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DETERIORATION OF BOOK AND RECORD PAPERS

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INTRODUCTION

Paper that becomes brittle or crumbly causes serious loss and expense to libraries, archives, and public offices charged with the keeping and storage of historical and legal records, important books, and scientific publications. It is the general opinion of librarians and other custodians of books and records who have given the matter serious consideration that much of the paper on their shelves, especially that made since about 1860, is not sufficiently durable. This opinion seems to be fully justified, especially in the case of books and papers subjected to frequent handling.

DETERIORATION OF OLD BOOK AND RECORD PAPERS [2]

There are serious difficulties in determining what deterioration has taken place in old papers. These include the lack of information concerning the chemical and physical properties of the papers when new, incomplete knowledge concerning conditions of storage, exposure, and use, and the lack of control samples which have been protected from deteriorating agencies. Old papers obviously afford no means of indicating what their properties were originally.

[1] At the time the work was conducted the authors held their respective positions in the Industrial Farm Products Division, Bureau of Chemistry and Soils.

[2] These experiments were conducted from 1928 to 1932.

The writers have noted that the outside margins of the leaves of many old books are very brittle and crack easily when handled, while the centers of the same leaves are, in most cases, apparently in a good state of preservation.

Although no control samples were available, it appeared that the center section, which had received relatively little exposure, would, when compared with the margin section, give fairly definite chemical and physical data as to the effect of normal conditions of storage and use.

REVIEW OF SIMILAR WORK

No attempt will be made here to review the literature. Only articles dealing with closely similar work will be briefly noted.

Since 1928, when this work was started, several investigators have studied the effect of air polluted with acidic sulphur compounds on the physical properties of paper. Richter (*10*) [3] and also Kimberly (*8*) exposed various kinds of paper for definite periods to an atmosphere containing sulphur dioxide, and found that the papers absorbed an appreciable quantity of acid. This absorbed acid caused a material decrease in the strength of the papers. Kimberly approved a "* * * modification of library ventilating systems so as to eliminate acid pollution." Richter in a later article (*11*) suggests that paper "* * * be loaded with a basic material which will tend to neutralize the condensed acid vapors that are continually brought in contact with the paper."

In 1933 Kimberly and Emley (*9*) published results on a number of different copies of the same edition of books submitted by city and country or suburban libraries. They stated that the paper from books stored in urban institutions was more deteriorated and more acid than that from the same edition kept in country libraries. They concluded that: "The greater deterioration of books stored in large cities is probably due to the harmful effect of contact with air polluted by sulphur dioxide."

In a previous publication (*7*), the writers demonstrated the injurious effect of added small quantities of aluminum sulphate, sulphuric acid, and hydrochloric acid on the strength of a high-grade waterleaf rag bond paper. The results emphasize the importance of using only the minimum quantity of alum in sizing the paper and of washing out excess chemicals which might form free acids.

As far as the writers know, in determining the deterioration of paper no examinations have been made of different sections of the same leaves taken from old books, magazines, or court records.

EXPERIMENTAL PROCEDURE

The work reported here was done on the following samples of paper:

Fifteen samples, numbered 1 to 10–B, were printing papers taken from old books and bound magazines collected from various sources. The publication dates of these books and magazines ranged from 1850 to 1913, and the leaves ranged in size from 6⅞ by 4⅜ inches (no. 1) to 11¼ by 8¾ inches (no. 7). The stocks of these papers were rag, bleached coniferous and bleached broadleaf chemical wood, either alone or in mixtures.

[3] Italic numbers in parentheses refer to Literature Cited, p. 20.

Five samples, numbered 11 to 15, inclusive, were blank leaves taken from volumes of public records (land deeds) on file in the Prince George's County Courthouse at Upper Marlboro, Md. The dates of these volumes ranged from 1763 to 1849. For comparison, a sample of new record paper was examined (no. 16).

Six samples, numbered 17 to 22, inclusive, were blank leaves taken from volumes of public records (land deeds) on file in the office of the recorder of deeds, Washington, D. C. The dates of these records ranged from 1797 to 1867.

Twelve samples, numbered 23 to 34, inclusive, were blank leaves taken from volumes of public records filed in the office of the register of wills, Washington, D. C. The dates of these records ranged from 1801 to 1868.

The record papers were all made of all-rag stock. The size of the leaves ranged from 12½ by 7 inches (no. 24) to 20 by 14 inches (nos. 18 and 19).

Each sample was divided into two subsamples indicated in the tables as margin and center. The margin subsamples were made up of strips 15 mm wide cut from the three exposed edges of the leaves (not including binding edge). The center subsamples represent that portion of the leaves remaining after strips were cut from each of the four edges. The strips from the book and magazine papers (samples 1–10) were 1½ inches wide; those from the court record papers (samples 11–34) were 3 inches wide. Comparative chemical and physical tests were made on these subsamples.

The folding-endurance tests were made both in the longitudinal and transverse directions of the paper with the Schopper machine (*13, p. 485*). Several of the stronger papers were tested with the machine set at the regular tension of 1,000 g (table 3), but it was found with practically all the samples that a significant number of double folds could not be obtained at this tension. Therefore, a tension of 500 g was used on all samples examined except no. 16, which was a new record paper (made in 1930) having a rather high folding value. This paper was folded at the regular tension of 1,000 g. All bursting-strength tests on margin subsamples were made as close to the edge as possible. The center strips for folding tests were taken in such a way that the actual folding point of the paper was at, or very near, the middle of the center subsample. The bursting-strength tests were made with the Mullen tester (*13, p. 482*).

All samples were conditioned at 50-percent relative humidity and 70° F. for at least 48 hours before physical tests were made on them.

For chemical analysis the samples were ground fine enough in a Wiley mill (*16*) to pass through a sieve having circular holes 2 mm in diameter. The rosin content was determined by the Sammet method (*12*). Total acidity was determined by the Minor method (*15*), which directs that the titration with 0.01 normal NaOH be conducted in the presence of the ground paper. To determine the hydrogen-ion concentration, 2½ g of the ground sample was transferred to a 250-cc pyrex glass Erlenmeyer flask, 125 cc of boiling distilled water having a pH of 6.9 to 7.1 was added, and the mixture was boiled gently for 15 minutes on an electric hot plate. The solution was then decanted into a 125-cc flask, which was tightly stoppered and allowed to cool. The pH value was determined by the electro-

metric method, using the quinhydrone electrode. The usual precautions were observed to eliminate carbon dioxide from the solutions.

Water-soluble sulphates were determined on the same solutions used in making the total acidity determinations. After being titrated with NaOH the solutions containing the ground paper were boiled for 15 minutes on an electric hot plate, filtered, and washed thoroughly with 200 cc of hot water. The filtrate was then evaporated to about 125 cc. A few drops of hydrochloric acid were added to the clear solution, and the sulphates precipitated in the usual way with barium chloride, filtered through a prepared platinum Gooch crucible, washed, ignited over a bunsen burner, and weighed as barium sulphate. Total sulphur by the magnesium nitrate method (*2, p. 110*) was determined only on the printing papers. The total acidity, water-soluble sulphates, and total sulphur results were calculated to SO_3.

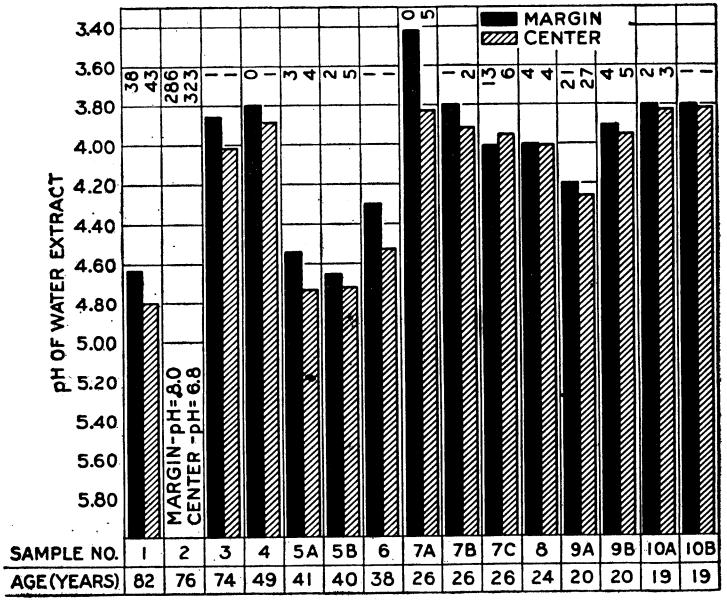

FIGURE 1.—Comparison of pH of water extract and folding endurance in margin and center sections of leaves form old books and magazines. (Figures above columns represent double folds at 500-g tension.)

The copper number was determined only on the printing papers. The tentative official method of the Technical Association of the Pulp and Paper Industry (*1*) was used. This method is essentially the Braidy modification (*3*) of the original Schwalbe method. Alpha cellulose was not determined, deterioration being judged chiefly by decrease in folding number.

RESULTS

The results of the examination of printed papers taken from old books and bound magazines are recorded in table 1. In table 2 are recorded the results of similar tests on blank leaves of record papers taken from bound volumes of county and city records. In table 3 are presented results of a comparison of folding-endurance tests made on the Schopper folding-endurance machines at tensions of 500 and

1,000 g. Nine of the samples in tables 1 and 2 were selected for this comparison. The results demonstrate the advantage, for the purpose of this investigation, of using a tension of 500 g rather than the usual

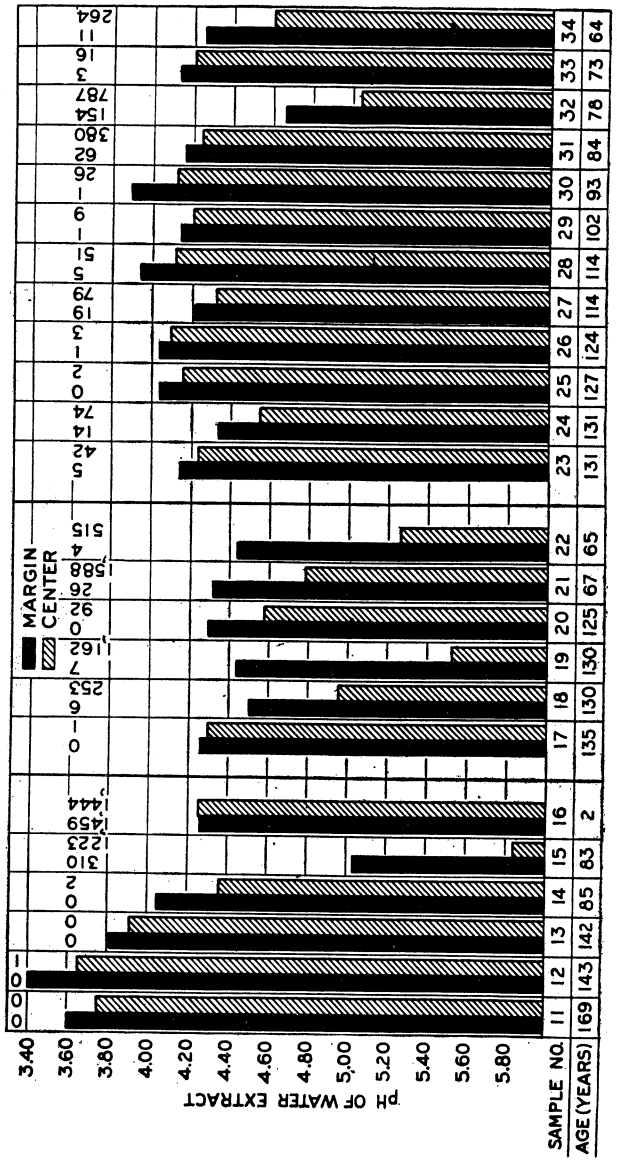

FIGURE 2.—Comparison of pH of water extract and folding endurance in margin and center sections of leaves from old court-record volumes. (Figures above columns represent double folds. Sample 16 made at 1,000-g tension. All others made at 500-g tension.)

tension of 1,000 g. Figures 1, 2, 3, and 4 show graphically a comparison of acidity and folding endurance in the marginal and center sections of all samples examined.

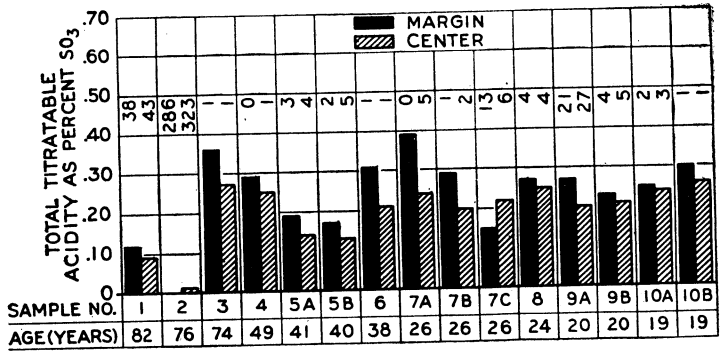

FIGURE 3.—Comparison of total acidity and folding endurance in margin and center sections of leaves from old books and magazines. (Figures above columns represent double folds at 500-g tension.)

TABLE 1.—*Results of examination of printed pages of old books and bound magazines*

Sample no.	Kind of publication	Date published	Where published	Where kept since publication	Weight of 500 sheets 25 by 40 inches	Thickness	Fiber composition			Ash	Starch
							Rag	Coniferous chemical wood (bleached)	Broadleaf chemical wood (bleached)		
					Lbs.	*0.0001 inch*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	
1	Book	1850	Boston	(2)	49.7	39	100			0.6	None.
2	do	1856	Germany	(2)	40.1	30	100			4.6	Do.
3	do	1858	England	(2)	61.1	47	100			4.1	Do.
4	Magazine	1883	New York	(2)	58.4	40	70		30	.9	Do.
5-A[3]	Scientific journal.	1891	Washington	Library, Bureau of Chemistry.	66.4	34		40	60	16.1	Do.
5-B	do	1892	do	do	62.8	34		45	55	20.0	Do.
6	Book	1894	Germany	do	73.8	40	20	80		13.9	Present.
7-A[4]	do	1906	Washington	New York Public Library.	60.7	44	100			.4	Trace.
7-B	do	1906	do	Superintendent of Documents' Library.	61.0	44	100			.4	Do.
7-C	do	1906	do	Library of Congress.	60.9	44	100			.4	Do.
8	do	1908	Boston	(3)	72.2	45	70	5	25	10.0	None.
9-A[3]	Scientific journal.	1912	Washington	Library, Bureau of Chemistry.	52.1	40	50	20	30	5.0	Present.
9-B	do	1912	do	do	64.3	44	80	20		.5	None.
10-A[3]	do	1913	do	do	51.8	42	80		20	.6	Present.
10-B	do	1913	do	do	52.4	42	75		25	.5	None.

Footnotes at end of table.

TABLE 1.—*Results of examination of printed pages of old books and bound magazines*—Continued

Sample no.	Rosin	Portion of sample represented by subsample	Degree of marginal discoloration	Present condition	Physical tests		Chemical tests				
					Folding endurance [1]	Bursting strength	Acidity		Water-soluble as sulphates SO_3	Total sulphur as SO_3	Copper number (corrected for ash and rosin)
							pH of water extract	Total as SO_3			
	Pct.				*Double folds*	*Points*		*Pct.*	*Pct.*	*Pct.*	
1	0.47	Margin	Slight	Good	38	11.8	4.63	0.12	0.10	0.13	1.74
		Center		do	43	12.0	4.80	.09	.05	.06	1.75
2	.63	Margin	do	do	286	12.0	8.00	.00	.11	.20	2.21
		Center		do	323	12.6	6.80	.01	.01	.03	2.15
3	1.42	Margin	Considerable	Brittle	1	8.7	3.86	.36	.22	.32	5.35
		Center		Somewhat brittle	1	9.7	4.02	.27	.05	.07	4.82
4	1.30	Margin	Some	Very brittle	0	3.9	3.80	.29	.09	.12	6.97
		Center		Brittle	1	5.9	3.89	.25	.02	.05	6.68
5–A [3]	.77	Margin	Slight	Fair	3	9.7	4.54	.19	.14	.22	4.81
		Center		do	4	9.7	4.73	.14	.09	.10	4.28
5–B	.87	Margin	Considerable	do	2	10.6	4.65	.17	.17	.29	5.64
		Center		do	5	11.9	4.72	.13	.11	.22	5.66
6	1.49	Margin	do	Brittle	1	17.4	4.30	.31	.23	.34	6.44
		Center		do	1	16.9	4.53	.21	.17	.19	6.29
7–A [4]	2.07	Margin	Some	Very brittle	0	2.0	3.42	.39	.27	.46	8.07
		Center		Fair	5	12.3	3.83	.24	.07	.09	4.44
7–B	2.19	Margin	do	Somewhat brittle	1	9.3	3.80	.29	.13	.15	4.72
		Center		Fair	2	12.2	3.92	.20	.03	.05	4.60
7–C	2.15	Margin	None	Good	13	13.0	4.01	.15	.05	.07	3.54
		Center		do	6	12.9	3.95	.22	.05	.05	4.24
8	.88	Margin	Slight	Fair	4	13.2	4.00	.27	.21	.30	5.57
		Center		do	4	13.3	4.01	.25	.18	.27	5.66
9–A [3]	.74	Margin	None	Good	21	13.8	4.20	.27	.25	.40	2.76
		Center		do	27	14.2	4.26	.20	.19	.33	2.59
9–B	1.11	Margin	Some	Fair	4	12.7	3.91	.23	.15	.19	4.51
		Center		do	5	13.1	3.95	.21	.09	.12	4.60
10–A [3]	1.16	Margin	do	Somewhat brittle	2	11.8	3.80	.25	.14	.19	3.87
		Center		do	3	12.9	3.83	.24	.09	.11	4.10
10–B	1.24	Margin	Considerable	Brittle	1	8.3	3.80	.30	.09	.14	6.43
		Center		do	1	8.9	3.82	.26	.06	.07	7.05

[1] All folding-endurance tests were made with Schopper tester set at tension of 500 g. Each result is an average of longitudinal and transverse directions.

[2] These publications were obtained from second-hand book dealers in Washington, D. C., and it is not known where and under what conditions they were kept since publication.

[3] A and B were taken from 2 different journal numbers of the same bound volume and stored under the same conditions.

[4] Samples 7–A, 7–B, and 7–C are different copies of the same edition stored in different places. Sample 7–C was kept well wrapped in paper since publication.

TABLE 2.—*Results of examination of blank leaves from old bound court records* [1]

KEPT IN OFFICE OF THE CLERK OF THE COURT, PRINCE GEORGE'S COUNTY, MD.

Sample no.	Date of records	Weight of 500 sheets, 25 by 40 inches	Thickness	Ash	Glue	Portion of sample represented by subsample	Degree of marginal discoloration	Present condition	Physical tests		Chemical tests		
									Folding endurance [2]	Bursting strength	Acidity		Water-soluble sulphates as SO_3
											pH of water extract	Total as SO_3	
		Pounds	*0.0001 inch*	*Percent*	*Percent*				*Double folds*	*Points*		*Percent*	*Percent*
11	1763	80.8	65	0.5	5.1	Margin	Considerable [3]	Very brittle	0	7.6	3.60	1.03	1.73
						Center		do	0	5.1	3.75	.75	1.25
12	1789	73.8	52	2.3	4.2	Margin	Some	Brittle	0	18.2	3.40	1.43	2.41
						Center		Somewhat brittle	1	19.4	3.65	.99	1.95
13	1790	83.1	57	2.5	4.1	Margin	Some	Brittle	0	15.9	3.81	.59	1.50
						Center		do	0	17.3	3.91	.50	1.34
14	1847	81.9	50	1.0	4.4	Margin	Slight	do	0	29.5	4.05	.49	.85
						Center		Somewhat brittle	2	35.0	4.36	.33	.67
15	1849	82.1	60	1.9	5.7	Margin	None	Good	310	43.6	5.03	.08	.84
						Center		do	1,223	44.3	5.84	.04	.44
16 [4]	1930	85.3	40	1.4	3.3	Margin	None	Excellent	1,459	79.3	4.26	.14	.31
						Center		do	1,444	79.0	4.25	.14	.32

KEPT IN OFFICE OF RECORDER OF DEEDS, WASHINGTON, D. C.

17	1797	62.1	50	3.7	3.6	Margin	Some	Very brittle	0	10.4	4.26	0.61	1.08
						Center		Somewhat brittle	1	12.4	4.29	.39	.91
18	1802	108.6	80	2.9	5.8	Margin	Slight	do	6	53.2	4.50	.23	.67
						Center		Good	253	64.7	4.95	.10	.46
19	1802	108.0	80	2.5	5.9	Margin	Some	Somewhat brittle	7	45.7	4.43	.25	.69
						Center		Excellent	1,162	69.2	5.52	.07	.56
20	1807	92.7	70	.5	8.1	Margin	Some	Brittle	0	33.9	4.29	.46	.56
						Center		Good	92	39.9	4.57	.21	.50
21	1865	79.2	45	.4	5.6	Margin	Slight	Fair	26	41.8	4.31	.23	.49
						Center		Excellent	1,588	61.3	4.78	.08	.32
22	1867	90.0	55	.6	5.4	Margin	Slight	Fair	4	37.7	4.43	.26	.41
						Center		Excellent	515	48.1	5.26	.08	.23

23	1801	83.2	75	0.7	5.3	Margin	Some	Somewhat brittle	5	28.8	4.14	0.36	0.46
						Center		Good	42	30.1	4.23	.28	.42
24	1801	59.1	50	2.9	3.3	Margin	Some	do	14	20.6	4.33	.28	.62
						Center		do	74	20.2	4.54	.17	.59
25	1805	94.3	74	3.5	5.6	Margin	Slight	Very brittle	0	24.4	4.04	.53	.99
						Center		Somewhat brittle	2	32.7	4.15	.40	.96
26	1808	85.0	65	3.0	5.6	Margin	Some	Brittle	1	28.7	4.03	.50	.97
						Center		Somewhat brittle	3	32.3	4.09	.47	.95
27	1818	81.1	73	1.7	7.6	Margin	Slight	Good	19	27.2	4.21	.46	.79
						Center		do	79	28.8	4.32	.32	.68
28	1818	63.2	50	.7	5.6	Margin	Some	Somewhat brittle	5	19.6	3.94	.60	.62
						Center		Good	51	23.5	4.11	.36	.48
29	1830	77.6	60	1.0	3.4	Margin	Slight	Brittle	1	18.2	4.14	.33	.65
						Center		Somewhat brittle	9	20.9	4.20	.26	.63
30	1839	88.7	70	1.8	7.6	Margin	Some	Brittle	1	37.4	3.89	.58	.79
						Center		Fair	26	51.3	4.12	.37	.64
31	1848	92.6	62	1.3	7.0	Margin	Slight	Good	62	42.9	4.16	.44	.69
						Center		do	380	48.4	4.24	.38	.65
32	1854	89.1	50	1.7	3.9	Margin	None	Excellent	154	50.6	4.66	.14	.43
						Center		do	787	52.2	5.04	.05	.30
33	1859	90.3	60	3.7	6.6	Margin	Slight	Somewhat brittle	3	36.8	4.13	.48	.84
						Center		Good	16	44.3	4.20	.42	.80
34	1868	86.1	48	1.1	7.9	Margin	Slight	do	11	37.9	4.26	.29	.59
						Center		do	264	41.4	4.60	.15	.46

[1] These papers were made of all-rag stock. Qualitative tests showed rosin absent in all samples except no. 16 and starch absent in all except no. 31.

[2] All folding-endurance tests made with Schopper tester set at a tension of 500 g except those on sample 16, which were made at 1,000-g tension. Each result is an average of longitudinal and transverse directions.

[3] The center portion of this sample was also considerably discolored.

[4] Sample 16, a relatively new record paper, is included in this table for comparison with the old papers.

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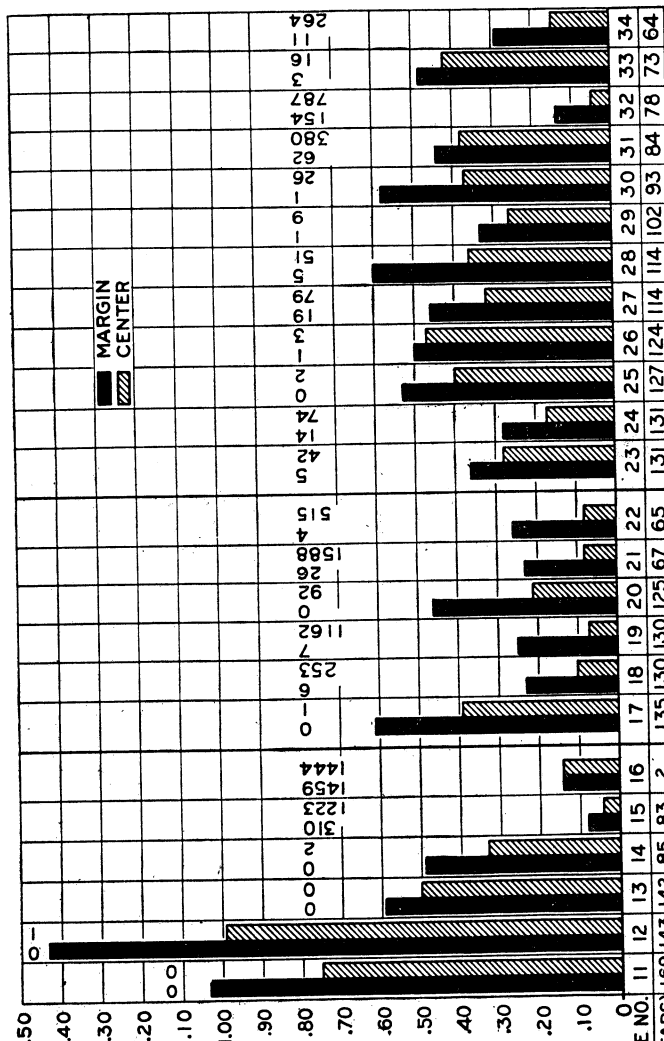

FIGURE 4.—Comparison of total acidity and folding endurance in margin and center sections of leaves from old court-record volumes. (Figures above columns represent double folds. Sample 16 made at 1,000-g tension. All others made at 500-g tension.)

TABLE 3.—*Folding-endurance tests at tensions of 500 and 1,000 g on Schopper folding-endurance machine*

Sample no.	Kind of paper	Age	Portion of sample represented by subsample	Condition of paper in 1932	Acidity (pH of water extract)	Folding endurance (average of both directions)		
						500-g tension	1,000-g tension	Ratio of 500-g to 1,000-g tension
		Years				*Double folds*	*Double folds*	
1	Book	82	Margin	Good	4.63	38	3	13
			Center	do	4.80	43	3	14
2	do	76	Margin	do	8.00	286	11	26
			Center	do	6.80	323	11	29
19	Court record	130	Margin	Somewhat brittle	4.43	7	0	
			Center	Excellent	5.52	1,162	25	46
20	do	125	Margin	Brittle	4.29	0	0	
			Center	Good	4.57	92	6	15
21	do	67	Margin	Fair	4.31	26	2	13
			Center	Excellent	4.78	1,588	47	34
22	do	65	Margin	Fair	4.43	4	0	
			Center	Excellent	5.26	515	14	37
31	do	84	Margin	Good	4.16	62	4	16
			Center	do	4.24	380	14	27
32	do	78	Margin	Excellent	4.66	154	7	22
			Center	do	5.04	787	16	49
34	do	64	Margin	Good	4.26	11	1	11
			Center	do	4.60	264	10	26

DISCUSSION OF RESULTS

It should be emphasized that definite correlation of the results of the examination of the various papers cannot be established. The history of manufacture and the exact conditions of use and storage, such as degree of exposure to light and air, and temperature and humidity range, are unknown. These conditions no doubt varied widely with the different papers, and this alone would account for some apparent inconsistencies in the results. Nevertheless, tests on the same paper exposed to different atmospheric conditions and use showed that the margins of the leaves contained more acid and deteriorated more rapidly than the centers. When considering the data it is well to bear in mind that the marginal subsamples can be compared only with the center subsamples cut from the same leaves. In the case of nos. 7–A, 7–B, and 7–C additional and striking data on the effect of different conditions of exposure and use of the same paper were obtained.

PRINTING PAPER

The results on the printing papers reported in table 1 show in general that there was somewhat more acid, more water-soluble sulphates and total sulphur, and a little less strength in the marginal than in the center sections of these papers. However, the differences are relatively small in most cases.

There is no way to determine whether the center portions of these different papers—that part of the leaves that had been least exposed and handled—had changed chemically or physically during their years of service. The differences between the margins and centers of the very old papers are no greater than between the margins and centers of the more recent papers. In most cases, the folding endurance of the papers is so low that correlation of folding endurance

and acidity is not warranted. However, the acidity of nearly all these papers was high enough to cause deterioration.

The results on the leaves of the book represented by sample no. 2, which was published in Germany about 75 years before this examination, are of special interest. This book was made of two kinds of paper. Most of the leaves were made of all-rag stock, while a few were composed of 85 percent rag and 15 percent mechanical wood. No acid was found in either the margin or center sections of the all-rag leaves, indicating that initially this paper contained little or no acid. The marginal sections, however, contained more than 10 times as much water-soluble sulphates and nearly 7 times as much total sulphur as the center sections. These results indicate that the portions of the leaves more fully exposed to the atmosphere absorbed sulphur compounds from the air, but the paper apparently contained a material which neutralized or counteracted the harmful effect of such compounds.

This paper contained 4.6 percent of ash. Examination of the ash showed that it contained 65.3 percent of material insoluble in hydrochloric acid, which upon fusion was found to be essentially aluminum silicate. The acid-soluble material contained 29.8 percent alumina, 2.8 percent calcium oxide, 1.1 percent sulphates expressed as SO_3, and a trace of magnesia (on the basis of the original ash). The water extract of the ash (0.5 g shaken in 500 cc cold water) contained 1.6 percent of calcium calculated as calcium oxide and was decidedly alkaline in reaction, containing 0.7 percent alkali calculated as calcium oxide. It is, therefore, probable that acid was absent from this paper because the filler used in its manufacture contained a basic or alkaline material which neutralized the acidic sulphur compounds of the air as they came in contact with it.

The copper numbers of both marginal and center sections of the all-rag leaves of this book were about the same, being relatively low and indicating little or no degradation of the cellulose. The paper still possessed good writing qualities, as shown by writing on it with ink. Glue and starch were absent. The folding endurance of both the marginal and center sections of this paper was much higher than that of any other old book paper examined—nearly eight times as much as the next highest book paper (no. 1) examined. The relatively high folding endurance and the generally good condition of this paper after about 75 years of service was undoubtedly due to the exceptionally good quality of the original paper and to the absence of acid from the paper. This in turn was unquestionably due to the incorporation of an alkaline substance in the paper.

The few leaves of book no. 2 that contained mechanical wood were greatly discolored and apparently much deteriorated, as shown by inspection and by folding endurance. This was to be expected, as it is well known that papers containing mechanical wood will not last as long as those made entirely of rag or chemical fibers. The folding endurance at 500-g tension and the pH of the water extract of the center sections of this paper were 12 and 4.26, respectively, while in the marginal sections of the same leaves they were 0 and 3.90, respectively. These results indicate that this paper absorbed harmful quantities of acids from the air.

The results on book-paper samples 7–A, 7–B, and 7–C are significant. These three books are copies of the same edition and were printed on the same lot of all-rag antique book paper by the United States Government Printing Office in 1906. Book 7–A had been kept on the reference shelves of the New York Public Library in New York City; 7–B had been kept on the shelves of the library of the Superintendent of Documents of the Government Printing Office, Washington, D. C., and 7–C, well wrapped in paper and thus protected from light and air, had been stored in the Library of Congress.

Greater acidity, more water-soluble sulphates, more total sulphur, and a lower folding endurance were found in the marginal sections of the leaves taken from the two copies kept on the shelves of the New York Public Library and the Superintendent of Documents' library than were found in the center sections of the same leaves. The leaves of the copy kept protected from light and air since publication (no. 7–C) gave practically the same results for acidity, water-soluble sulphates, and total sulphur in the marginal and center sections. The folding endurance, however, was somewhat higher in the former than in the latter. For this class and weight of paper the folding endurance was low, indicating that some deterioration had taken place. This was probably caused by its high acidity, the pH of the water extract being about 4.

It should be noted that the marginal sections of the leaves taken from the copy kept on the shelves of the New York Public Library (no. 7–A) contained much more acid, water-soluble sulphates, and total sulphur, and had less strength than the same sections of the leaves taken from the copy kept in the Superintendent of Documents' library (no. 7–B). In fact, the marginal sections of the leaves of the former book (no. 7–A) had a higher copper number and contained more acid, water-soluble sulphates, and total sulphur, and had apparently deteriorated more than the leaves of any other book or magazine examined. The marginal sections were very brittle, and were readily broken upon handling.

Numerous investigators (*5*) have shown that the air in large industrial centers is considerably polluted with sulphur compounds. For that reason it is not surprising that the leaves of book no. 7–A, which had been stored on the shelves of the New York City library, contained more acid and showed more deterioration than the leaves of book no. 7–B, which had been kept on the shelves of a library in Washington, D. C., and that both contained more acid and were more deteriorated than book no. 7–C, which had been kept thoroughly wrapped. After these papers had been examined the manufacturer stated that, by error, twice as much alum as the furnish called for had been put in this lot of paper.

BLANK RECORD PAPERS

Results of the examination of the blank record papers taken from bound volumes of old county and city records are in general agreement with those for the printing papers. These results are recorded in table 2. The marginal sections of all these samples (except no. 16, which was practically new) contained more acid and a greater quantity of water-soluble sulphates and had a lower folding endurance than the center sections.

Sample 16, essentially a new paper, was not included in the above comparisons. It should be noted that practically the same acidity, water-soluble sulphates, and folding endurance were found in both sections of this paper. This was to be expected and is in harmony with the results found on the leaves taken from the book kept well wrapped in paper in the Library of Congress (no. 7–C, table 1). The average folding endurance of paper no. 16 was 1,452 double folds when tested at 1,000-g tension in September 1930. After being well wrapped in paper and stored at room temperature for 3 years and 8 months, the folding test showed a 10-percent loss in strength. The acidity of this paper was rather high, which probably accounts for the loss in folding endurance. Of the court-record papers, only sample 16 gave a positive test for rosin, and only sample 31 contained starch. All contained glue ranging from 3.3 to 8.1 percent. The ash contents ranged from 0.4 to 3.7 percent.

Attention is directed particularly to the very low acidity in both the marginal and center sections of sample 15, which had been kept for 83 years. This paper contained less acid than any other record paper examined (fig. 2). The results indicate that when new it contained little or no acid, and also that practically no acidity developed in the paper during storage. This record paper had a much higher folding endurance than any of the other old papers collected from this office, due, no doubt, to its low acidity. On the otherh and, court-record paper no. 11, which is the oldest paper examined, having been stored for 169 years, had become much discolored and very brittle throughout. It cracked easily upon handling and had apparently deteriorated more than any other paper examined.

The comparative results of the folding-endurance tests at tensions of 500 and 1,000 g on Schopper folding-endurance machines are shown in table 3. These tests were made on two of the printing papers and seven of the court-record papers. They show that on these samples there is no constant relation between the double folds and the tension used, the folding endurance at 500 g being from 13 to 49 times as great as at 1,000-g tension.

Nearly all the samples listed in tables 1 and 2 were discolored along the margins of the leaves. No close correlation can be drawn between the degree of discoloration and the physical and chemical tests. In general, however, papers in the best state of preservation showed the least discoloration.

DETERIORATION OF RECORD PAPERS STORED UNDER NORMAL CONDITIONS[4]

Seven samples of commercial paper were kept under normal storage conditions without handling for 18 years. Physical tests were made to determine the deterioration of the papers during this period.

PROCEDURE

The papers, representative of high- and low-quality commercial bond and ledger papers, were made in 1914 and 1915 and were collected in the early part of 1915. They were tested in 1915[5] for folding endurance, bursting strength, and tensile strength. Stock, ash, rosin,

[4] J. M. Hankins did not assist in this investigation.

and glue determinations were also made at that time. In 1920 [5] and again in 1933, folding-endurance, bursting-strength, and tensile-strength tests were again made on the papers. It was not, however, until 1933 that acidity, as indicated by the pH of the water extract, was determined.

From 1915 to 1933, a period of 18 years, all these papers were stored in ream lots without handling in a dark, closed case in one of the halls of the brick building in Washington, D. C., in which this Bureau was located.

The folding-endurance tests were made with the Schopper machine. The bursting-strength tests were made with the Mullen tester, and the tensile-strength tests were made with a Schopper tester having a capacity of 30 kg. All these tests were made in both directions of the paper. In the last series of tests (1933), strips of these papers were also double folded once with Kirchner's creasing roller (*6, p. 50*). After folding with this roller, the strips were broken with the Schopper tensile-strength tester. In calculating the percentage decrease or increase in folding endurance and tensile strength, the average figures of both directions of the paper were used. All physical tests were made at 65-percent relative humidity and 70° F.

The rosin content of the papers was determined by the Sammet method (*12*). The pH value of the water extract of the papers was determined by placing 2 g of the ground sample in a pyrex Erlenmeyer flask and adding 100 cc of boiling distilled water having a pH of 6.9 to 7.1 when free of carbon dioxide (a 200-cc soil digestion flask with ground-in condenser was used). The mixture was boiled gently for 30 minutes. It was then allowed to stand for 1 minute, after which about 50 cc of the hot clear solution was carefully decanted into a 100-cc ground-in glass-stoppered pyrex Erlenmeyer flask. The flask was stoppered and the solution allowed to cool to room temperature. The pH value was measured within 18 hours after the solution was prepared. The electrometric method, with the quinhydrone electrode, was used.

In order to obtain test specimens from portions of the papers that had not been deteriorated by acidic sulphur compounds generally present in the air, samples for physical and chemical tests were always taken from near the center of the sheets and from sheets in the interior of each ream lot.

In table 4 are presented the results of comparative tests made on these papers shortly after the papers were manufactured (1915), about 5 years after manufacture (1920), and about 18 years after manufacture (1933).

[5] These tests were made by E. O. Reed, formerly of this Bureau.

TABLE 4.—*Variation in physical properties of commercial bond and ledger papers during 18 years' storage*

[All physical tests were made at 65-percent relative humidity and at 70° F.]

Sample no.	Kind of paper	Weight of 500 sheets, 17 by 22 inches	Stock		Thickness	Ash	Rosin	Glue	Starch	Acidity of water extract	Date examined	Folding endurance [1]			Bursting strength	Tensile strength [2]						Variation from strength in 1915		
																Not folded			Double folded once [3]					
			Rag	Coniferous chemical wood (sulphite)								Longitudinal direction	Transverse direction	Average, both directions		Longitudinal direction	Transverse direction	Average, both directions	Longitudinal direction	Transverse direction	Average, both directions	Folding endurance	Bursting strength	Tensile strength
		Lbs.	*Percent*	*Percent*	*0.0001 inch*	*Percent*	*Percent*	*Percent*		*pH*		*Double folds*	*Double folds*	*Double folds*	*Points*	*Kg*	*Kg*	*Kg*	*Kg*	*Kg*	*Kg*	*Percent*	*Percent*	*Percent*
31249	Ledger	22.0	100		32	1.0	1.0	3.5	Present		1915	3,489	1,626	2,558	62.0	10.7	5.8	8.3						
											1920	2,906	1,574	2,240	67.2	11.6	5.8	8.7				−12.4	+8.4	+4.8
										4.58	1933	2,241	1,697	1,969	54.3	11.1	5.9	8.5	10.3	6.0	8.2	−23.0	−12.4	+2.4
30857	Bond	17.2	100		27	.8	1.8	4.2	Trace		1915	2,686	877	1,782	39.5	8.0	4.4	6.2						
											1920	2,067	688	1,378	37.6	8.2	4.4	6.3				−22.7	−4.8	+1.6
										4.21	1933	1,754	706	1,230	39.5	7.5	4.2	5.9	7.0	4.2	5.6	−31.0	.0	−4.8
30730	do	20.3	100		33	.6	1.0	3.6	Present		1915	1,798	722	1,260	47.5	9.0	4.6	6.8						
											1920	1,192	535	864	47.2	9.9	4.6	7.3				−31.4	−.6	+7.4
										4.11	1933	649	306	478	44.0	9.4	4.2	6.8	8.0	4.2	6.1	−62.1	−7.4	.0
30855	Ledger	23.7	100		37	1.2	2.6	4.4	Trace		1915	2,138	1,206	1,922	59.5	10.8	5.9	8.4						
											1920	1,846	842	1,344	57.4	11.0	6.1	8.6				−30.1	−3.5	+2.4
										4.01	1933	773	480	627	54.8	10.4	6.1	8.3	7.9	5.9	6.9	−67.4	−7.9	−1.2
30856	Bond	20.2	53	47	33	.6	1.6	1.5	do		1915	400	131	266	33.0	6.5	3.8	5.2						
											1920	281	103	192	29.1	6.6	4.0	5.3				−27.8	−11.8	+1.9
										3.90	1933	73	46	60	28.7	5.8	3.3	4.6	4.7	3.2	4.0	−77.4	−13.0	−11.5
30858	do	20.7		100	33	2.3	1.2	None	None		1915	164	98	131	26.0	7.6	3.7	5.7						
											1920	71	43	57	22.8	7.5	3.4	5.5				−56.5	−12.3	−3.5
										4.52	1933	29	31	30	23.9	7.1	3.3	5.2	4.4	3.2	3.8	−77.1	−8.1	−8.8
31250	Ledger	20.5		100	30	3.6	1.5	None	Present		1915	270	58	164	28.5	7.2	3.8	5.5						
											1920	88	40	64	23.8	7.3	3.9	5.6				−61.0	−16.5	+1.8
										4.09	1933	10	11	11	23.5	6.5	3.5	5.0	3.3	2.9	3.1	−93.3	−17.5	−9.1

[1] Results of folding-endurance tests made in 1915 represent the average of 20 tests made on 2 machines; results for 1920 represent the average of 30 tests made on 3 machines; and those for 1933 represent the average of 30 to 40 tests made on 3 machines.

[2] All tensile-strength tests were made on strips 15 mm wide.

[3] Kirchner roller used.

DISCUSSION OF RESULTS

The pH value of the water extract from these samples ranged from as low as 3.90 in the rag and sulphite bond (no. 30856) to 4.58 in the all-rag ledger (no. 31249).

After 5 years' storage, tensile-strength tests did not indicate deterioration. Only in the rag and sulphite paper (no. 30856) and the two all-sulphite papers (nos. 30858 and 31250) did the deterioration indicated by bursting strength appear to be material. The folding-endurance tests on the other hand indicated material deterioration of all these papers except one of the all-rag ledgers (no. 31249), even after 5 years' storage. Generally speaking, the papers with the highest acidity as indicated by the pH of the water extract suffered the greatest deterioration.

In 18 years the folding endurance of the all-rag bonds and ledgers had decreased 23 to 67 percent. The bursting strength and tensile strength of the all-rag papers did not materially decrease during 18 years' storage. The bursting strength decreased 0 to 12 percent; and the tensile strength decreased not over 5 percent. The rag paper, no. 31249, which in 1933 had the lowest acidity as indicated by pH (4.58) showed the least decrease in folding endurance, and the rag paper, no. 30855, which in 1933 had the highest acidity (pH 4.01) showed the greatest decrease in folding endurance.

The folding endurance of the mixed rag and sulphite and of the all-sulphite papers decreased in 18 years 77 to 93 percent, the latter being an almost total loss of folding strength. The bursting strength decreased 8 to 18 percent, and the tensile strength decreased 9 to 12 percent during the same period. The acidity of the all-sulphite paper showing the least loss of folding endurance was pH 4.52, and that of the all-sulphite paper showing the greatest loss in folding endurance was pH 4.09.

A comparison of the tensile-strength tests made on strips in 1933 before double folding with Kirchner's creasing roller with those made at the same time on strips double folded once with the roller shows a decrease ranging from only 4 percent in the sample (no. 31249) having the greatest folding endurance, to as much as 38 percent in the sample (no. 31250) having the least folding endurance. These results indicate that the most brittle papers, as indicated by the loss in folding endurance, suffer the greatest decrease in tensile strength after being folded with the Kirchner roller.

The three papers (nos. 30856, 30858, and 31250) showing the greatest deterioration after 18 years' storage, as indicated by their folding endurance, tore easily. However, they showed no tendency to fall to pieces, and if kept in flat sheets with little or no handling and in an atmosphere free from acid fumes, would probably last for many years. Whether all of them would withstand handling and use appears problematical.

Neither the bursting-strength nor the tensile-strength results are in agreement with the folding-endurance results and do not appear to warrant the use of these tests as a means of indicating the extent of deterioration or the tendency to deteriorate. There appears to be no definite correlation between the results of the several types of physical tests. The folding-endurance test appears to give the best information as to the deterioration of these papers, and indicates

that acidity as indicated by the pH of the water extract is the chief factor in their deterioration.

The results of these tests indicate that there is a comparatively rapid loss in folding endurance of even the highest grades of record papers, if the acidity as expressed by the pH value of the water extract is moderately high. Moderately acid papers cannot be folded and unfolded many times, over even a comparatively short period of time, without serious weakening or even breaking at the fold. On the other hand, the bursting strength and tensile strength of these record papers showed comparatively little decrease over the period investigated, and deterioration of the papers as indicated by these tests would not appear to be serious.

SUMMARY AND CONCLUSIONS

Thirty-eight samples of paper taken from old books, magazines, and court records ranging in age from 19 to 169 years were examined. For comparison a sample of new record paper was examined. The leaves of each sample were divided into two subsamples representing marginal and center sections, respectively, and comparative chemical and physical tests were made on each section.

In general, more acid and more water-soluble sulphates were found in the marginal than in the center section of the same leaf. In some cases the quantity of acid in the margins was much greater than in the centers. The folding-endurance and bursting-strength results of the center section were equal to or greater than those of the marginal section for practically all the samples. In the samples where the strength of the center was less than that of the marginal section the difference was very small, being well within the experimental error.

The center and marginal sections of the leaves of one book, which had been kept well wrapped in paper and stored in the Library of Congress since publication in 1906, showed practically no difference in chemical and physical tests. However, the marginal section of the leaves of another copy of the same edition of this book, which had been stored unwrapped on the reference shelves of the New York Public Library in New York City for the same period, contained much greater acidity and water-soluble sulphates, and had much less strength, than the center sections of the same leaves.

The paper of another book, made of all-rag stock and published about 75 years before examination, was found free of acid in both the center and marginal sections. The latter section, however, contained more water-soluble sulphates and total sulphur than did the center section. This paper was in excellent condition throughout. The folding value was much higher than that of any other old book paper examined. It is significant that the water extract of the ash was alkaline in reaction. The filler used had undoubtedly neutralized the acidic sulphur compounds as they came in contact with the paper.

The results, which are in general agreement with those previously obtained by this Bureau on bookbinding leather (*4, 5, 14*) and by the National Bureau of Standards of the Department of Commerce on paper (*8, 9*), show that paper actually absorbs from the air harmful quantities of acidic sulphur compounds with which the air is generally polluted. The absorption is greater in the portions of the leaves more fully exposed to the atmosphere. Undoubtedly this is one

reason why in many old books and court-record volumes the leaves are more brittle near the outside edges than in the center.

It is significant, however, that with a few notable exceptions all the papers examined, and the printing and writing on them, are still intact and more or less serviceable. There is no reason to doubt that they will still be serviceable for a number of years if kept under proper storage conditions and not frequently used.

Most of the paper samples were discolored along the margins of the leaves. In general, the results indicate that the papers which showed little or no discoloration were in the best state of preservation.

Copper numbers were determined on the marginal and center sections of the 15 printing papers. The weakest samples, as indicated by the folding endurance and by general inspections and handling, gave relatively high copper numbers. However, in most cases the difference between the copper numbers of the two sections of any one sample was not great.

This investigation has shown that the paper in many valuable old books and court and other record volumes has greatly deteriorated and has become nearly worthless due to the absorption of acidic sulphur compounds from the air. In a previous investigation by this Bureau (7) on the effect of added small quantities of acids on the physical properties of waterleaf rag bond paper, it was found that when the pH of the water extract from the paper treated with sulphuric acid was 4.50 or less, the loss in folding endurance upon artificial aging by heating for 72 hours at 100° C. was more than 50 percent. In the present investigation nearly all the old papers examined gave a pH value of less than 4.50. Therefore it is to be expected that many records will steadily deteriorate and become worthless within a short time if much handled even though no further absorption of acid occurs.

These findings emphasize the need of further research to devise means of preventing or retarding deterioration caused by the presence of excessive quantities of aluminum sulphate and/or by the absorption of acidic sulphur compounds from the air. Libraries, especially those in cities and near coal-burning plants, should be so constructed as to permit conditioning and purifying of the air with which they are supplied. On the other hand, the incorporation in paper of suitable materials, such as a basic filler, to neutralize or counteract acidic gaseous sulphur compounds as such compounds come into contact with the paper may, it seems reasonable to think, decidedly prolong the life and serviceability of valuable book and record papers.

Seven samples of commercial bond and ledger papers, made in 1914 and 1915 and representative of high- and low-grade types, were collected in 1915, and tested for folding endurance, bursting strength, and tensile strength. They were stored under normal conditions in Washington, D. C., for 18 years. They were examined after 5 years' and again after 18 years' storage.

After 18 years the folding endurance of these papers had decreased from 23 to 93 percent, and the bursting strength had decreased from 0 to 18 percent. In most cases the tensile strength was affected but little, or not at all. In general, the papers with the highest acidity, as indicated by the pH of the water extract, suffered the greatest deterioration.

There were too few papers in these storage tests to permit any definite conclusions. The results are indicative, however, and they confirm other data that a moderately high acidity, that is, a pH of the water extract of less than 5, is a major factor in the deterioration of even the best classes of paper.

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