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Composition and Condition of Naturally Aged European Papers

ABSTRACT

We report the initial findings of a study of forty naturally aged papers of European origin dating from 1477 to 1793. The samples were analyzed for fiber type, gelatin content, pH, yellowness index (YI) and molecular weight (as degree of polymerization (DP)). Correlations were evaluated for gelatin content and pH compared to YI and DP, two measures of the condition of paper. Specimens with high pH values (pH = 7.0–9.9) showed a strong correlation to low YI and high DP values. These specimens were determined to be in good condition. Poor specimens were found to have low pH, high YI, and low DP values. Unlike pH, gelatin content was not strongly correlated with YI or DP. Specimens with high gelatin content (5.5–11.4%) exhibited high pH values and therefore had low YI and high DP values. Specimens containing less than 5.5% gelatin content showed a range of pH values (pH = 4.0–9.9) and consequently those papers ranged in condition from poor to good.

INTRODUCTION

For years conservators have been interested in understanding how changes in paper production have affected the aging of paper. Some aged papers have been known to yellow, embrittle, and fox. On the other hand, some aged papers are stable, remaining relatively white and strong over time. The reason for this stability is not fully understood, but there is a belief that certain factors—such as gelatin content, pH, degree of beating, trace metal content, and cellulose purity—play important roles.

Beginning in 1963, the William Barrow Laboratory (Barrow 1964; Barrow 1973; Barrow 1974) undertook a major project to determine what properties of a piece of paper influence its long-term stability. During the course of that study, roughly fifteen hundred book papers were examined. Using physical strength (a manifestation of the robustness of the cellulose chain), pH, alum, and metal carbonate tests, as well as measuring the retention of properties following thermal aging, the laboratory concluded that high-pH papers showed the best long-term stability. However, lacking in the study was a probe of the effect of gelatin content, a common ingredient in Western paper up until 1800, when rosin and alum internal size was introduced.

Barrett et al. (Barrett 1989; Barrett and Mosier 1995) analyzed the long-term stability of paper to investigate the effect of gelatin content. Results from those studies suggested that, in addition to pH, gelatin contributes to paper stability. However, both studies also concluded that more work needed to be completed to clarify the relationship between gelatin and long-term stability. Similarly, Dupont suggested that gelatin may retard the aging of cellulose if certain quantities of gelatin are used to size paper (Dupont 2003a).

For this study we measured the fiber type, gelatin content, pH, yellowness index (YI), and the degree of polymerization (DP) of forty naturally aged paper specimens dating from 1477 to 1793 to determine the chemical properties that enhance paper stability. Light microscopy and staining techniques were used to identify and measure the lengths of the fibers. We used gas chromatography-mass spectroscopy (GC-MS) to measure the gelatin content. The GC-MS method, which uses seven stable amino acids to calculate the gelatin content, differs from the TAPPI method used by Barrett and Mosier (Barrett and Mosier 1995), where only hydroxyproline content is used to calculate the gelatin content. The traditional method of measuring the pH from water extracts of the specimens was used; this technique is more representative of the pH of the entire paper than surface pH measurements (Strlič et al. 2004). A reflectance spectrophotometer

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was used to measure the yellowness index (YI), a potential indicator of the state of degradation. The degree of polymerization (DP) of the cellulose was measured using gel permeation chromatography (GPC).

RESULTS

The forty samples were first visually assessed and segregated into two categories, dark and light, based on color. The results are summarized in table 1. Dark specimens are identified by the prefix D and light specimens are identified by the prefix L.

Analysis of fibers from disintegrated papers indicated that all forty samples in the data set were made from flax bast fiber. However, polarized light microscopy, used to differentiate flax from hemp, can be inconclusive when the fibers are highly refined and beaten. Though tests did not positively identify hemp in any specific specimen, it is likely some of the specimens may contain hemp fiber.

Dark specimens D5, D7, and D20, as well as light specimens L2 and L18, showed the presence of small amounts of cotton fiber. Dark specimen D7 also had a small amount of shive fiber in it. Almost every specimen was fibrillated; dark specimens on the whole were more fibrillated than light specimens. Evidence of yellow staining from the application of Graff "C" stain was observed in some specimens and indicated the presence of nonfibrous or chemical material; the yellow staining was ascribed to the presence of gelatin.

The average fiber length of all forty samples was measured. Most specimens showed fiber lengths in the average range of 0.5 to 2.0 mm. Specimens D17, D20, L6, and L13 had slightly longer fibers. Dark and light specimens were not distinguishable based on fiber length.

The gelatin content measured for the specimens showed that the average dark specimen had less gelatin in it than the average light specimen. The gelatin content for the dark specimens ranged from 0.13–4.68%, and the light specimens ranged from 2.02–11.36%. It was noted that for this sample set, after 1570 only L3 and L15 showed a gelatin content above 5%; those two specimens were coincidentally the least yellow specimens in the entire data set.

The pH of the specimens showed that, in general, dark specimens were more acidic than light specimens. The pH range for the dark specimens was 4.0–7.9 while the range for light specimens was 7.3–9.9. It was interesting to observe that some of the specimens with the highest pH were also the oldest (L1, L2, L6, L7, L9, L11R, L12, L13, L20), and that eight of those nine specimens were made in Italy.

Barrow noted that after the introduction of alum, which he dated to around 1650, there was an overall decline in the pH values of paper (Barrow 1974). While it was observed that some of the more modern specimens had a lower pH than some of the older specimens, there were also some specimens made after 1650 that showed high pH values (L3, L4, L10R, L15, and L19). Three of five of those specimens were made in England.

The YI of specimen sheets showed that, on average, dark specimens were more yellow. The YI range for dark specimens was 16.7–38.6, while for light specimens the range was 9.2–18.1. Since yellowing was either the result of the chemical breakdown of cellulose molecules or the degradation of gelatin in the samples, it was initially inferred that dark specimens were more degraded than light specimens. However, the color of paper is not always an accurate indication of paper condition (Lee et al. 1994).

Molecular weight measurements showed that the dark specimens had lower DPs than light specimens. The DP range for dark specimens was 680–3290 while DP range for light specimens was 2030–3840. Though a DP of 680 is rather low, a piece of paper with that DP can still be considered to be viable; it is not until the DP falls below 500 that a piece of paper starts to be considered fragile (Jerosch et al. 2002).

DISCUSSION

Once the material property data were collected for all forty specimens, it was possible to identify relationships between the various properties. From figure 1, a plot of DP versus pH, it is evident upon first glance that these properties are strongly correlated. When the pH is alkaline, specimens show a high DP; conversely, when the pH is acidic, specimens show a low DP. This correlation between pH and DP is well established, for acid in papers catalyzes degradation in the form of hydrolysis (Whitmore and Bogaard 1994); hence, the DP is expected to be lower in acidic papers. Results from this study confirmed Barrow's

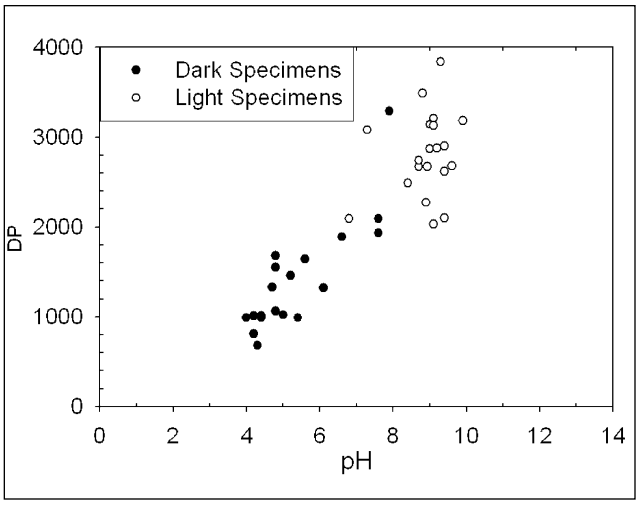

Fig. 1. Correlation between pH and degree of polymerization (DP)

Table 1. Summary of results for each specimen in the study

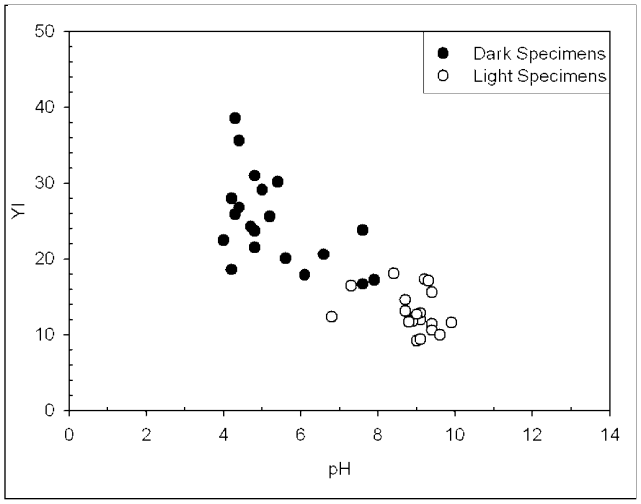

Fig. 2. Correlation between pH and yellowness index (YI)

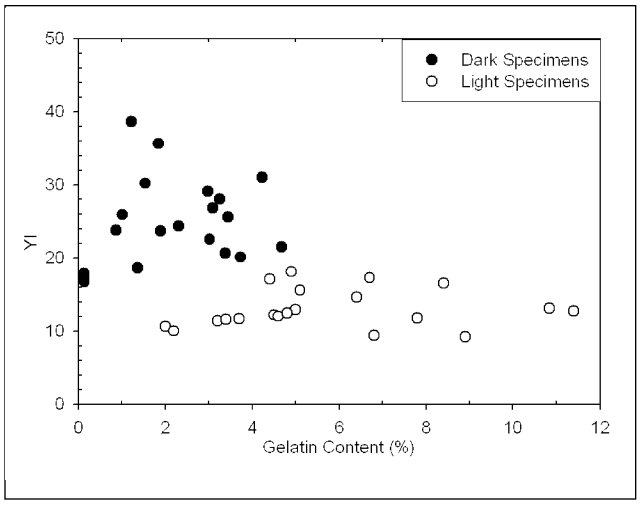

Fig. 3. Correlation between gelatin content and yellowness index (YI)

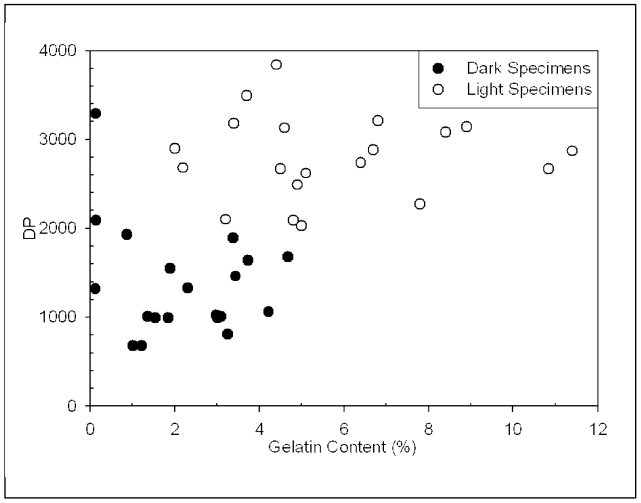

Fig. 4. Correlation between gelatin content and degree of polymerization (DP)

hypothesis that papers with high pH show good long-term stability.

In addition to breaking cellulose molecules apart, hydrolysis causes carbonyl groups to be formed at the ends of the cellulose molecules. Increasing amounts of carbonyls tends to lead to yellowing of the paper. Further, the color-forming chemistries are known to be more rapid at low pH. Figure 2, a plot of YI versus pH, shows that specimens with high pH were less yellow than specimens with low pH. Correlations between pH and either YI or DP indicated that under natural aging conditions, low-pH papers showed both physical (YI) and chemical (DP) signs of degradation.

After confirming that pH affects both YI and DP, we made the same comparison between gelatin content and DP and YI to determine the role of gelatin content on paper stability. Figure 3, a plot of YI versus gelatin content, showed that no strong correlation existed between the two. However, when the gelatin content was high, greater than 5.5%, specimens consistently showed low YI values. When the gelatin content was lower than 5.5%, it was not possible to predict the YI of the specimen.

Figure 4, a plot of DP versus gelatin content, showed an analogous relationship. Similar to YI, when a specimen contained more than 5.5% gelatin content, it also had high DP. When the gelatin content was less than 5.5% it was not possible to predict DP.

In order to understand the behavior of high gelatin content papers, see figure 5, a plot of pH versus gelatin content; this graph shows that specimens containing more than 5.5% gelatin content also exhibited high pH. Since we concluded that DP and YI values were strongly associated with pH, it was impossible to verify that high gelatin content alone contributed to high DP and low YI values. If there were specimens in the data set with high gelatin con-

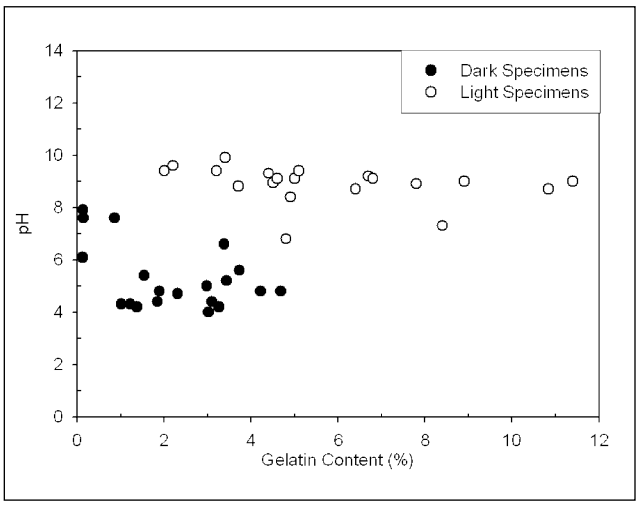

Fig. 5. Correlation between gelatin content and pH

tent and low pH, it might be possible to confirm whether gelatin is associated with high pH, high DP, and low YI—or not. To determine if gelatin does affect DP and YI, analysis of a larger set of specimens—all containing higher gelatin contents—would need to be analyzed before any final conclusions were made about the role of gelatin in long-term stability.

A Pearson's correlation and respective p-values were calculated using all the raw data collected in this study. The Pearson's correlation reflects an interconnection between two variables and values range from -1 to 1. Correlation values close to either extreme indicate strong relationships between the two variables: positive values imply a direct relationship; negative values imply an inverse one. The p-values calculated for the Pearson correlation values indicate the significance of the data; when p-values are $p<0.05$, the correlations are considered statistically significant.

Table 2 shows the result of the Pearson's and p-value analyses. The strongest Pearson relationship existed between pH and DP. It was a positive correlation, meaning that high pH was associated with high DP. The next strongest Pearson relationship was the negative correlation between pH and YI; that correlation meant that high pH was associated with low YI. The weakest calculated relationship was between gelatin content and pH. All of the correlations had $p< 0.05$; therefore the correlations were significant.

CONCLUSIONS

The role of pH and gelatin content in the long-term stability of forty naturally aged flax papers was probed. A strong correlation between pH and DP and pH and YI was found: high pH values were associated with high DP and low YI. A strong correlation between gelatin content and DP or YI was not observed; however, more analysis should be completed to confirm this conclusion. It is possible there exists yet another constituent—perhaps an alkaline salt in the high gelatin content papers and occasionally present in sheets having lower gelatin content—that contributes to the stability of naturally aged papers. The future work of this study is to perform quantitative trace metal analysis on these papers in order to better understand the influence of their concentrations on paper aging.

Table 2. Pearson correlations and p-values

Variable	Yellowness (YI)	pH	Gelatin Content (%)
YI	—	—	—
pH	-0.837**	—	—
Gelatin content (%)	-0.462*	0.458*	—
DP	-0.800**	0.891**	0.485*

* p<0.005
** p<0.0001

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APPENDIX

Paper Specimens

The forty specimen sample set was selected to span a range in gelatin content (0% to 11%), condition (dark to light in color), apparent strength (weak to strong), and overall quality (poor to good). "Poor" and "good" are subjective terms, but in general many of the specimens identified as "dark" in this study showed evidence of mixed fiber furnish, insufficient beating, unskilled sheet forming or couching, and other signs of rough workmanship. This contrasted with the other half of the specimens—identified as "light" in this study—where most showed evidence of uniform, high-quality rag selection, carefully executed beating, good formation quality, skilled couching, and overall superior attention on the part of the papermaker to producing a high-quality finished sheet.

Provenance and previous storage conditions for all the specimens are unknown but care was taken to avoid specimens where there was evidence of exposure of the entire leaf to water, conservation, or evidence of binder resizing such as an overly flat sheet lacking in type impression. An additional priority was to select sheets with the largest available homogeneous non-print area to permit the largest number of small-sample destructive and non-destructive tests.

The date cited for each specimen was either the original publication date of the book from which the specimen was taken when known or was an estimate of the date of production provided by the editor of the McBey Watermark Collection (Cohen 1981). The forty sheets in the final set were selected from a pool that included: more than five-hundred Barrett and Barrow book leaves printed between 1479 and the late 1700s (McBey unprinted leaves included); more than thirty-five early printed leaves specially purchased by University of Iowa (UI) Special Collections in November 2005; thirteen specimens supplied by Terry Belanger at University of Virginia (UVA) Rare Book School in December 2005; fifteen eighteenth-century bro-

ken books from the UI Libraries discard/rebinding training collection acquired in November 2005; twelve specimens supplied by Bill Cotter in December 2005; and thirty-two duplicate or new specimens specially pulled from Barrow's broken books at the Library of Congress in December 2005.

GC-MS Analysis

For each historical specimen, three samples, each 5 mg (air-dry (AD) weight), were used for gas chromatography-mass spectroscopy (GC-MS) analysis. Each sample was punched from ten different locations in the same historical leaf reserved for later nondestructive tests using a 1.2 mm Whatman Harris micropunch. For the thinnest sheets, weighing approximately 50 g/m^2, this required the equivalent of 1 cm^2 or about eighty-eight disks. For the heavier papers, weighing closer to 100 g/m^2, about forty-four disks were needed. Smaller pieces of the specimen remaining after repeated punching were sometimes cut into smaller bits and added to the total mass required to make up each sample. All of the lighter specimens were sampled using the same side of the Whatman supplied self-healing pad with a brief burst of Norazza Duster air to clear the punch tip between specimens. All of the dark specimens were then sampled in the same way using the opposite side of the pad during punching. After punching, disks were transferred to tared 2 mL screw-topped autosampler vials. At the Getty Conservation Institute, the sample vials were uncapped, dried for 30 minutes at 105ºC, then recapped and cooled in a desiccator. Each sample was subsequently transferred to a tared 2 mL vial and the AD weight recorded. The dry weights ranged from 4 to 7 mg.

Gelatin was extracted for GC-MS analysis using dilute aqueous hydrochloric acid following an established protocol (Halpine 1995). To each sample vial, 1.00 ml of 0.1N HCl was added. After capping, the vials were heated for 1 hour at 105ºC. Once cooled, a 100 μl aliquot of each extract solution was transferred to a Reacti-Vial, and evaporated to dryness with a stream of nitrogen on a Reacti-Therm heating block at 55ºC. To each Reacti-Vial were added 5 μl of a 200-ppm norleucine internal standard solution (in 0.1N HCl) and 100 μl of 6N aqueous HCL. The vials were heated in an oven for 24 hours at 105ºC, and then cooled to room temperature. Derivatization and quantitative GC-MS analysis were carried out using a silylating reagent (Schilling 2005).

Gelatin content, reported as a percent, is the ratio of the weight of the gelatin in the paper sample to the weight of the whole paper sample. Gelatin content was calculated from the concentrations of seven stable amino acids (alanine, glycine, L-valine, L-leucine, L-isoleucine, L-proline, and L-hydroxyproline) present in each paper extract. The total weight percent of the stable amino acids in each paper sample was converted to weight percent gelatin in the paper by a conversion factor (modern parchment contains 56.5 weight percent of stable amino acids). Reported gelatin content values were the average of three unique measurements.

pH, YI, and GPC measurements

All three tests, pH, yellowness index (YI), and gel permeation chromatography (GPC), were performed using a single sample, each 35 mg AD. Each sample consisted of one to two continuous pieces, totaling about 7 cm^2 for the thinner sheets and 3.5 cm^2 for the heavier sheets. Whenever possible these samples were taken from the same historical leaf reserved for later nondestructive tests. However, due to the limited size and thickness of some specimens, these samples were sometimes excised from like sheets from the same book.

The YI was measured according to the ASTM standard test method E313-00. A GretagMacbeth Color-Eye 7000 colorimeter controlled by Propalette Optiview Gold version 5.2 software was used to collect the data. Values reported are the average of four separate tests.

The TAPPI standard test method, TAPPI T-509, was used to measure the pH with several exceptions. The paper-to-water ratio was 0.0357 g paper in 2.5 mL water. All pH measurements were made in a sealed glove bag that was purged of carbon dioxide by using nitrogen gas. Water used for each sample was brought to pH 7.3 by distilling it according to Appendix A.3 of the TAPPI method. An Orion ROSS pH microprobe electrode attached to a Thermo-Orion model 720A benchtop pH meter was used to measure the pH. Due to the small quantity of sample, only one pH measurement was made per specimen.

A modification of the solvent exchange protocol developed by others (McCormick et al. 1985; Dupont 2003b; Strlič and Kolar 2003) was used to prepare specimens for GPC analysis. The specimen was first soaked in 2.5 mL of water for 24 hours. The specimen, while constantly stirred, was soaked twice in methanol for one hour followed by filtration. This procedure was then repeated twice using dimethylacetamide (DMAc). Finally, the specimen was dissolved in 5 mL of an 8% (w/v) solution of lithium chloride (LiCl)/DMAc, stirred continuously for 24 hours at room temperature, then stored at 4°C for 7 days. On the day of analysis, solutions were diluted to 0.0625% (w/v) cellulose in a 0.5% (w/v) LiCl/DMAc solution.

Molecular weight distributions (MWD) of the dissolved specimens were collected using a Waters 2695 Separations Module coupled to a Waters 2414 refractive index detector and Empower software, database version 5.0. Separations were carried out using three Waters HR Ultrastyragel columns in series, HR5, HR4 and HR3, held at 70°C. The refractive index detector was set to its highest temperature, 50°C. The mobile phase was a 0.5% (w/v) solution of LiCl/DMAc and flowed at a rate of 1 mL/minute. An

autosampler was used to inject 125 μL aliquots of sample solution into the GPC. Averages of three injections of each sample solution were used to determine the MWD and weight-average molecular weight (Mw). The degree of polymerization (DP) was calculated by taking the Mw and dividing by the monomer molecular weight of cellulose, 162 g/mol. Eight pullulan standards covering the range of molecular weights were dissolved in the LiCl/DMAC solvent and analyzed to generate a calibration curve.

Fiber Identification

Samples measuring 0.5 mm x 0.5 mm were pulped using a micro-disintegrator and analyzed to determine the type of fiber and the average fiber length. The TAPPI standard test method TAPPI T-401 along with polarized light microscopy were used to determine the fiber type of each sample. Light microscopy with a calibrated ocular micrometer was used to measure the average length of the fibers that comprised each sample.

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