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Sizing in Nineteenth-Century Book Papers

ABSTRACT

Recent research into nineteenth-century machine papermaking processes reveals that gelatin surface sizing for book papers was phased out during the early years of the machine period while alum-rosin internal size gained use. In this preliminary investigation, the authors tested for gelatin (protein) using biuret and ninhydrin reagents. A total of sixty American-imprint books—five from each decade spanning 1790 to 1910—were tested. Protein is present in a large majority of the tested book papers from the 1790s through the 1830s, but from 1840 to 1910 only a small minority of papers tested positive for protein. These results seem to support the premise that gelatin sizing decreased with the increased use of alum-rosin size. An iodine-potassium iodide test for starch was also carried out; starch was found in a few book papers starting in the 1830s, rising to a presence in a majority from 1880 on. This test confirms the addition of starch to alum-rosin sizing as found in contemporary papermaking recipes. The testing procedures were modified from standard ones. Samples in the ninhydrin test were not only heated, but also allowed to develop color (if positive) over several hours. For the starch test a standard commercial iodine-potassium iodide solution was diluted to different strengths to facilitate clear interpretation of the resulting color stain.

PAPER SIZING IN THE NINETEENTH CENTURY

The nineteenth century was a period of tremendous change in all aspects of American life, due to a progression away from hand-crafted articles toward mechanization. Increasingly, manufactured goods were made cheaply and efficiently by machines. Books both fueled this industrial revolution and were a product of it. Their three interdependent technologies—papermaking, printing, and bookbinding—saw incredible innovations as the century progressed.

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Early in the century the advent of both the fourdrinier and cylinder machines demonstrated that papermaking could be mechanized. Closely associated with these engineering inventions, a major chemical advance—alum-rosin sizing—made papermaking more efficient by giving the sheet enough internal strength at the wet end of the machine to allow the paper web to withstand the tension created as it traveled and shrank over the heated cylinders through the dry end. Although the discovery of alum-rosin sizing was first announced in 1807 by Moritz Illig, it was not used commercially in America until the 1830s, coinciding with the rise of the papermaking machines.

The traditional manner of sizing paper was to hand-dip loft-dried sheets in a tub of warm gelatin. Today this kind of sizing is called tub, surface, or external sizing. In the nineteenth century, it was called "animal sizing." The degree of gelatin sizing applied to paper depended on the anticipated use. Weak, soft, or slack sizing was appropriate for papers to be letterpress-printed with an oil-based ink. Slack sizing allowed book and news paper to be readily dampened before printing, which resulted in better impression, better ink deposition, and the consumption of less ink.

Conversely, strong or hard sizing was reserved for papers that had to withstand the application of water-based mediums and erasures. Additionally, intaglio plate papers required hard sizing because, once the paper was dampened, it had to be strong enough to stretch under great pressure.

Unfortunately tub sizing was a time-consuming and relatively wasteful practice. Gelatin solutions soured and putrefied in a few days, especially in the summer. In an effort to extend the working life of the gelatin, alum was added daily, and larger proportions of alum led to an increasingly acidic and softer sized sheet. Over several days this practice resulted in batches of paper that today exhibit differences in discoloration, acidity, and weakness. This progression, not noticeable at the time of printing, often can be seen across signatures in the same book.

Alum-rosin sizing occurred in the Hollander beater before sheet formation, and thus it is referred to as internal or engine

sizing—engine is another word for beater. In the nineteenth century it was called "vegetable sizing."

First, rosin soap was made by boiling powdered resin with caustic soda and water in a process known as saponification. An 1866 recipe for vegetable sizing called for the following (Proteaux 1866, 72):

100 parts by weight of dry pulp
4 parts of starch
8 parts of rosin soap
8 parts of alum

Perhaps surprisingly, starch was often added to the pulp when alum-rosin sizing. Contemporary sources reported that starch—usually potato or farina—made the paper stronger and less spongy, gave it a harder surface, which made glazing or calendering more effective, and rendered the sheet more moisture resistant, although Browning disputes this last claim (Browning 1977, 89). The starch was mixed in a small amount of warm water and added to the rosin soap solution.

Typical steps in alum-rosin sizing were:

- add processed pulp to the beater
- wash out the residues of any alkaline cooking liquor, bleach, or anti-chlor
- test the pulp to ensure the pH is between 7 and 9
- add alum to neutralize any alkalinity from processing residues or hard water
- add still more alum, which serves as a mordant, along with the rosin soap and starch
- beat the pulp for 3 to 5 hours

During beating the rosin and starch are precipitated and then melted onto the fibers as the paper travels over the drying cylinders.

Unfortunately, excessive amounts of alum result in acidic papers, whether it is added to the pulp in engine sizing or to the gelatin during tub sizing. Much of the gray-brown discoloration and overall weakness, but not necessarily embrittlement, of rag paper made during the nineteenth century can be attributed to the use of too much alum during sizing. The extreme embrittlement seen in some papers dating from the late 1880s into the twentieth century is the result of alum-rosin sizing added to groundwood pulp to make very cheap grades of news paper. This embrittlement is due to the large proportion of lignin in groundwood pulp, which, when combined with excess alum, contributes to severe cellulose degradation.

Cathleen A. Baker has been researching the technologies and materials of American nineteenth-century papermaking in preparation for a book to be published in 2010. From her research she concluded that alum-rosin sizing in machine-made book papers resulted in the virtual elimination of external, gelatin sizing as the century progressed. As always, there was a practical reason for this shift. By midcentury book and newspaper printing presses had evolved from the simple iron hand press to steam-powered, high-speed bed-and-platen and cylinder presses. Even though machine-made paper was available in reels, the roll was still cut into sheets to facilitate sheet-feeding these presses with dampened paper. By the end of the Civil War, however, it was increasingly common to find automatic web- or reel-fed presses in action. It was no longer necessary to manipulate dampened sheets into the grippers of the press, and so the need for gelatin-sized news and book papers decreased.

EXPERIMENT

To confirm that there was a trend away from surface-sized papers for letterpress-printed books in the nineteenth century, the authors devised the following experiment in the summer of 2008. The hypothesis was that the incidence of gelatin would be highest at the start of nineteenth century and decrease with time, while starch would show an inverse trend, increasing across the century as it was introduced into papermaking as an ingredient in alum-rosin sizing.

METHODOLOGY: COLLECTING AND PREPARING PAPER SAMPLES

Paper samples taken from five books from each decade between 1790 and 1910, for a total of sixty books, were tested for protein, i.e., for gelatin, with the biuret and ninhydrin reagents. The iodine-potassium iodide test was used to detect starch. Each book selected for testing was at least one hundred pages long, published or printed in the United States of America, still in the original binding, and without major repairs or conservation treatment. Additionally, selection preferred books that seemed to have had minimal handling because any residue left on paper after contact with skin may test positive for protein, and books with minimal disruption of the paper surface because most of any gelatin sizing will be found in the paper's outermost fiber layers. Finally, books were chosen without regard to paper condition, so as not to inadvertently select for or against gelatin, in case there is a correlation between gelatin sizing and paper condition after natural aging (Barrett 1992).

In selecting sample areas for testing, the first and last signatures were avoided because these sections are more frequently handled. Additionally, pages with inscriptions, such as underlining or marginalia, were not used because their surfaces have clearly been handled extensively by readers. Finally, samples were not taken from the gutter in case animal glue, which would test positive for protein, was used during binding.

All three analytical tests used in this project are destructive because they usually stain the paper surface. Of the sixty books sampled, destructive testing was possible on about half—in these cases testing was performed directly on a page taken from the book. When destructive testing was not possible, fiber samples scraped from the page surface were tested instead. To obtain fibers for testing, a clean scalpel held perpendicular to the paper surface was used to scrape fibers from both sides of the sheet onto a microscope slide. The area scraped was typically one to two square centimeters. As the test results are based on colored stains, each slide was examined under magnification before testing to find any colored fibers that would interfere with the test results. Colored fibers were occasionally found and removed from the slide.

METHODOLOGY: ANALYTICAL TESTS

In the biuret test for protein, two reagent solutions were used in sequence (Browning 1977, 103). First, a single drop of Reagent A (1.0 g copper sulfate dissolved in 50 ml deionized water; solution is a turquoise blue color) was deposited directly on the sample, without touching the paper or slide surface with the dropper. Next, after several minutes, a single drop of Reagent B (2.5 g sodium hydroxide dissolved in 50 ml deionized water; solution is colorless) was deposited on the same spot. To wick away excess reagent at each stage, a blotter corner was touched to the domed drop of reagent, with careful attention not to let the blotter touch the paper. This step was not necessary if the reagent absorbed quickly into the paper.

Interpretation of the biuret test is based on the color of the resulting stain. A violet color indicates the presence of proteins; a sky-blue color indicates a negative test result. Having known samples of positive and negative results to reference was essential for interpreting the results. The colored stains of both positive and negative tests changed again within a couple of days after the test was performed; in particular, positive tests showing a violet color consistently changed to a blue-green color, resembling negative tests. It was thus helpful to retest reference samples for each testing session in order to have a fresh sample to reference.

Because the biuret test is not sensitive to small concentrations of proteins or to certain amino acids, the extremely sensitive ninhydrin test for protein was used for some samples. Whereas interpreting the color results of the biuret test was difficult, positive and negative results of the ninhydrin test were much more easily distinguished.

The ninhydrin test for protein uses a single reagent composed of two solutions prepared separately (Browning 1977, 103). First, 0.14 g sodium hydroxide and 0.43 g citric acid are dissolved in 49 ml deionized water; separately, 0.5 g ninhydrin powder is dissolved in 49 ml acetone. Once both solutions are dissolved, they are mixed together. The resulting reagent is a transparent pale yellow color.

To perform the ninhydrin test, one drop of the reagent was placed on the paper and allowed to rest several minutes before heating. If necessary, excess reagent was drawn off with a corner of blotting paper. Fiber samples on microscope slides were not blotted out of a concern for removing fibers from the slide surface. Samples were heated for several minutes and examined for results.

Like the biuret test, the results of the ninhydrin test are indicated by color: red through violet to blue indicates the presence of some kind of protein, while a negative test is colorless. When the test was performed directly on the paper surface, colors ranging from dull red to magenta to violet were observed, and the intensity of the color varied greatly. Reference papers known to be heavily sized gave more intense, stronger colors, and the results appeared more quickly than reference papers sized with less gelatin, which yielded colors that were fainter and took longer to appear.

When the test was performed on fibers rather than on a page, colors from the ninhydrin test were most often visible only under magnification. A range of results were observed on the slides under magnification, including fibers stained entirely or partially red, and small globules stained red or violet, situated next to or tangled in fibers. (It is unclear what exactly these globules were; it is probable that they were accretions of gelatin that had dissolved in the testing reagent.) For this project, one of two results constituted a positive ninhydrin test: either multiple fibers or fiber portions stained red or violet, or the presence of multiple stained globules and some partially stained fibers.

The samples—both the pages and the microscope slides with fibers—were heated on a large tacking iron plugged into a rheostat and turned upside down (fig. 1). This set-up allowed the tester to place a sample on the tacking iron and have hands free to continue other tasks. The sample had to be heated for several minutes before a color appeared. If heated for too long, the slide surface showed areas of orange-brown film, although the red or violet color of a positive test was still visible under magnification.

The ninhydrin test proved also to give results without heating, although the reaction time is slower. During a review of the samples, it was observed that one test that had previously appeared negative showed a positive result several days later. A second round of testing was performed on that sample, as well as on some other previously tested samples, using new pages taken from the same books. These samples were not heated at all. The reagent was applied and allowed to air dry, and then each page was placed in a plastic bag. The next day, some test papers were plainly positive and others negative, for the most part corresponding to the results of the heated tests. After two hours the unheated test shows only a little color, while the heated test shows the strong purple

color of a positive result (fig. 2). After nearly two days however, the heated and unheated tests are equivalent (fig. 3).

The extreme sensitivity of the ninhydrin test can make it difficult to work with. A single fingerprint on a reference paper known to be gelatin-free can show a very slight purple color in this test (Barrett and Mosier 1992). The more contact a sheet has had with skin, the more distinct the positive result will be. For this reason, it is necessary to define the intensity of color constituting a positive test. Also, special care is required to handle the samples, slides, and other materials with forceps or gloved fingers so as not to contaminate the results.

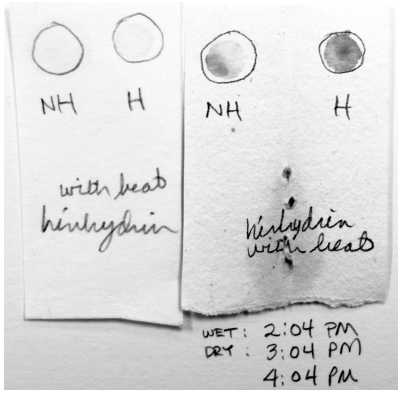
To test for starch, a prepared iodine-potassium iodide solution purchased from Fisher Scientific was used (Browning 1977, 91). The solution straight from the bottle is a dark yellow-brown color and is so concentrated that positive and negative tests are indistinguishable. When the solution was diluted down to 0.5% with distilled water, however, it became a straw color, and a drop applied to a known paper gave a distinctly blue positive result or a colorless negative result.

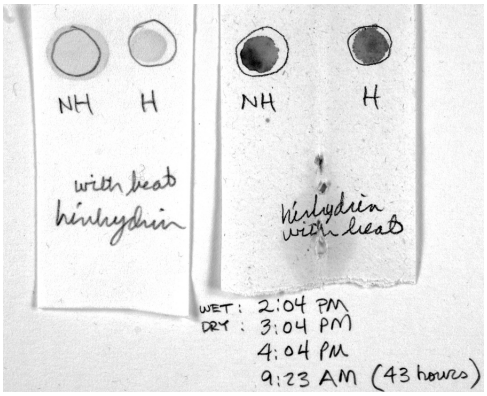
The results of the starch test were the most straightforward of the three tests to interpret. A blue color indicates the presence of starch. In practice a positive test shows a wide range of colors from blue to green to purplish-red, indicating starches from different plant sources as well as from different processing (Browning 1977, 88–100). In most cases, the stain of a positive test dried to a bluish color; occasionally the test showed a blue color initially and then dried colorless. These samples were retested with a more concentrated iodine-potassium iodide solution to confirm a positive or negative result.

Fig. 1. The ninhydrin test setup using a tacking iron connected to a rheostat for heating the sample

RESULTS

Samples from all sixty books were tested for protein, either with the biuret or the ninhydrin tests; some samples were tested with both. Positive tests for protein (represented in dark hatching in fig. 4) are most prominent in the early part of the century from 1790 to 1839, while negative tests dominate the latter part of the century from 1870 to 1910. The latest samples that tested positive for protein were from two books published in 1866. Forty-five of the sixty samples, representing all the decades, were tested for starch; fewer tests were performed on papers from earlier decades. Starch was detected in a sample as early as 1837, and most of the positive tests for starch (represented in light hatching in fig. 4) were in books published after 1870.





LEFT TO RIGHT

Fig. 2. The ninhydrin test on unheated (NH) and heated (H) samples after two hours. At the left is blotting paper testing slightly positive for protein due to handling; at the right is a gelatin-sized paper showing a strong positive test for protein. The heated tests show a stronger color change than the unheated tests.

Fig. 3. The same samples as in figure 2, showing the ninhydrin test on unheated (NH) and heated (H) samples after nearly two days. Color differences between the heated and unheated tests are negligible.

DISCUSSION

While these results suggest general trends in nineteenth-century American book paper sizing, the sample set is too small and too few tests were completed for the results to be statistically significant. To be more confident in the trends, it is necessary to increase the sample set, as well as to increase the repetitions of each test on each sample. It could also be useful to perform both the biuret and ninhydrin tests on all samples in order to compare the results. Another inconsistency in the experiment as performed is the fact that about half the sample papers were tested directly on intact pages, while the other half were tested as fiber samples. Because of the significant differences in procedure and interpretation between the two groups, it is possible that the results would vary if all books had been tested in exactly the same manner.

The location of the test area on the page is also a concern. The fore edge, top, and bottom margins are the areas of the page most likely handled by readers. In an attempt to avoid possible contamination by proteins transferred from skin in the past, samples were selected from the inner margin, hugging as closely to the text area as possible. Testing in the fold area was avoided, where glue from the binding might interfere with results. For paper that could be tested as intact pages, future experiments would do better to scatter multiple repeat tests across it, both in the inner margin and in the text area.

Lastly, the results of all three of these tests are based on the interpretation of colors appearing on the test papers. While interpreting colors is a simple enough task on bright white paper, it becomes increasingly difficult as the discoloration of the paper intensifies. A large proportion of the sample papers were discolored to some degree and interpretation of the results was sometimes difficult. A test that does not involve color interpretation would be useful in testing papers from this time period (Ormsby et al. 2005).

CONCLUSION

A major outcome of this sequence of tests has been the refinement of the testing procedures and the identification of areas for future research. One interesting implication of these tests is that starch, as a typical ingredient in alum-rosin internal size, can be detected with the starch test on the paper's surface. The starch test is by far the easiest of the three to perform, and the concentration of the iodine-potassium iodide test solution can be varied to give an appropriately obvious result.

The results of this research have revealed three important characteristics of nineteenth-century American book papers that impact directly on the conservation assessment of their condition and subsequent treatments, especially those that include washing and resizing book leaves.

First, by the 1850s, due to new kinds of printing presses being used to print books, the external sizing of paper with gelatin gave way in favor of the already well-established practice of internal sizing with alum-rosin. Thus machine-made news and book papers dating from about 1850 or 1860 on were probably never gelatin sized. Therefore, the gelatin resizing of washed book leaves from this period, which has been a typical treatment to replace the presumed washed-out

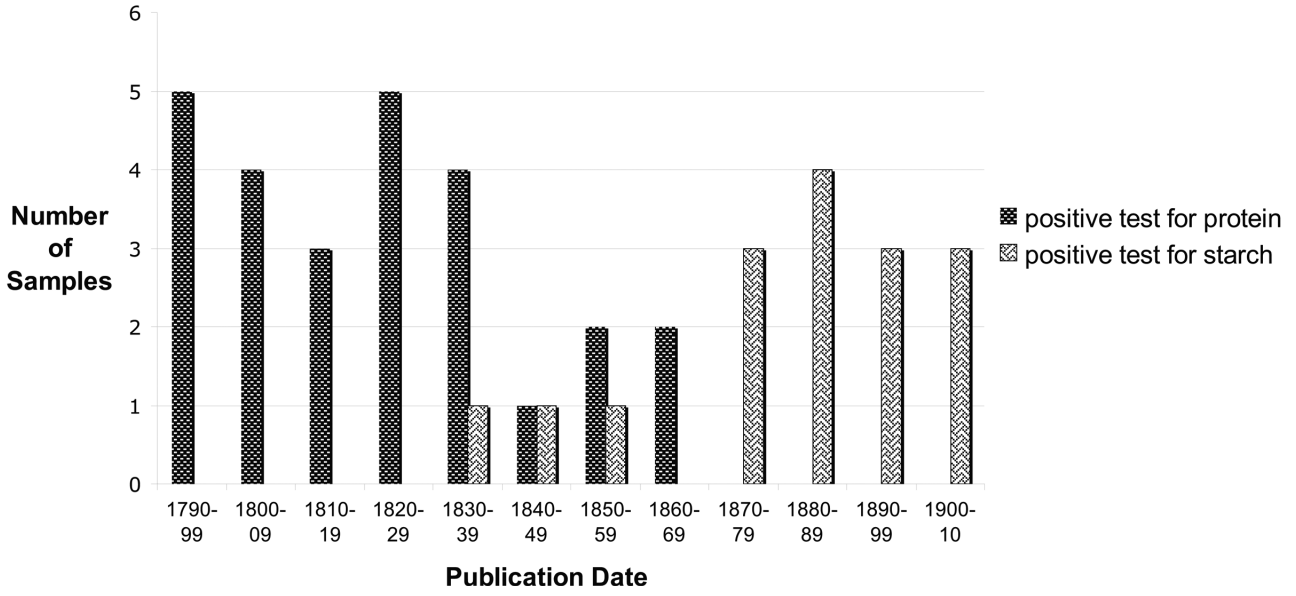


Fig. 4. Graph showing positive tests for protein and starch

gelatin, is an unnecessary treatment step. This is not to say that sizing washed book papers that remain weak is not a valid treatment, and either gelatin or an appropriate cellulose ether can be used to enhance strength and increase rattle.

Second, the presence of starch, an ingredient included in numerous alum-rosin sizing recipes, can lead to incorrect findings during certain typical analytical tests. For example, an unknown adhesive used for an overall lining or local repair undergoes an analytical test and a positive result for starch occurs. This test may actually detect the presence of starch in the sizing, not necessarily a starch-based adhesive. As a result, if a starch-specific enzyme treatment is used, it may not dissolve the adhesive but might remove a significant component of the internal sizing.

Finally, the presence of starch in alum-rosin sized papers may have led to certain kinds of discoloration, weakness, and even embrittlement that heretofore have not been considered by paper and book conservators.

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