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How copper corrosion can be retarded – New ways investigating a chronic problem for cellulose in paper

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ABSTRACT

To better assess the stabilization effects of chemical treatments on Cu(II)-catalyzed cellulose degradation, we developed Cu(II)-containing model rag paper with typical copper corrosion characteristics using e-beam radiation. The paper can be prepared homogeneously and quickly compared to tedious pre-aging methods. Using the Cu(II)-containing model rag paper, the stabilization effects of various chemicals on Cu(II)-catalyzed degradation of cellulose were tested. Benzotriazol was highly effective in retarding the degradation of the Cu(II)-containing model rag paper under hot and humid aging condition, as well as under photo-oxidative stress. Tetrabutylammonium bromide reduced Cu(II)-catalyzed degradation of cellulose, but its efficacy was dependent on the accelerated aging conditions. The results with the alkaline treatments and gelatin treatment suggested that their roles in the degradation mechanisms of cellulose in the presence of Cu(II) differ from those of benzotriazol and tetrabutylammonium bromide.

1. Introduction

The presence of transition metal ions in paper has long been a problem in paper conservation because they catalyze the degradation of cellulose. When copper ions in pigments or inks are in contact with a paper substrate, brown discoloration easily occurs and then disturbs the esthetic appreciation of the object and the readability of writing or illustrations on the paper. The paper substrate can also become extremely fragile and cease to function as a carrier of information. Historic manuscripts with green copper pigments are generally valuable objects, which do not lend themselves to comprehensive sampling and analysis of the composition of green paint and associated paper substrates. The compositions of green copper paints are complex. The pigment can be verdigris (basic or neutral copper acetate), malachite (basic copper carbonate), and/or atacamite or para-atacamite (basic copper chlorides) (Banik, 1989; Banik & Stachelberger, 1982). The binding medium of the paint can also vary: gum arabic, egg white, and animal glue have been used (Hendrie, 1847). Additional ingredients, such as plant extracts, may be also added to create a different hue of green color (Boltz von Ruffach, 1549). Therefore, apart from the material parameters of a sample (e.g., the thickness of the paint and paper, pigment size, and ways of applying the paint on the paper), the composition of the green copper paint poses further variations when

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trying to find a valid sample material to test stabilization chemicals for copper pigment-containing paper. The manifold conditions of samples sometimes lead to contradictory results as shown by the study of Ahn, Hartl, Hofmann, Henniges, and Potthast (2014) vs. that of Tse, Trojan-Bedynski, and St-Jacques (2012) on tetrabutylammonium bromide treatment of verdigris-containing paper.

Constructing a test paper sample in copper corrosion research is difficult for several reasons. Before any treatments can be tested, the pigment and the paper must be aged to be as close as possible to a naturally aged material. The simple approach of aging a paper sample is applying an elevated temperature. However, the verdigris transforms to browning copper oxide at an elevated temperature, which is an undesired effect not resembling natural aging. The transformation of copper acetate to copper oxides occurs even more rapidly under humid conditions (Potthast, Henniges, Hofmann, & Faerber, 2011) although humidity is required for extensive oxidative degradation (Williams, Fowler, Lyon, & Merrill, 1977) and for maintaining the moisture content of paper (Bansa & Hofer, 1984). Low-temperature methods, on the other hand, are much too slow to generate oxidation and hydrolytic degradation of a paper substrate. In addition to the paper, the verdigris stays water soluble under the conditions of low-temperature methods. The latter poses problems in subsequent treatment tests. Such treatments do not resemble naturally aged verdigris, which is much less prone to solubilization under aqueous treatments. Therefore, to study the effects of potential stabilization chemicals on copper-catalyzed degradation of paper, an appropriate model paper is necessary. Such paper should contain copper ions and exhibit oxidative degradation but not unsolicited transformation of copper pigments under accelerated aging conditions.

Other than using chemical methods, oxidative degradation of paper can be carried out using radiation energy. UV/visible light is commonly used to simulate degradation of paper in conservation. However, the absorption of UV/visible light is highly dependent on the composition of the paper, and the penetration depth of UV light is only around 70 μm (Hon, 2001). Therefore, it is not easy to apply the light homogeneously to a larger amount of sample materials that are required for subsequent testing. In contrast to UV/visible light, ionizing radiation, such as gamma and beta radiation (e-beam radiation), penetrates easily through paper and thus can be employed homogeneously and rapidly. The application of gamma radiation in the preservation of paper is versatile, depending on its dose and dose rate; it is used to disinfect paper and protect it from biological damage (Adamo, Magaudda, Trionfetti Nisini, & Tronelli, 2003; Gonzalez, Calvo, & Kairiyama, 2002; Magaudda, Adamo, Pasquali, & Rossi, 2000). E-beam radiation has not been used for the conservation of paper, but its abilities to enhance the reactivity of cellulose and to provide more efficient processing of cellulose have been widely tested (Kumakura & Kaetsu, 1983; Nemţanu et al., 2007). E-beam radiation results in severe loss of degree of polymerization (DP) and confers oxidative functionalities on cellulose (Henniges, Hasani, Potthast, Westman, & Rosenau, 2013; Potthast, Rosenau, & Kosma, 2006).

In the present study, we aimed at developing a Cu(II)-containing model paper in a easy and fast way for stabilizing tests of copper-catalyzed degradation of rag paper. For this purpose, e-beam radiation followed by Cu(II)-doping was applied to a fresh handmade rag paper to simulate degraded Cu(II)-containing historic manuscripts, creating homogeneously oxidized functionalities and severe hydrolytic degradation. A variety of chemical stabilization treatments followed to examine their stabilization effect on the Cu(II)-containing model paper. Employing gel permeation chromatography (GPC) with a multiangle laser light scattering detector (MALLS) and fluorescence detection after chemical labeling of the carbonyl groups of cellulose revealed the degradation mechanisms of the sample material with Cu(II) before and after accelerated aging. They eventually shed light on the stabilization ability of different chemicals and how these can influence Cu(II)-induced degradation mechanisms of cellulose. The advantages and limitations of the Cu(II)-containing model rag paper obtained with e-beam radiation are presented.

2. Methods and materials

2.1. Preparation of the Cu(II)-containing model rag paper

The selected paper species was a hand-made rag paper (Gangolf Ulbricht Papierwerkstatt, Berlin, Germany), as historic manuscripts containing copper pigments are usually composed of rag paper. The rag paper contained hemp and linen pulps with alum, in addition to gelatin as a sizing agent. Prior to copper impregnation, the rag paper was irradiated with an e-beam at 10 MeV (Rhodotron™ E-beam accelerator TT-100, IBA, Belgium) operated by Mediscan GmbH (Austria), using a 60 kGy dose to degrade and oxidize the cellulose. After e-beam radiation was performed, Cu(II)-doping was carried out based on the method by Shahani and Hengemihle (1995). The e-beam-irradiated papers were immersed in 0.1 M of verdigris, copper acetate pigment (Kremer pigmente GmbH, Germany) in water for 24 h, with gentle shaking at room temperature. The paper was subsequently washed with water until the conductivity of the washing water was 0.6 μS/cm using a conductivity probe (InLab™ 731, Mettler Toledo AG, Switzerland). The wet papers were placed between acid-free absorbent blotting papers (KLUG conservation GmbH, Germany) to remove excess water followed by air drying at ambient conditions for several days. 'The model paper' in the text refers to the rag paper that was irradiated by e-beam and Cu(II)-doped.

2.2. Chemical immersion treatments

Various chemicals were employed that are applicable to the field of conservation. Two common consolidation materials, hydroxypropyl cellulose and gelatin, were also included. Most of the chemicals were purchased from Merck™, Germany, unless otherwise mentioned in Table 1. Around 600 mg of the Cu(II)-containing model paper (approx. 60 mm × 80 mm) was immersed in 100 mL of each treatment solution described in Table 1 for 30 min, with gentle shaking at 23 °C. After immersion, each paper sample was placed between blotting papers (KLUG conservation GmbH, Germany) and pressed with an identical weight for 30 s to remove excess solution from the sample.

2.3. pH measurements

pH measurement was carried out with a semi-micro pH electrode (InLab™ Semimicro pH electrode, Mettler Toledo AG, Switzerland) which has proven to be useful for a small amount of sample material (Strlič et al., 2004). The measurement procedure was based on the TAPPI 509 om-02 (TAPPI, 2004) except the amounts of the sample and water that were reduced 40 times.

2.4. Accelerated aging

Two different accelerated aging methods were applied. The first method was carried out for 2 weeks at 80 °C and relative humidity (RH) of 65% (Q-Sun Xe-3, Q-LAB) based on ISO 5630-3:1996 (ISO, 2003). The second method for accelerated aging involved a photocatalyzed aging with light using xenon lamps with UV filters in a test chamber (Q-Sun Xe-3, Q-LAB). Twenty cycles between 12 h of light exposure, 1.10 W/cm^2 of irradiance, and 4 h of re-conditioning under dark at 23 °C and RH of 50% were applied in total. The same sides of the sample papers were exposed to the light, and their