Notes and Communications

The Effect of Alkali on the Long-Term Stability of Cellulosic Fibres

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Abstract

Excess acid has been shown to be the most important cause of the deterioration of paper. Almost all conservation processes which neutralize or remove acid from paper involve the introduction of alkaline chemicals into the paper fibres. Therefore, a detailed study of these processes and how they affect the permanence of cellulose, the principal component of paper, has the potential to influence greatly the preservation of Canadian archival and library materials. After two years of scientific investigation, a major research project sponsored by the Conservation Committee of the Canadian Council of Archives has reached the end of its first phase. The study, performed in conjunction with the Canadian Conservation Institute (CCI) in Ottawa, has concentrated upon the investigation of the effect of alkali on the long-term stability of cellulose fibres.

Introduction

Recently, the Conservation Processes Research Division of CCI, in cooperation with the Canadian Council of Archives, began scientific research into the effects of alkali on the long-term stability of cellulose, the principal component of paper. Although many conservation procedures involve the use of alkaline materials, the most important and frequently used are washing and deacidification treatments. The same hydroxide and bicarbonate salts of magnesium and calcium are used for both these processes. The main difference is one of concentration: low quantities (under 50 ppm magnesium or calcium) for the neutralization process used in extensive washing, and higher amounts (50-2500 ppm) for a full deacidification treatment involving neutralization, alkalization and buffer deposition.

Many questions about these treatments still remain unanswered. Some of the most important are whether different fibres react differently to alkalization; what role is played by lignin and the fibres' degree of oxidation in determining the effects of alkali; whether the optimum concentration of alkali is dependent on the individual fibre being treated; whether there is any advantage to one particular chemical or do they all work equally well; how different types of media are affected by alkalization.

The project initiated by CCI was carried out in direct response to such questions being asked by conservators, archivists, curators and librarians in the preservation community. As an expression of their interest in and support for the study, the

Conservation Committee of the Canadian Council of Archives is providing funds for the salary of a contract researcher to work on the project. On a continuing basis, they are also providing information and advice to the researchers regarding the needs of the archival field. The project is being coordinated by Helen D. Burgess. Other scientists who have contributed or are contributing to the work are Season Tse, Stephen Duffy and France Bertrand.

Materials Studied

One of the most important aims of the investigation is to make the results applicable to the material found in Canadian holdings. Therefore, it is essential that the papers used in some way typify many of the characteristics or problems of North American or European paper found in our institutions. Through the combined efforts of the Canadian Council of Archives and the National Archives of Canada, institutions across Canada donated examples of over one hundred different paper types to CCI for use in this project. These papers, added to those which CCI had collected over the years, were assessed and thirteen papers of widely varying age, degree of degradation and fibre type were chosen for the first phase of the project. Researchers have investigated these fibres in an effort to discover which ones are most likely to benefit from alkalization, and which types show no change or are harmed by the introduction of alkali.

The vast majority of the scientific literature concerned with the effects of alkali on paper deals with investigations which utilized "new" lignin-free fibres. The study under discussion in this article, therefore, represents an important departure from past experimental designs. As a consequence, it is hoped that the results will be useful in formulating realistic recommendations for the preservation of paper holdings in Canada.

The thirteen papers chosen for this project were as follows:

1. unbleached linen paper, watermark, *circa* 1734
2. light blue ledger paper (rag), water mark, 1821
3. rag paper, J. Whatman Turkey Mill, watermark, 1821
4. notebook (rag), watermark, *circa* 1827
5. blue journal paper (rag), *circa* 1857
6. Legal documents (processed wood pulp), *circa* 1870
7. dark blue ledger paper, "Cowan" watermark, *circa* 1877
8. ledger paper, "Owl Linen Bond" watermark, *circa* 1900
9. transparent copy paper, rag, *circa* 1903
10. bond paper, Wilson Stationery Co. Ltd. No. 2, watermark, *circa* 1922, fumigated in 1960s
11. bond paper, Rockland, watermark, *circa* 1950, fumigated in 1960s
12. scrapbook (ligneous wood pulp), *circa* 1952
13. modern newsprint (ligneous wood pulp), *circa* 1980.

Description of Experiments

The experiments involved the individual aqueous treatment of the thirteen papers with high (200 ppm) and low (20 ppm) concentrations of alkali in the form of magnesium bicarbonate. The higher concentration simulated a deacidification procedure while the ower one was similar to what would be used in a washing treatment. Experiments were also carried out using identical concentrations of a neutral magnesium sulphate salt. Appropriate control samples included materials which had only been washed in pure water and those which had had no treatment at all.

The effect of the water on the acidity of the papers was determined by the estimation of the cold extracted pH before and after washing. The papers were analysed before and after chemical treatment by electron beam x-ray microanalysis, using a scanning electron microscope. This technique gives data about the type and quantity of chemicals in the paper fibres. Information about the presence of aluminium, magnesium, calcium and sulphur in paper is particularly helpful, as it gives details about specific materials which are known to affect the stability of cellulose, e.g., alum, calcium carbonate and magnesium carbonate.

The long-term effects of the various treatment sequences were investigated through the analysis of samples before and after thermal accelerated ageing at 50 per cent RH and 70 degrees Celsius. Individual fibre types were aged from eight to twelve weeks, depending upon the initial condition of the material. Degradative changes in the papers were monitored by observing changes in the viscometric average degree of polymerization (DP). As DP provides a very good estimation of the average length of the cellulose molecule, measuring the magnitude of changes in this parameter provides an excellent means of determining the extent of chemical and physical break down of paper fibres. Therefore, if a particular chemical treatment destabilizes paper, deterioration of the fibres should take place during accelerated ageing, and a significant decrease in the DP of the cellulose should be observed.

Comparing results between the alkaline and the neutral salt treatments (relative to the control samples) will help to determine whether the observed effects are due to alkalinity or to the presence of the magnesium cations. The results for the control samples will give valuable information about the permanence or chemical stability of paper fibres which are washed with very pure water.

Discussion of Results

Previous work in the conservation field[1,2,3] indicated that washing with pure (e.g., distilled or deionized) water decreased the permanence of paper. The reason suggested was that pure water is an excellent solvent which is able to remove constituents of the fibre, such as calcium and/or magnesium salts, which chemically stabilize cellulose. The results given in this discussion have altered these conclusions in a number of ways.

First of all, the DP measurements demonstrated that there was a significant difference between the permanence of untreated and wash controls for six of the papers tested. Of these six papers, half showed significant improvement by washing, and half showed loss of permanence. Although only small changes were noted for the other seven papers, four of them gave results that showed greater permanence for the wash control (versus the untreated control), and three suggested a loss in stability.

The separation of the papers into two groups — those that are improved by pure water washing and those that are not — can be explained partially by the initial pH of the paper. The explanation for a gain in permanence may be that the fibres were extremely acidic, and soluble acids were removed during washing. As a consequence, the washed fibres underwent less acid-catalysed hydrolysis during accelerated ageing than did the unwashed control. Presumably, this positive influence offset the detrimental effects of the loss of calcium and/or magnesium during washing. In papers where the initial acidity level was lower, the fibres would not benefit so much from washing, and it would be expected that the loss of magnesium/calcium would cause a decrease in the permanence of the fibres.

However, not all of the results could be interpreted by using this theory. Nor was the presence or absence of lignin a sure clue to the effects of pure water washing. Therefore, it was necessary to investigate further and find out whether there was anything about the chemical make-up of the fibres which could further explain the results. This information was obtained to some extent by the electron beam x-ray microanalysis. These results showed that, contrary to previous theories, all of the calcium and magnesium were not removed by extensive pure washing. The proportion of the total amount of calcium or magnesium which was lost varied, probably due to the physical structure of the paper web, type and amount of sizes, fillers, additives, etc. Also, it was discovered that a number of the papers contained significant sodium or potassium, which has been correlated in the past to a loss of paper permanence. The degree to which these undesirable components are removed during washing can affect paper stability. After careful consideration of all of these factors, it was possible to come up with an adequate explanation of the results obtained for each of the thirteen papers.

The other important area of this study was the investigation of the effect of the alkaline treatments on the papers. In order to explain these results, it is convenient to look at the fibres as two groups — those that contain lignin and those which do not. The first group of rag and/or purified wood pulp papers showed, with only one exception, a clear improvement through alkalization, at both the washing concentration (20 ppm magnesium) and the deacidification concentration (200 ppm magnesium bicarbonate). As the concentration of chemical increased, so did the permanence of the paper. This trend was also observed with the neutral magnesium sulphate, although in general there was not so large a difference among the samples processed with 20 and 200 ppm magnesium. The benefit of the higher sample pH was also evident, as the neutral pH magnesium sulphate samples did not age so well as the alkaline magnesium bicarbonate papers. However, it is important to note that in general all the papers in this group, which were treated with a magnesium solution (whether alkaline or neutral), resulted in more permanent papers than those which were simply washed or left untreated.

The x-ray analysis of the treated papers showed that the magnesium levels of the samples increase when the paper is immersed in a magnesium solution. In the case of papers which originally contained calcium, the magnesium would displace the calcium during treatment. Sodium would also be lost as the magnesium content of the papers increased. The results correlate well with the hypothesis that magnesium stabilizes paper, and that an increase in its concentration in cellulose fibres results in an improvement in paper permanence.

The transparent copy paper (Paper No. 9) presented an interesting exception to the above general rule. The results indicated that paper treated with 20 ppm magnesium bicarbonate was not so permanent as those treated with the neutral 20 and 200 ppm magnesium sulphate solutions. This shows that, under some conditions, cellulose can be degraded by an alkaline pH. Why it happened with this paper and not the other lignin-free papers is not completely clear. Two possibilities are 1) some chemical (as yet undetermined) was added to the paper during its processing which made it more susceptible to degradation by alkali; and 2) the paper was very thin, and swelled considerably during aqueous treatments: this would magnify any chemical interactions between cellulose and the chemicals in the paper.

The second group of papers are the two fibres which contained significant quantities of lignin. The lignin complicates DP analysis tremendously; the lignin portion is not readily soluble in the cellulose solvent used, and impedes the dissolution of the cellulose component. Approximately one-third (by weight) of Papers No. 12 and No. 13 were soluble in the cellulose solvent, cadoxen. Therefore, conclusions are based upon changes to significantly less than the whole fibre, and consequently are not so clear as those obtained for the lignin-free papers.

However, these qualifications aside, the ligneous fibres did not show a uniformly positive response to the magnesium bicarbonate treatments. As mentioned above, papers free of lignin increased in permanence as the concentration of the alkaline magnesium bicarbonate increased. However, the 1950s scrap-book paper showed a significant decline in stability in going from the 20 to the 200 ppm treatment. In fact, the 200 ppm magnesium bicarbonate samples were approximately as permanent as the neutral 200 ppm magnesium sulphate-treated fibres. If treatments using concentrations higher than 200 ppm had been carried out, one can speculate that the neutral pH sulphate samples would have been significantly more stable than the alkaline papers.

The data for the second ligneous paper, 1980 newsprint, is not easily interpreted because of heterogeneity in the sample materials (hence the large variation in the initial DP of the individual samples); tendency of the DP to change with any chemical processing; and differences in the degree of solubility of the cellulose fraction before and after accelerated ageing. However, some sensitivity to alkali can be tentatively inferred from the fact that the 200 ppm magnesium bicarbonate sample was the same or slightly less stable than the 20 ppm sample. The magnesium sulphate samples were approximately the same or slightly better than the bicarbonate fibres. The significance of these observations are especially apparent when one compares them with the very clear-cut evidence of the benefit of alkalization of non-ligneous fibres. Alkalization seems to be a very beneficial treatment for most fibres which contain no significant quantities of lignin, but not necessarily for those that do.

These conclusions with regard to ligneous fibres are not considered to be final. This is especially true in light of the results of follow-up experiments on a 1989 newsprint, and a turn-of-the-century ground-wood book paper. These papers did yellow significantly as a result of alkalization, but physical strength measurements (zero span tensile strength) showed that the alkaline papers were stronger than the neutral papers after accelerated ageing. The DP measurements were inconclusive.

It is hoped that the issue of the alkaline sensitivity of ligneous fibres will be clarified by a current project using mixed fibre papers (linen and Kraft wood pulp) of varying lignin content. Initial experiments have demonstrated that the previous solubility problems with the DP measurements will not be so great with these papers. Therefore, it will be possible to obtain more accurate data, and hence reliable conclusions.

Conclusion

As a consequence of the fundamental nature of this investigation, the results of the research project should be of wide application in the field of paper conservation. Several important conclusions may be drawn from this research:

1. For six of the papers tested, there was a significant difference between the permanence of untreated samples and those subjected to pure water washing. Of these six papers, half showed significant improvement by washing, and half showed loss of permanence. Although only small changes were noted for the other seven papers, four of them gave results that showed greater permanence for the wash control (versus the untreated control), and three suggested a loss in stability. These results are important because, i) water washing is one of the most frequently carried

out processes in paper conservation; and ii) previous work in the conservation field (involving new paper) has only shown the degradative and not the stabilizing effects of pure water washing.

2. Calcium and/or magnesium salts are only partially removed by pure water washing; the extent of removal probably depends upon the physical structure of the paper and the quantity and type of sizes, fillers and additives. This result is significant because previous investigators have suggested that pure water washing removes calcium or magnesium from the paper, and thus causes loss in long-term stability.
3. All but one of the papers with no lignin (i.e., rag and processed wood pulp) benefited from alkalization; the benefit increased, as did the concentration of the alkaline magnesium salt used for processing. This result strongly supports the deacidification of lignin-free papers.
4. Treatment of the lignin-free papers with neutral magnesium sulphate increases their permanence (relative to wash or untreated control samples), although the benefit is not so great as alkalization. This result strongly supports the use of neutral salts for processing of lignin-free papers which contain alkaline-sensitive inks and colours.
5. In the case of the two ligneous papers tested, alkalization destabilized the fibres, relative to samples treated with neutral magnesium sulphate. This conclusion is not regarded as final because, i) subsequent experiments with other ligneous fibres show either no effect or a significant positive effect from alkalization; and ii) the problematic nature of the analysis of lignin fibres has made us cautious about prematurely finalizing our conclusions regarding the treatment of ligneous materials.

It is hoped that future experiments will allow the issues discussed in conclusion 5. to be resolved in a more definite manner. Until this information is available, it is suggested that institutions (at least temporarily) consider reducing the quantity of ground-wood papers which are being treated by aqueous deacidification methods. For example, priority for deacidification treatment could be given first to new books containing little or no lignin, second to older lignin-free material, and last to new or old ligneous books. Advice concerning the selection of these materials[4] can usually be obtained from the conservator or technician responsible for carrying out deacidification in the institution. It is not known to what extent these results apply to non-aqueous deacidification.

Notes

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1 Lucia Tang, and N.M. Jones, "The Effects of Wash Water Quality on the Ageing Characteristics of Paper," *Journal of the American Institute of Conservation*, 18 (1979), pp. 61-81.

2 Helen D. Burgess, "Gel Permeation Chromatography: Use in Estimating the Effect of Water Washing on the Long-Term Stability of Cellulosic Fibres," *Advances in Chemistry Series, No. 212*, "Historic Textile and Paper Materials: Conservation and Characterization," H.L. Needles & S.H. Zeronian, eds., American Chemical Society, 1986, pp. 363-376.

3 J. Nelson, A. King, N. Indictor, and D. Cabelli, "Effects of Wash Water Quality on the Physical Properties of Three Papers," *Journal of the American Institute of Conservation*, 21 (1982), pp. 59-76.

4 The presence of lignin in paper can be determined by a chemical spot test using a phloroglucinol solution. Information concerning the preparation and use of this reagent can be obtained from the following source: B.L. Browning, "Analysis of Paper," 2nd ed. (New York, 1977), pp. 72-73.