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Effect of Some Deacidification Agents on Copper-Catalyzed Degradation of Paper

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Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate

Page 1 of 12
www.loc.gov/preservation/

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Introduction

Paper conservators are all too familiar with artifacts in which iron gall ink or copper in verdigris pigment has caused severe deterioration of the paper base. But even trace concentrations of these metals, which are generally present in paper, contribute significantly to its aging by catalyzing oxidation reactions.[1,2,3] Copper and iron contaminants can also cause foxing in paper.[4,5]

Williams and his co-workers observed that paper samples containing copper acetate, which degraded rapidly when aged at 90˚C and 50˚C relative humidity (RH), were stabilized appreciably after deacidification treatment with magnesium bicarbonate.[3] However, deacidification by a Barrow two-step treatment with calcium hydroxide and calcium bicarbonate solutions did not stabilize against the degradative effect of copper acetate to a comparable extent. It was logical at that time to draw a parallel between the observed stabilizing influence of magnesium bicarbonate and the deactivation of iron species by "complexation" with magnesium carbonate in alkaline pulping processes.[6,7,8,9] In these systems, too, calcium carbonate had been reported to be ineffective in preventing transition-metal catalyzed oxidative degradation of cellulose under similar process conditions.[9]

In separate work, Williams and Merrill showed that magnesium acetate does not inhibit copper-catalyzed oxidation of cellulose.[10] This observation suggests that the formation of a complex between magnesium and copper species may not be the root cause of the observed inhibition of copper-catalyzed oxidative degradation of cellulose after a magnesium bicarbonate treatment. Nevertheless, deacidification treatments do appear to influence oxidative degradation of paper. Arney, Jacobs, and Newman have reported that deacidification of paper retards not only oxygen-independent degradation (acid hydrolysis) but also oxygen-dependent degradation (oxidation).[11] Margaret Hey has shown that manuscripts with iron gall inks, which are prone to oxidative degradation, can be stabilized by a deacidification treatment.[12]

In earlier works, the authors studied the effect of neutralization of acidic species in paper on the catalytic activity of copper and iron, taking care not to introduce any metal ions which could be inferred to complex with the transition metal catalysts.[13] To this end, soluble sodium bicarbonate was employed to neutralize acidic species, and any unreacted bicarbonate and reacted sodium salts were washed away. It was observed that paper containing copper or iron species aged more slowly after the neutralization treatment. In the same work, it was also shown that chelation of the catalytic transition metal species provided an uncertain solution. While iron acetylacetonate did not catalyze

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate

Page 2 of 12
www.loc.gov/preservation/

the degradation of paper at all, copper acetylacetonate was a more active catalyst than the copper species adsorbed and/or exchanged from a copper salt solution.

The most recent phase of this continuing work compared the effect of different aqueous deacidification agents on the aging of copper-doped paper.
The deacidification treatments selected for this purpose were magnesium bicarbonate, Barrow's two-step treatment with calcium hydroxide followed by calcium bicarbonate, and zinc bicarbonate. As far as is known, this work represents the first attempt at using a zinc bicarbonate solution for deacidification of paper.

Besides comparing the effectiveness of different deacidification agents, the work has revealed the reason for the effectiveness of magnesium bicarbonate and the relative ineffectiveness of the Barrow two-step treatment in inhibiting the catalytic effect of copper on the oxidative degradation of paper.

Experimental

Materials

Paper samples were 8" x 10" (20.3 cm x 25.4 cm) sheets cut from a continuous length of a single machine-made roll of bleached Kraft (50 lb [22.7 kg] basis weight). It was made by Neenah Paper Mills, Neenah, Wisconsin, from a wood-pulp stock composed of northern softwoods (60%) and Lake States hardwoods (40%). This paper was essentially waterleaf, as no additives were introduced in its manufacture.

All chemicals employed were analytical reagent grade, except where noted.
Water used for washing paper samples and the preparation of chemical solutions had a minimum resistivity of 15 MΩ.

Chemical Treatments

In all procedures described below, paper samples were interleaved with fibrous sheets of nonwoven polyester to facilitate penetration of solution between adjacent samples and to provide physical support for wet paper during its removal from a treatment bath. Plastic trays were used for all chemical treatment and washing operations. Generally, 1 liter of solution was used for every 10 sheets of paper.

Sorption of Copper on Paper

Paper samples were immersed in a dilute (104 mol/l) aqueous solution of copper sulfate for 16 to 18 hours. Intermittent agitation was provided during the first few hours of treatment. At the end of the treatment period, the paper samples were transferred to a water bath. The water was changed

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate

Page 3 of 12
www.loc.gov/preservation/

several times until the conductivity of the wash water in contact with the paper samples was under 10 μS (micromho).

Deacidification of Paper

Deacidification with magnesium bicarbonate was performed according to the procedure of Wilson and his co-workers.[14] The concentration of the magnesium bicarbonate solution prepared was 0.031 moles per liter (mol/l). Barrow's two-step method with calcium hydroxide and calcium bicarbonate was employed as described.[15] The concentrations of the calcium hydroxide and calcium bicarbonate solutions were 0.024 mol/l and 0.080 mol/l, respectively.

Zinc bicarbonate solution was prepared by saturating a suspension of 2 g of zinc carbonate hydroxide (Aldrich Chemicals Inc., 99% pure) per liter of water with carbon dioxide for at least one hour. The suspension was then centrifuged to obtain a clear solution. The concentration of the bicarbonate in the solution was determined to be 0.011 mol/l.

Upon completion of a deacidification or washing treatment, the paper samples were removed individually from the final bath along with the nonwoven polyester support sheet and were placed on a blotter to let excess water drain off. The treated sheets were then allowed to air-dry. While the samples were still moist, they were interleaved with untreated sheets of the same paper (which were discarded later) and were flattened in a book press. They were then conditioned at 23°C (73°F) and 50% relative humidity (RH) for at least 48 hours before being subjected to accelerated aging or testing.

Accelerated Aging of Paper

Chemically treated and control samples were aged in a humid aging oven at 90°C and 50% RH. Dry aging was not attempted, as it has been conclusively demonstrated that copper and iron species do not influence the aging of paper in the near-absence of moisture at 100°C.[3,13]

Testing and Analysis

The concentrations of bicarbonate solutions were determined by titration against a standard sodium hydroxide solution to a pH value of 8.0. The concentration of calcium hydroxide solution was determined by titration against a standard hydrochloric acid solution to a pH value of 6.0.

Copper concentration in the paper samples was determined by atomic absorption spectrometry. For each series of treated samples, a randomly selected 5 g sample was incinerated at 600°C. A 0.5 ml aliquot of concentrated nitric acid was added to the ash, followed by 1 ml of water. Dissolution of the ash was completed by intermittent agitation of the solution under an infrared lamp. The solution was diluted to 10 ml or more if necessary, and the absorbence was measured at 249.22 nm.

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate
Page 4 of 12
www.loc.gov/preservation/

The pH of paper was determined by a cold-extraction technique based upon Tappi Standard Test Method T509. In this method, 100 ml of a slurry was made up that contained 1.0 g of paper in distilled water. The paper sample was macerated in a Waring blender for 1 minute. The slurry was allowed to stand for 5 minutes before its pH was measured. To determine alkaline reserve, the same slurry was titrated to a pH value of 3.0 with standard 0.1 mol/l hydrochloric acid. The slurry was boiled for 2 minutes, was cooled, and then was back-titrated to a pH of 7.0 with standard 0.1 mol/l sodium hydroxide.

MIT fold endurance of paper was determined along the machine direction by Tappi Standard Test Method T511 with a modification which employed a reduced tension load of 0.5 kg. Brightness levels were determined by measuring blue reflectance with a Photovolt model 670 reflection meter. Six readings were taken from each side of the paper and were averaged.

Results and Discussion

Praskievicz and Subt, as quoted in Williams et al.,[3] found that new papers contained an average of 4 parts per million (ppm) of copper, and recycled paper contained an average of 12 ppm of copper. The highest amount of copper they found in a commercial paper sample was 77 ppm. By comparison, the average copper content of the copper-doped test samples in these experiments was 725 ppm. A high copper content was desired so that the paper samples would degrade mainly through copper-catalyzed reactions, which form the focus of this study. Also, it has been observed that, at lower concentrations, copper deposits in paper appear to be less uniform, with localized areas of high concentration. Figure 1 shows the devastating effect that copper exerted on the aging of paper samples in these experiments.

For a comparison of the effects of different deacidification methods to be relevant, the alkaline reserve concentrations imbibed during these processes must be of a similar order. The alkaline reserve concentration sought from the deacidification treatments in this work was 0.8%o + 0.1% (as grams of calcium carbonate per 100 grams of paper). An alkaline reserve of close to 1% can be easily attained after a single immersion in saturated magnesium bicarbonate solution, or after one two-step sequential treatment with calcium hydroxide and calcium bicarbonate. However, zinc bicarbonate solution, even when fully saturated under ambient conditions, is so dilute (0.01 mol/l) that to obtain an alkaline reserve of a corresponding order would have required repeated immersion and drying steps.

To avoid physical stress on the test samples due to repeated handling while moving them in and out of a deacidification bath, a spray technique for zinc bicarbonate deacidification was used. The sample sheets were alternately sprayed with zinc bicarbonate solution and were air-dried until the desired level of alkaline reserve was achieved. Magnesium bicarbonate treatment was applied by both immersion and spray techniques, so that this treatment would form the central reference point with which both calcium hydroxide bicarbonate (immersion) and zinc bicarbonate (spray) deacidification treatments could be compared. As will become clear shortly, this choice of experimental conditions was most fortunate.

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate

Page 5 of 12
www.loc.gov/preservation/

The deacidified test samples were aged at 90°C and 50% RH, and their fold endurance, brightness, and pH values were determined at intermittent intervals. The fold endurance data are presented in Figure 2. To facilitate an evaluation of the fold endurance data, the fold endurance values for different experimental systems have been compared at a single, arbitrarily selected point. For each treatment, the time taken for the fold endurance to fall to 1/8 of its initial value has been computed from the data in Figure 2. These data, along with the respective solution concentrations and alkaline reserves of the treated samples, are presented in Table 1. The corresponding brightness and pH data are presented in Tables 2 and 3, respectively. An examination of the fold endurance data in Figure 2 and Table 1 immediately provides new insight into the role of magnesium-based deacidification in copper-doped paper.

In conformity with the findings of Williams and his co-workers,[3] deacidification by the Barrow two-step treatment with calcium hydroxide and calcium bicarbonate was mildly effective in inhibiting copper- catalyzed oxidative degradation of paper, while the magnesium bicarbonate bath was much more effective. However, the same magnesium bicarbonate solution was surprisingly ineffective when applied as a spray. The zinc bicarbonate spray deacidification was also ineffective in stabilizing copper-doped paper.
The data for the spray-deacidified samples and the untreated copper-doped control are so close together on the plot that, in the interest of clarity, only a single regression line has been drawn to fit the data for the control sample points.

What role does magnesium bicarbonate deacidification play in retarding copper-catalyzed oxidative degradation? The deactivation of copper by magnesium through complexation or any other mechanism can be ruled out, because the sample deacidified with magnesium bicarbonate spray was loaded with magnesium but still aged at about the same rate as it did before the deacidification treatment. An examination of the data on the copper content of the treated samples, which are shown in Table 4, provides the solution.

Table 4 also presents the copper contents of similar copper-doped samples after immersion in aqueous calcium, zinc and sodium bicarbonates, a calcium hydroxide solution, and a non-aqueous methyl magnesium carbonate solution.
The samples deacidified by immersion in a magnesium bicarbonate bath lost most of their copper. The samples subjected to the two-step calcium hydroxide/calcium bicarbonate treatment lost a small fraction of the adsorbed copper, while the samples which had been spray-deacidified retained practically all of their copper content. All bicarbonate solutions were seen to be effective in dislodging the sorbed copper species from paper.

On the other hand, calcium hydroxide, magnesium acetate, and methyl magnesium carbonate were all equally ineffective. Calcium hydroxide must react with the adsorbed and/or exchanged ionic copper species to form insoluble calcium hydroxide within the paper matrix. Aqueous magnesium acetate and nonaqueous methyl magnesium carbonate were both ineffective, since magnesium does not complex copper or react with it in any other manner to deactivate it. The calcium bicarbonate treatment was much more effective if it was applied without a prior calcium hydroxide treatment. Precipitation of the sorbed copper species by calcium hydroxide renders it inaccessible to complexation by a subsequent bicarbonate treatment. This observation suggests that not all copper species in paper are susceptible to complex formation with bicarbonate ions.

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate

Page 6 of 12
www.loc.gov/preservation/

A simple qualitative test demonstrated that complexation of the adsorbed copper is indeed the key to its removal from paper, but the complexation effect takes place with bicarbonate ions rather than with magnesium species. If any of the bicarbonate solutions were added to a dilute solution of a copper salt, a precipitate was first formed. This precipitate dissolved on further addition of the bicarbonate solution as a soluble bicarbonate complex formed. Bicarbonate complexes of copper have been well characterized.[16,17,18,19]

The copper content data in Table 3 suggests that, unlike free copper ions, the soluble bicarbonate complex of copper has little affinity for sorption sites on the cellulose matrix. Earlier work reported a slower rate of copper-catalyzed oxidative degradation after neutralization with a sodium bicarbonate solution.[13]
It is possible that washing out of some of the adsorbed copper by the sodium bicarbonate solution might have been at least partly responsible for this observation.

In summary, aqueous bicarbonate solutions of magnesium, calcium, and zinc are all effective in dislodging adsorbed and/or exchanged copper species from paper. In the Barrow two-step treatment, on the other hand, the calcium hydroxide treatment fixes the sorbed copper species, making their removal by later treatments more difficult. Paper conservators who have a preference for this deacidification treatment can do better by employing only the second step, as originally recommended by Schierholtz.[20] The alkaline reserve imbibed from a calcium bicarbonate treatment alone is appreciably smaller. In conservation treatments where color changes are a concern, changes in pH need to be minimized. In such cases, a reduced reserve of calcium carbonate may even be advantageous. Deacidification treatments applied as sprays or from nonaqueous media, even if they contain magnesium, do not serve to inhibit copper-catalyzed degradation of paper.

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate
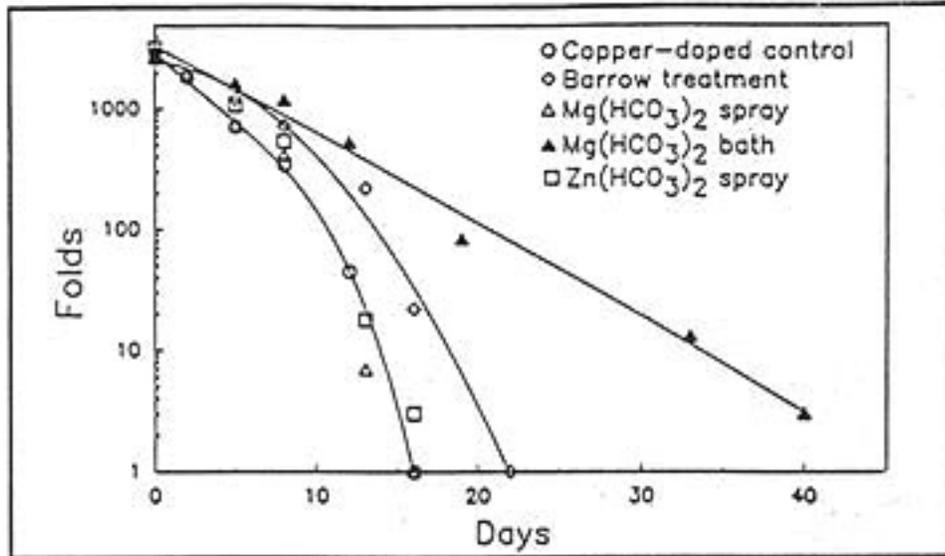Page 7 of 12
www.loc.gov/preservation/

Figure 1. Effect of copper on aging of paper.
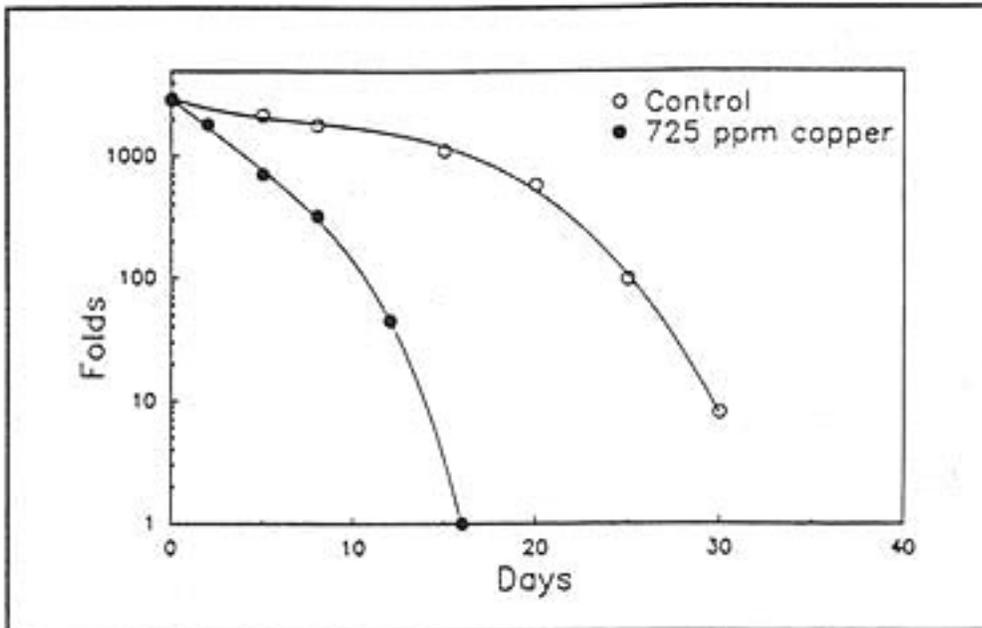
Figure 2. Effect of deacidification treatments on aging of copper-doped paper.

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate

Page 8 of 12
www.loc.gov/preservation/

Table 1
Effect of Deacidification Treatments on Relative Lifetime* of Copper-Doped Paper

Deacidification treatment	Concentration (mol/1)	Application technique	Alkaline Reserve (%)	Relative lifetime (days)
None	---	---	0	7.6
Magnesium bicarbonate	0.059	Immersion	0.81	14.7
Magnesium bicarbonate	0.059	Spray	0.91	7.5
Calcium hydroxide And Calcium bicarbonate	0.024 and 0.080	Immersion	0.76	10.8
Zinc bicarbonate	0.011	Spray	0.90	7.9

*Relative lifetime=time to 1/8 of fold endurance value before aging.

Table 2

Effect of Deacidification Treatment on Brightness (% Blue Reflectance)
of Samples Aged at 90˚ and 50% RH

Days aged	Control Water Washed Treatment	Copper Sorption only Treatment	Copper and Calcium 2-step Treatment	Copper and $Mg(HCO_3)_2$ Immersion Treatment	Copper and $Mg(HCO_3)_2$ Spray Treatment	Copper and $Zn(HCO_3)_2$ Spray Treatment
0	89.60	87.73	86.75	88.37	86.95	87.67
2	---	74.68	75.75	77.83	74.28	79.43
5	85.52	68.15	73.33	73.58	65.03	69.43
8	81.90	64.50	66.13	69.25	58.08	62.95
12	81.58	56.25	---	66.13	---	---
13	---	---	59.90	---	48.73	47.48

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate
Page 9 of 12
www.loc.gov/preservation/

Table 3
Effect of Deacidification Treatment on pH Values of Samples Aged at 90°C and 50% RH

Days aged	Control Water Washed Treatment	Copper Sorption only Treatment	Copper and Calcium 2-step Treatment	Copper and Mg(HCO$_3$)$_2$ Immersion Treatment	Copper and Mg(HCO$_3$)$_2$ Spray Treatment	Copper and Zn(HCO$_3$)$_2$ Spray Treatment
0	6.10	5.88	8.78	9.40	10.25	7.20
2	---	5.18	8.70	9.48	10.05	7.10
5	5.85	4.80	8.71	9.40	10.20	6.80
8	5.59	4.47	8.60	9.62	10.20	6.65
12	5.52	4.40	---	9.28	---	---
13	---	---	8.18	---	9.78	6.00

Table 4
Effect of Chemical Treatments* on Copper Content**

Treatment	Copper Content (ppm)	Copper Lost (%)
Calcium hydroxide, calcium bicarbonate (Barrow two-step deacidification)	609.0	16.0
Calcium hydroxide (0.23 mol/1)	638.0	12.0
Calcium bicarbonate (0.008 mol/1)	92.0	87.3
Magnesium bicarbonate (0.059 mol/1)	26.2	96.4
Zinc bicarbonate (0.012 mol/1)	53.0	92.7
Sodium bicarbonate (0.1 mol/1)	18.0	97.5
Magnesium acetate (0.05 mol/1)	613.0	15.4
Methyl magnesium carbonate (2% solution in Freon TF + methonal)	670.0	7.6

*All chemical treatments were by immersion in a chemical bath for 30 minutes, followed by gentle pressing between blotters, and air-drying.
**Initial copper content of paper=725 ppm

Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate

Page 10 of 12
www.loc.gov/preservation/

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Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995
Library of Congress ♦ Preservation Directorate

Page 11 of 12
www.loc.gov/preservation/

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Effect of Some Deacidifying Agents on Copper-Catalyzed Degradation of Paper
Preservation Research and Testing Series No. 9501
November 1995   Page 12 of 12
Library of Congress ♦ Preservation Directorate   www.loc.gov/preservation/