	*3.95*
21	1926	190	4.15	4.20	*3.85*	570	4.30	4.20	*3.85*
22	1923	145	3.80	4.15	*3.75*	445	4.45	4.45	*3.95*
23	1921	56	3.80	3.65	–	169	3.95	3.95	–
24	1906	34	4.60	*4.50*	*(4.55)*	110	4.95	4.75	*(4.35)*
25	1899	63	3.45	3.40	–	189	3.65	3.70	–

obtained during one series of measurements, the italic type ciphers represent pH values from another series, and the bracketed ciphers represent pH values obtained on a third testing occasion. On some occasions, replicate measurements were made and recorded. There are reasons to question the replicate values because wetting and drying may change the contact pH value of the paper. All the pH data are presented in Tables 8, 9, and 10 and no adjustments have been made for outlying data or for differences occurring between testing occasions. When replicate measurements were made, the first (higher lying) pH value was used for analyses in *3: Discussion of laboratory results*.

2.335 M. I. T. Folding Endurance

Folding endurance has been used more than any other test to evaluate the deterioration in paper caused by accelerated or natural aging. The M. I. T. folding endurance test was selected for use in this study because it measures the ability of papers to resist handling and use, it is very sensitive to the changes which occur in paper on aging, and it is a convenient and widely appreciated test. However, in fundamental research, folding endurance is not necessarily the best physical test to evaluate the effects of aging and use. Tearing energy absorbtion and fiber strength tests might be more suitable for such research and deserve consideration by future investigators.

The folding endurance test may be considered as a fatigue test. Actually, it is a modified tensile strength determination with the results determined by the ability of the paper to flex and stretch. The initial folding endurance folds do not greatly affect the tensile strength of papers in good condition, possibly because the fibers are being stretched. Thereafter, the tensile strength of the paper falls off.

This study generally followed the M. I. T. folding endurance procedure given by TAPPI method »Folding Endurance of Paper«,[29] except for the following variation. The test strips were prepared by mounting the die cut samples between two holding strips of paper with pressure sensitive (Scotch) tape. The tension or load on the M. I. T. folding endurance instrument was set at 0.5 kg. because the paper in many of the test books was already so weak that its folding endurance value at 1 kg. would have been zero folds.

The samples were positioned during the test to insure that the breaking point was approximately 3/8 inches from the end of the die cut sample closest to the text. The copies of each title were tested together and sequentially: (1) Lawrence University, (2) The Newberry and (3) The New York Public Libraries. All measurements were made by the same technician on the same M. I. T. folding endurance instrument. The instrument was overhauled before the testing commenced and was frequently standardized with a 500 gram weight during the testing.

The M. I. T. folding endurance raw data were tabulated in Table 11. In other work unreported to date, it has been verified that folding endurance data are distributed log-normally. Hence, the M. I. T. folding endurance data were changed to their logarithmic values in Table 12. The use of logarithmic data reduces the variance and otherwise improves the statistical analysis. The frequent practice of analyzing the logarithms of the means of

M. I. T. folding endurance replicates introduces a bias into the analysis and this practice was not followed in this study.

2.336 Sonic Dynamic Modulus of Elasticity

The study of deformation and flow of materials undergoing stress is called rheology. Rheology refers particularly to the study of materials whose elastic properties lie between those of ideal solids and ordinary liquids. Paper is such an intermediate material and its rheology is discussed by Mason[20] and Rance.[23]

The elasticity of any material is that property which enables the material to undergo deformation and to return to its original dimensions when the deforming stress (force) is removed. Such elasticity is determined more by the capability of the material to recover its original shape than by its ability to be deformed or extended. Paper, like many materials, can be extended or stretched by a certain amount and will return to its original size. That is, when the stretching force (deforming stress) is released, the paper will return instantaneously to its original dimensions. The dynamic modulus of elasticity of a paper largely defines the paper's ability to recover its original dimensions instantaneously.

In this investigation, it was not feasible to follow conventional practice when determining the dynamic modulus of elasticity. A non-destructive test which measured the speed of ultrasonic sound pulses through paper was selected instead with the intention of computing the sonic dynamic modulus of elasticity (sonic modulus) as a measure of paper embrittlement. The sonic modulus is determined by such paper properties as fiber orientation, machine or cross direction, stiffness, elasticity, resilience, and state of fatigue. The latter properties are particularly affected by aging. Unfortunately, the theory connecting the stress-strain property of porous materials like paper with the speed of sound is neither completely understood nor adequate. Nevertheless, the simplicity of the method and its non-destructive character made it appropriate to this investigation. Background on sonic modulus, details of earlier work, and additional references are available in Back, Htun, Jackson and Johanson,[1,2] Chatterjee,[7] Craver and Taylor,[9,10] Jackson and Gavelin,[16] and Yiannos and Taylor.[35]

The velocity of sound in solids is directly related to the force required to stretch or extend the solid and inversely related to its density. This occurs because a sound wave travels in solids as a mechanical but periodic strain. A sound wave typically travels fastest in materials with a high modulus of

Table 11: M. I. T. folding endurance data (1/2 kg tension)

Title no.	Year published	Lawrence						Newberry						New York					
		First page		Center page		Third page		First page		Center page		Third page		First page		Center page		Third page	
		Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin
1	1964	136	374	76	340	194	203	99	369	83	385	228	226	–	–	–	–	–	–
2	1960	74	362	75	199	60	161	54	285	37	384	56	131	60	403	100	280	57	209
3	1959	51	249	60	229	60	215	42	269	31	224	75	353	42	153	33	163	47	218
4	1958	23	19	5	11	12	22	20	17	19	17	20	24	14	7	9	8	11	20
5	1953	4	6	6	6	5	9	4	9	6	8	4	8	2	1	1	3	2	4
6	1953	1	2	2	2	4	4	3	4	4	5	3	5	–	–	–	–	–	–
7	1951	21	19	11	12	10	24	12	10	11	10	10	15	9	9	7	7	8	7
8	1951	4	2	3	1	4	2	8	7	7	5	5	4	1	1	1	2	3	2
9	1949	15	20	18	30	9	23	10	41	17	27	10	21	16	37	12	15	11	20
10	1948	12	9	11	10	8	13	13	13	15	22	13	13	4	4	7	4	3	7
11	1946	5	3	6	2	6	2	5	5	4	2	6	5	4	1	4	2	3	2
12	1941	11	19	15	22	12	10	14	18	31	34	33	36	6	7	5	9	5	13
13	1938	2	1	3	2	3	2	2	3	1	2	1	2	2	2	2	2	3	3
14	1938	6	1	7	1	8	2	9	5	6	3	8	4	3	2	3	1	3	1
15	1934	–	–	2	1	–	–	–	–	3	1	–	–	–	–	1/2	1/2	–	–
16	1934	36	30	62	29	69	35	31	28	19	24	28	20	26	16	7	20	18	25
17	1931	15	9	16	7	14	7	18	8	16	13	15	6	8	4	11	6	8	5
18	1931	18	10	13	8	13	6	10	10	16	9	14	11	6	10	6	5	6	6
19	1931	2	1	1	1	2	2	2	2	3	1	4	5	1	1	1	1	2	1
20	1930	7	7	18	14	9	7	6	7	19	11	7	12	3	2	1	3	10	6
21	1926	2	2	2	1	2	1	2	2	2	2	3	3	1	1/2	1	1	1	1
22	1923	2	1	2	2	3	3	1	1	2	2	3	2	1/2	1	1/2	1	1	1
23	1921	3	1	4	3	3	2	1/2	1	1	1	1	1	–	–	–	–	–	–
24	1906	2	4	4	5	2	3	1	2	2	5	2	2	2	2	1	3	1	2
25	1899	1	1/2	1	1/2	1	2	1	1/2	1/2	1/2	1	1	–	–	–	–	–	–

Table 12: Logarithms of M. I. T. folding endurance data (1/2 kg tension)

Title no.	Year published	Lawrence						Newberry						New York					
		First page		Center page		Third page		First page		Center page		Third page		First page		Center page		Third page	
		Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin	Side margin	Tail margin
1	1964	2.1335	2.5729	1.8808	2.5315	2.2878	2.3075	1.9996	2.5670	1.9191	2.5855	2.3579	2.3541	–	–	–	–	–	–
2	1960	1.8692	2.5587	1.8715	2.2989	1.7782	2.2068	1.7324	2.4548	1.5682	2.5843	1.7482	2.1173	1.7782	2.6053	2.0000	2.4472	1.7559	2.3201
3	1959	1.7084	2.3962	1.7782	2.3598	1.7782	2.3324	1.6232	2.4298	1.4914	2.3502	1.8751	2.5478	1.6232	2.1847	1.5185	2.2122	1.6721	2.3385
4	1958	1.3617	1.2788	0.6990	1.0414	1.0792	1.3424	1.3010	1.2304	1.2788	1.2304	1.3010	1.3802	1.1461	0.8451	0.9542	0.9031	1.0414	1.3010
5	1953	0.6021	0.7782	0.7782	0.7782	0.6990	0.9542	0.6021	0.9542	0.7782	0.9031	0.6021	0.9031	0.3010	0.0000	0.0000	0.4771	0.3010	0.6021
6	1953	0.0000	0.3010	0.3010	0.3010	0.6021	0.6021	0.4771	0.6021	0.6021	0.6990	0.4771	0.6990	–	–	–	–	–	–
7	1951	1.3222	1.2788	1.0414	1.0792	1.0000	1.3802	1.0792	1.0000	1.0414	1.0000	1.0000	1.1761	0.9542	0.9542	0.8451	0.8451	0.9031	0.8451
8	1951	0.6021	0.3010	0.4771	0.0000	0.6021	0.3010	0.9031	0.8451	0.8451	0.6990	0.6990	0.6021	0.0000	0.0000	0.0000	0.3010	0.4771	0.3010
9	1949	1.1761	1.3010	1.2553	1.4771	0.9542	1.3617	1.0000	1.6128	1.2304	1.4314	1.0000	1.3222	1.2041	1.5682	1.0792	1.1761	1.0414	1.3010
10	1948	1.0792	0.9542	1.0414	1.0000	0.9031	1.1139	1.1139	1.1139	1.1761	1.3424	1.1139	1.1139	0.6021	0.6021	0.8451	0.6021	0.4771	0.8451
11	1946	0.6990	0.4771	0.7782	0.3010	0.7782	0.3010	0.6990	0.6990	0.6021	0.3010	0.7782	0.6990	0.6021	0.0000	0.6021	0.3010	0.4771	0.3010
12	1941	1.0414	1.2788	1.1761	1.3424	1.0792	1.0000	1.1461	1.2553	1.4914	1.5315	1.5185	1.5563	0.7782	0.8451	0.6990	0.9542	0.6990	1.1139
13	1938	0.3010	0.0000	0.4771	0.3010	0.4771	0.3010	0.3010	0.4771	0.0000	0.3010	0.0000	0.3010	0.3010	0.3010	0.3010	0.3010	0.4771	0.4771
14	1938	0.7782	0.0000	0.8451	0.0000	0.9031	0.3010	0.9542	0.6990	0.7782	0.4771	0.9031	0.6021	0.4771	0.3010	0.4771	0.0000	0.4771	0.0000
15	1934	–	–	0.3010	0.0000	–	–	–	–	0.4771	0.0000	–	–	–	–	-0.3010	-0.3010	–	–
16	1934	1.5563	1.4771	1.7924	1.4624	1.8388	1.5441	1.4914	1.4472	1.2788	1.3802	1.4472	1.3010	1.4150	1.2041	0.8451	1.3010	1.2553	1.3979
17	1931	1.1761	0.9542	1.2041	0.8451	1.1461	0.8451	1.2553	0.9031	1.2041	1.1139	1.1761	0.7782	0.9031	0.6021	0.7782	0.6990	0.7782	0.7782
18	1931	1.2553	1.0000	1.1139	0.9031	1.1139	0.7782	1.0000	1.0000	1.2041	0.9542	1.1461	1.0414	0.7782	1.0000	1.0414	0.7782	0.9031	0.6990
19	1931	0.3010	0.0000	0.0000	0.0000	0.3010	0.3010	0.3010	0.3010	0.4771	0.0000	0.6021	0.6990	0.0000	0.0000	0.0000	0.0000	0.3010	0.0000
20	1930	0.8451	0.8451	1.2553	1.1461	0.9542	0.8451	0.7782	0.8451	1.2788	1.0414	0.8451	1.0792	0.4771	0.3010	0.0000	0.4771	1.0000	0.7782
21	1926	0.3010	0.3010	0.3010	0.0000	0.3010	0.0000	0.3010	0.3010	0.3010	0.3010	0.4771	0.4771	0.0000	-0.3010	0.0000	0.0000	0.0000	0.0000
22	1923	0.3010	0.0000	0.3010	0.3010	0.4771	0.4771	0.0000	0.0000	0.3010	0.3010	0.4771	0.3010	-0.3010	0.0000	-0.3010	0.0000	0.0000	0.0000
23	1921	0.4771	0.0000	0.6021	0.4771	0.4771	0.3010	-0.3010	0.0000	0.0000	0.0000	0.0000	0.0000	–	–	–	–	–	–
24	1906	0.3010	0.6021	0.6021	0.6990	0.3010	0.4771	0.0000	0.3010	0.3010	0.6990	0.3010	0.3010	0.3010	0.3010	0.0000	0.4771	0.0000	0.3010
25	1899	0.0000	-0.3010	0.0000	-0.3010	0.0000	0.3010	0.0000	-0.3010	-0.3010	-0.3010	0.0000	0.0000	–	–	–	–	–	–

elasticity, that is, resistance to stretch. Hence, the speed of sound increases in the following series of materials: rubber, wood, steel.

The sonic pulse velocity was measured using the Dynamic Modulus Tester PPM-5R with the Planar Mount Option manufactured by H. M. Morgan Co., Inc., Cambridge, Mass. In the PPM-5R instrument, a ceramic piezoelectric transducer propagates a longitudinal sonic pulse in the leaf at a frequency low enough to ensure complete damping before the succeeding pulse is generated. A receiving transducer at a measured distance from the transmitter is used to convert the sonic pulse into an electronic signal. The sonic pulse velocity is obtained from the distance and time interval between the emission and reception of sonic pulse. The velocity might be used to compute Young's modulus of elasticity, E:

$$E = \sigma V^2 (1 - \rho^2) \qquad (7)$$

where σ is the apparent density and ρ is Poisson's ratio. The fiber or apparent density of paper, »σ«, ranges from 0.6 to 0.7 for book papers. Poisson's ratio, »ρ«, is small for paper and it is conventionally neglected when computing the sonic modulus. This disregard of ρ means the equation:

$$E_s \approx \sigma V^2 \qquad (8)$$

does not represent Young's modulus but rather some function thereof, namely the sonic modulus.

Originally, it was planned to use Craver and Taylor's equation to compute the sonic modulus because the basis weight of the papers in the duplicate copies was anticipated to be approximately the same. However, the paper from New York Public Libraries books had consistently lower basis weights than the paper from the books of the other two libraries. This raised a question as to the appropriate value for the fiber density. An analagous difficulty was encountered when thickness was substituted into the equation. Another objection developed because the basis weight and thickness measurements were made at the edges of the leaves whereas the sonic velocity was determined for the center of the leaves. There seemed to be no satisfactory solution by which the use of this equation could be justified.

The quantity E_s/σ, however, provides a reason to evaluate V^2. This is particularly true if one assumed, as this investigator did, that the fiber densities are identical in the duplicate copies of a title. When paper having equal fiber density and basis weights is tested, the paper sample that stretches least per unit width under a given load is the sample with the

TABLE 13: (Sonic velocity)^2 = V^2

Title no.	Year published	$V^2 = \sqrt{\sum_1^3 (V_c^2)(V_m^2)/3}$		
		Lawrence	Newberry	New York
1	1964	5.53	6.22	–
2	1960	5.67	6.31	5.95
3	1959	5.11	5.52	5.26
4	1958	5.69	5.44	5.45
5	1953	3.85	4.11	3.79
6	1953	4.61	7.50	–
7	1951	4.85	5.07	4.95
8	1951	5.94	5.78	5.36
9	1949	4.51	4.70	4.79
10*	1948	5.86	5.59	6.49
11	1946	4.80	5.47	5.06
12	1941	4.82	5.53	4.74
13	1938	4.69	4.93	4.79
14	1938	5.73	6.52	5.69
15	1934	4.02	4.94	6.37
16	1934	6.04	6.18	6.24
17	1931	6.10	5.35	6.35
18*	1931	5.73	5.97	5.32
19	1931	4.80	4.85	5.15
20	1930	5.15	5.60	5.70
21	1926	4.89	5.35	4.85
22	1923	4.63	5.05	8.36
23	1921	5.53	5.69	–
24*	1906	3.93	4.50	4.74
25	1899	3.44	3.92	–

* Identical pages were not tested.

highest E_s/σ. This implies that the value of V^2 should increase with increase in embrittlement. That is, a decrease in resilience and elasticity should parallel an increase in stiffness and state of fatigue.

The sonic velocity for each test page was determined in both directions along the center two axes of the page. Several measurements of sound velocity were made in microseconds over distances from 2 to 10 centimeters and recorded on the graph of the instrument. The average transit time in microseconds over a 10 centimeter span was computed from the slope of the time-distance plot of these measurements. This transit time value was subsequently converted to V^2, sonic velocity. A typical instrument graph and example set of computations are given in Appendix 2.

The V^2 values, as measures of change in E_s/σ, are tabulated in Table 13, as the square root of the means of the products of the cross direction and machine direction V^2 values for each copy:

$$\sqrt{\sum_{1}^{3} (V_c^2)(V_m^2) / 3} \tag{9}$$

The V^2 values for the cross and machine directions of the pages tested in the various copies are given in Appendix 2. The raw data are available from the author.

Chapter 3

Discussion of Laboratory Results

3.1 Introduction and Storage Conditions

One purpose of this investigation was to determine whether the condition of paper in identical books is affected by storage conditions. Hence, before discussing the experimental results, it is desirable to establish what these storage conditions might have been. The elevations and latitudes of Appleton, Chicago, and New York are similar, and all are located on or near bodies of water. Appleton might be somewhat cooler and drier, but on the other hand, the Lawrence University Library book stack would be heated for a longer period each year.

The Lawrence University and Newberry Libraries have been air conditioned since 1961. The humidity and temperature levels are controlled and dusts are removed by filtering. In addition, the air of the Newberry Library is washed to remove acidic gases. Plans have been formulated but as yet the general collections of The Research Libraries in New York are not protected by air conditioning.

Table 14, »Quality of Air in Appleton, Chicago, and New York«, is based on data from the U.S. National Air Surveillance Networks of the U.S. National Air Pollution Control Administration.[33] There are no state or federal sampling stations in Appleton or vicinity and data is given for Madison and Eau Claire, Wisconsin, where the air quality is believed to be similar to that of Appleton. The Chicago sampler is located on the City Office Building, 320 North Clark Street; the Eau Claire station at 314 East Grand Avenue; the Madison station on the City-County Building, 202 Monona Avenue; and the New York station on the Harlem Courthouse, 170 East 121st Street. Three fractions are listed under suspended particulates, the benzene soluble organic matter (B. S. Organic), water soluble nitrate compounds, and water soluble sulfate compounds. The SO_2 and NO_2 are collected in reagent-filled bubblers. Each annual average is derived from twenty to twenty-six 24-hour samples collected throughout the year.

New York City is more seriously polluted than Chicago, and by comparison to these cities, Eau Claire and Madison appear to be practically non-polluted. In another publication,[24] the author has reviewed the effect

TABLE 14: Air quality in Appleton, Chicago, and New York City[1]

Library	Pollutant[2]	1960	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970
LAWRENCE												
Eau Claire	Suspended particulates					65	48	70	50	43	41[3]	56[3]
	B. S. organic					3.7				3.5	3.1[3]	
Madison	Suspended particulates		76		73		79		55	62	59	68
	B. S. organic		6.6		6.0		4.5		4.4	4.3	4.1	
	Sulfates						8.9		5.0	6.1	9.5	
	Nitrates						3.0		1.5	1.6	0.9	
	Suspended particulates	182	190	123	144	176	140	124	143	111	135	112
	B. S. organic	14.5	13.6	9.4	10.0	9.5	7.8	7.3	5.7	7.4	7.4	
	Sulfates		24.9	15.5	16.9	19.0	15.9		12.4	13.4	18.8	
NEWBERRY	Nitrates		2.7	1.2	1.7	2.5	2.2		1.5	2.7	2.0	
	Sulfur dioxide			246	278				232	174	184	119
				0.21	*0.24*				*0.20*	*0.15*	*0.16*	*0.10*
	Nitrogen dioxide			113	109				271	299	301	255
				0.10	*0.09*				*0.23*	*0.25*	*0.26*	*0.22*
	Suspended particulates	162	173	179	215	197	179	134	186	128	105	123
	B. S. organic	13.7	14.0	15.2	17.1	12.2	9.6	10.3	12.2		8.9	
	Sulfates			25.3	31.3	33.1	28.8		32.2	21.0	19.1	
NEW YORK	Nitrates			1.4	3.0	2.2	2.4		1.4	1.2	1.3	
	Sulfur dioxide	152	314	409	401	448	374	352	364			
		0.13	*0.27*	*0.35*	*0.34*	*0.38*	*0.32*	*0.30*	*0.31*			
	Nitrogen dioxide	181	153	151	136	171	157		336			
		0.15	*0.13*	*0.13*	*0.12*	*0.13*	*0.12*		*0.28*			

1. Source: U. S. National Center for Air Pollution Control, Cincinnati, Ohio, and U. S. Environmental Protection Agency, Research Triangle Park, North Carolina. Personal correspondence.
2. Body face ciphers present the measured concentrations of pollutants in micrograms per cubic meter of air. Italic face ciphers present estimated concentrations of sulfur dioxide or nitrogen dioxide in parts per million of air computed by the author.
3. Sampling site changed in 1969.

of air pollution on library materials. His findings indicate that the quantities of either NO_2 or SO_2 which occur in the atmospheres of Chicago and New York City would provide more than enough hydrogen ions to destroy unprotected books.

3.2 BOOK EVALUATION

The books from The New York Public Library were used much more frequently than the copies from the Lawrence University and The Newberry Libraries. The degree of difference in use levels can be appreciated by an analogy with the conditions of books in most other libraries. The New York Public Library books look like heavily used ready reference books while the books from the other two libraries look like the remainder of a library's collection. The appearance of the Lawrence University books suggests that they were used somewhat more frequently than those of The Newberry Library. The bookbinding cloth, particularly at the spines, of the copies from The New York Public and The Newberry Libraries appears more embrittled than the cloth of the Lawrence University Library copies. The top-edge of the books from The Newberry Library were the most dirty, the top-edges from The New York Public Library were intermediately dirty, and the top-edges from the Lawrence University Library books were the cleanest.

The high level of rebinding at The New York Public Library (52%) as contrasted to that of The Newberry Library (8%) and to the entire lack of rebound copies from the Lawrence University Library invites speculation about the cause of rebinding. The amount of rebinding must correlate with patron use, particularly since selection for rebinding must occur principally during sorting for reshelving. That is, the binding breaks when the book is taken from the shelf or during some other use related procedure and the need for repair is noted prior to reshelving. Observations based upon selection for rebinding are valid measures of effect but they are not necessarily related to the cause (or causes) of binding failure. The real cause (or causes) is defined as that cause (or causes) which sets up the conditions for binding failure. This cause might be patron use, but it is more likely that the chemical reactions which occur during storage make binding failure inevitable.

Various components of book bindings, for example, binding cloth, hinges, tapes, cord and thread, end papers, head caps, etc., are cellulosic and consequently have chemical properties similar to those of paper fibers.

Kimberly[17] demonstrated that sulfur dioxide, at concentrations approaching those of polluted urban enviroments, caused the average paper to loose 15 per cent of its folding endurance in only ten days. The bindings of the books in this study were not evaluated for pH, but an observation based on studies of the deterioration of leather bookbindings can be made. Veitch, Frey, and Leinbach[34] reported pH values lower than 1.5 for leather removed from the spines of books obtained from the collections of the John Crerar Library, Chicago, Illinois, The New York Public Library, and various libraries in Washington, D. C. The air around The Research Libraries of The New York Public Library has been and is highly polluted with acidic gases such as nitrogen and sulfur dioxides. The unprotected spines of cellulosic bookbindings presumably take up substantial quantities of these gases in polluted atmospheres and the rapid deterioration of the spines of such books should not surprise librarians. It is doubtful whether the most resistant cellulosic bookbinding component could have much, if any, durability or permanence at one hundredth (a pH of 3.5) of the hydrogen ion content reported by Veitch, Frey, and Leinbach. It is likely that book spines composed of ordinary bookbinding components deteriorate significantly within a few months of receipt and their premature failure is determined by library practices when books are stored in the highly polluted atmospheres of some American cities.

Librarians might weigh the costs of book repair and replacements against the costs of reducing the rate of acidic gas pick-up. Methods of removing acidic gases from library air and improving the resistance of bookbinding materials to acidic attack are appropriate subjects for discussion and further investigation. Librarians do not control book manufacturing practices, but they can set an example through specifications for binding originating in libraries. Librarians can seek sources for and then specify the use of hinges, tapes, and cords, etc., containing an alkaline buffering agent and bookbinding cloths coated with an impermeable barrier layer, such as a polyester plastic film like Mylar. It might also be rewarding for librarians to deacidify and seal the spines of newly received books which have porous, cellulosic bindings.

3.3 Basis Weight, Thickness, and Groundwood Fiber Content Tests

The results of the basis weight, thickness, and groundwood fiber content tests imply that the paper in the various test pages was not precisely the

same from one »identical« copy to another »identical« copy. The actual picture is unclear because random test samples were used for the thickness and groundwood fiber content tests and, as a consequence, identical leaves were not compared. Certain samples tested from some of the titles contained small and, insofar as permanence is concerned, probably insignificant quantities of groundwood fibers. Commercially speaking, a paper containing less than 5 per cent of groundwood fiber in its fiber furnish is defined as groundwood free. The presence of less than 5 per cent of these fibers in some copies suggests that the paper in certain leaves came from different production runs or from different locations during a given run. These variations probably indicate that the papermaker was recycling small quantities of scrap or feeding in some deinked material which contained groundwood fibers. These fluctuations were too small to preclude a comparison of other test data, but they were sufficient to make computation of the sonic dynamic modulus of rupture undesirable. It is unclear why the paper from The New York Public Library copies was thinner and lighter than the paper in the duplicate copies from the other two libraries. The differences might have been caused by errors of measurement or moisture hysteresis, but such differences could also be a result of deterioration and/or patron use. The need for clarification of this difference presents an interesting opportunity for future investigation.

3.4 Contact pH

The contact pH data given in Tables 8, 9, and 10 are tabulated in Table 15 and interpreted by Figures 4–9 as regression lines of the hydrogen ion content on the age of paper. Table 15 and Figures 4–9 imply that paper as typically manufactured is acidic enough to undergo severe deterioration and that storage conditions have a powerful influence upon the present day acidity of library paper materials. The paper in the books of The New York Public Library is most acidic, in The Newberry Library books intermediately acidic, and in the books of the Lawrence University Library the least acidic. The margins of the leaves in the books of The New York Public Library and The Newberry Library are more acidic than the center of the leaves but this acidity relationship is reversed in the leaves from the books from the Lawrence University Library. The percentage distribution of the contact pH values given in Table 8 is tabulated in Table 15.

The contact pH values summarized in Table 15 are very acidic and 52.4 % fall below a pH of 4. By contrast, only 0.7 % of the TAPPI cold extraction

TABLE 15: Percentage distribution of contact pH values at middle of center page

pH values between	Lawrence	Newberry	New York
3.00–3.99	54.1	48.0	55.6
4.00–4.99	29.7	36.0	34.9
5.00–5.99	4.1	4.1	–
6.00–7.05	12.2	12.0	9.5
Total	100.1	100.1	100.0

pH[30] values reported by the Barrow Research Laboratory[3] and Church[8] fall below a pH of 4.

The initial step in graphing the contact pH data was to change each pH value into a factor reflecting the number of hydrogen ions in a liter of aqueous solution as explained in footnote *, p. 2. (Hydrogen ion content theoretically provides a better guide to the probable rate of deterioration than the pH value does because hydrogen ions, not pH values, catalyze the hydrolysis of cellulose. As noted previously, pH values can be misleading because pH values are computed from a logarithmic function of the hydrogen ion concentration). Then the hydrogen ion factors were regressed according to Brownlee[5] (pp. 338–42) on the number of years since the book was published to obtain the least squares regression lines in Figures 4–9. The number of years since publication or printing were assumed to be an accurate estimate for the age of the paper. The pH and year of publication are given as secondary axes at the bottom and right side of the figures to serve as guidelines.

Appendix 3 tabulates the hydrogen ion data used to compute Figures 4–9 as well as the equations of the regression lines and their intercept values. The hydrogen ion data for Titles 1, 6, 23, 24, and 25 were excluded from all analyses because of incomplete, non-comparable, or out-lying (time) data. In addition, no first and third pages were tested in Title 15.

Figures 4 and 5 interpret the data of Table 8 as the middle of center page contact pH regression lines. Figure 4 arranges the regression lines by time of exposure and Figure 5 organizes the same lines by individual library. The regression lines for the paper in books from the Lawrence University and The Newberry Libraries have negative slopes while those for the paper in the books from The New York Public Library have positive slopes. The

pattern of decreasing acidity with increasing age for the Lawrence and Newberry books probably occurs because the paper in some of the more recent books is unusually acidic. The effect of these acidic values is to see-saw the lines downwards retrospectively and to imply falsely that the older books have less acidic pH values. In contrast, the paper in the books from The New York Public Library becomes increasingly acidic with time. The sample of books studied appears to be unusual and probably does not reflect the true situation in libraries for two reasons. First, the low pH values for the paper in some of the more recently published books cause the regression lines representing the books from Lawrence University and The Newberry Libraries to have negative slopes. These slopes imply falsely that a paper may become more alkaline as it grows older. The paper in books from *The New York Public Library* apparently is so strongly affected by air pollution that the acidic values for recent publications are overridden and the paper in the older books becomes the most acidic.

Second, the data from the original Newberry Library study suggest that it is unlikely for more than one book out of twenty-five to have paper with a pH above 6. There were three such books in this study, all found among the most recent publications.

The effect of extraction time has implications of interest to librarians. The pH values for paper in the Lawrence books became more acidic with the increase in extraction time. This suggests that the paper's secondary components or fiber furnish act as sources of hydrogen ions. In case of The New York Public Library, however, there was a decrease in acidity from twelve to thirty and sixty seconds exposure indicating the paper's secondary components or fiber furnish are taking up the hydrogen ions. Hence, it seems that the greatest acidity in New York books occurs on the surfaces of the paper components, presumably as a consequence of storage conditions, whereas the greatest acidity of the Lawrence books occurs within the components, perhaps as a consequence of manufacture or natural degradation reactions. The acidity of the paper in books from The Newberry Library books fell in between the acidity of the paper in the books from New York and Appleton at time of test suggesting a balance between the surface and interior effects had been established.

This pattern of acidity suggests that inter-fiber bonding and fiber surface materials probably were attacked more severely in The New York Library books than in the books from the other two libraries. Further investigation is warranted because this external acidity could have destroyed the bonding between paper fibers and may explain the more rapid deterioration of

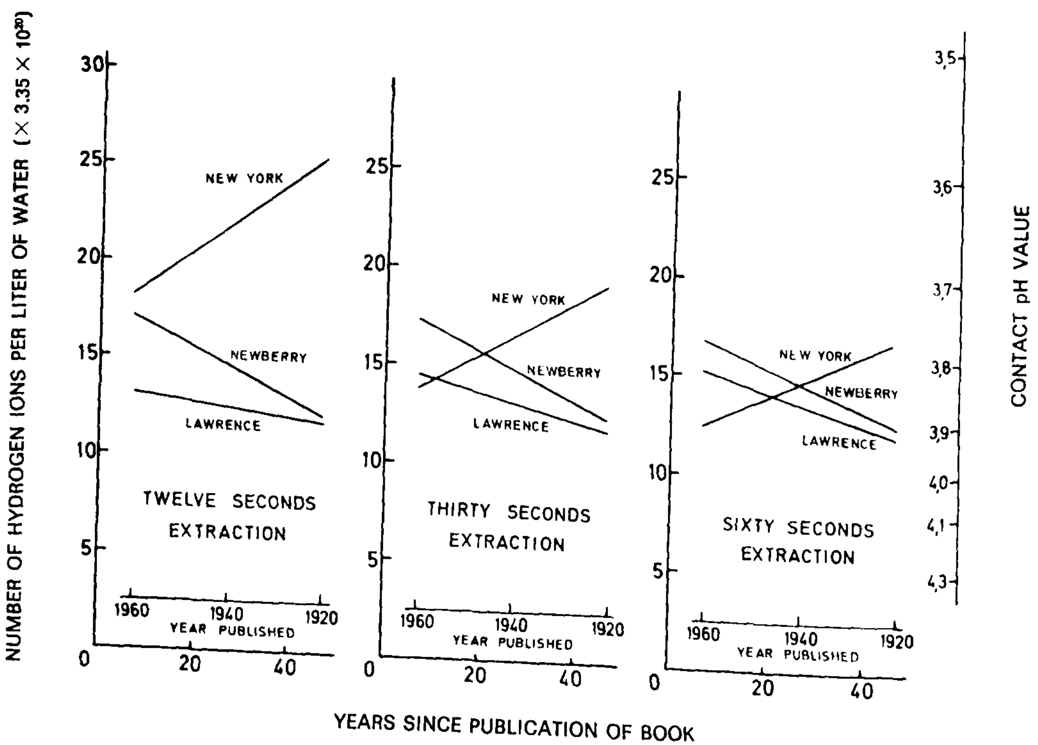


FIG. 4. Middle of center page contact pH regression lines arranged by time of extraction.

paper at The Research Libraries. Figures 4 and 5 also indicate that acidic gases of air pollution penetrate throughout The Newberry and The New York Library books.

Figures 6 and 7 interpret the data from Tables 8 and 9 as the middle of page 12 sec. contact pH regression lines. Figure 6 arranges the regression lines by pages tested and Figure 7 organizes the same lines by library. The pattern of increasing acidity from the Lawrence to The Newberry to The New York Public Library continued although the regression lines for the third page imply a slightly less acidic condition in The Newberry books than in those from Lawrence. It is not clear why the third page is least acidic, the first page intermediately acidic, and the center page most acidic. Presumably, the pattern is correct because the pH data for the Lawrence University and The Newberry Libraries were obtained primarily on a single occasion and most of The New York Public Library data were obtained at another time. The explanation probably goes back to the point of manufacture. It is also possible that the back cover of the book provided

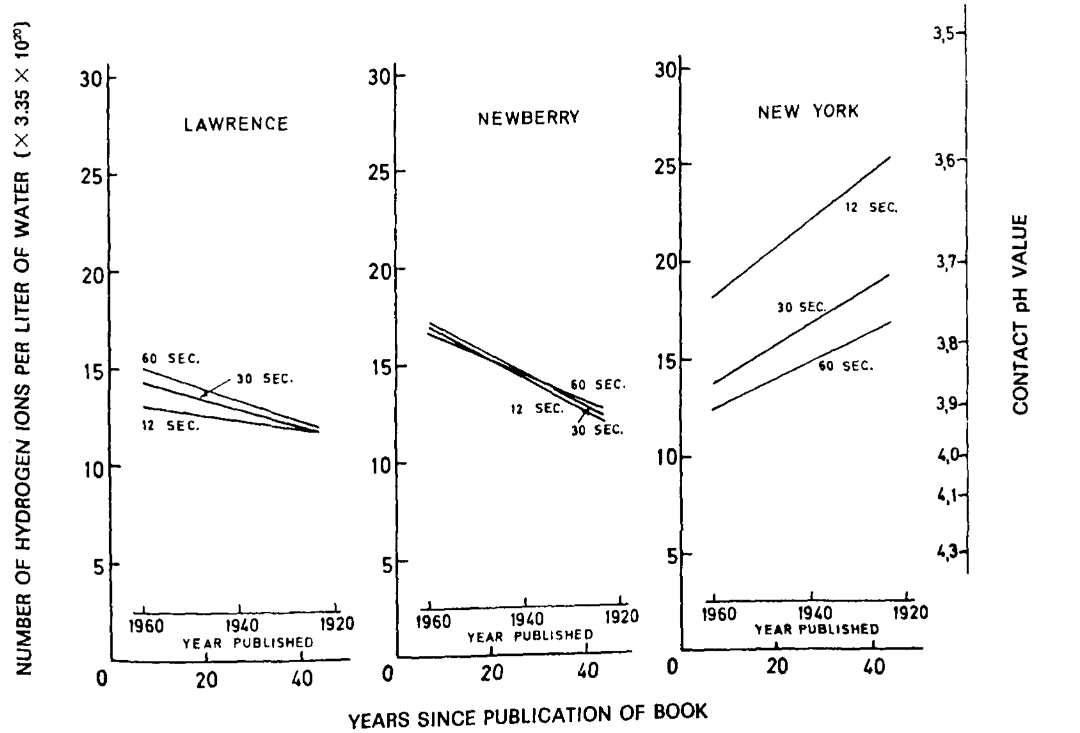


FIG. 5. Middle of center page contact pH regression lines arranged by library.

protection to the leaves in the last signature. In any event, whether or not the fluctuation in pH goes back to time of paper manufacture, the variation in pH is not very great. It would be difficult, if not impossible, for paper manufacturers to reduce the variaion of about 0.1 pH unit implied by the Lawrence Library regression lines.

Figures 8 and 9 interpret the margin pH data of Table 10 as the margin of center page 12 sec. contact pH regression lines. The 12 sec. regression lines for the middle of the center page are included to provide a basis for comparison. In Figure 8, the regression lines are arranged by library and in Figure 9, the same lines are organized by location on the center page. The pattern of increasing acidity is maintained from the paper in the books from the Lawrence University to the paper in the books from The Newberry and The New York Public Library. In fact, the differences in the levels of acidity at the margins are so marked that it seems almost impossible for the lines to represent pH data for identical copies of the same titles.

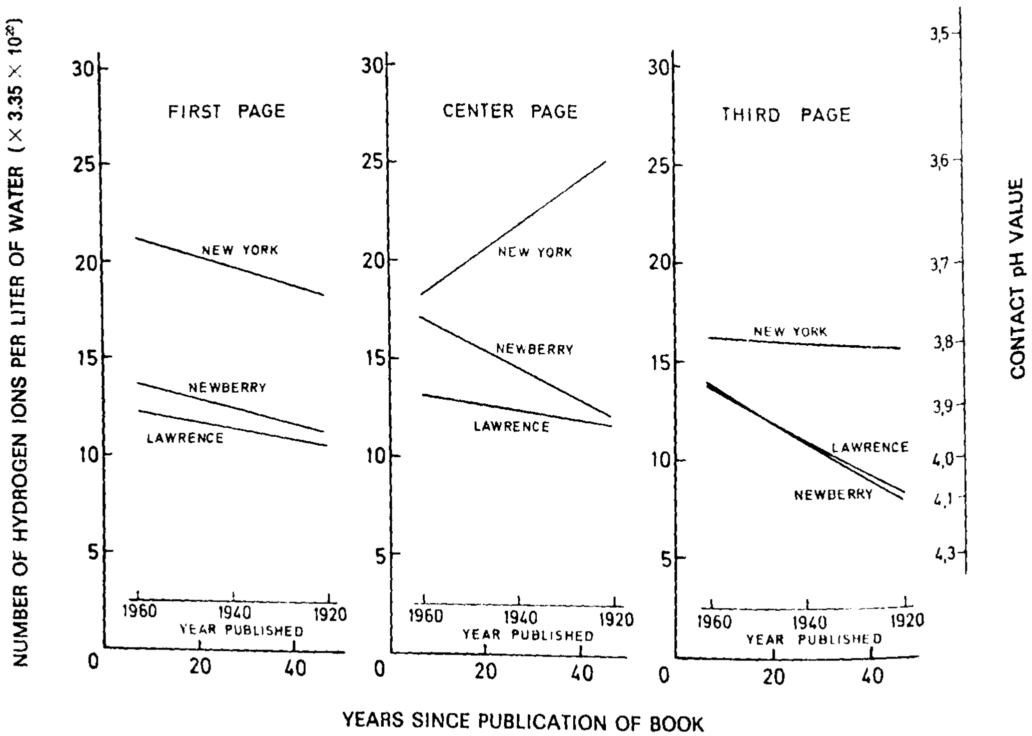


FIG. 6. Middle of page 12 sec. contact pH regression lines arranged by page tested.

The margin of the leaves was less acidic than the middle of the leaves in books from the Lawrence University Library. This increase in acidity at the middle of the leaves apparently is a consequence of acidic reaction products from ink medium degradation[24] (p. 179). This relationship between the margin and the middle of leaves supports Table 14 which says air pollution is not a critical problem in Appleton[24] (p. 167). The distribution of hydrogen ions is precisely the opposite in The Newberry and The New York Public Library books where the margin of the leaves is substantially more acidic than the middle of the leaves. There appears to be no other explanation for the data except that air pollution made the major contribution to the increased acidity of the paper in the books of The Newberry and The New York Public Library. The increase of acidity at the middle of the leaves in The Newberry and New York Public Library books follows the degree of increase at the margin. This increase indicates that acidic gases from polluted air do reach the innermost parts of books.

The hydrogen ion content of the fore edge margin is greater than it is at

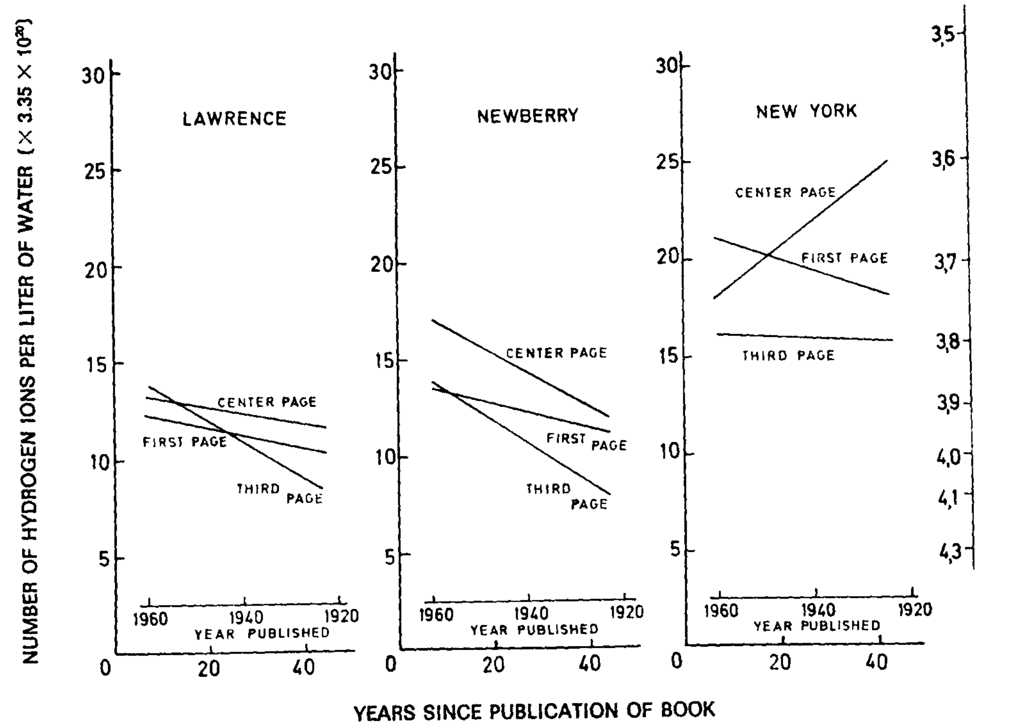


FIG. 7. Middle of page 12 sec. regression lines arranged by library.

the top margin of leaves in The Newberry Library books. This difference might have been caused by a protective layer of dirt or gilding on the top-edge and by a higher rate of air travel along the vertical fore edge of the book. This same pattern occurs in the leaves of books from The New York Public Library in their original bindings. The pattern in the margins of rebound books from The New York Public Library does not reveal such a difference. The rebound books from The New York Public Library were cropped approximately 1/4 inch at the fore edge margin and 1/8 inch at the top and tail margins. This cropping is most likely the principal reason why the acidity levels of the top and fore edge margins of The New York Public Library books are similar. It is also probable that the pH values for the margins of cropped leaves from The New York Public Library books are conservative. These pH measurements for the books from New York were taken at a greater distance from the original edges of the leaves than the pH measurements for the books from Appleton and Chicago were taken.

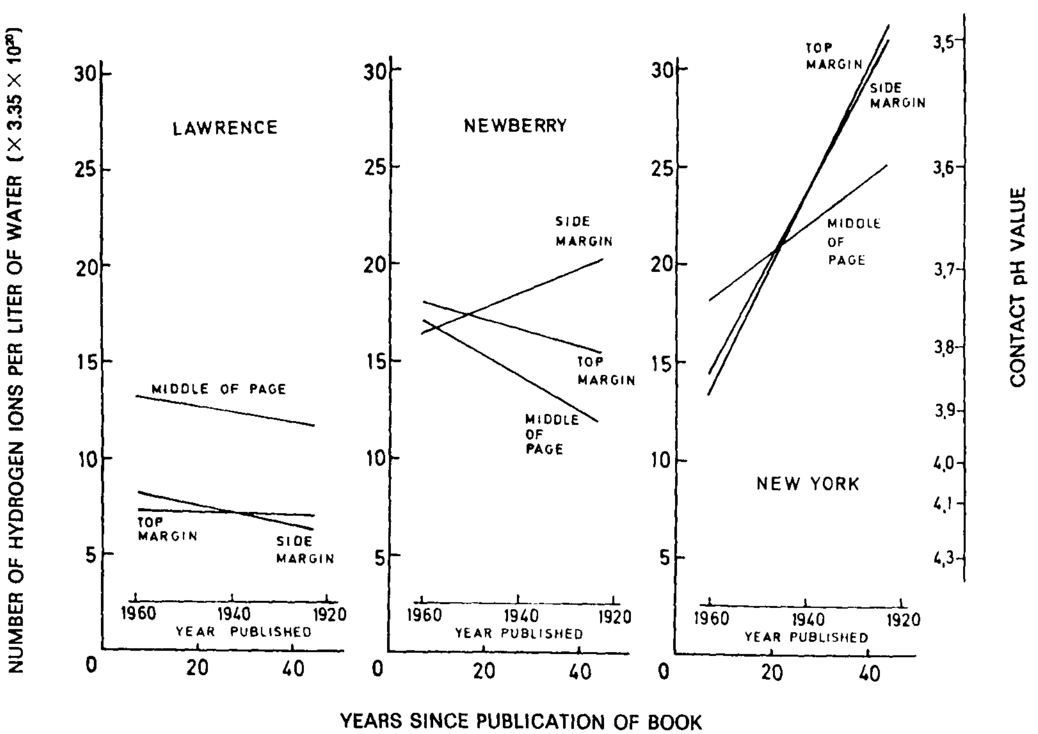


FIG. 8. Center page 12 sec. contact pH regression lines arranged by library.

The higher pH data for the margins of leaves from books in the Lawrence University Library can be compared with results reported by the Barrow Research Laboratory[3] for the leaves of books discarded from libraries in the Richmond, Virginia, area. The Barrow Research Laboratory investigated the paper in 500 books published between 1800 and 1899 and reported TAPPI cold water extraction data for the printed and unprinted portions of the leaves. One hundred and two books had a higher pH in the printed portions than in the unprinted portions, 95 books had an equal pH value for both printed and unprinted portions, and 303 books had a higher pH in the unprinted than in the printed portions. Presumably, the printed leaves averaged more acidic in three out of five books because the ink medium (linseed oil?) degraded to form acidic oxidation products. The regression lines of Figures 8 and 9, therefore, suggest that the conclusions based upon investigations of books discarded from libraries in the Richmond, Virginia, area are probably not an appropriate guide for most research libraries because research libraries are located frequently in badly polluted

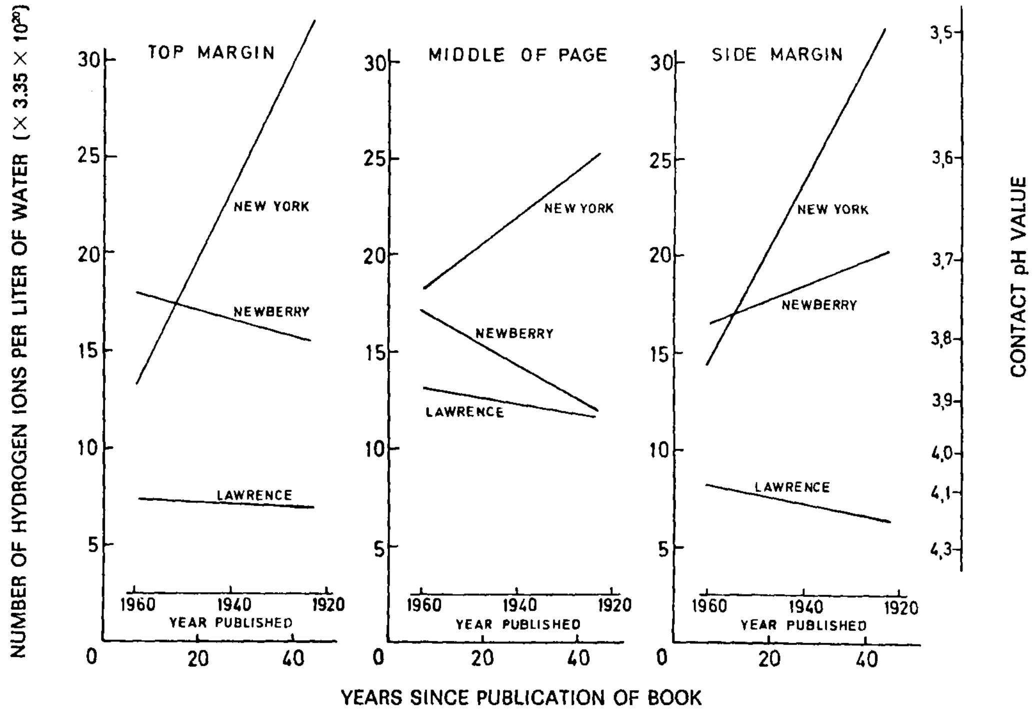


FIG. 9. Center page 12 sec. contact pH regression lines arranged by test location.

metropolitan areas such as Chicago and New York. The air pollution in these urban areas differs radically from the air pollution in places like Appleton and Richmond.

In summary, although the differences in acidity between the three libraries are affected by ink degradation products, these differences in acidity are determined primarily by the effects of atmospheric pollution. Experimental data[24] indicate that acidic gases like NO_2 and SO_2 are taken up by paper from polluted air and these gases permeate into the innermost parts of books. The differences in pH value observed between the Lawrence Library and The Newberry and The New York Public Library books parallel the differences reported by Hudson[13] for the paper in seventeenth and eighteenth century books from the Chatsworth and Portico Libraries in England. The paper in many rare and unique records, such as incunabula, held in the collections of urban American libraries has probably become so acidic that these records now have a very much shorter life expectancy than history.

This sample of 21 books is probably biased in favor of high pH values for the books in The Newberry Library. In other words, Figures 4–9 naturally contain a conservative factor. It is not known whether these twenty-one books faithfully represent the total collections of the Lawrence University Library and The Research Libraries of The New York Public Library, but presumably this sample represents a very substantial proportion of the holdings of these libraries. The high level of acidity in the holdings of the Lawrence University Library indicates that the paper in the University's books has deteriorated greatly. The paper in the books of The Newberry Library may be approaching a state of crisis and the data from the original larger study may speak to this question. The exceedingly high level of acidity in the paper of the books in The Research Libraries of The New York Public Library is almost unbelievable, particularly since most of these books can still be used with appropriate care.

3.5 M. I. T. Folding Endurance

The M. I. T. folding endurance data given in Table 12 are interpreted by Figures 10–14 and Table 16. The M. I. T. folding endurance data for Titles 1, 6, 23, 24, and 25 were excluded from the analysis because of incomplete, non-comparable, or outlying (time) data. In addition, no first and third pages were sampled in Title 15.

Before considering Figures 10–14, it is desirable to review the equation by which a paper is said to loose folding endurance on aging:

$$\text{Log } Y_i = \overline{\log y} - b\,(x_i - \bar{x}), \tag{10}$$

where »Log Y_i« is the logarithm of the folding endurance to be estimated, »$\overline{\log y}$« is the mean of the logarithms of the M. I. T. folding endurance experimental data, »b« is the slope of the regression line, x_i is the aging time when the »log y_i« were measured, and »$\bar{x}$« is the mean of the aging times x_i. The regression line equation is one method by which the folding endurance data from accelerated aging studies are analyzed. This equation is used conventionally to obtain straight lines by graphing the logarithm of folding endurance against time of aging. A variation of the usual graph offers an insight into the deterioration of paper in libraries. The regression equation is computed as usual, but folding endurance (the antilogarithm, not the logarithm of folding endurance) is plotted against time. Such a graph forcefully demonstrates the greatest loss in folding endurance occurs in relatively new, strong paper and shows that the rate of folding endurance loss decreases with the increase of aging time. Hence, the optimum time to preserve books occurs when the books are new and strong.

The regression lines in Figures 10–14 were obtained according to Brownlee[5] (pp. 338–42) and the pertinent equations, given in Appendix 4, have the exponential characteristics described above. Figure 10 interprets the M. I. T. folding endurance data for the tail margin specimens (machine direction of paper) for the first, center, and third pages regressed on the number of years since the book was published. The greatest loss in folding endurance occurred in the paper from The New York Public Library books. An intermediate loss took place in the Lawrence University Library books and the least loss was found in The Newberry Library books. The parallel and close relationship between the three libraries indicate the loss of folding endurance follows a similar path in each library.

The nature of the differences in folding endurance, demonstrated by Figure 10, reflects the storage history of these papers. The test specimens purposely were not treated by a humidity cycle to reduce any residual dried-in strains or to equalize the moisture content in the paper. A humidity cycle of 95 %, 11 %, and 50 % relative humidity for 24 hours respectively can change folding endurance by as much as 50 %. Such a cycle could have reversed the relationship between the Lawrence University and The Newberry Libraries and might have explained the apparent contradiction of acidity levels. The specimens were not humidity cycled because this study was interested in the differences which existed between paper in the three libraries and not in the possibilities for improvement of folding endurance through air-conditioning.

Storage temperature also could have caused the differences between the paper in the books of the two libraries. An average higher temperature of only one or two degrees could account for the lower folding endurance of the paper in books from Lawrence University Library compared with the folding endurance of the paper from books of The Newberry Library[24] (pp. 181–87).

Figure 11 interprets the M. I. T. folding endurance data for the side margin (cross machine direction of paper) specimens regressed on the number of years since the book was published. Folding endurance decreases more slowly in the cross machine direction where the fibers are in compression than in the machine direction where the fibers are dried in tension. The increased acidity in the side margins of the leaves from The New York Public Library books may explain the disparity between the folding endurance of the paper in The New York Public Library books and the

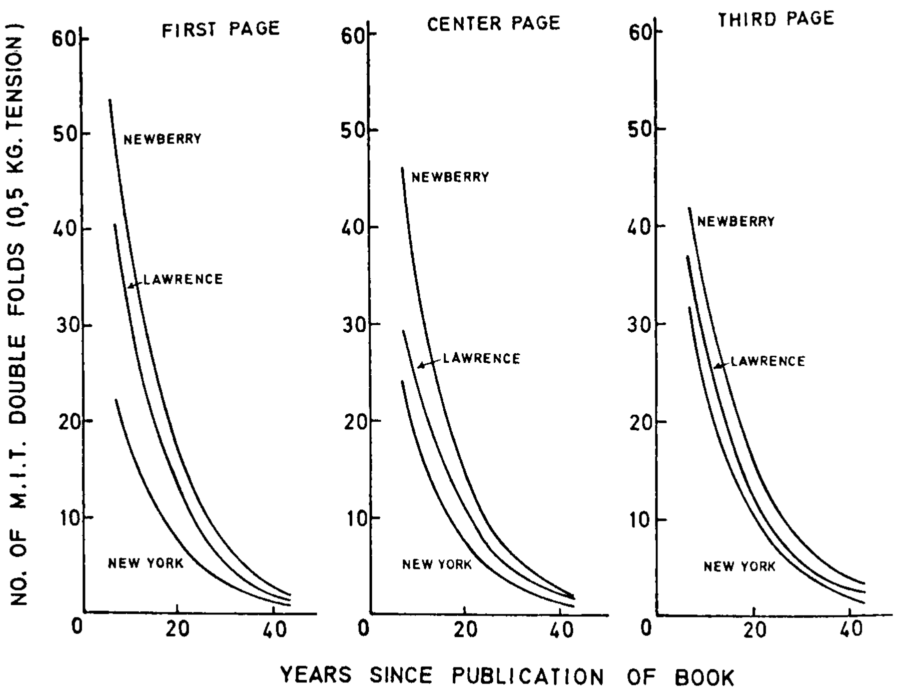


FIG. 10. Tail margin folding endurance regression lines arranged by page tested.

paper in the books from the Lawrence University and The Newberry Libraries. The similarity in folding endurance suggests that the acidity levels in the tail margins of the books from the Lawrence and Newberry Libraries are more alike than the acidity levels in their side margins, but this is only a possibility because contact pH measurements were not made in the tail margins.

Figures 12, 13, and 14 contrast the M. I. T. folding endurance data by page and library for the first, center, and third pages. The pattern of relationship appears to be consistent between the pages and the libraries. The tail margin samples on the average were stronger originally, deteriorated more rapidly, and are now weaker than the side margin samples in the older books.

The regression line equations for Figures 10–14 are given in Appendix 4. Since these equations have characteristics of a first-order reaction rate equation, their slope »b« can be used to approximate the logarithmic folding endurance half-life »$t_{\frac{1}{2}}$« of paper in each of the libraries. This technique is the method used when studying radio-active decay. The under-

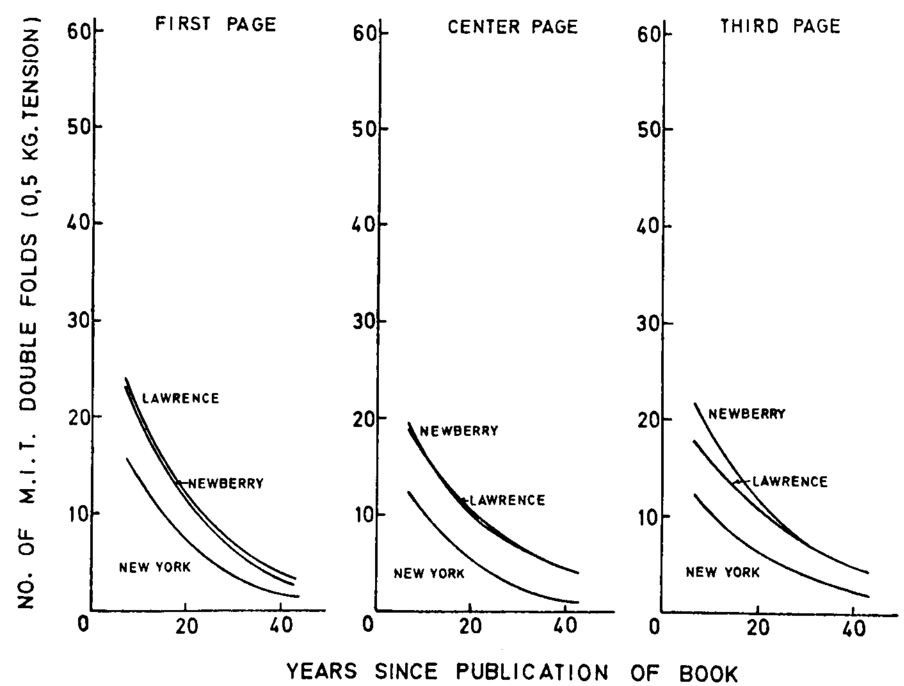


FIG. 11. Side margin folding endurance regression lines arranged by page tested.

lying theory is available in chemistry or physics textbook discussions of chemical kinetics. The first approximations of paper half-life given in Table 16 were computed by dividing the slope of the regression lines according to the equation:

$$t_{\frac{1}{2}} = -\frac{0.301}{b} \tag{11}$$

The half-life summation of Table 16 is valuable as an expression of the past but it must be used with caution when considering the future. The air-conditioning practices of the Lawrence University and The Newberry Libraries presumably have reduced the rates of folding endurance loss and probably will provide an even greater benefit in the future. The number of books studied in this investigation was small and neither the book selection nor the experimental procedures were designed to support rigorous predictions based on a variable like M. I. T. folding endurance. The exponential process of paper deterioration has proceeded so far that there is less difference between the properties of paper from books in the three libraries than had been anticipated. The similarities in rates of deterioration are

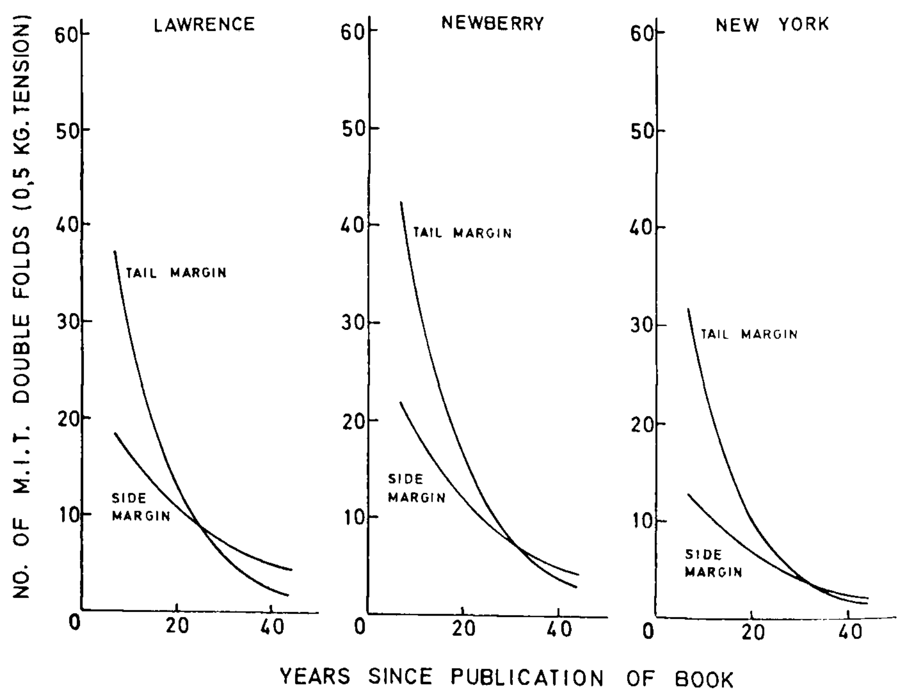


FIG. 12. First page M.I.T. folding endurance regression lines arranged by library.

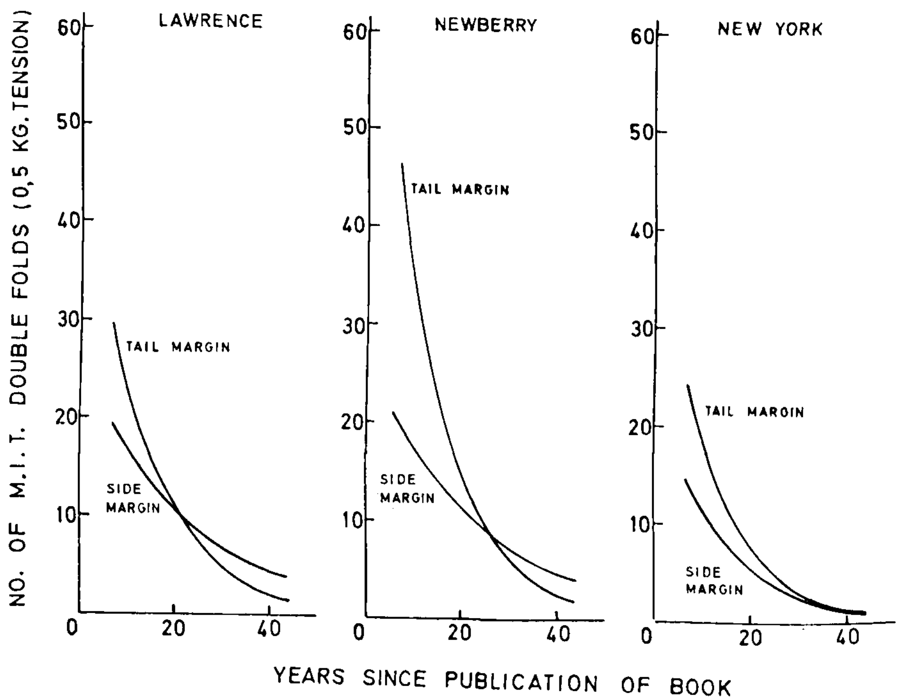


FIG. 13. Center page M.I.T. folding endurance regression lines arranged by Library.

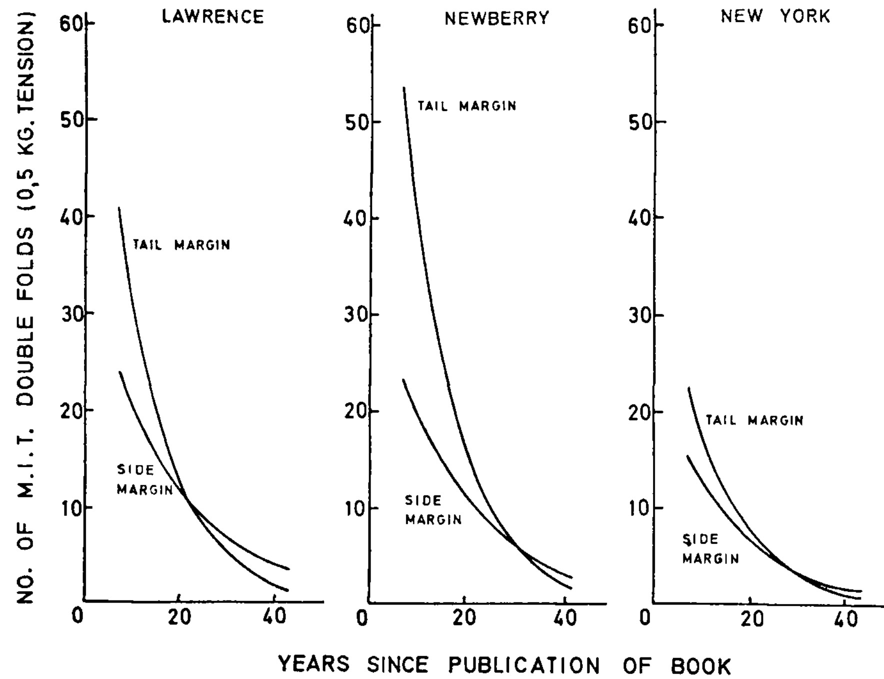


FIG. 14. Third page M.I.T. folding endurance regression lines arranged by library.

A

2:885m), N69

Table 16: M. I. T. folding endurance half-life in years

N72-2

Test location and page	M. I. T. folding endurance half-life in years		
	Lawrence	Newberry	New York
Tail margin			
First page	7.67	7.74	8.15
Center page	8.70	7.88	7.77
Third page	8.47	9.46	7.85
Average	8.28	8.36	7.92
Side margin			
First page	13.0	12.4	10.6
Center page	15.7	15.6	9.3
Third page	17.7	15.8	13.3
Average	15.5	14.6	11.1
Overall average	11.9	11.5	9.5

shown by the half-life values of Table 16. The half-life data for the tail margins are particularly ominous because the machine direction properties are a more sensitive barometer of paper condition than are the properties in the cross machine direction. The tail margin interpretations of Figures 10–14 and Table 16 indicate that although the differences in folding endurance are both real and significant, these differences are barely measurable when they are contrasted with the original properties of the paper. Figures 10–14 and Table 15 show that 1) the best time to preserve books is when they are new and strong and 2) the collections in Lawrence University and The Newberry Libraries will be in the same condition as the collections of The New York Public Library within a relatively short period of time.

3.6 Sonic Dynamic Modulus of Elasticity

The (sonic velocity)^2 data given in Table 13 are interpreted by Figure 15 as regression lines of the V^2 values on the age of paper. The relationship of the (sonic velocity)^2 lines between libraries follows the pattern of the hydrogen ion content lines rather than the pattern of the folding endurance lines. The test data for titles 1, 6, 10, 18, 23, 24, and 25 were excluded from the analysis because the data were incomplete or different leaves were tested in the copies of these titles.

The negative slope of the lines of Figure 15 suggests that the paper in the older books of the Lawrence University and The Newberry Libraries may have slightly less inter-fiber contact than the paper in more recent books. The positive slope for paper in The New York Public Library books implies that older papers may have more inter-fiber contact. The higher C^2 values and the more acidic condition of the paper in The Newberry Library books suggest this paper should be more deteriorated than the paper in the books of the Lawrence University Library. However, this expectation is not supported by the folding endurance data. The paper in The Newberry Library books was found to have better folding endurance than the paper in books of the other libraries. This anomaly could have been caused by variation in the moisture content of the paper. It was undesirable to put the books through a humidity cycle to insure equivalent moisture content prior to testing. In addition, the sonic dynamic modulus of elasticity measures a quite different magnitude of stress-strain relationship than do folding endurance or tensile strength tests. No body of experience exists with which to evaluate the effect of paper deterioration

on sonic modulus. For these reasons, the meaning of Figure 15 remains unclear. Consequently, the usefulness of a sonic modulus of elasticity test for studying the deterioration of paper in libraries remains to be demonstrated.

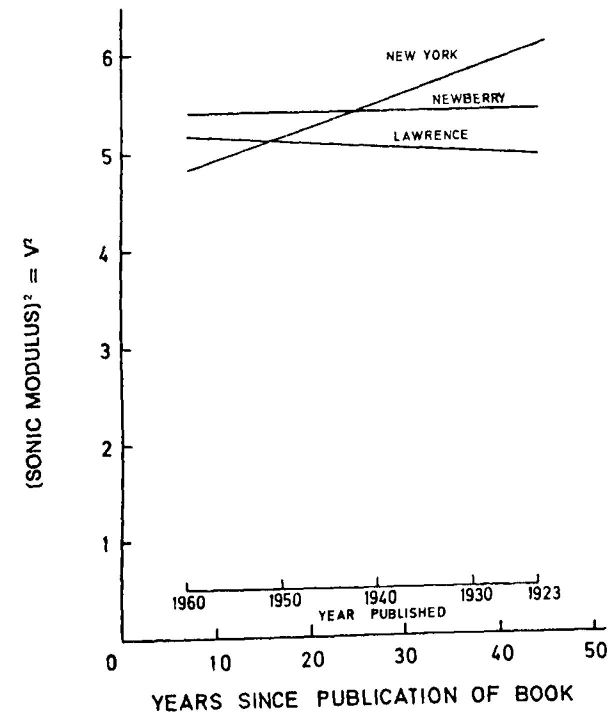


FIG. 15. (Sonic velocity)^2 regression lines.

Chapter 4

Conclusions and Summary

This study attempted to determine why 50% of the contact pH values for the paper in a group of books from The Newberry Library were below 4.0 and what effect these very acidic pH values have on the permanence of these books. The background and methodology of the tests used in the study were reviewed. Contact pH measurements were found to estimate the true pH of paper in libraries just as accurately as the TAPPI cold extraction procedure estimated true pH values for the same paper. No reason was established to suspect that the contact pH values would be consistently higher or lower than the pH values obtained by cold extraction procedures.

21 books from The Newberry Library, Chicago, Illinois, were compared with identical copies from the collections of the Lawrence University Library, Appleton, Wisconsin, and The Research Libraries of The New York Public Library. The paper in books from The Research Libraries of The New York Public Library was found to be most acidic, the paper in The Newberry Library books intermediately acidic, and the paper in the Lawrence University Library books least acidic. The margins of the leaves in books from The Research Libraries of The New York Public Library and The Newberry Library were more acidic than the centers of the same leaves; but in the books from Lawrence University Library, the centers of the leaves were more acidic than the margins of the same leaves. The differences in the acidity level of the books in the three libraries were determined primarily by the effects of atmospheric pollution in Chicago and New York. The degradation products of ink mediums such as linseed oil produced a significant but less substantial increase in acidity than airpollutants.

The more acidic pH values for the leaves of books from The Newberry and The New York Public Libraries indicate that estimates of pH values based upon investigations of books discarded from libraries in the Richmond, Va. area are not reliable guidelines for many research libraries. Most research libraries are located in badly polluted metropolitan areas such as Chicago and New York City. The degree of air pollution in these urban areas is much more severe than the degree of air pollution in places like Appleton.

The pH values for the margins of the leaves in most of the books from the Lawrence University Library suggest that the paper in these books was manufactured under acidic conditions and would deteriorate rapidly on aging. This implication is supported by the M.I.T. folding endurance strength which deteriorates rapidly at first and then more slowly with increasingly older books. The margins of the leaves in books from Lawrence University probably have greater folding endurance than the paper at the center of the leaves because the center of the leaves is more acidic due to ink degradation products.

The M. I. T. folding endurance results for The Newberry Library books were not in accord with the findings on acidity. The paper in the books from The Newberry Library had greater folding endurance, but this paper was more acidic than the paper from books of the Lawrence University Library. An explanation for this anomaly was not established, possibly because detailed information about the storage history of the books studied was not available. It was noted, however, that a small difference in storage temperature, moisture content, or residual strains from manufacturing could account for this difference and that the bindings of books from The Newberry and The New York Public Libraries had deteriorated far more than the bindings of books from the Lawrence University Library.

The acidity in the paper from books of The Research Libraries of The New York Public Library in New York City had reached an almost unbelievable level, particularly since these books came from a very heavily used collection. The physical condition of this collection is critical and both air-conditioning and remedial steps appear to be urgent if the collection is to be maintained for use in the future.

The M. I. T. folding endurance data was summarized as exponential curves to demonstrate that 1) the paper deteriorated in parallel patterns in each library, 2) the books from The Newberry and the Lawrence University Libraries will soon reach the same condition as the books from The Research Libraries of The New York Public Libraries in New York City, and 3) the optimum time to treat unstable library books for preservation is when the books are relatively new and strong. The similarity of the deterioration curves suggests also that heavier use by patrons in The New York Public Library does not significantly affect the rate at which the collections of The Research Libraries are deteriorating.

The average M. I. T. folding endurance half-life of the paper tested was 11.9, 11.5, and 9.4 years respectively for books from the Lawrence University, The Newberry, and The New York Public Libraries. These half-life figures are not comforting to the librarian who has assumed that his collection is not directly involved with major deterioration problems and that conventional preservation practices are adequate for his library. Radical changes in library practices appear to be essential for every library.

Appendices

APPENDIX 1: Books Tested arranged by Increasing Age

*1. Hanson, Lawrence & Elizabeth Hanson: *Prokofiev: A biography in three movements.* New York: Random House, 1964.
2. Nest'ev, Izrail' Vladimirovick: *Prokofiev.* Stanford, Calif.: Stanford University Press, 1960.
3. Conkin, Paul K.: *Tomorrow a new world: The New Deal community program.* Ithaca, N. Y.: Published for the American Historical Society by Cornell University Press, 1959.
4. Chapman, Hester W.: *The last Tudor king: A study of Henry VI.* London: Jonathan Cape, 1958.
5. Rossiter, Clinton Lawrence: *Seedtime of the Republic; The origin of the American tradition of political liberty.* New York: Harcourt, Brace and Company, 1953.
*6. Fowlie, Wallace: *Mallarmé.* Chicago: University of Chicago Press, 1953.
7. Roberts, Owen Josephus: *The Court and the Constitution.* The Oliver Wendell Holmes Lectures, 1951. Cambridge, Mass.: Harward University Press, 1951.
8. Weinstock, Herbert: *Chopin: The man and his music.* New York: Alfred A. Knopf, 1949.
9. Marek, George Richard: *Puccini, a biography.* New York: Simon and Schuster, 1951.
10. Smith, Herbert Maynard: *Henry VIII and the Reformation.* London: Macmillan, 1948.
11. Nest'ev, Izrail' Vladimirovich: *Sergei Prokofiev, his musical life.* New York: Alfred A. Knopf, 1946.
12. U. S. War Industries Board. *American industry in the war: A report of the War Industries Board.* By Bernard M. Baruch, Chairman. New York: Prentice-Hall, Inc., 1941.
13. Read, Conyers, (ed.): *The Constitution reconsidered.* New York: Columbia University Press, 1938.
14. Howells, William Dean: *Life of Abraham Lincoln.* Springfield, Ill.: Abraham Lincoln Association, 1938.
15. Wallace, Henry Agard: *America must choose...* World Affairs Pamphlet No. 3. New York: Foreign Policy Association, Boston: World Peace Foundation, 1934.
16. Pickthorn, Kenneth William Murray: *Early Tudor government: Henry VIII.* Cambridge, Eng.: The University Press, 1934.
17. Hertz, Emanuel: *Abraham Lincoln, a new portrait. Vol. I.* New York: Horace Liveright, Inc. 1931.
18. Hertz, Emanuel: *Abraham Lincoln, a new portrait. Vol. II.* New York: Horace Liveright, Inc., 1931.
19. Puccini, Giacomo. *Letters of Giacomo Puccini...* Edited by Giuseppe Adami. Philadelphia: J. B. Lippincott Company, 1931.

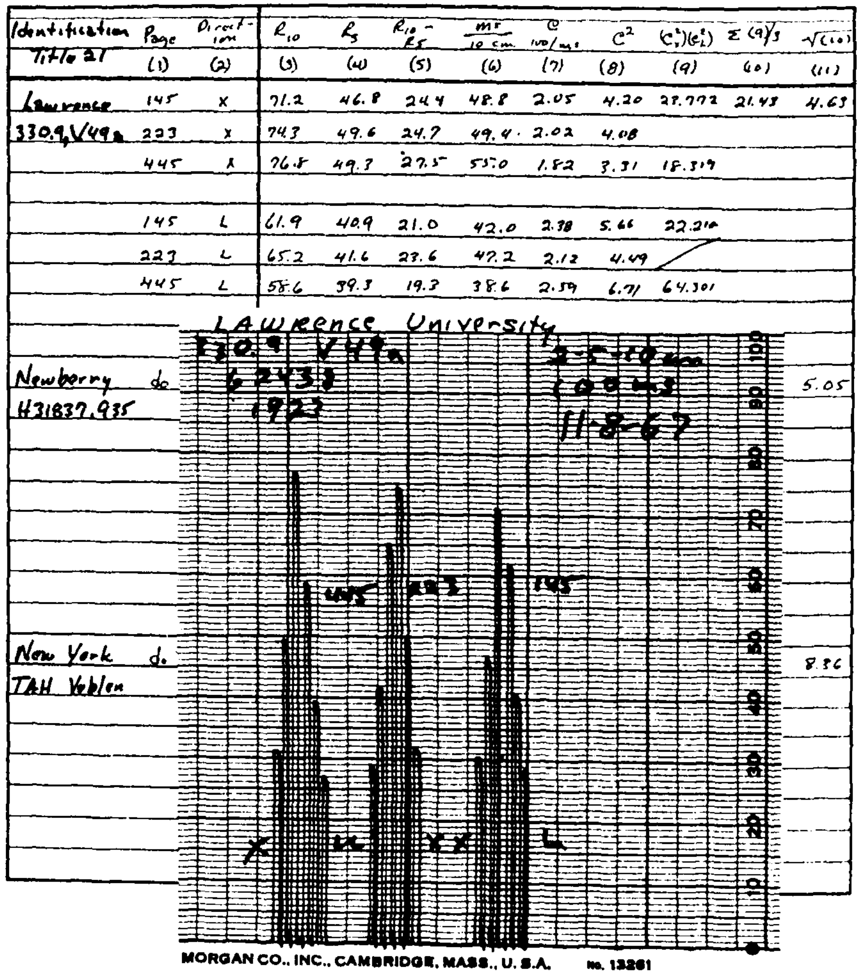
* Not available in this edition from The Research Libraries of The New York Public Library.

20. Van Hise, Charles Richard: *Conservation of our natural resources. Based on Van Hise's The Conservation of Natural Resources in the United States*, by Loomis Havemeyer, editor, et al. New York: The Macmillan Company, 1930.
21. Randall, James Garfield: *Constitutional problems under Lincoln*. New York: D. Appleton & Co., 1926.
22. Veblen, Thorstein: *Absentee ownership and business enterprise in present times: The case of America*. New York: B. W. Huebsch, Inc., 1923.
*23. Veblen, Thorstein: *The engineers and the price system*. New York: B. W. Huebsch, Inc., 1921.
24. Dry, Wakeling: *Giacomo Puccini*. New York: J. Lane Co., 1906.
*25. Montaigne, Michel Eyquem de: *...Montaigne, the Education of Children*. Selected, translated and annotated by L. E. Rector. New York: D. Appleton and Co., 1899.

* Not available in this edition from The Research Libraries of The New York Public Library.

APPENDIX 2: (Sonic velocity)² data for individual specimens and sample computation

Title no.	Year published	Years since publication	First page						Center page						Third page					
			Cross direction			Machine direction			Cross direction			Machine direction			Cross direction			Machine direction		
			L	N	Y	L	N	Y	L	N	Y	L	N	Y	L	N	Y	L	N	Y
1	1964	–	3.06	3.84	–	9.18	8.64	–	4.41	4.00	–	8.47	10.30	–	3.13	4.24	–	8.35	9.80	–
2	1960	7	3.92	3.96	3.69	9.99	9.30	10.56	3.20	3.65	4.08	7.90	10.69	9.80	3.69	4.33	3.42	8.64	10.11	7.95
3	1959	8	3.10	4.58	3.50	5.34	7.95	8.07	3.20	3.31	3.53	8.64	7.95	7.40	3.76	3.80	3.35	9.06	7.56	8.47
4	1958	9	4.28	4.20	3.96	9.86	7.02	7.90	7.72	4.49	3.69	2.89	6.76	7.40	8.07	7.90	7.08	4.04	3.61	4.28
5	1953	14	2.50	2.79	2.22	6.05	5.95	7.08	2.96	3.06	2.46	5.76	6.25	5.29	2.46	2.50	2.40	5.02	5.95	5.95
6	1953	–	4.12	7.08	–	6.50	8.76	–	3.69	7.40	–	5.57	11.09	–	2.46	3.31	–	6.71	7.90	–
7	1951	16	3.72	4.00	4.16	6.66	6.25	5.66	3.57	3.92	7.84	5.71	7.13	6.25	3.57	3.76	3.65	7.08	6.40	7.08
8	1951	16	4.33	3.28	3.20	8.35	8.88	7.90	3.28	3.50	3.31	9.99	8.76	9.18	3.92	4.33	3.50	9.43	9.30	8.76
9	1949	18	2.92	2.96	3.20	7.78	7.73	7.95	2.50	3.13	3.24	7.13	8.35	6.45	2.59	2.56	3.20	7.90	6.76	7.02
10	1948	19	7.95	7.73	8.80	4.28	8.84	3.57	3.57	4.28	4.71	8.64	8.47	9.30	4.80	7.29	5.86	7.95	3.80	8.76
11	1946	21	2.40	2.96	2.62	6.05	7.90	8.76	3.28	3.13	3.50	8.18	10.30	7.40	3.24	3.39	3.42	8.35	9.55	8.18
12	1941	26	2.82	3.80	3.13	7.62	6.86	7.62	3.13	4.00	3.42	7.62	7.90	5.66	3.17	3.46	3.42	7.73	9.80	7.08
13	1938	29	3.20	3.17	3.10	6.55	6.76	7.08	3.39	3.39	3.53	7.13	7.29	7.45	2.69	3.39	3.03	7.78	7.90	6.76
14	1938	29	4.54	5.57	3.92	6.92	9.06	8.47	5.06	5.20	4.54	7.08	7.08	7.24	4.45	5.20	4.49	7.08	7.73	6.92
15	1934	33	–	–	–	–	–	–	6.25	2.96	13.91	2.59	8.24	2.92	–	–	–	–	–	–
16	1934	33	7.78	9.06	4.54	4.33	4.67	8.35	9.06	9.80	5.15	4.33	4.37	7.56	8.88	7.08	8.88	4.12	4.16	4.49
17	1931	36	4.75	4.80	4.00	7.90	6.71	7.08	4.71	4.80	4.04	7.90	7.08	7.45	3.84	5.15	3.57	7.90	7.90	7.45
18	1931	36	5.15	4.24	4.12	7.62	6.76	6.92	4.80	4.37	5.11	6.40	6.55	7.90	4.67	3.50	4.33	7.73	7.08	7.24
19	1931	36	3.50	3.57	3.96	7.24	5.71	6.92	3.42	3.39	4.12	6.76	6.20	7.29	3.53	3.92	3.92	5.86	7.45	5.66
20	1930	37	3.96	4.33	4.80	7.02	8.64	8.94	3.65	3.69	3.69	7.08	4.78	6.86	3.42	3.92	3.92	7.56	7.13	7.45
21	1926	41	3.72	4.33	3.96	7.56	7.08	8.18	3.03	3.57	3.24	5.57	7.08	5.02	3.76	3.84	3.50	7.13	7.73	6.25
22	1923	44	4.20	4.67	11.90	5.66	6.92	5.06	4.08	3.61	12.04	4.49	5.90	5.15	3.31	3.88	14.82	6.71	5.90	5.90
23	1921	–	4.08	5.15	–	7.29	5.95	–	3.13	4.75	–	7.18	8.18	–	4.88	3.80	–	8.18	7.34	–
24	1906	–	2.79	3.50	1.69	4.16	6.30	12.53	5.50	4.00	2.04	4.93	6.30	8.64	2.96	3.34	2.10	5.86	4.16	13.69
25	1899	–	5.76	5.20	–	2.59	3.03	–	4.71	5.10	–	2.16	2.52	–	4.67	6.25	–	2.22	2.76	–



V^2 sample computation and instrument graph.

The notation used in this example computation differs from the notation used in the text. (Sonic velocity)² is represented by »C²« instead of by »V²«. The average transit time in microseconds for the sonic pulse to travel over a 10 cm span is given by »2(R_{10}–R_5)«. The direction of the paper in which transit time was measured is represented by »x« and »l« for cross (width of leaf) and machine (length of leaf) directions respectively. The »Identification Title 21« in this example computation is numbered »21« instead of »22« because the sequence of the title numbers was changed in the process of preparing the work for publication.

APPENDIX 3: HYDROGEN ION REGRESSION LINE DATA

DATA FOR FIGURES 4–9: Hydrogen ion content regression line equations and average ($\bar{y}$) and intercept (y) values of hydrogen ion content.

	Test location and time	Regression line equation $\hat{Y}_i$ =	Values of $\hat{Y}$: x = 1960, y =	Values of $\hat{Y}$: x = 1923, y =
LAWRENCE	First page			
	Middle 12 sec.	12.62 — 0.04978 x_i	12.27	10.43
	Center page			
	Middle 12 sec.	13.41 — 0.04058 x_i	13.13	11.63
	Middle 30 sec.	14.91 — 0.07314 x_i	14.39	11.69
	Middle 60 sec.	15.69 — 0.08629 x_i	15.09	11.89
	Top 12 sec.	7.40 — 0.01050 x_i	7.33	6.94
	Side 12 sec.	8.51 — 0.04821 x_i	8.18	6.39
	Third page			
	Middle 12 sec.	14.76 — 0.14403 x_i	13.76	8.43
NEWBERRY	First page			
	Middle 12 sec.	14.01 — 0.06535 x_i	13.55	11.14
	Center page			
	Middle 12 sec.	14.58 — 0.13613 x_i	17.06	12.03
	Middle 30 sec.	18.12 — 0.13038 x_i	17.20	12.38
	Middle 60 sec.	17.45 — 0.11141 x_i	16.67	12.55
	Top 12 sec.	18.39 — 0.06552 x_i	17.93	15.51
	Side 12 sec.	15.76 + 0.09744 x_i	16.44	20.04
	Third page			
	Middle 12 sec.	15.03 — 0.16009 x_i	13.91	7.99
NEW YORK	First page			
	Middle 12 sec.	21.70 — 0.08168 x_i	21.13	18.11
	Center page			
	Middle 12 sec.	16.88 + 0.18772 x_i	18.19	25.14
	Middle 30 sec.	12.69 + 0.14911 x_i	13.73	19.25
	Middle 60 sec.	11.59 + 0.11934 x_i	12.42	16.84
	Top 12 sec.	9.77 + 0.50900 x_i	13.33	32.16
	Side 12 sec.	11.08 + 0.46524 x_i	14.33	31.55
	Third page			
	Middle 12 sec.	16.27 — 0.01215 x_i	16.18	15.73

Notes: $\hat{Y}_i$ is the hydrogen ion content value ($\times$ 3.35 $\times$ 10^{20}) to be estimated. x_i is the age of the paper in years since publication to 1968 when the pH measurements were made. x are the years, 1923 or 1960, for which values of y, the estimated hydrogen ion content values, are given.

Data for Figures 4 & 5: *Number of hydrogen ions per liter of water* (× 3.35 × 10^{20}) for the »Contact pH values for the Middle of the Center Page« (Refer to Table 8, page 23).

Title no.	Year published	Page no.	Lawrence			Newberry			New York			Years since publication
			12 sec.	30 sec.	60 sec.	12 sec.	30 sec.	60 sec.	12 sec.	30 sec.	60 sec.	
1	1964	181	–	–	–	–	–	–	–	–	–	–
2	1960	265	0.05	0.04	0.04	0.04	0.04	0.03	0.06	0.04	0.03	7
3	1959	175	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	8
4	1958	150	12.60	14.10	14.10	14.10	12.60	12.60	14.10	10.00	7.94	9
5	1953	275	15.80	22.40	25.10	31.60	31.60	28.20	44.60	31.60	28.20	14
6	1953	149	–	–	–	–	–	–	–	–	–	–
7	1951	50	6.31	6.31	6.31	11.20	10.00	10.00	10.00	8.91	7.94	16
8	1951	200	50.10	50.10	50.10	50.10	56.20	56.20	79.40	56.20	50.10	16
9	1949	166	0.18	0.32	0.36	0.45	0.45	0.40	1.78	1.41	1.12	18
10	1948	215	19.90	17.80	17.80	28.20	25.10	25.10	15.80	17.80	19.90	19
11	1946	100	11.20	12.60	12.60	10.00	11.20	12.60	15.80	12.60	12.60	21
12	1941	250	17.80	19.90	22.40	15.80	17.80	17.80	15.80	14.10	12.60	26
13	1938	210	25.10	28.20	31.60	31.60	31.60	28.20	63.10	39.80	31.60	29
14	1938	45	12.60	14.10	15.80	15.80	15.80	15.80	22.40	17.80	12.60	29
15	1934	15	15.80	15.80	15.80	25.10	25.10	25.10	17.80	17.80	19.90	33
16	1934	280	1.78	2.24	2.51	3.16	3.55	3.98	5.62	5.01	3.55	33
17	1931	247	3.98	5.01	6.31	3.55	5.01	6.31	6.31	5.62	5.62	36
18	1931	750	11.20	7.08	5.01	7.94	7.08	6.31	10.00	7.94	7.94	36
19	1931	165	25.10	25.10	25.10	25.10	25.10	25.10	35.50	31.60	25.10	36
20	1930	275	5.01	6.31	6.31	4.66	4.46	4.46	22.40	14.10	12.60	37
21	1926	285	5.01	5.62	5.62	7.94	7.08	6.31	12.60	8.91	7.94	41
22	1923	223	7.94	7.94	7.08	5.01	6.31	7.94	39.80	28.20	25.10	44
23	1921	85	–	–	–	–	–	–	–	–	–	–
24	1906	57	–	–	–	–	–	–	–	–	–	–
25	1899	95	–	–	–	–	–	–	–	–	–	–

Data for Figures 6 & 7: *Number of hydrogen ions per liter of water* (× 3.35 × 10^{20}) for the »Contact pH values for the Middle of the First and Third Pages« (Refer to Table 10, page 25).

Title no.	Year published	First page				Third page				Years since publication
		Page no.	L	N	Y	Page no.	L	N	Y	
1	1964	121	–	–	–	365	–	–	–	–
2	1960	188	0.03	0.03	0.06	525	0.04	0.05	0.07	7
3	1959	117	0.07	0.06	0.10	349	0.08	0.06	0.14	8
4	1958	100	17.80	15.80	19.90	280	17.80	12.60	19.90	9
5	1953	180	19.90	19.90	39.80	550	19.90	22.40	14.10	14
6	1953	100	–	–	–	299	–	–	–	–
7	1951	33	1.12	11.20	5.62	100	5.01	5.01	7.94	16
8	1951	133	31.60	35.50	63.10	400	39.80	50.10	63.10	16
9	1949	111	1.41	0.79	25.10	333	1.26	1.58	3.16	18
10	1948	140	19.90	22.40	17.80	420	28.20	19.90	15.80	19
11	1946	66	8.91	10.00	19.90	190	10.00	12.60	17.80	21
12	1941	166	15.80	14.10	15.80	495	11.20	11.20	15.80	26
13	1938	141	25.10	39.80	35.50	420	22.40	25.10	44.60	29
14	1938	31	19.90	15.80	44.60	91	12.60	10.00	28.20	29
15	1934	–	–	–	–	–	–	–	–	–
16	1934	180	2.51	2.51	7.08	550	2.51	2.51	3.55	33
17	1931	161	0.79	1.26	3.55	493	6.31	6.31	8.91	36
18	1931	665	12.60	8.91	11.20	1006	11.20	8.91	7.94	36
19	1931	110	14.10	15.80	19.90	320	8.91	8.91	15.80	36
20	1930	187	2.51	7.94	12.60	551	6.31	2.51	11.20	37
21	1926	190	6.31	6.31	14.10	570	5.01	6.31	14.10	41
22	1923	145	15.80	7.08	17.80	445	3.55	3.55	11.20	44
23	1921	56	–	–	–	169	–	–	–	–
24	1906	34	–	–	–	110	–	–	–	–
25	1899	63	–	–	–	189	–	–	–	–

DATA FOR FIGURES 8 & 9: *Number of hydrogen ions per liter of water* ($\times 3.35 \times 10^{20}$) for the »Contact pH values for the Margins of the Center page« (Refer to Table 9, page 24).

Title no.	Year pub-lished	Page no.	Top margin			Side margin			Years since pub-lication
			L	N	Y	L	N	Y	
1	1964	181	–	–	–	–	–	–	–
2	1960	265	0.02	0.04	0.07	0.03	0.02	0.08	7
3	1959	175	0.02	0.02	0.09	0.02	0.03	0.08	8
4	1958	150	8.91	14.10	15.80	8.91	14.10	17.80	9
5	1953	275	11.20	22.40	22.40	14.10	31.60	39.80	14
6	1953	149	–	–	–	–	–	–	–
7	1951	50	6.31	8.91	11.20	5.62	10.00	14.10	16
8	1951	200	31.60	44.60	50.10	22.40	39.80	50.10	16
9	1949	166	0.71	1.12	5.62	0.45	0.71	5.01	18
10	1948	215	12.60	44.60	15.80	14.10	44.60	17.80	19
11	1946	100	10.00	19.90	15.80	10.00	11.20	17.80	21
12	1941	250	14.10	28.20	31.60	12.60	25.10	31.60	26
13	1938	210	17.80	50.10	50.10	5.01	35.50	35.50	29
14	1938	45	6.31	12.60	35.50	3.55	25.10	19.90	29
15	1934	15	6.31	11.20	35.50	14.10	28.20	31.60	33
16	1934	280	2.24	12.60	28.20	2.51	10.00	25.10	33
17	1931	247	1.26	10.00	25.10	2.24	10.00	14.10	36
18	1931	750	5.01	14.10	25.10	4.46	11.20	12.60	36
19	1931	165	6.31	17.80	19.90	11.20	22.40	22.40	36
20	1930	275	3.55	7.94	15.80	3.16	19.90	35.50	37
21	1926	285	3.55	6.31	25.10	5.01	12.60	22.40	41
22	1923	223	5.62	7.94	25.10	6.31	12.60	44.60	44
23	1921	85	–	–	–	–	–	–	–
24	1906	57	–	–	–	–	–	–	–
25	1899	95	–	–	–	–	–	–	–

APPENDIX 4: M. I. T. FOLDING ENDURANCE REGRESSION LINE DATA.

DATA FOR FIGURES 10–14: M. I. T. folding endurance regression line equations and average ($\bar{y}$) and intercept (y) values of folding endurance.

	Test location and page	Regression line equation Log $\hat{y}_i$ =	Values of $\hat{Y}$		
			$\bar{y}$ =	x = 1960 y =	x = 1923 y =
LAWRENCE	First page				
	Side margin	$1.542 - 0.0232\, x_i$	9.2	24.0	3.3
	Tail margin	$1.885 - 0.0392\, x_i$	8.0	40.8	1.4
	Center page				
	Side margin	$1.411 - 0.0192\, x_i$	8.4	18.9	3.7
	Tail margin	$1.710 - 0.0346\, x_i$	6.8	29.4	1.5
	Third page				
	Side margin	$1.381 - 0.0170\, x_i$	9.0	18.3	4.2
	Tail margin	$1.818 - 0.0355\, x_i$	8.5	37.1	1.8
NEWBERRY	First page				
	Side margin	$1.533 - 0.0243\, x_i$	8.4	23.1	2.9
	Tail margin	$2.003 - 0.0389\, x_i$	10.7	53.8	2.0
	Center page				
	Side margin	$1.429 - 0.0193\, x_i$	8.7	19.7	3.8
	Tail margin	$1.933 - 0.0382\, x_i$	9.2	46.3	1.8
	Third page				
	Side margin	$1.461 - 0.0191\, x_i$	9.7	21.8	4.1
	Tail margin	$1.847 - 0.0318\, x_i$	11.3	42.1	2.8
NEW YORK	First page				
	Side margin	$1.399 - 0.0285\, x_i$	4.9	15.8	1.4
	Tail margin	$1.609 - 0.0370\, x_i$	4.8	22.4	1.0
	Center page				
	Side margin	$1.389 - 0.0323\, x_i$	3.6	14.6	0.9
	Tail margin	$1.655 - 0.0387\, x_i$	4.7	24.3	0.9
	Third page				
	Side margin	$1.269 - 0.0227\, x_i$	5.0	12.6	1.9
	Tail margin	$1.769 - 0.0383\, x_i$	6.5	31.7	1.2

Notes: Log $\hat{y}_i$ is the logarithm of the folding endurance to be estimated. x_i is the age of the paper in years since publication to 1968 when the M. I. T. folding endurance measurements were made. $\bar{y}$ is the antilogarithm of the mean of the logarithms of the folding endurance measurements. x represents the years, 1923 or 1960, for which values of y, the estimated folding endurance values, are given.

APPENDIX 5: (Sonic velocity)^2 Regression line data, Figure 15.

DATA FOR FIGURE 15: (Sonic velocity)^2 regression line equations and average ($\bar{v}$) and intercept (v) values of (sonic velocity)^2.

Library	Regression line equation $\hat{V}_i =$	Values of $\hat{V}$		
		$\bar{v}$	x = 1960 v =	x = 1923 v =
Lawrence	$5.0511 - 0.00611\, x_i$	5.05	5.16	4.94
Newberry	$5.4094 - 0.00011\, x_i$	5.41	5.41	5.40
New York	$4.5981 - 0.003330\, x_i$	5.43	4.83	6.06

Notes: $\hat{V}_i$ is the (sonic velocity)^2 value to be estimated. x_i is the age of the paper in years since publication to 1968 when the (sonic velocity)^2 measurements were made. $\bar{v}$ is the mean of the (sonic velocity)^2 values. x are the years, 1923 or 1960, for which values of v, the estimated (sonic velocity)^2 values, are given.

Summaries and Explanations for the Figures and Tables

A comparison of paper in identical copies of books from The Lawrence University, The Newberry, and The New York Public Libraries.

This study was conducted in 1967 and 1968 to confirm the unusually acidic condition of paper in books selected at random from the general collections of The Newberry Library, Chicago, Illinois.

To investigate the causes and effect of this acidity, twenty-five books from The Newberry Library were compared with identical copies from the Lawrence University Library and The Research Libraries of The New York Public Library. The Lawrence University Library, located in Appleton, Wisconsin, was selected because the climate in Appleton is similar to the climate in Chicago, the level of book use in the Lawrence University Library is about the same (possibly 50 percent more) as the use level in The Newberry Library, but there is considerably less air pollution in Appleton than there is in Chicago. The New York Public Library research collection was selected because the New York climate is similar to the Chicago climate, but the level of air pollution is greater than it is in Chicago, and the books in The Research Libraries are heavily used. The contact pH values for paper in these books is compared with the cold extraction pH values reported by W. J. Barrow for paper in books discarded from libraries located in the Richmond, Virginia, area.

The appearance and condition of the books from these three libraries are reported and discussed. The paper in three leaves (selected at the one third and center points of the book and from the final signature) was tested for basis weight, thickness, presence of groundwood fibers, contact pH value, M. I. T. folding endurance, and sonic dynamic modulus of rupture. The procedures used for these tests are explained and references to additional information are provided. The test data and interpretations of this data are summarized in fifteen figures and sixteen tables.

The results of the tests conducted in this study suggest that: 1) the paper in books from the general collections of The Newberry Library probably is ten times more acidic than the paper in comparable books discarded from libraries in the Richmond, Virginia, area, 2) this high level of acidity is one consequence of the more severe level of air-pollution in Chicago than in Richmond, 3) the use of books by the patrons of most research libraries is not a significant factor in the physical deterioration of their collections, 4) the paper in books from The New York Public Library is the most acidic of the books tested in this study, 5) the M. I. T. folding endurance half-lives of the papers tested were 11.9, 11.5 and 9.4 years respectively for books from the Lawrence University, The Newberry, and The New York Public Libraries, and 6) most research library collections will be in the same, critical state of deterioration as the research collections of The New York Public Library are unless remedial measures are taken in the near future.

Explanations for the figures in text.

Figure 1. A comparison of the number of pH values at different levels of acidity between the paper in books from The Newberry Library and the paper in books discarded from libraries in the Richmond, Virginia, area. Acidity is expressed as pH values and as numbers of hydrogen ions per liter of water ($\times$ 3.35 $\times$ 10^{20}).
Figure 2. Buffering capacity of six naturally aged book papers versus the difference between their cold extraction and contact pH values. Buffering capacity is expressed in milliequivalents ($\times$ 100) of the acid or alkali required to change the pH of a 70 milliliter extract of one gram of paper by one pH unit at a pH of 7.
Figure 3. Age of paper (no. of years since publication date) versus the differences between the cold extraction pH values and contact pH values for paper from the same book.
Figure 4. Contact pH values for the middle of the center page versus the age of the paper (number of years since publication). Regression lines arranged by time of wetting until pH measurement (twelve, thirty, and sixty seconds). Contact pH values are expressed as the number of hydrogen ions per liter of water ($\times$ 3.35 $\times$ 10^{20}).
Figure 5. The information given in Figure 4 with the regression lines arranged by the library which provided the books.
Figure 6. Contact pH values for twelve seconds wetting time for the middle of the page versus age of paper (no. of years since publication). Regression lines arranged by first, center, or third page.
Figure 7. The information given in Figure 6 with the regression lines arranged by the library which provided the books.
Figure 8. Contact pH values for twelve seconds wetting time for the margins and the middle of the center page versus the age of paper (no. of years since publication). Regression lines arranged by the library which provided the books.
Figure 9. The information given in Figure 8 with the regression lines arranged by test location.
Figure 10. Folding endurance of paper in tail margin of page versus the age of paper (no. of years since publication). Regression lines arranged by page tested.
Figure 11. Folding endurance of paper in side margin of page versus the age of paper (no. of years since publication). Regression lines arranged by page tested.
Figure 12. Folding endurance of paper in the first page versus the age of paper (no. of years since publication). Regression lines arranged by library.
Figure 13. Folding endurance of paper in the center page versus the age of paper (no. of years since publication). Regression lines arranged by library.
Figure 14. Folding endurance of paper in the third page versus the age of paper (no. of years since publication). Regression lines arranged by library.
Figure 15. Sonic dynamic modulus of elasticity (expressed as the velocity of a specified sound wave) versus the age of paper (no. of years since publication).

Explanations of tables in text.

Table 1. Bibliographic data for the twenty-five books investigated.
Table 2. Pages tested and special comments regarding the twenty-five books investigated.
Table 3. Visual estimate of book usage and condition of binding.

Table 4. Classification of tests for evaluating the condition of paper.
Table 5. Basis weight and thickness (caliper) of paper.
Table 6. Presence of groundwood fibers in paper.
Table 7. pH values for paper determined by different methods; i. e., the true (graphic), cold extraction, and contact methods.
Table 8. Contact pH values for the middle of the center page.
Table 9. Contact pH values for the middle of the first and third pages.
Table 10. Contact pH values for the middle of the center page.
Table 11. M. I. T. folding endurance data (0.5 kg tension) arranged by library for the first, center, and third pages.
Table 12. The information given in Table 11 with the data transformed into logarithmic values.
Table 13. Average $(\text{velocity})^2$ of a specified sound wave in the three test leaves.
Table 14. Air quality in Appleton, Chicago, and New York City. Air quality, i. e., degree of air pollution, expressed as the quantity of certain contaminates in air.
Table 15. Percentage distribution of contact pH values at the middle of center page.
Table 16. M. I. T. folding endurance half-life in years.

Étude comparative du papier provenant d'exemplaires identiques de livres conservés dans les bibliothèques municipales de New York, la Bibliothèque Newberry ainsi que dans la bibliothèque de la Lawrence University.

Cette étude, faite en 1967 et en 1968, avait pour objet la vérification de l'acidité exceptionnelle du papier provenant de livres choisis au hasard parmi les fonds de la Bibliothèque Newberry à Chicago, Illinois.

Afin de déterminer les causes et les effets de cette acidité, une comparaison a été faite entre vingt-cinq livres de la Bibliothèque Newberry et des exemplaires identiques des mêmes ouvrages provenant de la bibliothèque de la Lawrence University et des bibliothèques de recherche de la Bibliothèque municipale de New York. La bibliothèque de la Lawrence University, située à Appleton, dans le Wisconsin, a été choisie parce que son climat est semblable à celui de Chicago et que le taux d'utilisation des livres à la bibliothèque de la Lawrence University est à peu près le même (peut-être de 50 pour cent plus élevé) que celui de la Bibliothèque Newberry; cependant, l'air est bien moins pollué à Appleton qu'à Chicago. Le choix de livres de la collection de recherche de la Bibliothèque municipale de New York est fondé sur le fait que le climat de New York est semblable à celui de Chicago; cependant, le niveau de pollution de l'air et le taux d'utilisation de livres sont plus élevés qu'à Chicago. Le pH de contact du papier de ces livres a été comparé au pH de l'extraction à froid indiquée par W. J. Barrow pour le papier des livres mis au rebut par les bibliothèques situées dans la région de Richmond en Virginie.

L'apparence et l'état de conservation des livres provenant de ces trois bibliothèques est décrit et étudié. Des expériences concernant le poids de base, l'épaisseur, la présence de fibres de pâte de bois, le pH de contact, la résistance au pliage d'après M. I. T., et le module sonore dynamique de rupture ont été faits sur deux feuilles de papier prises au

tiers et à la moitié des livres ainsi qu'au dernier cahier. Les techniques utilisées au cours de ces expériences sont expliquées; l'étude comprend une documentation relative aux informations supplémentaires. Les données concernant les expériences et les interprétations de ces données sont résumées en quinze figures et seize tableaux.

Les résultats des expériences qui ont fait l'objet de cette étude indiquent que: 1) Le papier provenant des livres des fonds généraux de la Bibliothèque Newberry a une acidité qui est, probablement, dix fois plus élevée que celle du papier provenant de livres semblables mis au rebut par les bibliothèques de la région de Richmond en Virginie; 2) Ce niveau élevé d'acidité est une conséquence du niveau plus élevé de la pollution de l'air à Chicago; 3) Le taux d'utilisation des livres de la plupart des bibliothèques ne constitue pas un facteur significatif de la détérioration matérielle des fonds de bibliothèque; 4) Le papier provenant des livres de la Bibliothèque municipale de New York a le taux d'acidité le plus élevé de tous les livres soumis à des essais dans le cours de cette étude; 5) La période de résistance au pliage des papiers soumis à l'expérience, d'après M. I. T. a été de 11,9, 11,5 et 9,4 années respectivement pour la bibliothèque de la Lawrence University, la Bibliothèque Newberry et les bibliothèques municipales de New York; 6) Les fonds de livres de la plupart des bibliothèques de recherche se trouveront dans le même état de détérioration critique, à moins que des mesures de protection ne soient prises dans un avenir proche.

Explications des figures du texte.

Figure 1. Comparaison des valeurs de pH mesuré à différents taux d'acidité entre le papier des livres de la Bibliothèque Newberry et le papier des livres mis au rebut par des bibliothèques de la région de Richmond, Virginia. L'acidité est exprimée par le pH, c'est-à-dire le nombre d'ions hydrogène par litre d'eau ($\times$ 3.35 $\times$ 10^{20}).

Figure 2. Capacité – tampon de six échantillons de papier de livres naturellement vieillis en fonction de la différence entre le pH de l'extraction à froid et le pH de contact. Cette capacité est exprimée en milliéquivalents ($\times$ 100) de l'acide ou de la base nécessaire pour faire varier d'une unité le pH d'un extrait de 70 millilitres d'un gramme de papier avec un pH de 7.

Figure 3. Age du papier (nombre d'années depuis la date de publication) en fonction de la différence entre le pH d'extraction à froid et le pH de contact pour du papier d'un même livre.

Figure 4. Le pH de contact mesuré au milieu de la page centrale en fonction de l'âge du papier (nombre d'années depuis la publication). Les lignes de régression sont disposées selon la durée du mouillage jusqu'à la mesure du pH (douze, trente et soixante secondes). Le pH de contact est exprimé comme le nombre d'ions hydrogène par litre d'eau $\times$ (6 $\times$ 10^{18}).

Figure 5. Mêmes données que dans la figure 4, mais les lignes de régression sont disposées par la bibliothèque qui a fourni les livres.

Figure 6. Le pH de contact pour une durée de mouillage de douze secondes, mesuré au milieu de la page en fonction de l'âge du papier (nombre d'années depuis la publication). Les lignes de régression sont disposées sur la première page, la page centrale ou la troisième page.

Figure 7. Mêmes données que dans la figure 6, mais les lignes de régression sont disposées par la bibliothèque qui a fourni les livres.

Figure 8. Le pH de contact pour une durée de mouillage de 12 secondes, mesuré dans les marges et au milieu de la page centrale, en fonction de l'âge du papier (nombre d'années depuis la publication). Les lignes de régression sont disposées par la bibliothèque qui a fourni les livres.

Figure 9. Mêmes données que dans la figure 8, mais les lignes de régression sont disposées d'après des tests locaux.

Figure 10. Résistance au pliage dans la marge inférieure de la page en fonction de l'âge du papier (nombre d'années depuis la publication). Les lignes de régression sont disposées par page examinée.

Figure 11. Résistance au pliage dans la marge latérale de la page, en fonction de l'âge du papier (nombre d'années depuis la publication). Les lignes de régression sont disposées par page examinée.

Figure 12. Résistance au pliage du papier de la première page en fonction de l'âge du papier (nombre d'années depuis la publication). Les lignes de régression sont disposées par la bibliothèque.

Figure 13. Résistance au pliage du papier de la page centrale en fonction de l'âge du papier (nombre d'années depuis la publication). Les lignes de régression sont disposées par la bibliothèque.

Figure 14. Résistance au pliage du papier de la troisième page en fonction de l'âge du papier (nombre d'années depuis la publication). Les lignes de régression sont disposées par la bibliothèque.

Figure 15. Module dynamique sonore d'élasticité (exprimé comme la vitesse d'une onde sonore déterminée) en fonction de l'âge du papier (nombre d'années depuis la publication).

Explications des tableaux du texte.

Tableau 1. Données bibliographiques des vingt-cinq livres examinés.
Tableau 2. Pages examinées et remarques spéciales concernant les vingt-cinq livres étudiés.
Tableau 3. Estimation visuelle de l'usure du livre et de l'état de la reliure.
Tableau 4. Classification des tests visant à établir l'état du papier.
Tableau 5. Poids de base et épaisseur (calibre) du papier.
Tableau 6. Présence de fibres de pâte de bois dans le papier.
Tableau 7. Le pH du papier déterminé par différentes méthodes: la méthode exacte (graphique), l'extraction à froid, et la méthode de contact.
Tableau 8. Le pH de contact pour le milieu de la page centrale.
Tableau 9. Le pH de contact pour le milieu des première et troisième pages.
Tableau 10. Le pH de contact pour les marges de la page centrale.
Tableau 11. Données du M. I. T. de la résistance au pliage disposées par la bibliothèque pour la première page, la page centrale et la troisième page.
Tableau 12. Mêmes données que dans le tableau 11, mais les chiffres sont exprimés en valeurs logarithmiques.
Tableau 13. Moyenne (de la vitesse)^2 d'une onde sonore déterminée dans les trois feuilles examinées.
Tableau 14. Qualité de l'air à Appleton, Chicago, et New York City. La qualité de l'air, c'est-à-dire son degré de pollution, est exprimée par la quantité de certaine impuretés qu'il renferme.

Tableau 15. Pourcentage de distribution du pH de contact mesuré au milieu de la page centrale.
Tableau 16. Période de la résistance au pliage M.I.T., en années.

Результаты сравнения бумаги в идентичных экземплярах книг из библиотеки Лоуренского университета, библиотеки им. Ньюберри и Нью-Йоркской публичной библиотеки

Настоящее исследование проводилось в 1967 и 1968 гг. с целью подтвердить необычное кислотное состояние бумаги в книгах, произвольно отобранных из общей коллекции книг библиотеки им. Ньюберри в Чикаго (Иллинойс).

Чтобы выявить причины возникновения и действие этой кислоты, сравнивали 25 книг библиотеки им. Ньюберри с идентичными книгами Лоуренской университетской библиотеки и научных библиотек Нью-Йоркской публичной библиотеки. Лоуренская университетская библиотека, расположенная в Эплтоне, Висконсин, была выбрана, потому что климат в Эплтоне сходен с Чикагским климатом, уровень спроса на книги в Лоуренской университетской библиотеке приблизительно таков же, как и в Ньюберрийской библиотеке (возможно на 50% выше); однако воздух в Эплтоне значительно менее загрязнен, чем в Чикаго. Научные фонды Нью-Иоркской библиотеки были выбраны потому, что Нью-Иоркский климат сходен с Чикагским, в то время как уровень загрязнения воздуха в Нью-Йорке выше, чем в Чикаго и книги научных библиотек пользуются большим спросом. Значения контактного pH бумаги в этих книгах сравниваются со значениями pH, сообщенными В. И. Барроу и полученными при холодной экстракции, для бумаги из книг, списанных в библиотеках, находящихся в окрестностях Ричмонда, Виргиния.

Дается описание и обсуждение внешнего вида и состояния книг в вышеназванных библиотеках. Три листа бумаги, отобранные в первой трети, в центральной части книг и взятые из конечного сфальцованного листа, были подвергнуты испытанию на основной вес, толщину, наличие древесных волокон, контактное pH, на сопротивление излому по М.И.Т. и звуковой динамический модуль на разрыв. Дается обьяснение методов, применяемых для данных испытаний и библиография с дополнительной информацией. Данные испытаний и их интерпретация приводятся в пятнадцати рисунках и шестнадцати таблицах.

Результаты испытаний говорят о том, что 1) бумага в книгах из общего книжного фонда Ньюберрийской библиотеки, по всей видимости, в десять раз более кислотна, чем бумага в сравниваемых книгах, списанных в библиотеках Ричмонда, Виргиния; 2) этот высокий уровень кислотности является следствием более значительного заражения воздуха в Чикаго, по сравнению с Ричмондом; 3) спрос на книги в большинстве научных библиотек не является существенным фактором для физической изношенности их фонда; 4) бумага книг из Нью-Йоркской публичной библиотеки является самой кислотной из всех исследуемых; 5) полупериод выносливости на излом по М.И.Т. равен 11.9, 11.3 и 9.4 лет для исспытуемой бумаги соответственно для книг из Лоуренского университета, библиотеки Ньюберри и Нью-Йоркской публичной библиотеки; и 6 большинство фондов научных библиотек в билжайшем будущем окажется так же сильно повреждено, как и научные фонды Нью-Йоркской публичной библиотеки, если не будут приняты меры к их сохранению.

Рис. 1. Сравнение числа значений pH на разных уровнях кислотности бумаги книг Ньюберрийской библиотеки с бумагой списанных книг из библиотек Ричмонда, Виргиния. Кислотность выражена в значениях pH, т.е. числом ионов водорода на литр воды (6×10^{18}).

Рис. 2. Буфферная емкость 6-ти видов печатной бумаги для книг естественного старения в зависимости от разницы между и значениями pH холодной экстракции и контактного pH. Буфферная емкость выражается в миллиэквивалентных ($\times 100$) кислоты или щелочи, необходимой для изменения pH экстракта из 70 миллиметров одного грамма бумаги на одну единицу pH, при pH равной 7.

Рис. 3. Возраст бумаги (количество лет после даты опубликования книги) в зависимости от разницы pH холодной экстракции и контактного pH для бумаги из той же книги.

Рис. 4. Контактное pH значения для середины центральной страницы в зависимости от возраста бумаги. Линии регрессии расположе - ны согласно времени смачивания до измерения pH (12, 30 и 60 секунд). Контактное pH выражено числом ионов водорода на 1 литр воды ($\times 3.35 \times 10^{19}$).

Рис. 5. Данные, указанные на рис. 4 с линиями регрессии, расположенными согласно библиотекам, предоставившим эти книги.

Рис. 6. Контактное pH для 12-ти секундного смачивания середины, в зависимости от возраста бумаги. Линии регрессии расположены по первой, центральной или третьей странице.

Рис. 7. Данные как на рис. 6 с линиями регрессий, расположенными согласно библиотекам, предоставившим эти книги.

Рис. 8. Контактные pH значения для 12-ти секундного смачивания краев и середины центральной страницы в зависимости от возраста бумаги. Линии регрессии расположены согласно библиотекам, предоставившим эти книги.

Рис. 9. Данные как на рис. 8 с линиями регрессии, расположенными согласно местоположению библиотеки.

Рис. 10. Выносливоеть на излом бумаги по краю нижнего поля страницы в зависимости от возраста бумаги. Линии регрессии расположены согласно испытуемой странице.

Рис. 11. Выносливость на излом бокового края страницы в зависимости от возраста бумаги. Линии регрессии расположены согласно испытуемой странице.

И-метил-а-пирролидон является органическим растворителем старого клейстера, растворяющим мучной клей, и применимым в процессе отделения документов или рисунков от поддерживающих материалов без заметной потери краски галложелезного Танната.

Рис. 12. Выносливость на излом бумаги на первой странице в зависимости от возраста бумаги. Линии регрессии расположены согласно библиотекам.

Рис. 13. Выносливость на излом бумаги центральной страницы в зависимости от возраста бумаги. Линии регрессии расположены согласно библиотекам.

Рис. 14. Выносливость на излом бумаги на третьей странице в зависимости от возраста бумаги. Линии регрессии расположены согласно библиотекам.

Рис. 15. Звуковой динамический модуль эластичности (выраженный в виде скорости фиксированной звуковой волны) в зависимости от возраста бумаги.

Заголовки таблиц встречающихся в тексте

Таби. 1. Библиографические данные 25 исследованных книг.

Таби. 2. Исследованные страницы и специальные комментарии относительно 25 исследованных книг.

Табл. 3. Визуальная оценка износа книги и состояния переплета.

Табл. 4. Классификация испытаний, проведенных для оценки состояния бумаги.

Таби. 5. Основной вес и толщина бумаги.

Табл. 6. Наличие древесинных волокон в бумаге.

Табл. 7. Показатели pH для бумаги, определяемые различными методами, т.е. истинным (графическим), холодной экстракцией и контактным методами.

Табл. 8. Контактные pH значения для середины центральной страницы.

Ттбл. 9. Контактные pH значения для середины первой и третьей страницы.

Табл. 11. Данные о выносливости на излом по М.И.Т. (0,5 кг напряжения), расположенные по библиотекам, для первой, центральной и третьей страниц.

Табл. 12. Данные таблицы 11, преобразованные в логарифмические величины.

Табл. 13. Средняя (скорость)[8] фиксированной звуковой волны в 3-х испытуемых листах.

Табл. 14. Качество воздуха в Эплтоне, Чикаго и в Нью-Йорке. Качество воздуха, т.е. степень его загрязнения, выраженная количеством некоторых загрязняющих веществ.

Табл. 15. Процентное распределение контактных pH значений посередине центральной страницы.

Табл. 16. Полупериод выносливости на излом (по М.И.Т.).

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