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# Oops, I thought that those books had been deacidified

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Major libraries have been placing increasing reliance upon non-aqueous mass deacidification in an effort to avoid hydrolytic decomposition of the cellulose during storage of bound volumes. Such decomposition is especially a problem when the printing papers used in manufacture of the books have been prepared under acidic conditions, using aluminum sulfate. But there is reason to doubt that the widely used non-aqueous treatments, in which "alkaline reserve" particles are deposited in the void spaces of the paper, can achieve neutralization of acidity throughout the paper structure under the conditions most commonly used for treatment and storage. Anecdotal evidence suggests that alkaline particles such as $CaCO_3$, MgO, $Mg(OH)_2$, or ZnO can be present for long periods of time adjacent to acidic parts of cellulosic fibers without neutralization of the acidity, especially the acidity within the fibers. If these phenomena can be better understood, then there may be an opportunity to use a high-humidity treatment of certain "deacidified" books in order to achieve more pervasive protection against acid-induced degradation.

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## The Problem

Paper-based materials can suffer from embrittlement and depolymerization of the cellulose during storage (Zervos 2010; Area *et al.* 2011). The effects can be particularly severe in cases where the paper was manufactured under acidic conditions. Indeed, most printing papers manufactured between the early 1800s and the mid-1980s were prepared at pH values in the range 4 to 5.5 in the presence of aluminum sulfate, which is an acidic compound conferring pH buffering capability to paper. Accelerated aging tests have shown that such "acidic paper" loses its folding endurance during storage.

If one can separate a bound volume into its component pages, then it is possible to thoroughly deacidify the paper by immersion in an aqueous solution having a pH above about 7. To guard against the possible future emergence of additional acidity, the paper can be simultaneously treated by adding sufficient alkaline buffering capacity so that the extract pH will remain weakly alkaline for many years. But single-item treatment of this kind is out of the question for large collections. Even in small collections, aqueous treatments may contribute to such problems as cockling, bleeding of dyes, and formation of mildew. An elegant solution to the problem involves suspending inherently alkaline particles, such as 1 μm MgO, in a low-energy, perfluorinated solvent (Baty *et al.* 2010). Such a solvent has minimal interaction with ink. It transports the alkaline particles into the voids of the paper without causing the books to become soggy and wavy. The non-aqueous solvent then can be recovered by evaporation, leaving behind a substantial alkaline reserve, as has been specified for paper products designed for archival purposes (Public Law 101-423, http://www.loc.gov/preservation/resources/rt/perm/pp_x1.html).

## Suspicions and Clues

Until recently I had always assumed that some form of neutralization reaction would take place between a solid alkaline particle and the acidity of the cellulosic fibers in the deacidified paper, perhaps located within about 10 μm of each other. After all, Middleton, Scallan, Zou, and Page (1996) had shown that deacidification can be achieved even by temporarily placing $CaCO_3$-filled paper sheets between the pages of a book. In such cases the alkaline particles are as much as 100 μm from the acidic sites on and within cellulosic fibers that need to be neutralized. What I had failed to pay attention to was the fact that the cited authors had employed both high humidity and high pressure for extended periods in order to achieve such effects. Even during the course of co-authoring a recent review article on deacidification (Baty *et al.* 2010), it never occurred to me to question my own assumption that non-aqueous treatment of paper with alkaline particles would be sufficient to protect the paper from acid-induced breakdown.

But I ought not to have been so sure. About 20 years ago, while carrying out research related to a now-closed linerboard mill, I wanted to find out whether it was possible to make a two-ply sheet in which the bottom ply was acidic (extract pH about 5) and the top ply was alkaline (pH about 8 or higher). We were concerned that draining of the alkaline process water through the acid-treated ply would "kill" the intended hydrophobic sizing effect, which depends on a reaction between the acidic form of aluminum sulfate and resin acids in unbleached softwood kraft pulp. Remarkably, however, I found that even the passage of a column of about 30 cm of pH=9.5 water was not sufficient to remove the hydrophobic effect of the complex formed between alum and the wood resins. In other words, I found that the acidity-dependent hydrophobic sizing within paper can be quite resilient to subsequent exposure to an alkaline solution.

Another clue involves inconsistencies when testing different de-acidified papers by means of different accelerated aging protocols. There has been a general consensus in favor of running accelerated aging tests at 90 °C with either 25% or 50% relative humidity (TAPPI Method T-544, original *vs.* current specifications). The rate of decomposition has been found to depend mainly on temperature, moisture content, and pH (Zou *et al.* 1996). Recently I had a chance to view some preliminary data comparing initially acidic paper sheets that had been treated, respectively, with a particle-based and a reagent-based deacidification system, each involving immersion in a non-aqueous medium. The two systems yielded similar improvements in retention of folding endurance, compared to a non-deacidified control sheet, when aged in the presence of 25% relative humidity. But the reagent-based deacidification was more effective when parallel accelerated aging tests were carried out under nearly dry (~1.3% relative humidity) conditions (TAPPI Method T-453). There were only a few samples tested in this preliminary study, but clearly there is a need for follow-up research. One possible explanation is that the more humid conditions during accelerated aging at least partly facilitated localized mixing of acidity and basicity, by some mechanism yet to be determined. These results were brought to my attention by Dick Smith, who has been working for many years to provide mass deacidification systems and the related equipment to conservators and library organizations.

Documents printed in the years 1450 to 1750 using linseed oil-carbon black ink often contain irregular brown mottles. Hansen (1937) showed that acids from degraded linseed oil caused the severe hydrolytic attack except in places where irregularly distributed $CaCO_3$ particles in the handmade paper had neutralized the acids. The protection was limited to the immediate vicinity of such particles. This was despite the lack of air conditioning, with many years of humid conditions. Thus, the conditions of relative humidity, typical of library storage, had not been sufficient to cause equilibration.

Another important clue comes from work done on behalf of the Library of Congress (Whitmore 1994). Paul Whitmore, who is presently at Yale University, investigated the deacidification of various acidic papers by means of the Bookkeeper process, in which MgO particles are suspended in a perfluorinated solvent, which is used to transport the particles into bound books. An innovative approach was used, pretreating the paper with pH-indicator dye before the deacidification. Certain papers retained the initial "acidic" coloration even after the treatment, suggesting that the local environment on the cellulosic fibers was still acidic. Exploratory tests, not reported at that time, were carried out in which such sheets were left over night in a high humidity environment. After such treatment the dye in the paper indicated a uniformly alkaline condition.

If one accepts the premise that diffusion mechanisms govern the rates of equilibration between local sites to acidity within cellulosic fibers and nearby alkaline particles, it follows that there ought to be a great advantage of employing nanoparticulate alkaline materials. By preparing the particles much smaller than typical MgO or $CaCO_3$ particles, the same amount of material can be distributed through the paper as a much larger number of individual particles. In addition, those particles will have a greater ability to enter into yet smaller void spaces within the paper. Such a theory has been recently supported by Wojciak (2015), who compared nano-sized $Mg(OH)_2$ particles to conventional $Mg(OH)_2$. The nanoparticles were much more effective in their deacidification work, yielding higher extract pH values in the paper. Unfortunately, the cited work did not also include accelerated aging tests.

In retrospect, it appears that some of the most important clues had been spelled out in the already-cited article by Middleton *et al.* (1996) and also in the 1994 report to the Library of Congress (Whitmore 1994). Both of these sources provide evidence that high-humidity treatment might be required to bring about neutralization of acidic groups at fiber surfaces if alkaline particles have been brought very close or into the acidic paper sheet in the absence of moisture.

## Making Good Use of "Sunk Costs"

According to their website (http://loc.gov/preservation/about/deacid/index.html), the Library of Congress has used deacidification treatments to extend the useful lives of at least 3.78 million bound volumes. Because of a lack of research dealing with the critical issues raised in this editorial, it is very difficult to be sure whether, and to what extent, various deacidified books might still be at risk of relatively rapid acid catalyzed hydrolysis during further storage. The climate control systems in a modern library could conceivably be having the perverse effect of avoiding conditions under which the local mixing of acidity and alkalinity could go to completion in order to render the books more fully protected. It is also quite unknown at this point what conditions of relative humidity, temperature, and time might be required in order to bring about completion of the desired effects. And it is also unknown whether or not a sufficiently long storage under typical conditions in a modern library might be sufficient, in itself, to bring about completion of the deacidification process.

While keeping in mind the uncertainties just mentioned, it would appear that research is needed to shed light on two possible outcomes, both of which point to favorable roles of alkaline particles such as $Mg(OH)_2$, ZnO, or $CaCO_3$, *etc.* that have been used already under non-aqueous conditions to impart an alkaline reserve to initially acidic papers. On the one hand, it may turn out that the rate of localized mixing of acidity with alkaline particles is sufficiently rapid, compared to the rate of aging of the paper, even under typical library conditions, so that no further action is needed regarding these deacidified books. On the other hand, the results of future experiments might imply a need for relatively benign and chemical-free post-treatment in humid environments, maybe with vacuum re-drying to achieve a favorable combination of effects.

## Research as the First Order of Business

As a faculty member at a major research university I have to admit that I have a preference for studying things in great detail before suggesting any implementation. Much has been happening in the fields of nano-science and in the development of analytical methods. We now are able to find out things that previously had been unknowable. Some of the questions that I wonder about are as follows:

1. Is it possible to quantify the protonated *vs.* other forms of carboxyl groups within the cellulosic fibers that make up paper in the presence of alkaline particles?
2. Is it possible to quantify the rates of local mixing of acidity with alkaline particles within microscopic regions under different levels of humidity?
3. Can such mixing be induced by exposure of books to conditions of humidity, temperature, and time that do not raise concerns about wrinkling, cockling, or other unintended effects?
4. Is the level of relative humidity associated with the "moist" accelerated aging protocol (currently 50% at 90 °C, TAPPI Method T544) sufficiently low so that it does not inadvertently complete certain deacidification processes?

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