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Neutralizing Acids for Book Preservation

Despite present efforts to conserve paper by protecting trees and to remedy the degradation of paper by reducing its corrosive properties, the world has accepted wood pulp as the dominant material for making paper. The acidic properties of manufactured paper are the major cause of the paper degradation that now afflicts a plethora of books and documents. Mass deacidification is the current process to preserve books in many libraries, including the Library of Congress.

<u>The Shift to Acidic Paper</u>

The origin of acidic paper can be traced back to the late 19th century when book producers began to experience shortages of previously-used materials such as linen and cotton rag. In 1838, while experimenting with methods for conserving cotton rags at his local paper mill, Charles Fenerty was able to make paper from wood pulp. Paper made from wood pulp became widespread with the aid of steam-driven printing presses such as the Fourdrinier machine.[1] As the wood-pulp process for paper production became more efficient, the use of wood pulp was established as a response to the limited supply of linen and cotton-based fibers.

Current chemical processing of wood fiber is unable entirely to remove lignin from the main ingredient of paper: cellulose fiber.[2] Lignin must be removed from the wood pulp to produce paper that is durable yet easily used. The structure of lignin is formed by aromatic polymers that provide structural support for wood, but are a hindrance in the paper-producing process. Bleaching processes “delignify” or target the chromophores[a] in lignin. These chromophores are the major source of the yellow, natural color of paper. Lignin is either oxidized or reduced to smaller compounds that contain oxygen. The compounds are soluble in

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[a] Chromophores are parts of molecules that selectively absorb light.

water and are washed away. The major process used in the United States is the Kraft process that is able to pulp many types of wood. The pulp is immersed in an aqueous solution of sodium hydroxide and sodium sulfite that is approximately 90% effective in delignifying the pulp.[3] Before chlorine dioxide was identified as a source of carcinogenic dioxins and furans,[5] it was used industrially to delignify and bleach pulp.[17] Safe paper-bleaching processes are now categorized as totally-chlorine free (TCF) or processed-chlorine free (PCF).

Waste products are produced during the process of manufacturing paper. Paper mills are sources of pollution such as acid and alkaline waste, toxic wastewater, and sludge. The acid and alkaline waste are mainly produced during the processes of pulping wood. Toxic wastewater and sludge result from bleaching, coloring, coating, and cleaning of paper.[17]

Hydrolysis of Cellulose

The main cause of paper deterioration is the undesired hydrolysis of cellulose by acids within the fibers. Cellulose is composed of anhydroglucose moieties linked as a linear polymer by 1,4-β-glycosidic bonds as shown in Figure 1.[6]

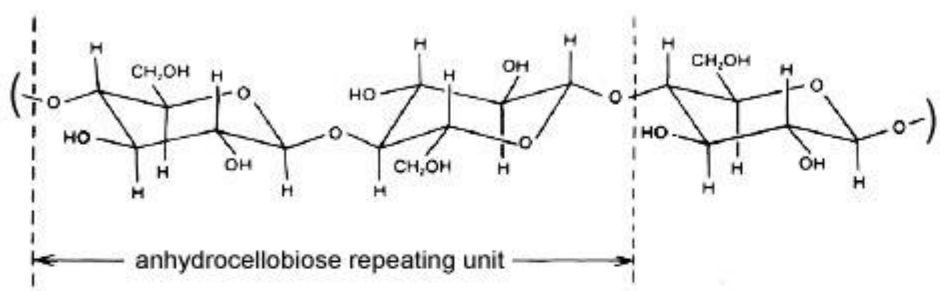

Figure 1: Three β-linked anhydroglucose units of the cellulose chain

The degree of polymerization (DP) indicates the number of anhydroglucose units that are beta-linked to form one cellulose chain. In wood, the DP of cellulose is approximately 10,000, but the DP declines to approximately 1,000 during the production of paper. As shown in Figure 2, the beta-acetal portions that link units of cellulose are broken due to the acid-catalyzed hydrolysis of cellulose.[6]

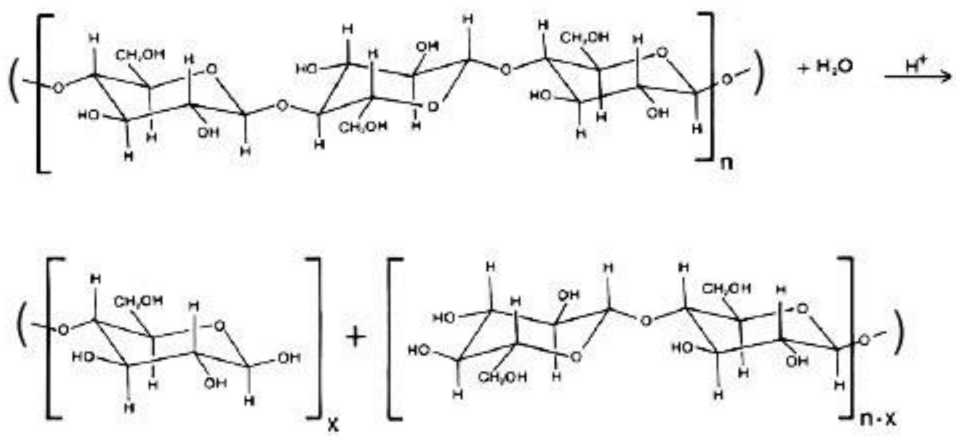

Figure 2: Hydrolysis of the cellulose chain catalyzed by acid

In Figure 2, n refers to the number of cellulose units and x refers to the number of broken portions of the cellulose chain. The hydrolysis reaction produces an acidic proton to propagate the breakdown of cellulose. The DP is further lowered by hydrolysis. The durability of the paper decreases when the DP is 400-500 or less.

The acidic environment of the paper-production process is the major source of acids in paper. Alum-precipitated rosin[b] is usually applied to paper to prevent it from decaying due to water damage.[15] However, aluminum sulfate, $Al_2(SO_4)_3\cdot 18H_2O$, in aqueous solution, produces an acidic solution through the following hydrolysis:[6]

[b] a mixture of acidic chemicals produced during the pulping process

$$[Al(H_2O)_6]^{3+} + H_2O \leftrightarrow [Al(OH)(H_2O)_5]^{2+} + H_3O^+$$

There is no process that removes all of the lignin in the paper fibers. As lignin decays with aging, cellulose hydrolysis produces acetic, oxalic, formic, and lactic acids.[7]

Currently, the widespread method for the preservation of paper is alkalinization. This involves adding an alkaline salt that reacts with and neutralizes the acidic compounds inherent in and external to the paper.[8] At the Library of Congress, this practice of deacidification is now fully accepted; the Library estimates that over one quarter of all its documents have already deteriorated beyond normal usage.[9]

<u>The Bookkeeper Process at the Library of Congress</u>

The purpose of deacidification is to neutralize the acid present in the paper and prevent further damage by using an alkaline compound.[10] Although there are various processes used to neutralize acids in paper, the Bookkeeper Process is used by archives and universities worldwide, including the Library of Congress. Bookkeeper Deacidification was patented by Pennsylvania-based Preservation Technologies, L.P. It satisfies the environmental and industrial standards set by the Occupational Safety and Health Administration (OSHA), Federal Trade Commission (FTC), and Environmental Protection Agency (EPA).[16] The chemicals used in the process are neither hazardous nor toxic.[11]

In this process, books are dipped in a non-aqueous solvent containing particles of magnesium oxide (MgO). Due to the detrimental effect of chlorofluorocarbons (CFCs) on the atmosphere, the solvent has been changed from CFC-113 to perfluorohydrocarbon solvents.[10] The solvent evaporates from the paper and leaves the alkaline particles incorporated within the structure of the paper. During a few weeks after the treatment, the magnesium oxide particles react with the moisture in the air to produce magnesium hydroxide. This alkaline buffer neutralizes acids that continue to be produced within the paper. Compared to the cellulose fibers in the paper, the buffer of magnesium hydroxide reacts at a faster rate with acids.[11] The Bookkeeper Process is a permanent treatment;[11] it increases the pH level of the paper to the more basic range 6.8 to 10.4. This is the requirement set by the Library of Congress.[12]

Efforts to neutralize the acidic properties of paper are of paramount importance because a voluminous amount of documents is in danger of becoming permanently damaged. Even with the shift to digital media, care must be given to preserve the original sources for future reference.[13] As indicated by research conducted by the Library of Congress, there is need for a continued international effort to improve the efficacy and costs of paper deacidification.[14] Further research on Bookkeeper Deacidification is conducted by Preservation Technologies, L.P., including the effect of deacidification on the strength of paper.[11]

Techniques are under development by research departments at universities and paper-producing companies to improve the production and type of paper.[c] The Paper Pilot Plant at Western Michigan University uses Fourdrinier paper machines to produce paper from non-cellulosic fibers and other non-wood fibers.[18] Non-wood fibers are categorized in three different groups: fine-textile crops that are soft fibers; packing crops that are rough fibers; and soft-cordage crops that are strong fibers.[20]

During the production process of paper from wood pulp, paper treated with calcium carbonate ($CaCO_3$) becomes alkaline paper.[19] Although alkaline paper is naturally acidic and susceptible to its acidic environment, the alkaline treatment is able to neutralize most of the acids before the cellulose chains are damaged.[7] This paper has a neutral or weakly basic pH. The alkaline properties of calcium carbonate allow it to act as a buffer and neutralize acids that form

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[c] Refer to the Testing page at PaperOnWeb.com (http://www.paperonweb.com/test.htm) for a list of companies and institutions, as well as their websites.

from the natural decay of cellulose. Production operates at lower costs because calcium carbonate is a relatively cheap resource and the manufacturing process is faster with alkaline paper. Products that are recycled from alkaline paper are stronger than those that are not treated with alkaline compounds.[19]

Literature Cited

1. About.com. The History of Papermaking http://inventors.about.com/od/pstartinventions/a/papermaking.htm (accessed Feb 22, 2010).

2. Rice Paper. Fiber Used in Rice Paper. http://www.rice-paper.com/about/fiber.html (accessed Mar 12, 2010).

3. Ghoreishi, S.M., and M.R. Haghighi. Chromophores Removal in Pulp and Paper Mill Effluent Via Hydrogenation-biological Batch Reactors. *Chemical Engineering Journal*. [Online] **2007,** 127, 59-70 doi:10.1016/j.cej.2006.09.022 (accessed Mar 13, 2010).

4. Sillanpää, Mervi. Studies on Washing in Kraft Pulp Bleaching. Ph.D. Dissertation, University of Oulu, Oulun Yliopisto, Oulu, 2005.

5. Natural Resources Defense Council. Avoiding Chlorine in the Paper Bleaching Process. http://www.nrdc.org/cities/living/chlorine.asp (accessed Mar 14, 2010).

6. Carter, Henry A. Chemistry in the Comics: Part 3. The Acidity of Paper. *J. Chem. Educ.* [Online] **1989,** 66, 883-886 http://pubs.acs.org/doi/abs/10.1021/ed066p883 (accessed Mar 18, 2010).

7. The Library of Congress. The Deterioration and Preservation of Paper: Some Essential Facts. http://www.loc.gov/preserv/deterioratebrochure.html (accessed Feb 25, 2010).

8. Alkalinization. *The Book Conservation Catalog* [Online] 2009. http://www.conservation-wiki.com/index.php?title=Book_Conservation_Catalog (accessed Feb 22, 2010).

9. Library of Congress Preservation Directorate. *Library of* Congress*: Technical Specifications for Mass Deacidification;* The Library of Congress: Washington, D.C., 2004.

10. Carter, Henry A. The Chemistry of Paper Preservation: Part 1. The Aging of Paper and Conservation Techniques. *J. Chem. Educ.* [Online] **1996,** 73, 417-420 http://pubs.acs.org/doi/abs/10.1021/ed073p417 (accessed Mar 18, 2010).

11. Preservation Technologies, L.P. Bookkeeper: Frequently Asked Questions. http://www.ptlp.com/faq.html (accessed Mar 18, 2010).

12. The Library of Congress. Saving the Written Word: Mass Deacidification at the Library of Congress. http://www.loc.gov/preserv/deacid/massdeac.html (accessed Mar 7, 2010).

13. Waters, Peter. Phased Conservation. *The Book and Paper Group Annual* [Online] **1998,** 17 http://cool.conservation-us.org/coolaic/sg/bpg/annual/v17/bp17-17.html (accessed Mar 2, 2010).

14. The Library of Congress. Services of the Preservation Research and Testing Division. http://www.loc.gov/preserv/rt/ (accessed Mar 7, 2010).

15. North Carolina State University. Mini-Encyclopedia of Papermaking Wet End Chemistry. http://www4.ncsu.edu/~hubbe/SOAP.htm (accessed Apr 6, 2010).

16. Preservation Technologies, L.P. About PTLP. http://www.ptlp.com/about.html (accessed Apr 7, 2010).

17. PaperOnWeb.com. Environment and Effluent Treatment http://www.paperonweb.com/envrn.htm (accessed Apr 7, 2010).

18. Western Michigan University. Paper Pilot Plant. http://www.wmich.edu/pilotplants/paper/index.html (accessed Apr 7, 2010).

19. Lundeen, G.W. Preservation of paper based materials: Present and future research and developments in the paper industry. In *K.L. Henderson and W.T. Henderson (eds),*

Conserving and preserving library materials, Papers presented at the Allerton Park Institute, November 15-18, 1981.

20. Kugler, D. E. Purdue University. Non-wood Fiber Crops: Commercialization of Kenaf for Newsprint. http://www.wmich.edu/pilotplants/paper/index.html (accessed May 4, 2010).