Chemical Degradation of Cellulose in Paper over 500 Years

by DAVID ERHARDT & CHARLES S. TUMOSA

INTRODUCTION

Paper had been introduced into Europe by the 12th century by Arabs, who in turn had obtained the technology from the Chinese much earlier[1]. The development of the printing press greatly increased the quantity of paper required and by the end of the 15th century considerable amounts of paper had been produced, printed upon and bound into books. The large amounts of paper available from the 14th century onwards provide an opportunity to examine the chemical and physical changes brought about by time and essentially uncontrolled environments. These changes, in turn, allow us to evaluate how changes in the manufacture of paper affected its ageing behaviour.

Developments in the papermaking process

By the 15th century paper consisted primarily of beaten, soaked and macerated linen fibers. Cotton fibers were also becoming an important component. Other materials have been used but in general the best paper was made from linen and cotton rag fibers. Initially, both the pulping process and the conversion of pulp to paper were slow manual processes. Flax or rags were retted and bleached in the sun, a process that could take months. The material was pulped using pestle and mortar, or later using mechanical stampers. Paper was often produced near mountain streams that provided the clean water needed for the process. In Europe, such water was often hard, containing lime, which contributed to the alkalinity and permanence of the resulting paper. Gelatin sizing was applied by dipping the paper in a solution of gelatin. The tubs of sizing were subject to spoiling. Around 1650, the addition of alum to the sizing solution was introduced. The alum had some sizing ability of its own, but primarily served to harden the gelatin and prevent the solution from putrefying. Unfortunately, alum usually contained some residual sulfuric acid, and alum-sized paper was not as permanent. Faster, more

efficient and larger scale mechanical processes gradually were developed. The Hollander beater was introduced in 1680. It was much faster and more productive than mechanical stampers, but its pulping action resulted in shorter fibers. Around 1749, "bucking and crafting", i.e. treatment with alkali followed by mild acid (such as sour milk) was introduced. Later, sulfuric acid was used to speed up the process! In 1774 Scheele discovered chlorine, and chlorine bleach soon followed. It took a while for the bleaching process to be perfected, however, and quantities of paper were produced that were either unusable or crumbled soon after manufacture. By the 19th century the demand for paper was such that other sources of cellulose fibers, such as straw and grasses, were being explored. The development of the cotton gin in 1794 made much greater amounts of cotton fiber available, and reduced the urgency of developing other fiber sources for some time. The demand for paper kept increasing, though, especially with the introduction of the Fourdrinier machine for the continuous, rather than batch, production of paper. By the mid to late 19th century methods and processes were developed that enabled the use of wood, the largest single reservoir of cellulose, as a source of paper fibers. Because mechanical treatment of wood alone did not produce very good quality pulp or paper, chemical processes were developed to remove some of the non-cellulosic components such as lignin and colored material to produce higher quality paper. These included the soda process in the 1850s, the sulphite process in the 1870–1880s, and the sulphate (Kraft) process at the end of the 1800s.

The process of making paper fibers changed with the introduction of new fiber sources, new chemical and physical pulping processes, and the adoption of chemical bleaching techniques. A more thorough discussion of the developments listed above, as well as other developments in the manufacture of paper, can be found in the article by Clapp[2]. These changes significantly altered the ageing behaviour of paper. These changes can be roughly divided into three categories: changes in the fiber sources (and additives), changes in the mechanical production of pulp and paper, and changes in the chemical treatment of the pulp.

Chemical changes during ageing

Paper is a mixture of cellulose fibers. Other components such as hemicelluloses and lignin (from wood) may also be present depending on the composition of the fiber sources used for a specific paper. Added components include such materials as rosin, calcium carbonate, titanium dioxide or clay to alter the properties of the final sheets of paper[3]. All of these components change with time or alter the ageing characteristics of other components of the paper. The present condition of old

paper is affected by a number of factors: the component fibers (and additives), the process of manufacture, the cumulative effects of use and the storage environment and, finally, the handling of the paper as a utilitarian object. Except for conditions of extreme heat or dryness, the primary deterioration mechanism (aside from biological attack at high RH) is hydrolysis. This results in depolymerization of the cellulosic chain, and the resulting products include glucose (the basic chemical compound from which cellulose is derived) and oligomers (short chain polymers) containing two or more units of glucose. Similarly, other sugars such as xylose and arabinose result from the hydrolysis over time of components such as xylan and hemicellulose.

Paper samples spanning the time period from the late 15th century to the present were analyzed to determine the amounts of glucose and xylose produced from the cellulose polymer and xylan, respectively, as the paper ages over the course of centuries. Hydrolysis of the cellulose to yield glucose as a final product is an expected reaction of cellulose with absorbed water, and glucose serves as an indicator of the extent of hydrolysis of the terminal unit of the cellulose in paper. Similarly, xylose serves as an indicator both of the presence of xylan (usually from wood pulp) and its hydrolysis. In an initial attempt to determine if the non-polymeric sugar concentrations varied in any discernable fashion, it was decided to examine a range of papers of varying properties.

EXPERIMENTAL METHODS

Paper was acquired from discarded documents, books, or fragments of books that had no known prior treatments. Areas were sampled near the edge of the sheets, avoiding areas with obvious water staining, foxing or mechanical damage. Samples tested were approximately 0.1 to 1 grams in weight. All of the specimens were in a reasonable state of preservation, and could be handled and tested without special precautions.

Gas chromatographic analyses of saccharides were performed after aqueous extraction and a two-step derivatization to convert carbonyl groups to oximes and to trimethylsilylate reactive hydroxyl groups as described previously[1]. Identification of components was made by comparison of retention times with standard samples. Concentrations were determined by comparison of peak areas with that of an internal standard (O-phenyl-β-D-glucopyranose). This method allowed the detection and quantification of simple sugars as well as their oligomers up to tetramers (four sugar units) in length.

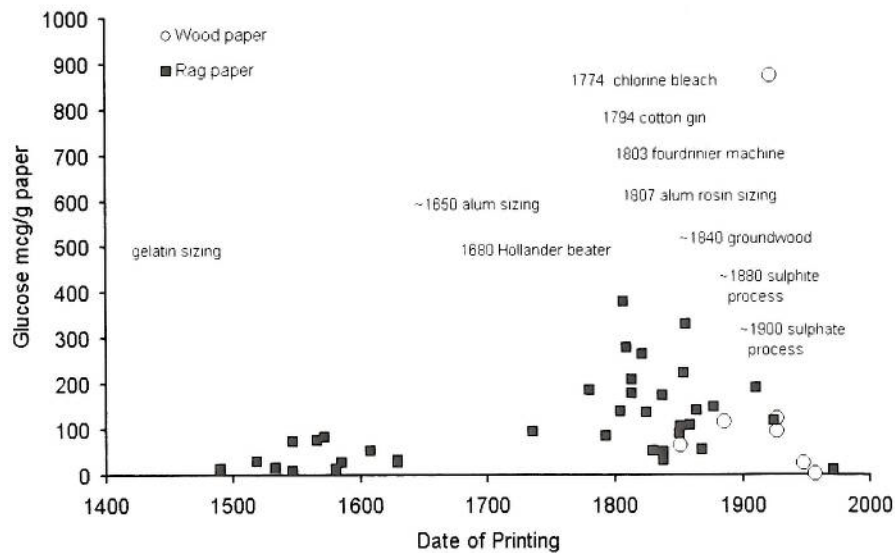Microscopic examination was used to identify the composition of the paper fibers.

Fig. 1: Concentrations of glucose in paper samples plotted versus date of printing. Dates of important developments in the papermaking process are also indicated.

RESULTS AND DISCUSSION

Fig. 1 shows a plot of the soluble glucose content of papers from the 15' to the 20" centuries. The data show that the earliest papers (pre-1650) have produced the lowest amounts of glucose, even though they have aged for over 200 years longer than most of the other papers. As the demand for paper increased through the centuries, changes in the processing of paper occurred. The newer papers (mostly post-1800) have produced much more glucose than the older papers. Since these papers come from a variety of sources, it is unlikely that the differences are due to post-production treatment, use, or environment. The differences are more likely due to the changes in papermaking that occurred during this time span, a number of which could result in higher amounts of glucose during ageing. The older processes may have removed much more of the easily hydrolyzed components (possibly through fermentation) than the newer processes in which the pulp is not soaked for nearly as long and in which biological growth is minimized or prevented. The greater degree of mechanical maceration and shorter fiber length achieved by the Hollander beater may have also resulted in shorter cellulose chain lengths, meaning more end units exposed to hydrolysis. Most likely, though, is the fact that the newer processes either created or deposited acidic compounds that catalyze hydrolysis. Alum sizing, alum rosin sizing (and later, aluminum sul-
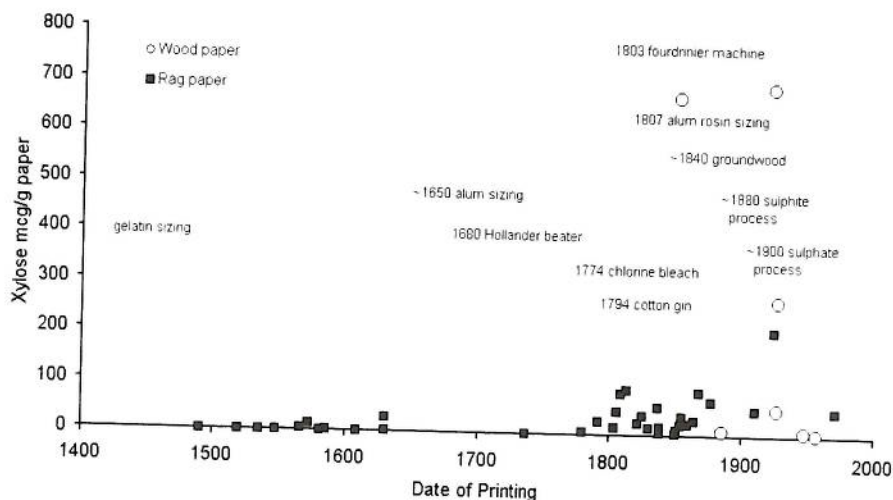
Fig. 2: Concentrations of xylose in paper samples plotted versus date of printing. Dates of important developments in the papermaking process are also indicated.

fate rosin sizing), bucking and crofting, and the sulfite and sulfate processes all involve treatment with acidic materials that resist being washed out during manufacture. Chlorine bleaching, as well, may oxidize the cellulose and produce carboxylic acid groups. It is interesting to note that the use of groundwood does not by itself seem to result in greater amounts of glucose, since, with one exceptionally high value, all of the glucose concentrations in the tested wood pulp papers are within the low range of values for rag papers manufactured during the same time span. The increase in the rate of glucose predates the introduction of groundwood and is probably due more to the introduction of acidic processes, especially the use of alum and alum rosin sizing. Also of note is that the increase in use of cotton, made possible by the development of the cotton gin, did not result in a significant decrease in glucose levels, except possibly for newer papers in which the lower levels are more likely the result of shorter ageing times. The general perception is that the "best" paper is made from cotton, because it is the purest naturally occurring source of cellulosic fibers generally available. As with the perception that wood pulp papers are inherently bad, the perception that cotton papers are consistently better is also not uniformly true. The primary factor that determines the ageing behaviour of paper is whether or not the manufacturing process results in an acidic paper. More extensive testing, especially of papers manufactured during the 1600–1800 time period, should allow better correlation of changes in processes with changes in ageing behaviour.

Fig. 2 shows a plot of the soluble xylose content of papers from the 15th to the 20th centuries. The amount of xylose in the earliest papers was found to be either undetectable, or minimal when compared to more recent specimens of paper from the 19th and 20th centuries. Two factors may explain this. First, as with the results for glucose, the non-cellulosic, xylose-containing material may have been more effectively removed during the prolonged retting and associated bacterial action. Second, the generally alkaline early processes, as opposed to later acidic processes, result in less acid-catalyzed hydrolysis of any xylose-containing material that remains. Unlike the results for glucose, however, most of the papers with the highest levels of xylose are wood pulp-containing papers. This is to be expected, especially for wood pulp papers that were minimally processed and in which much of the woody, non-cellulosic material remains. It is possible, through more severe chemical and mechanical treatment, to remove most of the woody material, although such treatment also results in shorter fibers and weaker (although "cleaner") paper. This is probably the case with the wood pulp papers that have levels of xylose comparable to non-wood papers.

CONCLUSION

The plots of the amounts of sugars versus date of manufacture show trends and discontinuities that may be explained by changes in paper manufacturing materials and processes. The oldest papers (pre-1650) were probably produced by similar procedures, and it is interesting that the amounts of both glucose and xylose in these papers are both consistent and very low despite the age of the papers. This is probably due to a papermaking process that tended to produce an alkaline paper that contained little non-cellulosic material. Later papers tend to have larger amounts of both glucose and xylose, even though they have aged for substantially shorter times. The higher levels are probably due to the introduction of new chemical and mechanical processes that resulted in more degraded fibers and acidic papers that contained more non-cellulosic material. The primary factor is the acidity of papers produced by the newer processes, as demonstrated by consistently high levels of the sugars only after the introduction of acid processes, but both before and after the introduction of other fibers and mechanical papermaking.

Rag and linen papers contain almost no xylose, while the amounts in wood pulp papers range from very large amounts to small amounts comparable to rag papers. Testing of more samples may allow better correlations of glucose and xylose levels with changes in the papermaking process. However, even the results so far have demonstrated the effects of the changes.

SUMMARIES

Chemical degradation of cellulose in paper over 500 years

Concentrations of soluble sugars including glucose and xylose in papers produced over a range of 500 years were determined. Extraction of samples from the unprinted areas of the paper was followed by concentration, derivatisation, and analysis of the extracts by gas chromatography. The identification of the sugars was made by comparison of retention time to authentic samples and the sugars quantified against an internal standard. Initial data showed differences in the oldest (14th–17th century) specimens in comparison to later 18th, 19th, and 20th century papers. Higher levels of simple sugars were found in the newer papers, indicating a combination of larger amounts of easily hydrolyzed material and processes that yielded acidic papers in which the hydrolysis of these components is much more rapid.

Dégradation chimique de la cellulose dans le papier au cours d'une période de 500 ans

On a procédé à une évaluation des quantités de sucres solubles comme le glucose et le xylose dans des papiers dont la date de fabrication s'étale sur une période de cinq siècles. On a extrait des échantillons du bord du papier non imprimé qui ont été soumis à des compressions, des conversion et des analyses au moyen de chromatographie gazeuse. Pour l'analyse qualitative on a procédé à la comparaisons des durées de rétention avec des échantillons authentiques et on a utilisé un standard interne pour l'analyse quantitative. On a constaté des différences entre les spécimens les plus anciens (entre le 14e et le 17e siècle) et les plus récents (fin du18e, 19e et 20e siècle). Les plus hautes concentrations de sucres à basses molécules ont été décelées dans les papiers les plus récents, c'est un indice permettant d'affirmer que les substances facilement hydrolisables dans le papier résultent d'un procédé de fabrication favorisant l'acidité dans le papier, celle-ci ayant pour effet d'accélérer l'hydrolyse.

Chemischer Abbau von Cellulose in Papier über einen Zeitraum von 500 Jahren

Es wurden die Mengen an löslichen Zuckern wie Glucose und Xylose in Papieren aus fünf Jahrhunderten bestimmt. Proben vom unbedruckten Rand der Papiere wurden extrahiert, die Extrakte komprimiert, konvertiert und mittels Gas-Chromatographie analysiert. Zur qualitativen Analyse wurden die Retentionszeiten mit denen authentischer Bezugssubstanzen verglichen, zur quantitativen diente ein interner Standard. Es ergaben sich Unterschiede zwischen den ältesten (14.–17. Jh.) und jüngeren Proben (spätes 18., 19., und 20. Jh.). Die größeren Mengen an niedermolekularen Zuckern wurden in den neueren Papieren gefunden, was ein Anzeichen dafür ist, daß leicht hydrolisierbare Substanzen im Papier die Folge von Herstellungsprozessen sind, die zu Säure im Papier führen, welche deren weitaus raschere Hydrolyse bewirken.

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David Erhardt, Charles S. Tumosa
Senior Research Chemists
Smithsonian Center for Materials Research and Education (SCMRE)
Museum Support Center
4210 Silver Hill Road
Suitland, Maryland, 20746
E-mail: ErhardtD@si.edu
          TumosaC@si.edu