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Permanence in Book Papers

Investigation of deterioration in modern papers suggests a practical basis for remedy.

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The deterioration of paper in the books of libraries has been a matter of increasingly acute concern for nearly a century. Although sporadic attempts have been made over this period to ascertain the causes of the deterioration and to find means for preventing it, the problem continues to grow. In this article are presented the results of a recent attempt to determine its magnitude and to open some profitable avenues toward solution.

Background

Books, which were once a principal end product of paper manufacture, now absorb only a small fraction [less than 2 percent (*1*)] of all paper production. By far the greater part of this production has very ephemeral uses—in newspapers, shopping bags, shipping containers, towels, and so on. As a result, the qualities of permanence which once were among paper's most important characteristics now take a much lower place in the scale of importance and may, for most uses, be appropriately ignored. The literature of paper technology is enormous, but this literature typically shows little interest in the product beyond the immediate point of its conversion into consumer goods, and a paper technologist who feels completely at home with new paper may be quite nonplussed when confronted with a piece of paper which may be anywhere from 100 to 1000 years old.

At the other extreme are those for whom permanence is still one of paper's most important characteristics—the custodians of libraries and archives. By living with old papers, the members of these professions may acquire a "feel" for them which is lacking in the paper technologist, but they are usually quite naive with respect to the origin of the qualities which they esteem—a naivete which is betrayed in their urgent though uncritical specification of "all rag" content whenever permanence is desired.

Because libraries cannot prescribe the characteristics of the paper which enters their collections but must take what the market affords, it is no wonder that increasingly, since the introduction of the ground wood and chemical wood fiber papers of the last decades of the 19th century, the custodians of these institutions should find themselves piling up mountains of paper only to watch these mountains disintegrate before their eyes. With respect to newspapers, this situation became so acute and concentrated that it has been met to a considerable extent—with concomitant gains in space saving—through the techniques of microfilming; but for the generality of books the problem is more diffused and complex, and microfilming would consequently be so costly and so wasteful, and would impose so many inconveniences, that these institutions have looked for other solutions or—at the very least—for an improvement in the quality of currently used book papers.

These hopes have been largely unrealized through a combination of circumstances; among these the economics of the situation undoubtedly plays the largest part, but there are other factors also. One of these is lack of appreciation of the exact state of affairs with respect to the deterioration of book papers, the rate and extent of such deterioration, the expectations of permanence which may legitimately be held regarding papers in current use, and so on. Still another is the lack of understanding of the real causes of deterioration and the consequent paucity of economically feasible techniques for preventing it.

In the very recent past, even when publishers, librarians, and papermakers have cooperated in efforts to produce a durable book, the lack of understanding of the real causes of deterioration has too often led to failure. For example, when, in 1906, the Library of Congress commenced publication of the important records of the Virginia Company of London which it had inherited from Thomas Jefferson, it arranged for publication on all-rag paper made by one of the country's oldest and best paper manufacturers (*2*). But by 1928 the resulting volumes (the first two of a set of four) were falling to pieces because of an excessive use of aluminum sulfate and rosin in the sizing.

Deterioration in paper—a process which occurs even under storage conditions which are "normal" with respect to temperature, humidity, and cleanliness, and which is distinguished from the impairment resulting from insects, molds, or use—is evidenced by progressive embrittlement, which eventually prevents ordinary handling. Such deterioration is generally ascribed either to the polluted air of cities or to injurious agents introduced into the paper during the course of manufacture. Considerable attention has been given to the first of these factors, and especially to the effects of sulfur dioxide on paper and to its removal from the air of libraries (*3–5*). It has been found that books stored in urban areas are more acid than those kept in

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rural locations (*4, 5*); in one case the paper in copies of a book stored in cities showed, over a 25-year period, 2 to 9 percent greater loss in folding endurance than copies of the same book held in rural repositories, but the difference seemed to be ascribable to differences of use rather than of storage conditions (*6*). One study, however, indicates that the greatest absorption of acid occurs in the outer edges of the leaves (*4*). Thus, these studies have shown that while removal of acidic gases from the atmosphere is desirable, such gases account for only a small part of the total deterioration. And they do not explain the phenomenon, frequently observed by the librarian who has stored different books under the same conditions for years, that the leaves of 25- to 50-year-old volumes are cracking while those of 300-year-old volumes remain flexible and strong (Fig. 1). Storage conditions could not by themselves have caused the deterioration of the later books. In spite of this fact, far too little attention has been given to identifying and to inactivating or removing the other probable causes of deterioration—agents introduced into the paper at the time of manufacture.

Yet the history of writing materials suggests avenues of inquiry into this matter. Many early materials have shown amazing stability under storage conditions in which most modern papers would last only a few decades. Papyrus, for example, was a principal vehicle of written records from at least 3000 B.C. down to the advent of paper, 4000 years later, and abundant examples survive. While the relation of acidity to the permanence and retention of flexibility of papyrus has not been adequately explored, two very embrittled examples of about 1000 B.C., examined in the course of our study (*7*), showed high acid levels (*p*H 3.8 and 3.9, respectively). From some time before the beginning of the Christian Era, papyrus was (in the West) in increasingly keen competition with vellum and parchment. These were prepared by a lime process from the skin of sheep, calves, and other animals, and it has been conjectured that their excellent lasting qualities (as evidenced in the Dead Sea Scrolls, some of which date from the 1st century B.C.) are due to the presence of residual calcium carbonate from the manufacturing process. These, in general, have lasted much better than their counterpart, leather, whose acidity varies with the method of tanning.

It took paper a thousand years to travel from China to Europe, which it reached only in the 12th century. But well before the end of the Middle Ages it had become the most common material for record-keeping and had outstripped parchment and vellum as the material used for all but the most important permanent records. Linen rags were the principal source of cellulose fiber in the manufacture of the earlier European papers (*8*), and many of these have lasted well. Several investigators (*4, 9, 10*) have found that the strongest early papers are either very slightly acid (*p*H 6.0 and above) or mildly alkaline, and they attribute this condition to the presence of calcium and magnesium compounds. These compounds may have been introduced either during the bleaching of the rag with extract of wood ashes or through washing the rag with water containing bicarbonates of these elements. It is unlikely that lime was used in the preparation of the pulp (though its use would account for the presence of calcium), since such a process does not appear in the literature until much later. Regardless of the source of these compounds, however, they are associated with preservation, while the acid papers of the same period are today either quite brittle or have altogether disappeared.

Confirmation of these clues is afforded by the history of inks. In the course of the Middle Ages the carbon inks were gradually supplanted in the West by iron gall inks. These contained sulfuric acid, as a result of the interaction of ferrous sulfate with oak gall tannins, in varying degrees of concentration corresponding with the very considerable variations in the old formulae (*9*). Highly acid inks have often done considerable damage to paper, even to the extent of eating holes in it (Fig. 2), while the low-acid inks caused little or no damage, and in some cases the alkalinity of the paper was sufficient to neutralize the acid. The damage done to vellums and parchments by these inks was similarly small, due to the high lime content.

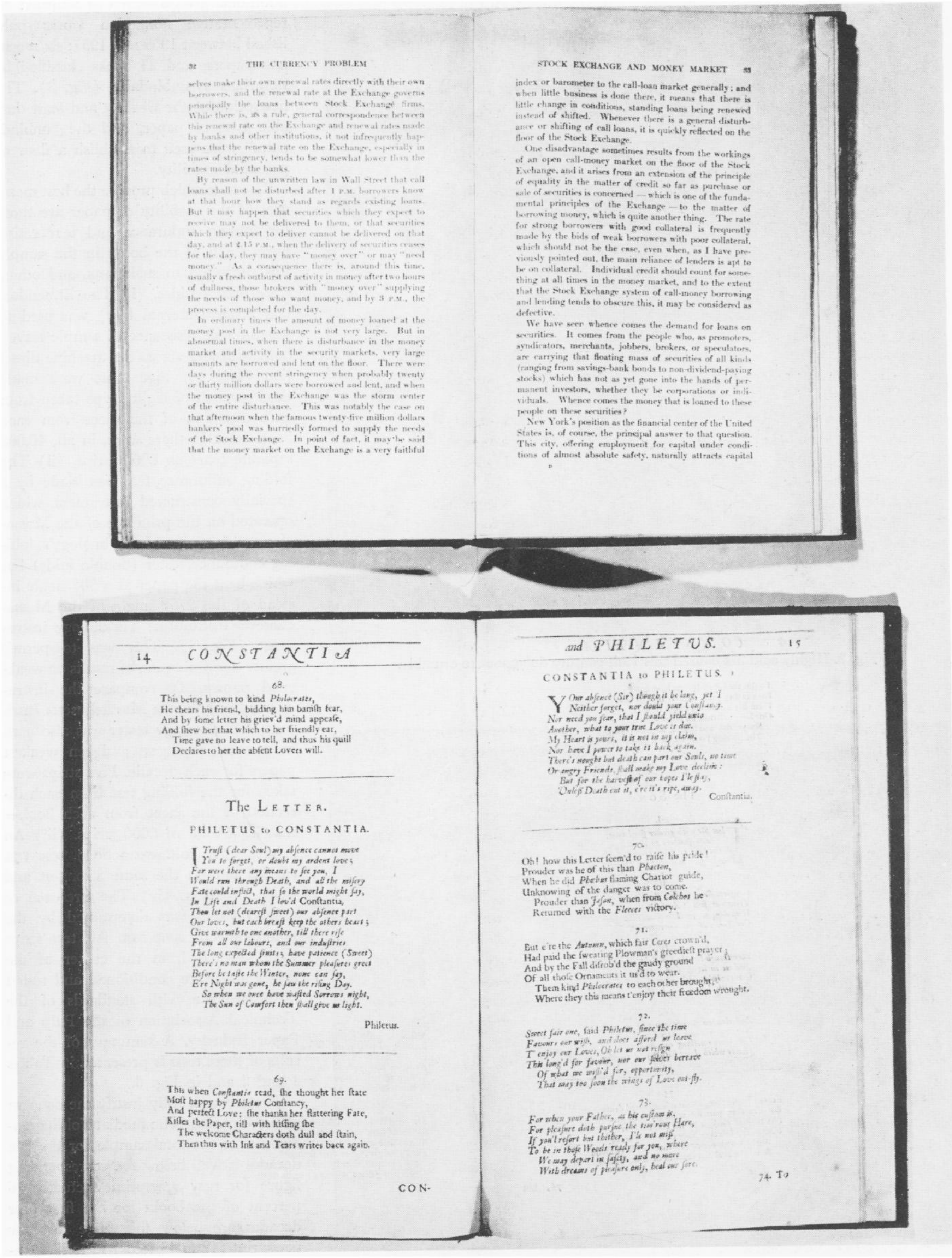
It was paper, as much as any one thing, that made possible the transition from the Middle Ages to the modern world, for it was only through paper that the world could fully benefit from the invention of printing. Printing may, in consequence, be said both to owe its success to paper and at the same time to have ushered in the modern age of paper. Yet there is a certain ironic quality in the observation that this very invention so assisted in stimulating the needs and uses for paper and so advanced the technology by which those needs have been met that it resulted in the progressive loss of that very permanence which it had seemed to insure (*8, 9, 11*).

The use of potassium aluminum sulfate in sizing had already commenced before the end of the 17th century. This was only the first of a number of additives which threatened eventually to shorten the life of paper. Forced by rising demand to resort to less than the best or to other than traditional raw materials, the papermaker found that he could employ weakened rag if he corrected its yellow tint by blueing, and (after 1774) that he could bleach other discolored (and often weak) material with chlorine. Even the relatively pure source of cellulose that became available with the invention of the cotton gin (1793) did not long satisfy the spiraling demand, and the last decades of the 19th century found grass (from 1860) and wood (from 1880) firmly established as raw materials, bringing with them new threats to permanence, either through unwanted constituents of the raw material or through residues or effects of the reagents used to remove such constituents (chlorine, sodium hydroxide, sodium sulfate, calcium bisulphite, and so on).

Meanwhile, as striking evidence of the high degree of stability which a well-made paper can possess and with which the papers of important books and documents should be endowed, every great library can show examples—and in some cases many thousands of examples—of books printed or written five and more centuries ago on paper which is still white, strong, and flexible, though kept under the same storage conditions as books one-tenth as old which have long ceased to be usable.

Physical Strength of Modern Book Papers

In the light of the foregoing facts, it appeared desirable to ascertain, in the first place, just what has happened and is happening to books printed on modern book papers. For this purpose, a representative sample was assembled, consisting of 500 nonfiction books issued by American publishers during the period 1900 to 1949 and comprising 100 books for each decade. None of these books bore signs of having suffered from adverse storage conditions or wear. Three



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selves make their own renewal rates directly with their own borrowers, and the renewal rate at the Exchange governs principally the loans between Stock Exchange firms. While there is, as a rule, general correspondence between this renewal rate on the Exchange and renewal rates made by banks and other institutions, it not infrequently happens that the renewal rate on the Exchange, especially in times of stringency, tends to be somewhat lower than the rates made by the banks.

By reason of the unwritten law in Wall Street that call loans shall not be disturbed after 1 P.M. borrowers know at that hour how they stand as regards existing loans. But it may happen that securities which they expect to receive may not be delivered to them, or that securities which they expect to deliver cannot be delivered on that day, and at 2.15 P.M., when the delivery of securities ceases for the day, they may have "money over" or may "need money." As a consequence there is, around this time, usually a fresh outburst of activity in money after two hours of dullness, those brokers with "money over" supplying the needs of those who want money, and by 3 P.M., the process is completed for the day.

In ordinary times the amount of money loaned at the money post in the Exchange is not very large. But in abnormal times, when there is disturbance in the money market and activity in the security markets, very large amounts are borrowed and lent on the floor. There were days during the recent stringency when probably twenty or thirty million dollars were borrowed and lent, and when the money post in the Exchange was the storm center of the entire disturbance. This was notably the case on that afternoon when the famous twenty-five million dollars bankers' pool was hurriedly formed to supply the needs of the Stock Exchange. In point of fact, it may be said that the money market on the Exchange is a very faithful

STOCK EXCHANGE AND MONEY MARKET 33

index or barometer to the call-loan market generally; and when little business is done there, it means that there is little change in conditions, standing loans being renewed instead of shifted. Whenever there is a general disturbance or shifting of call loans, it is quickly reflected on the floor of the Stock Exchange.

One disadvantage sometimes results from the workings of an open call-money market on the floor of the Stock Exchange, and it arises from an extension of the principle of equality in the matter of credit so far as purchase or sale of securities is concerned — which is one of the fundamental principles of the Exchange — to the matter of borrowing money, which is quite another thing. The rate for strong borrowers with good collateral is frequently made by the bids of weak borrowers with poor collateral, which should not be the case, even when, as I have previously pointed out, the main reliance of lenders is apt to be on collateral. Individual credit should count for something at all times in the money market, and to the extent that the Stock Exchange system of call-money borrowing and lending tends to obscure this, it may be considered as defective.

We have seen whence comes the demand for loans on securities. It comes from the people who, as promoters, syndicators, merchants, jobbers, brokers, or speculators, are carrying that floating mass of securities of all kinds (ranging from savings-bank bonds to non-dividend-paying stocks) which has not as yet gone into the hands of permanent investors, whether they be corporations or individuals. Whence comes the money that is loaned to these people on these securities?

New York's position as the financial center of the United States is, of course, the principal answer to that question. This city, offering employment for capital under conditions of almost absolute safety, naturally attracts capital

D

14 *CONSTANTIA*

68.

This being known to kind *Philocrates*,
He chears his friend, bidding him baniſh fear,
And by ſome letter his griev'd mind appeaſe,
And ſhew her that which to her friendly ear,
Time gave no leave to tell, and thus his quill
Declares to her the abſent Lovers will.

The LETTER.

PHILETUS to CONSTANTIA.

I Truſt (dear Soul) my abſence cannot move
You to forget, or doubt my ardent love;
For were there any means to ſee you, I
Would run through Death, and all the miſery
Fate could inflict, that ſo the world might ſay,
In Life and Death I lov'd Conſtantia,
Then let not (dearest ſweet) our abſence part
Our loves, but each breaſt keep the others heart;
Give warmth to one another, till there riſe
From all our labours, and our induſtries
The long expected fruits; have patience (Sweet)
There's no man whom the Summer pleaſures greet
Before he taſte the Winter, none can ſay,
E're Night was gone, he ſaw the riſing Day.
So when we once have waſted Sorrows night,
The Sun of Comfort then ſhall give us light.

Philetus.

69.

This when *Conſtantia* read, ſhe thought her ſtate
Moſt happy by *Philetus* Conſtancy,
And perfect Love: ſhe thanks her flattering Fate,
Kiſſes the Paper, till with kiſſing ſhe
The welcome Characters doth dull and ſtain,
Then thus with Ink and Tears writes back again.

CON-

and PHILETUS. 15

CONSTANTIA to PHILETUS.

YOur abſence (Sir) though it be long, yet I
Neither forget, nor doubt your Conſtancy.
Nor need you fear, that I ſhould yield unto
Another, what to your true Love is due.
My Heart is yours, it is not in my claim,
Nor have I power to take it back again.
There's nought but death can part our Souls, no time
Or angry Friends, ſhall make my Love decline:
But for the harveſt of our hopes I'le ſtay,
Unleſs Death cut it, e're it's ripe, away.

Conſtantia.

70.

Oh! how this Letter ſeem'd to raiſe his pride!
Prouder was he of this than *Phaeton*,
When he did *Phebus* flaming Chariot guide,
Unknowing of the danger was to come.
Prouder than *Jaſon*, when from *Colchos* he
Returned with the *Fleeces* victory.

71.

But e're the *Autumn*, which fair *Ceres* crown'd,
Had paid the ſweating Plowman's greedieſt prayer;
And by the Fall diſrob'd the gaudy ground
Of all thoſe Ornaments it us'd to wear.
Them kind *Philocrates* to each other brought,
Where they this means t'enjoy their freedom wrought.

72.

Sweet fair one, ſaid *Philetus*, *ſince the time*
Favours our wiſh, and does afford us leave
T' enjoy our Loves, Oh let us not reſign
This long'd for favour, nor our ſlower bereave
Of what we wiſh'd for, opportunity,
That may too ſoon the wings of Love out-fly.

73.

For when your Father, as his cuſtom is,
For pleaſure doth purſue the tim'rous Hare,
If you'l reſort but thither, I'le not miſs
To be in thoſe Woods ready for you, where
We may depart in ſafety, and no more
With dreams of pleaſure only, heal our ſore.

74. To

Fig. 1. Two volumes, printed 227 years apart. The upper one (1908) has a *p*H of 4.3 and has deteriorated to such an extent that it has a folding endurance of 0 folds; the lower one (1681) has a *p*H of 5.7 and a folding endurance of 1117 folds.

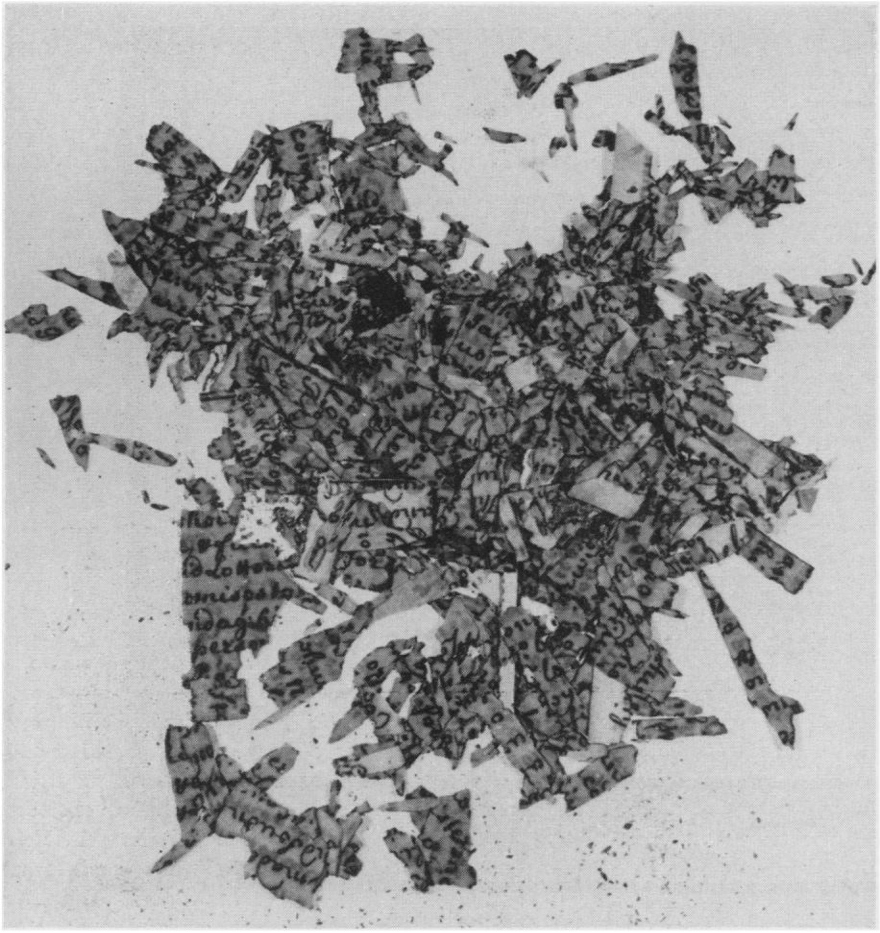

Fig. 2. Highly acid ink caused this 18th-century document to crumble.

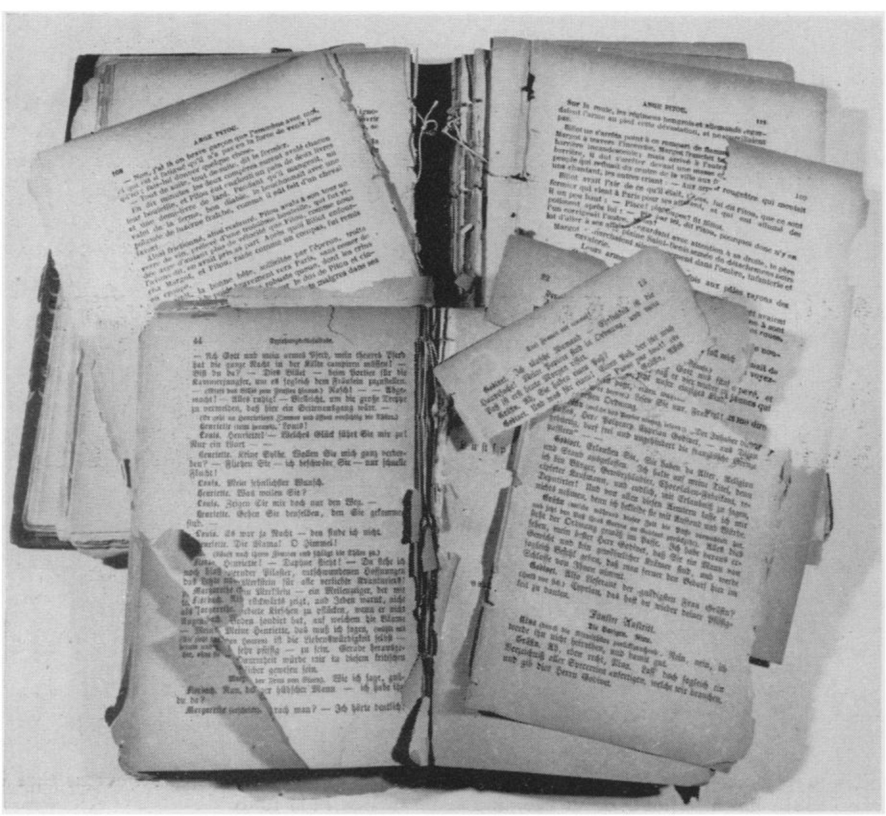

Fig. 3. "Unbindables."

additional groups served as controls: 32 representative nonfiction works published between 1955 and 1957; six recent newspapers; and 25 books classified by librarians as unbindable (Fig. 3). The newsprint, as the weakest and least durable type of paper, and the "unbindables" were used to establish a floor of potential usability.

The tests which provide the best measures of the usability of paper are those for folding endurance and tear resistance. Each of the books in the sample was subjected to such tests, and others were used besides. (i) The Elmendorf tear tester (internal tear) was used to test the tear resistance of sample leaves, both with and across the machine direction (Fig. 4). Five tears were made through each of eight strips taken from each direction of the sheet from each book—that is, there were, in all, 40,000 separate tears on 8000 strips. (ii) The folding endurance test was made by a specially constructed instrument which operated on the principle of the Massachusetts Institute of Technology's folding endurance tester (double folds) but which bent the paper at a 90° angle instead of the 270° angle of the Massachusetts Institute of Technology instrument (Fig. 5). This was to permit greater discrimination of results on weakened papers. To compare the instruments, however, the Massachusetts Institute of Technology tester was also used on the ten strongest and ten weakest papers for each decade. Five strips were taken for the folding test from each direction of the sheet from each book—that is, a total of 5000 strips. (iii) An acidity (*p*H cold extraction) test was carried out on the same strongest and weakest papers. (iv) The presence of ground wood was determined by the phloroglucinol spot test. All test strips were selected from the center of the leaves and were conditioned and tested in accordance with standards of the Technical Association of the Pulp and Paper Industry. A summary of the results of these tests is presented in Tables 1 and 2 and in Fig. 6.

These results fully justify the concern of the librarian. The median folding endurance of the total sample for the five decades is well below the corresponding figure for new newsprint. Actually 76 percent of the books for the first four decades are below the range for new newsprint (12 to 45 folds) in folding endurance; 17 percent are within that range, and only 6 percent are stronger. If it may be assumed that the folding endurance of the 1955 to 1957 books (average, 291 folds) is typical of the entire sample when new, it is evident that there has already been a very steep falling off in the books of the 1940 to 1949 decade (average, 106 folds). But the deterioration of the books of this decade has not as yet shown itself sufficiently for full evaluation of its rate or extent.

Acidity may well be the principal cause of deterioration in these papers. Ground wood was found in only 21 of the 500 volumes, and in only six made before 1940, while the role of acidity from other sources is strongly suggested by a comparison of the *p*H values of the weakest and strongest papers (Table 2). In such a comparison it appears that the acidity of the weakest papers is, on the average, from six to ten times as great as that of the strongest. It may be suspected, accordingly, that many of even the stronger papers will continue to deteriorate, since few have a *p*H above 6.0.

The principal sources of this acidity are probably alum rosin sizing, residual chlorides from the bleaching, and a breakdown in some of the oxidizable carbohydrates found in chemical wood fibers. Of course, a small amount may be due to deteriorated cellulose, but failure to wash the chlorides from the fibers and the use of alum in the sizing probably account for most of the acid present.

It also appears from these results that the folding endurance test is the most meaningful for measuring the physical effects of aging. Because a pattern of deterioration similar to that found here, in terms of progressive loss of folding endurance, results from accelerated aging by baking at 100°C [each 72 hours of baking has been found to be the approximate equivalent of 25 years of aging under normal storage conditions (*12*)], the reliability of that method for predicting the permanence of a paper receives additional confirmation.

Stabilization of New Book Papers

It appears both from this and from other studies that in older papers and—as is discussed below—in the newer papers as well, acidity (*p*H of less than 6.0) is associated with deterioration and that mild alkalinity is associated with stability (*4, 5, 9–11, 13–15*). If, then, acidity is a principal enemy of paper, it should logically be expected that stability would be improved through the use of neutralizing agents. Previous investigations (*9*) have shown that the hydroxides and bicarbonates of calcium are effective in counteracting acidity in paper and in stabilizing it under artificial aging tests; further, that the small amounts of calcium carbonate precipitated in paper through soaking in solutions of these compounds appear, upon accelerated aging, to have no ill effects and serve as a buffer for acids which may later be absorbed. However, soaking papers in two solutions seemed to be too

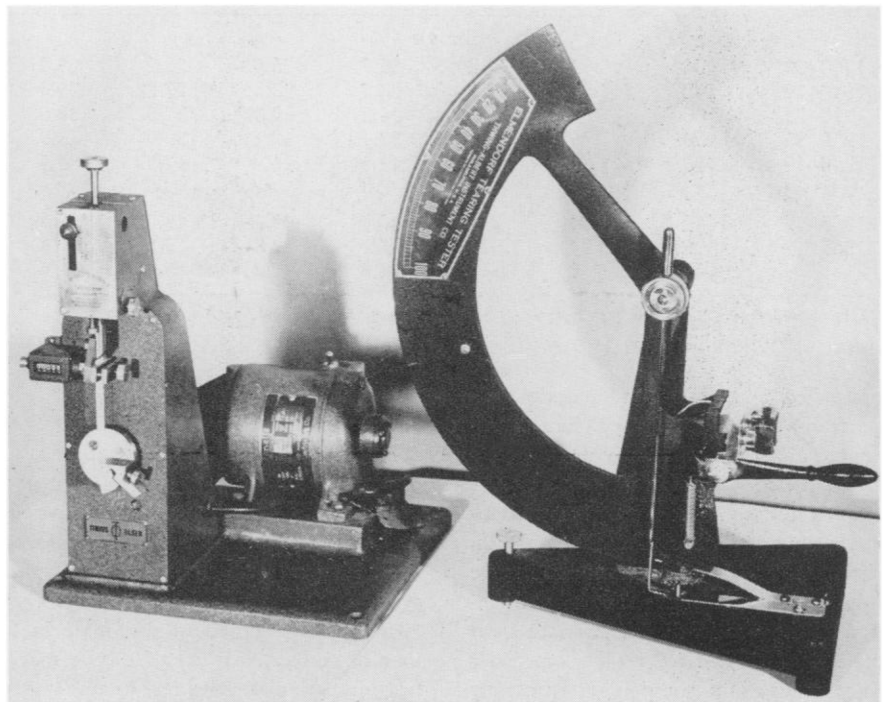

Fig. 4. (Left) The MIT folding endurance tester, used to measure flexibility. (Right) The Elmendorf tear resistance tester, used to measure tear resistance. When the left-hand clamp is moved upward by the swinging pendulum, the paper is torn and the number of grams required to make a continuous tear across the sheet is registered on the dial.

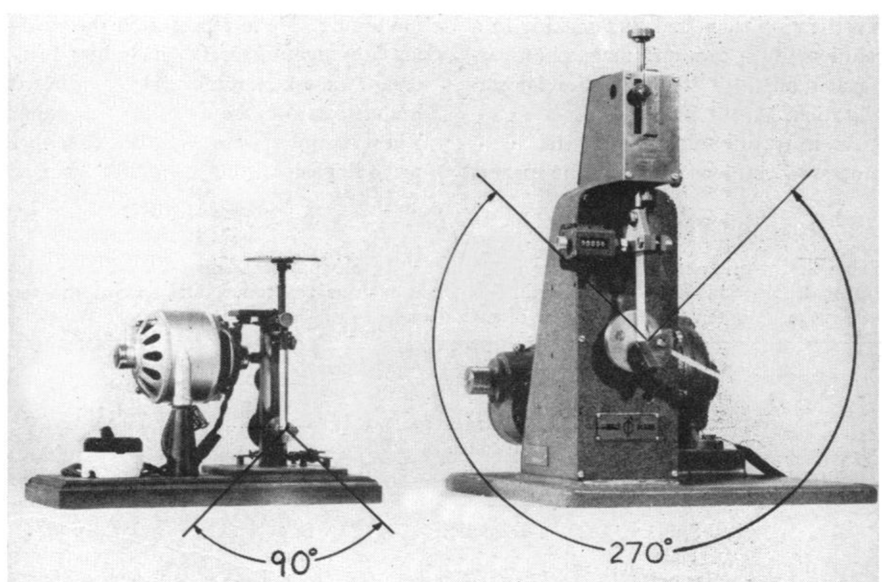

Fig. 5. (Left) The special fold tester used in this study. (Right) the MIT folding endurance tester. In the latter, the paper specimen is fastened first in the upper clamp and then in the oscillating lower jaw. Both ends of the specimen are held tight by screw clamps, and the desired tension is applied. The lower jaw bends or folds the paper at a 270° arc until it breaks; the number of folds is recorded on a counter. The special fold tester operates on a similar principle but folds the paper strip at a 90° arc. This tester is suitable for very weak papers.

Table 1. Present strength of paper in nonfiction books published in the United States during the period 1900–1949.

Period	No. of books	Folding endurance* (folds)		Tear resistance (g)			
				Median		Average	
				Direction in leaf		Direction in leaf	
		Median	Average	Long	Short	Long	Short
			Sample				
1900–09	100	4	12	25.7	25.8	28.2	29.6
1910–19	100	3	9	24.7	22.6	27.2	29.0
1920–29	100	4	8	26.2	28.3	27.6	30.0
1930–39	100	9	51	37.4	42.1	38.6	43.3
1940–49	100	19	106	41.5	44.0	42.0	44.5
			Controls				
1955–57	32	164	291	46.2	49.3	46.2	49.3
1957	6†	24	27	16.1	19.3	16.1	19.3
	19‡	1	3	14.8	15.8	15.0	14.0

* Tension of 1 kg on the special fold tester. † Newsprint. ‡ Very weak (unbindables).

prolonged and costly an operation for general adoption, while calcium bicarbonate alone is not entirely effective because of its low solubility.

Consequently, since magnesium carbonate has characteristics similar to calcium carbonate and is at the same time more soluble, it was thought that a combination of the two in the bicarbonate form might give the desired results, especially since magnesium compounds (probably in the original form of carbonates or phosphates) are found together with calcium in well-preserved old papers—prima facie evidence, at least, that such compounds are not harmful to cellulose (*9*). Preliminary experiments during our investigation suggested that soaking in a solution of calcium and magnesium carbonates offers good possibilities for stabilization.

As it was developed, the stabilizing process consists of soaking the papers overnight in a saturated solution of calcium and magnesium bicarbonates. The bicarbonates left in the sheet after soaking revert upon air-drying to the carbonate form. The solution is prepared by passing carbon dioxide for 2 hours through a solution containing 1.5 to 2 grams of calcium carbonate and 15 to 20 grams of magnesium carbonate in 1 liter of water. Nearly half of the magnesium carbonate and about one-tenth of the calcium carbonate is converted to bicarbonates. After the undissolved particles settle, the clear solution is decanted for use.

Twenty-six reams of different papers commonly used in books were obtained for testing. These represented the products of manufacturers (including principal manufacturers) in the United States east of the Rocky Mountains. These samples were classified as either text, English finish, or coated papers. Comparison was made of the physical and chemical characteristics of specimens of each of these papers, with and without the stabilizing treatment, and both before and after accelerated aging.

For the physical tests the MIT folding endurance tester (double folds) and the Elmendorf tearing resistance tester (internal tear) were employed, since the characteristics tested by these machines are those chiefly involved when the pages of a book are turned.

For the folding endurance test, five consecutive sheets were selected from each ream. Ten test strips were cut from each sheet in each direction; of these five served as controls and five were subjected to accelerated aging. The total of these was 2600 strips. For the tear-resistance test a similar process of selection was employed, except that four strips were taken instead of five; the total of these was 2080 strips. Letter-size sheets were cut from each ream and were subjected to the stabilizing process; the same numbers of test strips were similarly cut from these. The grand total of test strips was consequently 9360. All samples, treated and untreated, were conditioned and tested according to standards of the Technical Association of the Pulp and Paper Industry.

Accelerated aging was effected by heating for 72 hours at 100° ± 2°C, in accordance with the procedure developed at the National Bureau of Standards (*12*). The temptation to use higher temperatures in emulation of certain other investigations, in order to hasten the accelerated aging test, was resisted because it was suspected that these higher temperatures induce a breakdown in the cellulose which does not occur in natural aging.

Exploratory tests were made for copper number, water extractables, alkali solubles, and viscosity; but, though viscosity data exhibited a small trend, they showed no relation to folding endurance or tear resistance, and none of these tests proved satisfactory for evaluating the stability of the papers following accelerated aging, the indications being that chemical tests of this type are not sensitive enough to uncover the subtle changes that are occurring. In addition, however, test specimens were subjected to *p*H measurement, to fiber analysis, and to a spot test with dilute hydrochloric acid to detect the presence of carbonates through the evolution of carbon dioxide. Of all tests, those for folding endurance, tear resistance, and *p*H were found to be the best indicators for

Table 2. Present strength of paper in nonfiction books published in the United States during the period 1900–1949. Folding endurance, tear resistance, and *p*H of the ten weakest and the ten strongest papers of each decade.

Decade	Weakest					Strongest				
	*p*H*	Folding endurance (double folds)		Tear resistance (g)		*p*H*	Folding endurance (double folds)		Tear resistance (g)	
				Direction					Direction	
		Special tester†	MIT tester‡	Long	Short		Special tester†	MIT tester‡	Long	Short
1900–09	4.3	0	0	12.4	14.3	5.3	71	14	40.9	41.1
1910–19	4.2	1	0	13.2	15.6	5.2	29	8	41.9	42.1
1920–29	4.4	1	1	15.2	16.5	5.0	30	10	37.4	36.1
1930–39	4.4	2	2	22.9	27.7	5.1	398	73	55.0	65.0
1940–49	4.4	5	4	26.0	30.0	5.1	530	180	59.4	55.4

* Relative hydrogen-ion concentrations (cold extraction.) † Tension, 1 kg. ‡ Tension, ½ kg.

relating the effects of natural aging to accelerated aging for different papers.

The principal results of these tests are given in Tables 3 and 4, where text papers and English finish papers are differentiated from coated papers and where the samples are arranged in ascending order of relative retention of folding endurance after accelerated aging.

Because it was found that three out of four of the total sample of 532 books (published between 1900 and 1957) tested in the previous investigation were constructed with the machine direction of the paper parallel to the spine, it appeared that the significant tests for measuring the resistance of paper to the strains imposed upon it in the natural use of books are those for folding endurance in the cross direction and for tear resistance in the machine direction. These, in consequence, are the tests reflected in Table 3. Table 4, however, shows retention of the characteristics of physical strength expressed in percentages of average values obtained for both directions of the papers and relates these to the respective *p*H values.

It will be seen from Table 3 that while seven of the text papers and English finish papers, when new, were able to withstand more than 100 folds, after a cycle of accelerated aging only four remained in this category, and that the average drop in folding endurance after a cycle of accelerated aging was from 126 to 58 folds—a loss of 54 percent. By way of contrast, it may be noted that new rag bond papers often survive 3000 folds and that many book papers from 200 to 400 years old can still endure 300 to 1500 folds.

Table 3 also shows what happens to the tear resistance of these papers upon accelerated aging. Two books in the entire sample tore at 30 grams or less when new; after accelerated aging there were eight in this category, and the drop for the text papers and English finish papers (chiefly used for text, in contrast to the coated papers, which are chiefly used for illustrations) was from 54.9 to 42.4 grams—a loss of 23 percent.

The seven coated papers tested showed greater folding endurance but a lower tear resistance than the other two types. It is interesting to note that these papers were found to be mildly alkaline when the entire sheet was ground and tested. However, when they were laminated with cellulose acetate, split into four layers, and delaminated with acetone, the two inside layers were found to be either acid or less alkaline that the two outer layers. This suggests that in coated papers the acidity may be localized. Further work is required to determine the significance of this observation. It is doubtful whether the coated papers will withstand much more wear than the uncoated, because of their low tear resistance.

The fiber analyses on all papers showed that chemical wood fibers were used almost exclusively; rag and ground wood were found only in traces. Hardwood fibers prepared by the sulfite and soda processes predominated, while softwood fibers and the sulfate process were identified less frequently. Thus, the type of chemical wood fiber principally used was itself not conducive to stability.

Again, as with the older papers represented in Tables 1 and 2, the relation of acidity to deterioration is clearly seen in these new papers. Those which showed the highest rate of deterioration following accelerated aging, as indicated by loss in folding endurance and tear resistance, also have the greatest acidity. The three papers among the text and English finish papers which held up best after accelerated aging (samples No. 24, 25, and 26) had the least acidity. Again, it appears that acidity is the principal cause of deterioration, and that it occurs in new papers as well as in old.

None of the 26 papers tested may be considered to have either sufficient original strength or sufficient permanence to qualify them for use in books having a prospect of moderate usage over a long period of time. Under conditions of normal use in libraries, it is doubtful whether they would hold up much better than the 500 volumes tested for the period 1900 to 1949. It may be predicted with some assurance that the high rate of deterioration among most of the new papers will present quite a problem to librarians some three to six decades hence.

So much for the 26 new book papers prior to the stabilizing treatment. These

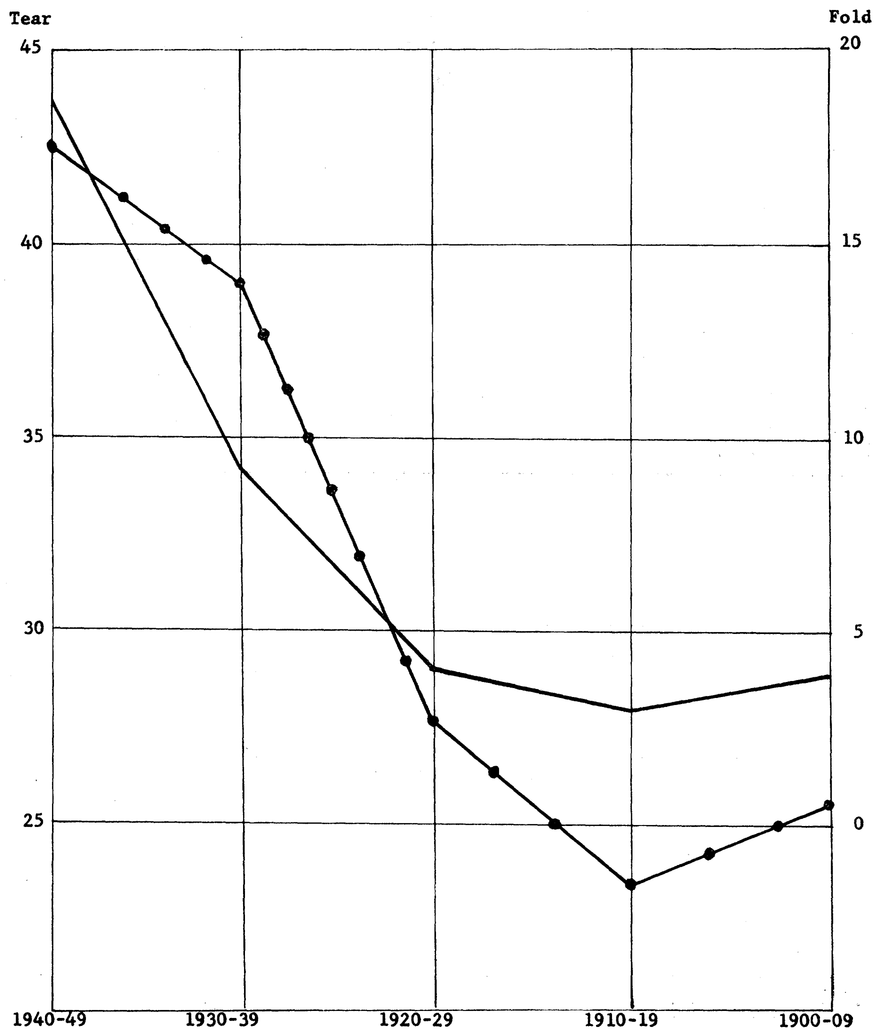

Fig. 6. Median fold and tear, plotted by decades. Smooth line, fold; dotted line, tear (average for both directions).

Table 3. Principal folding-endurance and tear-resistance data for 26 treated and untreated modern book papers before and after accelerated aging for 72 hours at 100°C. CD, cross direction of the sheet; MD, machine direction of the sheet; ½ kg tension used on all fold-test specimens (MIT tester).

Sample	Untreated				Treated			
	Folds, CD		Tear (g), MD		Folds, CD		Tear (g), MD	
	Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging
			Text and English finish papers					
1	459	101	101.0	64.2	459	381	103.9	92.6
2	44	18	63.6	41.8	64	53	64.9	64.8
3	275	95	25.8	12.7	263	289	26.6	23.0
4	235	53	76.7	57.2	324	228	79.9	75.4
5	81	39	73.4	52.4	104	116	72.3	71.4
6	384	122	67.6	47.8	401	323	72.7	70.8
8	41	22	43.7	29.8	60	65	40.3	41.8
9	107	50	46.5	31.8	98	101	52.9	48.6
10	57	36	50.4	43.3	94	83	56.2	55.8
12	186	100	53.4	46.6	235	187	61.8	59.0
14	44	32	29.2	21.6	46	38	31.4	29.8
15	59	48	59.4	46.7	99	117	62.3	57.9
16	13	9	33.9	25.8	15	16	31.2	31.0
17	91	63	81.0	72.8	123	88	84.5	76.9
18	17	12	43.9	40.5	26	26	42.2	40.9
22	24	20	50.1	43.8	31	30	48.6	44.6
24	136	126	66.5	57.8	113	124	64.6	58.2
25*	59	63	34.3	29.2	73	57	38.6	35.6
26*	77	89	43.6	40.7	107	88	48.7	45.8
Average	126	58	54.9	42.4	144	127	57.0	53.9
			Coated papers					
7	71	29	33.6	28.2	68	39	37.6	32.7
11*	358	186	35.3	30.6	361	395	41.8	37.9
13	315	208	38.9	33.5	414	376	40.2	37.3
19	272	241	26.0	23.8	546	357	31.3	27.8
20	201	156	38.6	18.1	355	317	24.0	21.6
21*	334	271	34.2	30.8	507	368	39.6	36.5
23*	431	316	41.9	39.8	314	278	44.7	45.0
Average	283	201	35.5	29.3	366	304	37.0	34.1

* Spot test indicates presence of calcium carbonate.

Table 4. Relative retention of folding endurance and tear resistance, and *p*H, of 26 treated and untreated modern book papers before and after accelerated aging for 72 hours at 100°C.

Samples*	Untreated				Treated			
	*p*H		Retention of folding endurance after aging† (%)	Retention of tear resistance after aging† (%)	*p*H		Retention of folding endurance after aging† (%)	Retention of tear resistance after aging† (%)
	Control	After aging			Control	After aging		
			Text and English finish papers					
1–4	5.0	5.3	26	64	9.0	9.1	86	93
5, 6, 8, 9	5.0	5.0	36	70	8.9	9.0	94	97
10, 12, 14	5.0	5.0	53	80	8.9	9.1	82	95
15–18	5.3	5.3	63	83	8.9	9.0	93	93
22, 24–26	5.8	5.7	92	89	8.9	9.0	92	93
			Coated papers					
7, 11, 13	9.4	9.3	50	87	8.9	9.1	86	91
19, 20, 21, 23	9.4	9.2	80	82	9.1	9.2	84	93

* Average of groups of papers. † Average, both directions.

same papers, after being soaked in the solution of calcium and magnesium bicarbonates, exhibited a decided increase in stability. This is seen in Table 3 in their increased retention of both folding endurance and tear resistance following accelerated aging. In contrast to the average 46-percent retention of folding endurance in the cross direction after accelerated aging shown by untreated text and English finish papers, these papers after treatment show 88 percent retention. The corresponding figures for tear resistance in the machine direction are 77 and 95 percent. If the two characteristics of folding endurance (in the cross direction) and tear resistance (in the machine direction) are combined as a general indication of strength, then the retention of the untreated papers is 67 percent and that of the treated papers is 92 percent. Table 4 shows averages of characteristics for both directions.

The sampling procedure upon which this finding is based was computed for the 95-percent confidence level; in consequence, it is believed that errors due to sampling variations have been avoided, and that the percentages of improvement shown have a high degree of reliability.

It is significant, too, that the higher *p*H of the papers after treatment changes little when the papers are subjected to accelerated aging (Table 4). This would suggest that sufficient buffer salts are present to prevent the paper from becoming acidic for many years. (An interesting development shown in Table 4 is the loss of alkalinity of the coated papers following treatment. This may be tentatively ascribed to loss of alkaline compounds from the coatings during soaking.)

Calcium carbonate is used as filler in some modern papers (*14*), and the spot test indicated its presence in two of the text and English finish papers in the sample (Nos. 25 and 26). These proved to be among the most stable papers of the lot.

Comparative Deterioration Curves for New and Old Papers

When batches of the treated and untreated papers were subjected to accelerated aging for 6, 9, 12, and 24 days, respectively (multiples of the 3-day Bureau of Standards procedure), it was found that their decline in folding endurance followed exponential decay curves similar to those exhibited by other organic materials. The tear resistance followed a similar pattern. Meanwhile, the acidity of the less stable papers was found to increase.

Because the new papers tested during this investigation showed a considerable range in rate of deterioration, it appeared that it might be useful to establish some arbitrary limits to the range, so as to provide measurements with which performances of an intermediate character might be compared. For this purpose, several of the most unstable of the new papers were selected to serve as the floor. For the ceiling, seven old papers (1534 to 1713), still in good condition after 200 to 400 years, were available. Within the range limits set by these papers, the characteristics of the weakest papers, after receiving the stabilizing treatment, can now be observed. All these papers were subjected to accelerated aging, presumptively equivalent to 25, 50, 75, 100, and 200 years of natural aging, respectively.

The results are shown in Fig. 7. The rapid deterioration of the untreated new papers needs no comment. In contrast, the much slower rate of deterioration of even these inferior papers after the stabilizing treatment may be noted as comparing favorably with the rate of deterioration of the very stable old papers.

The plotting on a logarithmic scale of the folding endurance of papers after three or more cycles of accelerated aging (72 hours per cycle) offers the following possible advantages: (i) Relative rates of deterioration may be established which will permit the comparison of a paper with papers of known stability; (ii) estimates of strength properties of a paper may be extended many decades into the future; (iii) irregularities resulting from testing a typically weak or strong portion of a sheet can be detected either in the control or in the artificially aged specimens.

While this method of testing and analysis has been used to check the effectiveness of the experimental stabilizing process, more investigation is needed to explore other relationships between the naturally aged and the artificially aged papers.

Application of Stabilizing Procedure

Practical application of the stabilizing procedure has not been fully developed, but experimental or "trial" runs have been made. The equipment developed is relatively simple and inexpensive. The process can be carried out by a semiskilled person; and the expected production is approximately 2500 pages (6 by 9 inches) per day. Larger sheets and books that present special problems take longer. Bound books must be removed from their covers for treatment and must be resewed, backed, and so on, before recasing. This entails little or no additional expense since many of the books in need of the stabilizing treatment would require rebinding at some future time in any case. Therefore, the cost of the stabilizing procedure for books of lasting value is moderate when compared with the other costs of purchase, cataloging, storing, rebinding, and so on. Since the stabilizing procedure has not presented any major problems, it provides the librarian with a process which will increase several times the life expectancy of the works which he accumulates and stores for posterity.

Summary

Deterioration of paper in the book stock—especially among books of recent decades—has become a serious problem for libraries, but exact measures of the extent or rate of this deterioration have not been available. By the same token, no good indications have been available of the expected useful life of paper in

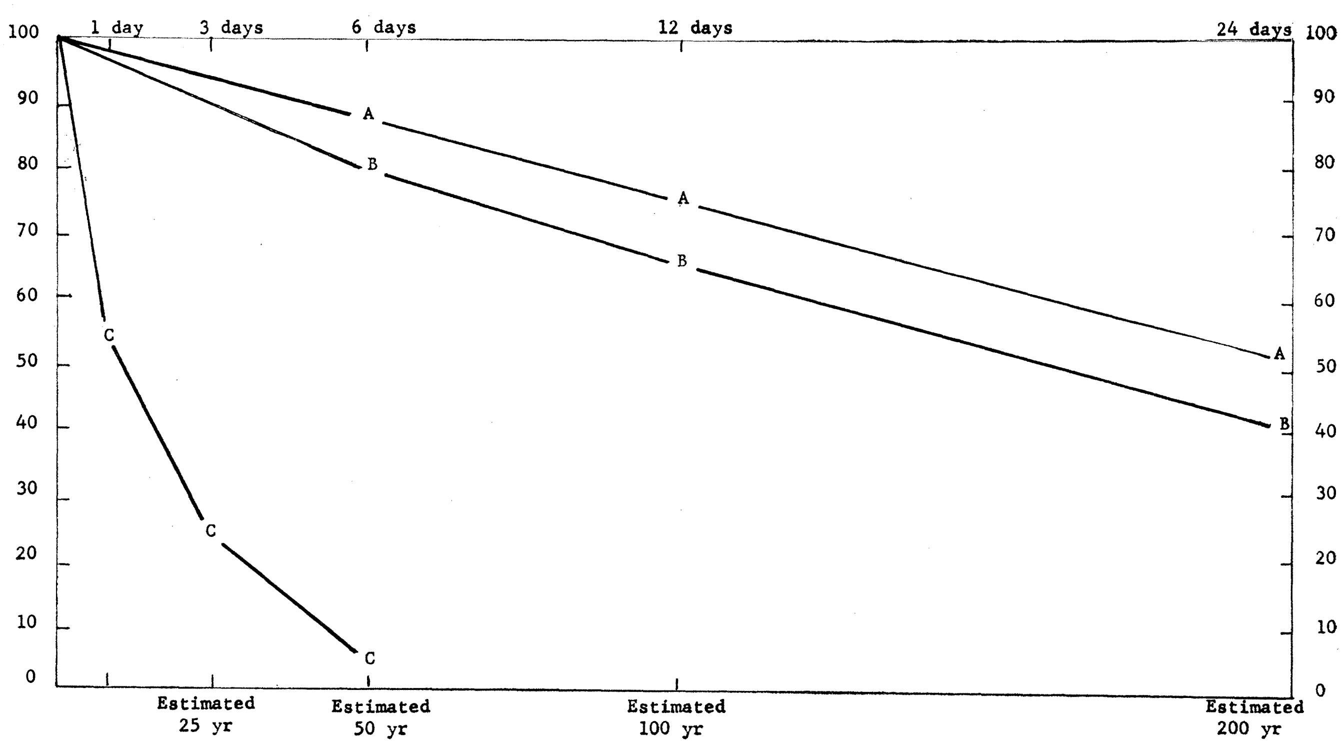

Fig. 7. Retention (percentages) of folding endurance (average for both directions) after heating at 100°C for from 1 to 24 days. *A,* Average for seven old papers made between 1534 and 1713; *B,* average for the papers shown as C after treatment with the bicarbonate solution; *C,* average for six untreated modern book papers with a rapid rate of deterioration.

books currently coming off the press. Furthermore, although attention has been given to means of counteracting one of the recognized causes of deterioration —pollutants absorbed from the atmosphere—similar attention has not been given to the problems of identifying and counteracting the other recognized source of deterioration—agents left in or introduced into the paper at the time of manufacture. Our investigation was undertaken in an attempt to fill some of these gaps in our knowledge.

It has been found that modern books —even those written with a serious or scholarly purpose ("nonfiction") and published ("to last!") in hard bindings —are deteriorating rapidly, and many of those issued 25 to 50 years ago are now almost unusable. The paper of an average American publication of the first decade of this century retains only 4 percent of the folding endurance of a typical new book paper of today; even the paper in the average publication of the 1940's has already declined in folding endurance to 36 percent of today's new book paper.

Meanwhile this typical new book paper itself shows low initial strength (for example, folding endurance on the order of only 20 percent of that of book papers already 200 to 500 years old) as well as indications that it is subject to rapid deterioration.

Acidity appears to be the principal cause of deterioration, both in the older papers and the new. A stabilizing process for neutralizing this acidity was developed and was brought during the investigation to an initial stage of economic feasibility. This process appears to inactivate the most injurious properties found in new book papers and precipitates compounds into the fibers which should, in addition, counteract the effect of pollutants absorbed from the air.

A principal technique used for predicting the durability of paper is the accelerated aging procedure developed by the National Bureau of Standards; by extending the use of this technique, interesting decay curves have been obtained which facilitate comparison of modern papers with papers which have already demonstrated their stability for several centuries. These curves offer other values as well for the study of permanence in paper and suggest that a principle exists relating extended accelerated aging to even longer periods of natural aging than those with which it has hitherto been equated.

During the past 300 years the papermaker has done an excellent job in meeting the demand for more and cheaper paper. A by-product of this accomplishment has been the production of many weak and unstable papers. This does not give rise to any problem where strength or stability are not critical, but where permanence is important, as in libraries of record, the problem becomes serious. While the present study describes a procedure for stabilizing initially unstable paper, much more remains to be done if relatively stable papers are to be made for books of lasting value. There is evidence that this is possible—that such papers can be made from certain types of chemical wood fibers at but little additional cost. But more research is needed, and the cooperation of the scientist, papermaker, printer, publisher, and librarian will be required to assure permanent books for the future.

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