Effect on Paper pH and Alkaline Reserve from Magnesium Bicarbonate Introduced via Ultrasonic Humidification

by

Bonnie Rose Curtin*

This research got started when I was working as a Conservator Aide at the National Archives conservation laboratory and I wondered if the ultrasonic humidifier that we normally used with deionized water could also disperse aqueous magnesium bicarbonate so that the system could be used to buffer paper.

Susan Lee-Bechtold, supervisory chemist, and I pursued the possibility through four experiments in 1986 and 1987 with cooperation and encouragement from Norvell Jones, then supervisory conservator of the Document Conservation Branch, Bill Minter, a book conservator, and later from Professor Paul Banks of the Columbia University, School of Library Service, Preservation Program. Despite this expert support, there were limitations and problems with the research and thus, the resulting information. However imperfect, it seemed worthwhile to do rather than leave undone and worthwhile to submit this limited report rather than leave the research unshared.

One of our first steps was to see if the ultrasonic humidifier would actually expel the whole alkaline solution. The one gallon tank of a Brookstone Model 7088 ultrasonic humidifier was filled with 0.06 molar aqueous magnesium bicarbonate generally used for immersion alkalization. The humidifier's settings were turned to their highest and the mist coming from the spout was collected into a beaker. According to a Taylor Drop Test titration, the pH of the solution mist matched the pH of the liquid put into the tank.

*Director, Preservation Planning Project
National Association of Government Archives and Records Administrators (NAGARA)

The fume hood served as a chamber (two different fume hoods were used for the experiments). The fume hood openings were blocked with blotter paper and polyester film sheets. The ultrasonic humidifier was centered at the base of the fume hood chamber with the spout aimed towards the fume hood's back wall. Two paper samples were used for each run. Each sample was supported by unused blotter paper and placed flat upon an eleven inch high platform made of a rigid plastic open grid. The humidifier's settings were turned to their highest, the fume hood was closed, and the timer was set as the chamber quickly filled with mist.

We selected two types of paper for our samples. One type was an old gelatin-sized ledger paper that had been used by our chemistry laboratory for other pH experiments. We also used a modern alum-rosin sized paper that the chemistry laboratory was considering as a standard sample. Descriptions of the samples are on the preceding page.

The experiments involved two-sheet sets of samples. In three experiments, each "set" consisted of one unwashed, untreated, paper sheet and one paper sheet that had been washed for 10 minutes in deionized water and air dried for a minimum of 30 hours.

One of the experiments exposed sample sets to the alkaline ultrasonic mist for 10, 30, and 60 minutes. A cold extraction method (TAPPI 509-OS-77) was used to determine the pH. The modern alum-rosin sized paper starting with a pH range of 4.9 to 5.3, rose to a range of 8.3 to 8.5 in 60 minutes. The gelatin sized ledger paper starting with a pH range of 4.3 to 4.6 rose to a range of 4.7 to 5.5 in sixty minutes. A (subjective) visual examination showed a barely perceptible movement of the media at this point.

A least squares analysis of the pH results for the unwashed paper indicated that the gelatin sized ledger paper would require 7 hours of exposure to achieve a pH of at least 7.

The test paper samples consisted of:

- "Old Ledger Paper"
  - pH range before treatment: 4.2 - 4.4
  - content: linen and cotton fiber
  - sizing: gelatin, tested positive for alum
  - dimension: 8 1/2" x 14"
  - form: wove, heavily calendered
  - date of manufacture: circa 1890
  - media: black, pink, & blue printed inks

- "Modern Paper"
  - pH range before treatment: 4.5 - 5.0
  - content: fiber - 53% softwood bleached sulfite
    - 47% hardwood kraft sulfite
  - fillers - 21% kaolin clay
    - 9% talc
  - sizing - 3% rosin
    - 5% alum
  - dimension: 8 1/2" x 11"
  - form: wove, calendered
  - date of manufacture: circa 1985
  - media: none

The experimental apparatus consisted of:

- 40" x 27" x 42" fume hood
- two 12" x 20" x 1/2" rigid plastic grid supports
- eight 1 liter polyethylene squeeze bottles
- unused blotter paper (4% cotton, 96% woodpulp)
- Aspirating psychrometer
  polyester film sheets

(inch measurements are approximate)

In experiments that followed (which were performed in the second hood) unwashed and washed samples of the "old ledger paper" were exposed for 1, 3, and 7 hours to the alkaline ultrasonic mist. For the unwashed samples, cold extraction pH tests resulted in a pH of 6.3, 8.5, and 8.9 respectively. An ASTM test (D3301-74-reapproved in 1979) for alkaline reserve indicated an alkaline reserve of 1.3% at 3 hours and 2.2% at 7 hours. For the washed samples, these tests resulted in pH's of 5.6, 8.5, and 7.9 at 1, 3, and 7 hours respectively. At 7 hours there was an alkaline reserve of 0.8%.

We were a little surprised at the lower pH and alkaline reserve in the washed sheet. Dr. Lee-Bechtold, who performed this particular experiment, had the impression that there was more alkaline mist flowing to the side of the chamber with the unwashed sheet - opposite from the side with the washed sheet. We also guessed that the experiment in the second fume hood, which involved only unwashed sheets, produced a somewhat higher pH and alkaline reserve overall due to the fume hood being smaller and less leaky.

The effect upon media was evaluated only by our subjective visual examination. There are magnified view photographic slides of the ledger paper sample support surface with black, pink, and blue printing ink media after treatment, but not before treatment. All of the alkalization methods which brought the pH level up to at least 6.4, moved the inks significantly. The aqueous alkalization immersion method moved the inks the most, and the aqueous ultrasonic method somewhat less.

ANALYSIS

It is helpful to review the research parameters before considering conclusions and possible applications.

First, the experiments and testing are limited, not comprehensive, nor without some problems. These limitations include the fact that only single sheets were used, not bound or stacked paper. Also, only one type of experimental set-up was used, other configurations are possible. For instance, the alkaline mist might be delivered through a flexible tube in conjunction with a suction table treatment. A further limitation is that the tests performed do not determine the distribution of pH or alkaline reserve within the "layer" of the sheet. Also, there were no aging tests performed.

What the tests do seem to indicate is that:

(1) it is possible to buffer paper using an alkaline solution in an ultrasonic humidifier,
(2) different results will be obtained with different papers in different application configurations,
(3) with a fairly new alum-rosin sized paper, deionized water washing makes little difference with respect to both initial pH and the pH's achieved from ultrasonic humidification,
(4) with a fairly new alum-rosin sized paper, adequate buffering and alkaline reserve can be achieved in a reasonable time,
(5) for sheets which we think to be gelatin sized, there is a difference between the pH's achieved in washed and unwashed papers exposed to alkaline ultrasonic humidification, but this difference is not immediately apparent,
(6) aqueous ultrasonic alkalization does not leave a visible coating on the paper's surface,
(7) aqueous ultrasonic alkalization does not remove any components from the paper (which could be undesirable or desirable in a given treatment challenge),
(8) the distribution of pH and alkaline reserve tends to vary slightly across the area of a paper sheet buffered by the ultrasonic method,
(9) magnesium bicarbonate leaves magnesium deposits in the ultrasonic humidifier which need to be cleaned and which may limit its usefulness; though we are not sure about the potential for damage to the ultrasonic humidifier, it is something to be alert to, and
(10) considerations for aqueous ultrasonic alkalization are similar to those of humidification with deionized water and to processes that change pH.

Certainly, it is up to conservators as individuals and as a community to decide whether to explore this option further and when, or if, to apply it in treatments.

Given this limited research, I do not see the ultrasonic method as an across the board replacement for existing alkalization options. However, in specific cases, it may prove to be an appropriate alternative. One example of a potential application would be a treatment plan in which humidification seems necessary, but alkalization (though it would be desirable) does not warrant the extra step. Humidification and some degree of alkalization could be combined into a single step via aqueous ultrasonic alkalization.