A Review of Paper Quality and Paper Chemistry

JOHN C. WILLIAMS

HANDMADE PAPER OF THE Middle Ages and earlier, housed in the rare book rooms of libraries, is often in excellent condition. The machine-made paper of the last 150 years, in the general collection, is as often brittle and crumbling. The failure of machine-made paper to endure has been a disaster for the records of this civilization. Recently, however, methods of making long-lasting paper on the paper machine have been developed. Now there is reason for optimism.

The new paper not only shows improved life, but is more economical to produce, causes less erosion of the paper-making equipment, and gives a cleaner effluent, or none. Companies have been changing to the new methods, particularly in Europe. American producers are lagging behind. This situation must not be allowed to continue. The problem of caring for disintegrating books in American libraries is already unmanageable and should not be allowed to grow larger. Now is the time for librarians, bibliophiles and, indeed the paper-makers to unite to ensure that long-lasting paper is again available and used in publishing.

The Condition of Paper in Libraries

Paper fails by gradually losing flexibility and finally becoming brittle. The change is apparent to the librarians only when the pages begin to crack and break as the book is used. Folding endurance mea-

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surements, however, can show the progressive loss of flexibility. To follow the condition of paper from the initial good properties to its final useless and degraded state would take a long time. Even poor paper lasts for twenty-five years, while the best paper has already been in existence two thousand years. Exposing paper to higher temperatures—accelerated aging—speeds the process of degradation so that it can be studied in the laboratory.

Folding endurance is generally measured by the Technical Association of Pulp and Paper Industry (TAPPI) MIT folding endurance test.[1] A strip of paper 1.5 centimeters wide is put under one kilogram tension and folded by machine over a specified radius 135° to the right and 135° to the left. The number of folds required to bring the initial tensile strength down to the applied load, where the strip must break, is recorded as the "folding endurance." Tensile strength remains essentially constant while the folding endurance drops toward zero, so the folding endurance change accurately gives the increase in brittleness.

William Barrow, who did important work in the field of conservation, considered that when folding endurance had dropped to a value of one, the book was in the restoration category and was essentially unbindable. In one experiment he studied 500 recent books. Those published from 1900 to 1939 were composed of paper so weak that he employed a specially built fold tester, one that folded the test strip through only a 90-degree angle. Thirty-nine percent of the samples showed a median fold of 3 or less, which put them in his "very weak" category; 49 percent showed a median fold of 24 or less, falling in his "low strength" category; 9 percent showed 24-75 folds, which he termed "medium strength"; and 1 percent gave 200 folds, for his "high strength" rating. "That the figure of 200 folds for high strength classification is not too high can be shown by the fact that random tests of modern rag papers and old rag papers of the 16th, 17th, and 18th centuries often show from 300 to 4000 folds, even on the MIT tester which is much more severe than the special tester used for the samples."[2] Paper made in the 1940s had aged only seven to eleven years at the time the tests were made, yet 57 percent were already in the low strength category.

Tomer examined 500 books, published from 1777 to 1969, from the Freiburger Library of Case Western Reserve University. Of these books, 74 percent were from the twentieth century. Two test strips were cut from the margin running the length of the pages. The standard fold angle was used, but with only 0.5 kilogram tension on the strip. Tomer reported: "The folding endurance of the paper in the sample was generally low. Only five percent of the papers had retained a high degree of strength (more than 200 folds). Ninety-two percent of the samples exhibited relatively low levels of strength (less than 24 folds) and sixty-nine percent had deteriorated to extremely low levels of strength (3 folds or less)."[3] He agreed with Barrow that modern paper is in deplorable condition.

Magrill and Rinehart sampled books at the University of Michigan Library and concluded that 45 percent of the collection in Western European literature required immediate attention.[4] Frazer Poole reported that a sampling at the Library of Congress made in 1972 indicated that: "perhaps as many as 6 million volumes, out of some 17 million books in the total collection, are in the advanced stages of deterioration. In thousands of instances the paper has become so brittle that to turn a page is to break it off."[5]

According to *Reprographics Quarterly*, France's national library is experiencing similar difficulties. The chairman of the Bibliothèque Nationale reports:

> 90,000 volumes are in extremely poor condition, 7,000,000 pages of periodicals have deteriorated to the point where they can no longer be consulted while 36,000 maps, 375,000 prints and 300,000 photographs together with manuscripts and musical documents are in a critical condition. The major factors blamed for this situation all relate to the poor quality of modern paper. Modern papers apparently include numerous impurities one of which—lignin (comprising between 20 and 30 percent of poor grade papers like newsprint)—decomposes when exposed to daylight. Even better quality papers tend to contain acidic elements used in the sizing operation which can sharply reduce life expectancy. The Library proposed two courses of action to deal with the problem: like the British Library it is to expand its micro-filming programme, secondly a massive preservation programme is to be initiated. The preservation programme is to concentrate on the development of a suitable process for the large scale deacidification of paper. Probably the major issue about preservation efforts of this kind is the danger that they will fail to keep pace with the problem—while money is being expended on deteriorated material, other material, at present in usable condition, is subject to the same process. It is a paradox of the present time that expendable packaging seems to be made of indestructible plastics while the World's knowledge is stored on materials with a short life expectancy.[6]

There are many more such comments on paper quality in the literature, some not so restrained.

What Went Wrong with Paper?

Paper quality dropped in the seventeenth and eighteenth centuries. The supply of rags from which paper was made could not keep up with the demand. The discovery of chlorine by Scheele in 1774 allowed colored and stained rags to be bleached and used, but bleaching harmed the fiber. As demand continued to grow, the paper-maker was forced to find fibers elsewhere. Wood was at hand in abundance; however, in wood the fibers are firmly bonded together by lignin. Wood can be directly ground to produce the low-grade lignocellulose fiber used in newsprint. In processes developed in the nineteenth and twentieth centuries, lignin is chemically dissolved and is washed away from the cellulose fiber. The fibers are then bleached. The chemical treatments used are vigorous, and the cellulose fiber is degraded in the process. It would be logical to blame the short life of modern paper on this degradation, which is partly true. However, Barrow has shown that reasonably long-lasting paper can be made from refined wood fiber.[7]

Another, more serious mistake has been made by the paper-makers. Paper made from pure cellulose fiber is like a blotter. It absorbs water readily, swelling in the process.When it is written on with ink, the ink line feathers out in a disconcerting way. The early paper-makers of Italy[8] corrected these defects by dipping or "sizing" the paper in dilute gelatin solutions. This made paper like vellum and parchment, and was much more acceptable to the scribes; thus gelatin-sized paper became the standard for centuries.

In 1807 Moritz F. Illig disclosed that when rosin soap is stirred into beaten fiber and precipitated by adding alum solution, the paper made from this mixture becomes sized merely on drying.[9] The invention allowed sized paper to be made conveniently and directly on the paper machine. This method continues in use. Unfortunately, the amount of alum ordinarily added leaves the paper acid, and acid cellulose becomes brittle in twenty-five to fifty years. People have come to believe that this embrittlement is a characteristic of refined wood fibers, and that only rag will give long-lasting paper. These beliefs are strongly held even today, and are quite untrue.

At the turn of the century, several investigators placed the blame where it belongs: on the acidity of paper. In 1903, Winkler demonstrated that papers soaked in dilute solutions of sulfuric or hydrochloric acids after a few years lost all resistance to rubbing or creasing.[10] Herzberg showed that paper degraded more rapidly at high temperatures.[11]

Kohler and Hall brought together these techniques in landmark studies.[12] Degradation of paper was accelerated by the use of the 100° oven, to bring investigations into a reasonable time frame. They recognized folding endurance as the most sensitive indicator of degradation. The acidity resulting from the use of rosin-alum sizing was shown to be responsible for rapid degradation.

Studies by Van Royen and by Barrow indicated that seventy-two hours at 100° are approximately equal to twenty-five years at ambient conditions.[13] This relation has been used to predict the life of paper from data obtained using accelerated aging. While not everyone agrees with the relation and procedure, it gives reasonable and conservative predictions which are in accord with what is known of paper from the past, i.e., that a good-quality alkaline paper lasts over a thousand years, while highly acidic paper is brittle in fifty. The latter figure can be validated by a study in one's personal collection.

An interesting long-term experiment was initiated by Edwin Sutermeister at the S.D. Warren Company in 1901—five rosin-sized, clay-filled papers of various mixtures of rag and refined wood fiber were set aside for observation.[14] A sixth paper composed wholly of refined wood fiber with a calcium carbonate filling was added to the series. The sized clay-loaded papers were acid, with pH values ranging from 3.6 to 4.3. The calcium carbonate paper was not rosin-sized, since alum and calcium carbonate are incompatible. The pH of this paper was 8.9. The presence of the alkaline salt, calcium carbonate, ensured that it would remain alkaline. When Sutermeister examined the samples in 1929, he reported that all the acid samples were badly discolored and were absolutely without strength. The calcium carbonate paper had remained white and seemed as strong as when it was made. In this experiment, the rag papers failed and the refined wood fiber paper lasted, which shows that the common belief that rag is necessary for permanence is wrong.

For a thesis at the Institute of Paper Chemistry, Hanson studied a copy of a text on physics and natural science dated 1576. Some sheets had aged considerably and were brown and weak, while others were white and still possessed considerable strength. The fibers of the two sheets appeared to be identical; neither sheet was sized. The white sheets contained around 2.5 percent calcium carbonate, while the degraded sheets had none. The water extract from the white sheets had a pH of 7.5, while that of the brown sheets was 4.9. Hanson concluded: "The results obtained in this investigation suggest that, at least in the case of a $CaCO_3$ filled sheet, the effect of the filler in maintaining a favorable pH within the sheet may be the explanation of the increased permanence. If there is sufficient $CaCO_3$ present, it can act as a buffer and resist the changes in pH resulting from the formation of acid degradation products of cellulose."[15] (And acid from polluted atmospheres.)

Jarrell, Hankins and Veitch in 1932, working with an unfilled and unsized all-rag paper, brought sheets to various pH values with hydrochloric and sulfuric acids, and with aluminum sulfate solutions.

The papers were then given seventy-two hours in the 100°C oven, and after being reconditioned, the folding endurance was determined. The folding endurance of the neutral paper did not change in the aging period. The more acid papers dropped substantially. At pH 4.5, one-half the folding endurance was lost, and at pH 4 the loss was complete.[16] The results are shown in figure 1. Again, a rag paper is seen to be impermanent if acid. A great deal of library paper is at pH 4.5 or below, and will have the rapid rate of degradation shown in the figure. In 1936, the same researchers noted that, "incorporation in paper of suitable materials, such as a basic filler,...prolongs the life and serviceability of...book and record papers."[17]

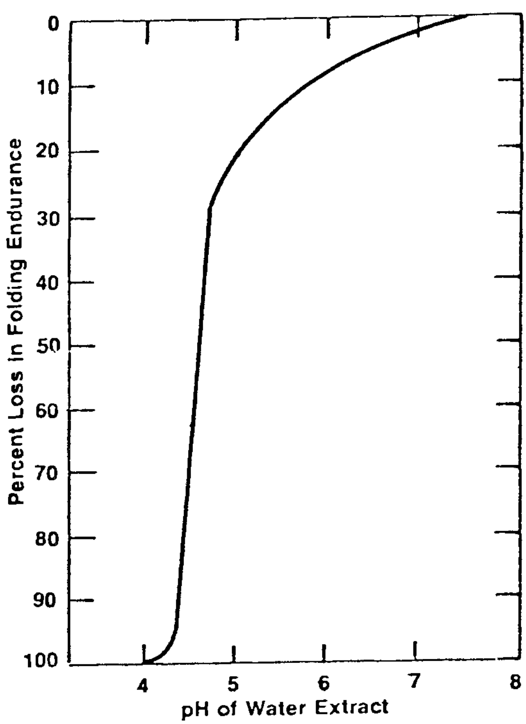

Fig. 1. The Effect of 72 hours at 100°C on the Folding Endurance of Paper
Source: Jarrell, T.D., et al. "The Effect of Inorganic Acids on the Physical Properties of Waterleaf Rag Bond Paper." *USDA Technical Bulletin*, no. 334(1932).

Surprisingly, acid hydrolyzed cellulose fiber is used commercially. Battista and Smith hydrolyzed the fiber and then worked it vigorously in water. The fiber fell apart into a short microcrystalline cellulose, which has proved useful as a commercial thickening agent for aqueous material.[18]

Production of Long-Lasting Paper Rediscovered

Barrow, following extensive experiments on the deacidification of acid paper to lengthen and improve its life span, proceeded to make sized alkaline wood fiber paper on the paper machine:

> The specifications include initial strength of fold and tear, acceptable deterioration of fold and tear under artificial aging, and minimum acidity. To meet these specifications it appears necessary that papers contain a high percentage of long and stable fibers and be sized with a material compatible with alkalinity. It also appears desirable that they be filled with an acid buffer such as calcium carbonate.
>
> Evidence indicates that most modern papers have a reasonable life expectancy of about fifty years. It is estimated that papers manufactured under new specifications will have a comparable expectancy of more than four hundred years.[19]

This was a great step forward in the history of paper-making, one made by a conservator rather than a paper-maker! This solved the problem which has been with the industry since the time of Illig; but the paper industry has not responded to the solution!

The major portion of the American paper industry has continued to make rosin-alum-sized acid impermanent paper. European paper-makers, however, have been more responsive. Gestetner Papers Ltd. in Scotland is producing excellent calcium carbonate filled papers. Hugh Bryson, Process and Technical Manager for Gestetner, has been helpful and generous in sharing his experiences:

> The considerable upsurge in the last five years of non-rosin derivatives for neutral sizing of paper, coupled with the use of calcium carbonate fillers, has opened a new realm of papermaking. Neutral-sized, calcium-carbonate-loaded papers are now firmly established in the European market, not only, as was originally thought, for specialty lines, but competing successfully in the popular lines of lithography (stationery sizes as well as conventional litho sheets), industrial papers, chart papers, continuous stationery, archive text, photocopying, and coated stock (on machine-blade and off-machine coated).
>
> What has the technique of neutral, i.e., non alum-rosin sizing to offer? The answer is very simple, better paper at a lower cost.[20]

In a letter, Bryson added:

> *Economics*—Brilliant!—and getting better each year as the cost of energy rises, that is in comparison with nonalkaline paper-making. At present, we see a 32% reduction in energy in comparison with acid paper-making. [There is] a reduction in the number of drying cylinders one would normally use for acid paper-making due to the ease of drying the increased carbonate filler one can more readily carry in an alkaline system. The reduction in oil, water and steam makes the picture an even greater financial success, and the big punch line [is] no capital investment to change to neutral sizing and carbonate filled papers.
> *Special equipment*—Paper-making-wise—none; laboratory-wise—nothing that is not normally found in progressive technical laboratories, whether they are acid or alkaline paper mills.[21]

Samples of Gestetner paper have been given accelerated aging tests at the Library of Congress Preservation Research and Testing Laboratory and found to have an excellent life span.

Hoppe and Karle wrote an instructive account of a German paper mill's successful changeover to an alkaline system. The mill now makes 250,000 metric tons per year of "an offset-paper with the best printability and runability containing approximately 25% filler."[22] A substantial drop in energy requirements and water consumption was realized.

Penniman expressed the situation well:

> The evidence is now in. The calcium carbonate-alkaline size paper-making process offers overwhelming benefits as compared with the traditional alum-rosin size process. It requires less energy, is significantly cheaper, produces a much better product, is easier to control and creates a great deal less waste.
> *The latest report from Europe.* It is actually becoming embarrassing to continue to have an endless stream of European visitors come over here and lecture us on the merits of the calcium carbonate process while we take so little action to implement it and realize the benefits.[23]

Alkaline paper-making was considered at a paper-makers conference held in Boston in 1979.[24] Riddell of Wolvercote Mill in England stated that alkaline paper-making not only pays off in material costs, but there are hidden benefits, such as cleanliness, reduced down-time, improved runability, and lower energy and effluent costs. "There is no way that we would ever attempt to go back to acid paper-making,"[25] he said. Similar experiences were recounted by a spokesman for American Israeli Paper Mills, who reported a saving of $27.50 per ton of paper. Dumas of Hercules, Inc. listed advantages of alkaline sizes and calcium carbonate filled paper as: (1) a better, stronger sheet is made so that a reduction basis weight is possible; (2) expensive, high-brightness pigments may be replaced, and increased filler loadings are possible;

(3) there is reduced energy consumption in refiners and driers; (4) there is reduced effluent load, and white-water closure is possible; and (5) there is improved productivity, with less down-time and maintenance.[26]

These impressive statements do not even mention the librarian's interest, that the alkaline paper made is long-lasting. Paper-makers themselves should be interested in permanence. According to Williams, acid paper degrades so rapidly that it is scarcely worth recycling.[27] Fifty percent of the vast quantity of garbage that is taken out of American cities is fiber. This would be a valuable resource if the paper were properly made so that fiber strength was retained!

Changing the Industry: The Informed Customer

In the several years that the Preservation Office of the Library of Congress has specified alkaline paper for file folders, film jackets, film boxes, etc., it has been brought from a curiosity to a standard item of supply. Vendors now feature alkaline paper in their catalogs and dwell on its virtues. More purchasers should specify alkaline paper. More purchasing agents should be familiar with the appropriate specifications.

The *Annual Book of ASTM Standards*[28] covers the following:

D3290-76 Bond and Ledger Papers for Permanent Records
D3458-75 Copies from Office Copying Machines for Permanent Records
D3301-74 File Folders for Storage of Permanent Records
D3208-76 Manifold Papers for Permanent Records

Methods of analyzing for calcium carbonate content are given.

The National Historical Publications and Records Commission subvention programs asks for the following quality:

> All volumes for which subsidies are requested must be produced under the following standards:
>
> *Paper*
>
> Book text paper should have:
> —minimum pH of 7.5 (cold extraction, TAPPI method T-435)
> —minimum alkaline reserve (calcium or magnesium carbonate or both) of 2%, based upon oven dry weight
> —minimum C.D. (Cross Direction) folding endurance of 30 double folds at 1 kilogram tension (25 replicates, TAPPI method T-511)
>
> *Printing*
>
> Inks which contain acids or chlorides should not be used in the production of these volumes.
>
> *Binding*
>
> Books should be Smyth-sewn and casebound and have acid-free

endpapers, no synthetic fabrics, and no polyvinyl cloride adhesives. Volumes published after December 31, 1981, shall have no pyroxylin fabrics.[29]

Barrow Research Laboratory published condensed specifications for permanent/durable book papers:

The following specifications are recommended for uncoated permanent and durable papers; it is shown that there are commercial papers which meet them.
A. Minimum cold extraction pH of 7.5 (TAPPI method T-435).
B. Minimum C.D. folding endurance of 30 at 1 kg. tension (MIT, 25 replicates, TAPPI method T-511).
C. Minimum M.D. tear resistance (Elmendorf, 10 replicate 8-ply tears, TAPPI method T-414) of 70 grams for 60-lb. (25 x 38″—500) paper and proportionally more for heavier weights. For lighter weights:

Basis Weight	Minimum Acceptable M.D. Tear
40	40.0 gm
45	47.5
50	55.0
55	62.5

D. Minimum retention of M.D. folding endurance after 24 days of aging at 100°C in a forced circulation oven (as calculated from multipoint regression line) of 50 percent *or* M.D. folding endurance of one or more after 118 days of aging as determined by extrapolation.[30]

"Permanence," in paper vocabulary, indicates a high degree of chemical stability as evidenced by very slow deterioration. The retention of 50 percent machine-direction folding endurance after twenty-four days aging at 100°C is a difficult requirement. Not all alkaline papers will meet this. The degree of oxidation of the cellulose fiber is probably the deciding factor.

The *National Union Catalog* carries the properties of its paper on the front page:

The paper on which this catalog has been printed is supplied by P.F. Bingham Limited and has been specially manufactured by the Guard Bridge Paper Company Limited of Fife, Scotland. Based on requirements established by the late William J. Barrow for a permanent/durable book paper. It is laboratory certified to meet or exceed the following values:
Substance 89 gsm
pH cold extract 9.4
Fold endurance (MIT ½kg. tension) 1200
Tear resistance (Elmendorf) 73 (or 67 x 3)
Opacity 90.3%[31]

Every book printed on alkaline paper should carry the information on the title page, since the individual purchaser cannot test pH as he buys the book. The information would have definite sales appeal, and this will increase as the public becomes more educated on the subject. The statement will have other value, e.g., it will allow good-quality books in the library to be separated from the acid volumes being taken for deacidification treatment. The term *acid-free* should not be used. This phrase is subject to too many interpretations. The calcium or magnesium carbonate content and the pH of the paper as made are key points.

Theory of Paper-Making

Cellulose, A Natural Polymer

Polyethylene, nylon, polyester, etc., are familiar materials, which have resulted from recent advances in polymer chemistry. In such polymers, many small molecules are linked together to make larger molecules which exhibit new properties, including strength. The number of small molecules linked is termed the degree of polymerization, or "D.P." Nature has been dealing in advanced chemistry for ages. Cellulose is a natural linear polymer made up of linked anhydroglucose units. The D.P. of cotton and flax cellulose is in the 7000-12,000 range. Refined wood cellulose which has been separated chemically from the lignin binder in wood, and bleached, is in the 2000-3000 D.P range.

The Cellulose Fiber

The fiber is made up of cellulose molecules lined up in a high-density crystalline array. Occasionally, the regular arrangement fails and lower density, more open, amorphous regions occur. Crystalline cellulose is not highly pliable. However, the amorphous regions absorb moisture from the atmosphere, and this imparts greater flexibility to the fiber. An extensive discussion on these matters is given by Housmon and Sisson.[32]

Beating or Macerating Cellulose Fiber

Cellulose fibers become self-adhesive when worked or beaten in water. Tapa of the South Sea Islands, papyrus of Egypt, huun and amatl of the Mayans and Aztecs, and paper are all prepared by beating fiber. Paper is unique in this group, being the only one in which the fibers have been beaten, dispersed in water, and formed into the desired sheet by filtering the dispersion through a screen.

Beating develops a microfibril fuzz on the surface of the fibers. As the sheet is dried, the surface tension forces the fibers together and the microfibrils make a bond. If the wet, freshly formed sheet is frozen and then dried while frozen, this mechanism does not operate and the dried sheet has little or no strength.

Predicting the Life of Paper; Types of Degradation

Acid from polluted atmospheres or from alum-rosin sizing can enter the low-density, open, amorphous regions of the fiber and cut the polymer chain by hydrolysis. This releases the molecules from restraint, and the cut ends are free to crystallize. The degree of crystallization thus can go up during degradation and the water-holding power of the fiber go down. Under the influence of acid, water molecules may split out between cellulose chains, giving a cross link, which also drops water absorption.

Oxidation of the cellulose polymer introduces side groups, aldehyde and ketone, which make the molecule more easily hydrolyzed.[33] Free radicals generated by oxidation or by light can also cut the cellulose chain. The presence of catalysts such as copper, cobalt or iron compounds can step up the rate of oxidation. Tang[34] has shown that foxing degradation in paper can be produced by iron compounds. In some foxed spots, there is a central particle of iron oxide which was originally struck off, as a metal particle, from the beater bed plate.

The fiber-to-fiber bond in paper does not disappear as folding endurance is lost. The microfibrils form a bond with a crystalline character. When new paper is torn, there is a fiber fringe at the tear. The strong fibers pull out of the fiber-to-fiber bond. When degraded paper is torn, the tear edge is sharp. The fiber-to-fiber bond holds but the brittle fibers break.

Importance of the Alkaline Reserve

Figure 1 shows that paper at a pH of 5.5-7 is quite stable, with good lasting qualities. Such paper is often sold as "acid free." However, in the absence of an alkaline reserve such as 3 percent calcium carbonate, the pH can readily fall into the danger zone of 4.5 and below, by acids either absorbed from polluted air or generated in the paper by oxidation. If sulfur dioxide is absorbed, and oxidation catalysts are present, it can be readily oxidized to sulfur trioxide and hydrated to nonvolatile sulfuric acid, with a consequent drastic drop in the pH of the paper. This action can be seen to have taken place in the degraded margins of book paper. Langwell[35] has written on inactivating the catalysts; Tang and Troyer[36] discuss their removal. Williams[37] considered that oxidation is more in evidence under humid conditions.

Libraries, including the Library of Congress, have installed systems to remove sulfur dioxide from the air. Very thorough early studies on the subject have been given by Kimberly.[38] Data to show the effectiveness of the systems are generally lacking, perhaps due to difficulties with the air analysis in the past. At the present time a number of instruments giving direct readout of gaseous sulfur dioxide are on the market. These have been rated and compared in a recent article.[39] Certainly, libraries in large cities should control the sulfur dioxide in their buildings.

The Arrhenius Equation

In accelerated aging, folding endurance changes rapidly. To use the rate of change established at 100°C to predict the useful life of paper, the rate must be reduced to the much slower rate at room temperature. The Arrhenius equation has been used for the purpose:

$$\text{Log rate} = \frac{-E}{2.303RT} + \text{constant}$$

where E is the activation energy, R is the gas constant, and T is the absolute temperature. This equation has been successfully applied to chemical reactions. Its use to follow change of rate of loss in folding endurance with temperature implies that this change depends on a single chemical reaction. Such a reaction could be the acid hydrolysis which destroys water-holding amorphous regions and reduces the plasticizing action of water. To use the equation, the activation energy must be shown to be a constant. Depending on conditions, E has been shown, for certain papers, to be essentially constant from 120°C down to 80°C. At the lower oven temperatures, the experiment becomes too long to carry out, so it is necessary to assume the constancy at lower temperatures.

Values of E from 16 to 34 k cal/mole have been reported. The variation is at least partially due to using different (and changing) pH values, and different conditions of humidity and ventilation. The relation that seventy-two hours at 100°C represents twenty-five years at room temperature calculates out to an activation energy of 21.8 k cal/mole. High values of E expand the relation so that seventy-two hours at 100°C is made to represent several hundred years. The 21.8 value therefore gives conservative and, as has been mentioned, reasonable predictions. Excellent articles on the application of the Arrhenius equation to paper life have been written by Browning and Wink[40] and by Gray.[41]

The curve of figure 1 is quite definite in showing that acid paper is unstable. Arrhenius determinations should, therefore, best be carried out on paper with an alkaline reserve, in the pH range of 7.5-9.5, where accurate prediction of life is of most interest. According to Golova and Nosova, the state of oxidation of the cellulose has a great deal to do with its stability on the alkaline side: "The dominant effect of carbonyl groups on the degradation of oxidised cellulose in an alkaline medium is evident also from the conversion of alkali-unstable oxidised celluloses into stable materials by reduction with sodium tetrahydroborate in a weakly alkaline medium, i.e., under conditions such that aldehyde groups are converted into alcoholic groups. The stability of oxidised celluloses is considerably enhanced also when carbonyl groups are oxidised to carboxy groups."[42]

The difficult part of the Barrow Laboratory specification for alkaline paper is that folding endurance should not drop more than 50 percent after twenty-four days accelerated aging in the 100°C oven. Tang and Troyer have shown that treating paper or fiber with sodium borohydride allows this test to be passed with ease.[43] In other words, the treatment greatly extends the life of alkaline paper.

Storage at Low Temperatures

The Arrhenius equation clearly indicates that paper will last longer if stored at low temperatures. This was proposed earlier by Gordon Williams, director of the Center for Research Libraries:

> It also occurred to us, at that earlier time that, since the standard test of paper permanence involved heating it to accelerate the aging process, it would be logical to assume that cooling the paper would slow the rate of deterioration. Therefore, Barrow was asked to investigate this assumption and, indeed, it turned out to be the case. The Barrow Laboratory, in continuing to investigate this process, has had a sample of books under cold storage for some time. The general indication at the moment appears to be that the longevity of any particular paper will be increased about seven and a half times for each drop of 36° Farenheit in the temperature of the atmosphere in which it is stored. By combining deacidification with low temperature housing, the untreated life expectancy of a paper probably can be increased about 40-fold. For example, a book with a present life expectancy of only 25 years if untreated, and left in a normal library stack, would have a life expectancy of about 600 years if deacidified and stored at 34° Farenheit. This figure would increase to over 4000 years if the paper were deacidified and stored at -2° Farenheit.[44]

Treatments for Acid Paper

Deacidification of acid paper should be carried out as soon as possible, before the paper has lost its strength and flexibility. The necessary alkaline agent is applied from water or solvent solutions, or as a vapor. The procedure selected must be first tested to see that it will not harm the artifact.

Aqueous Deacidification

The paper, supported on a plastic screen, is washed to remove products of degradation. Barrow immersed the paper first in dilute calcium hydroxide solution and followed this with calcium bicarbonate solution. He also used a single solution, spray or dip, of magnesium bicarbonate.[45] A satifisfactory solution can be made using eight grams of basic magnesium carbonate powder per liter of water and dissolving this by bubbling with carbon dioxide. The paper, still supported on the plastic screen, is immersed in the solution until saturated; it is then air dried. The paper will pick up 1-2 percent of magnesium carbonate, which is a respectable alkaline reserve. (Accelerated aging of treated and untreated paper is shown in figure 2.)

A method of deacidification which avoids the use of carbon dioxide is described in U.S. Patent 3,898,356.[46] The paper is first immersed in a calcium chloride solution, dried, and then immersed in ammonium carbonate solution. This precipitates calcium carbonate in the paper. The byproduct salt, ammonium chloride, is then washed out of the paper. Loadings of 10 percent of calcium carbonate can be obtained by this method; the calcium chloride and ammonium carbonate solutions are easily made up and are stable.

The use of aqueous solutions involves taking the book apart, treating and drying the paper, and then rebinding the book. This may easily cost two or three hundred dollars per book. There is however, the advantage that the paper is washed and brightened in the process. The paper swells slightly, and often there is a 10 percent increase in folding endurance, which is not seen in other methods.

Solvent Deacidification

Baynes-Cope[47] deacidified paper using 1 percent barium hydroxide in methanol. His data showed the treatment to be as effective as magnesium bicarbonate. Barium compounds, however, are quite toxic and should be used with care.

R.D. Smith[48] disclosed in U.S. Patent 3,676,182 the use of magnesium methoxide in Freon/alcohol solutions. The solvent was chosen to be one which would have little effect on colors or inks. George B. Kelly[49] of the LC Preservation Research and Testing Office was granted U.S. Patent 3,939,091 for methyl magnesium carbonate which he also uses in

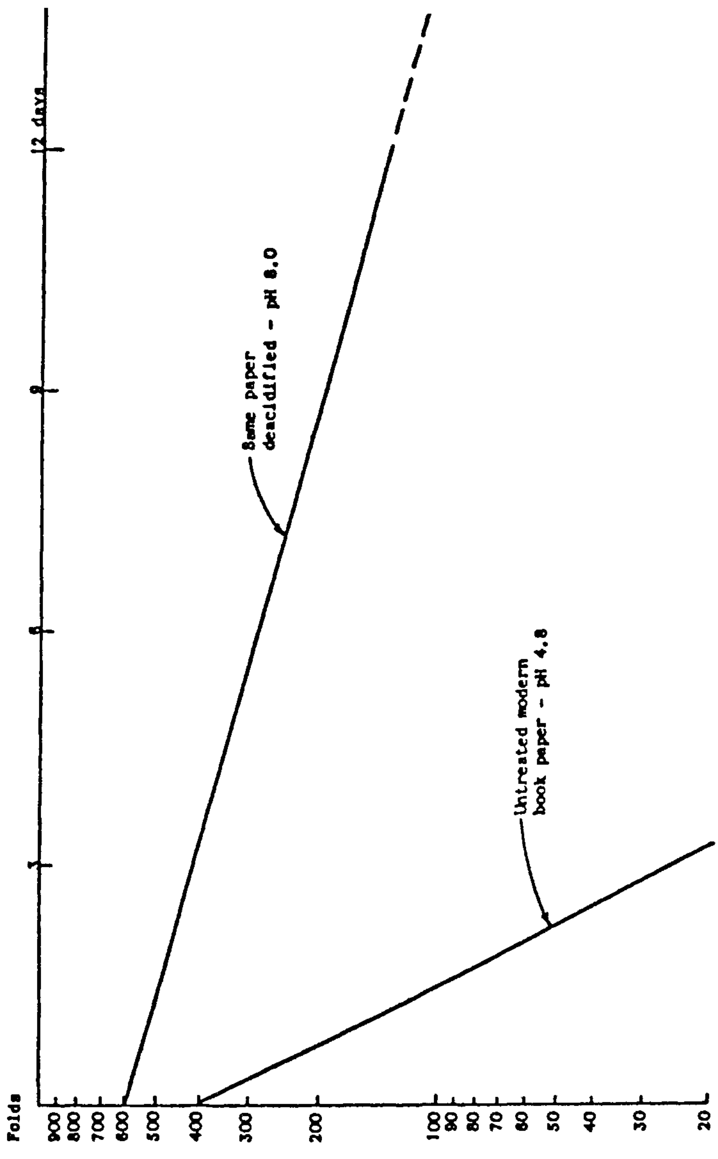

Fig. 2. Effect of Deacidification on Deterioration

Source: W.J. Barrow Research Laboratory. *Permanence/Durability of the Book II: Test Data of Naturally Aged Papers*. Richmond, Va.: 1964, fig. 2.

the alcohol/Freon solutions. This material shows an improved tolerance for the water of humidity in paper. The magnesium/solvent-based treatments are available from Wei T'O Associates in Chicago in spray cans. Smith has been applying similar materials for a mass deacidification treatment being developed for the Public Archives of Canada. The books are immersed for a period, the solution is drained away, and the residual solvent in the books removed by vacuum evaporation.[50]

Koura and Krause immerse paper in liquid ammonia or concentrated ammonium solutions to deacidify and improve folding endurance, perhaps by cellulose decrystallization.[51] This method holds promise, but needs more investigation.

Vapor Phase Deacidification

Kathpalia deacidified paper with ammonia gas. He considered the treatment to be effective for thirteen years.[52] Langwell's U.S. Patent 3,472,611 disclosed the use of cyclohexylamine carbonate.[53] This is sold in packets which may be folded into books. The vapor permeates the book in the course of several weeks to deacidify the paper. Barrow Laboratory, U.S. Patent 3,771,958, described a process of impregnating books with morpholine in a vacuum chamber.[54] The books are set on their feet on a shelf with covers interleaved. The pressure in the chamber is oscillated between 35 and 40mm which makes the leaves pulsate and gives excellent exposure. The morpholine process was summarized by Walker.[55] It may be licensed from Research Corporation in New York City.

Ammonia and the amines will leave paper under humid conditions. A library filled with books treated with these chemicals may prove to be a health hazard to librarians and patrons.

The Library of Congress Preservation Office has been studying the deacidification of books using gaseous diethyl zinc. The method is described in U.S. Patent 3,969,549 and by Kelly.[56] The compound is pyrophoric and must be handled by trained operators using the proper equipment: books are first thoroughly dried under high vacuum, then the diethyl zinc is introduced into the chamber. Three days are required for the gas to penetrate the closed books and to react with the cellulose. After the reaction is complete, the unused diethyl zinc is distilled off and saved. Carbon dioxide gas and water are introduced to convert the zinc cellulosate to zinc carbonate. Final pH is around 8. Two percent zinc carbonate is left in the paper as an alkaline reserve. Results obtained on oven-aging a commercial paper, treated and untreated, are shown in table 1. Runs of four hundred books have been carried out at the General Electric Space Center at Valley Forge, Pennsylvania. A run of five

TABLE 1
FOLDING ENDURANCE, DEZ-TREATED FOLDUR KRAFT PAPER

Days Aging	Control[3] CD	Control[3] MD	Treated[4] CD	Treated[4] MD
Humid Oven[1]				
0	747.0 ± 117.0	935.0 ± 194.0	582 ± 215	877 ± 289
3	138.0 ± 30.0	190.0 ± 52.0	564 ± 164	642 ± 112
6	36.0 ± 10.0	32.0 ± 14.0	342 ± 104	509 ± 125
12	10.4 ± 2.7	4.0 ± 0.7	281 ± 77	284 ± 73
18	4.4 ± 0.5	2.0 ± 0.0	206 ± 48	258 ± 42
24	1.0	1.0	105 ± 39	96 ± 17
Dry Oven[2]				
0	747.0 ± 117.0	935.0 ± 194.0	582 ± 215	877 ± 289
3	152.0 ± 48.0	288.0 ± 49.0	426 ± 138	527 ± 134
6	54.0 ± 21.0	38.0 ± 8.0	161 ± 48	325 ± 120
12	21.0 ± 9.5	5.3 ± 1.3	131 ± 54	153 ± 25
18	3.8 ± 0.6	2.0 ± 0.0	77 ± 19	70 ± 14
24	2.0	1.0	37 ± 11	19 ± 6

[1] 90°C, 50% r.h.
[2] 100°C, no added moisture
[3] pH 4.8
[4] pH 7.8

Source: George B. Kelly, Preservation Office, Library of Congress.

thousand books is planned; however, it is first necessary to find a large vacuum chamber for this purpose.

Conditions in the Library

From the preceding discussions it is clear that the library should be as cool as is consistent with comfort, 65-68°F, and at a low relative humidity, 40-45 percent. Humidity above 70 percent is quite dangerous because it permits mold growth. Very low humidities extend the life of paper, but stiffen it slightly.

Cycling conditions of temperature and humidity have been considered by many to speed degradation. There is not a great deal of information on the subject. A paper by Kelly, Williams, Mendenhall and Ogle shows that chemiluminescence—an indicator of oxidation—is increased as temperature is cycled.[57] Williams, Verna and Stannett have shown that changing humidity can create free radicals in paper, which contribute to degradation.[58]

Disasters: a broken pipe, fire or flood can lead to many wet books. First aid for a wet book is to freeze it immediately, usually at a local food locker, so that it does not mold. The frozen book can then be freeze- or vacuum-dried.[59]

Conclusions

For the first time in many years there is reason to believe that paper-makers will change their process and start to make lasting paper again. There are so many advantages to them in the new process that this must come about. To speed the change to alkaline paper, every paper consumer, every magazine subscriber, every librarian, and every purchasing agent must make their voices heard.

In regard to the great masses of acid paper on hand, the library community is waiting for and needs an operational mass deacidification method. While much progress has been made, further work is required.

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