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Degradation of cellulose at the wet–dry interface. II. Study of oxidation reactions and effect of antioxidants

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ABSTRACT

To better understand the degradation of cellulose upon the formation of a tideline at the wet–dry interface when paper is suspended in water, the production of chemical species involved in oxidation reactions was studied. The quantitation of hydroperoxides and hydroxyl radicals was carried out in reverse phase chromatography using triphenylphosphine and terephthalic acid, respectively, as chemical probes. Both reactive oxygen species were found in the tideline immediately after its formation, in the range of micromoles and nanomoles per gram of paper, respectively. The results indicate that hydroxyl radicals form for the most part in paper before the tideline experiment, whereas hydroperoxides appear to be produced primarily during tideline formation. Iron sulfate impregnation of the paper raised the production of hydroperoxides. After hygrothermal aging in sealed vials the hydroxyl radical content in paper increased significantly. When aged together in the same vial, tideline samples strongly influenced the degradation of samples from other areas of the paper (multi-sample aging).

Different types of antioxidants were added to the paper before the tideline experiment to investigate their effect on the oxidation reactions taking place. In samples treated with iron sulfate or artificially aged, the addition of Irgafos 168 (tris(2,4-ditert-butylphenyl) phosphate) and Tinuvin 292 (bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate and methyl 1,2,2,6,6-pentamethyl-4-piperidyl sebacate) reduced the concentration of hydroperoxides and hydroxyl radicals, respectively. Tinuvin 292 was also found to considerably lower the rate of cellulose chain scission reactions during hygrothermal aging of the paper.

1. Introduction

Tidelines (brown lines) in paper can affect degradation of cellulose in the brown area itself and in neighboring areas (Jeong, Dupont, & De la Rie, 2012; Souguir, Dupont, & De la Rie, 2008). They can form in historical papers and books at the wet–dry interface upon local exposure to water or high relative humidity (Bone & Turner, 1950; Dupont, 1996a; Eusman, 1995; Hofenk de Graaff, 1994; Madaras & Turner, 1953). Understanding the degradation of cellulose due to a tideline is therefore important for paper conservation purposes. Various degradation products evidencing oxidation have been identified in tidelines (Bogaty, Campbell, & Appel, 1952; Dupont, 1996b; Jeong et al., 2012; Souguir et al., 2008). Among those, low molar mass organic acids, can directly affect cellulose via acid catalyzed hydrolysis, which results in a decrease in the molar mass (Fengel & Wegener, 1984; Souguir et al., 2008). Hydroperoxides have also been found in tidelines in larger quantities than in other areas of the paper (Souguir et al., 2008).

Cellulose oxidation may involve the often cited oxidation of the C2 and C3 hydroxyl groups to ketone groups and of the C6 hydroxyl group to a carboxylic acid group (Lai, 2001). Much more destructive oxidation involves free radical reactions. Free radical oxidation in organic materials encompass a complex series of reactions and has been studied widely, although perhaps less so in cellulose. Some of the free radical reactions possible in cellulose are presented in Scheme 1 (Luo, Abbas, Zhua, Deng, & Tang, 2008; Prousek, 2007; Scott, 1993). They involve hydrogen abstraction from a cellulose molecule and formation of an alkyl radical. Certain hydrogen atoms are more easily abstracted than others, such as those in an α-position to a double bond and those attached to a tertiary carbon atom. In Scheme 1 examples are indicated of H-abstraction on C3,

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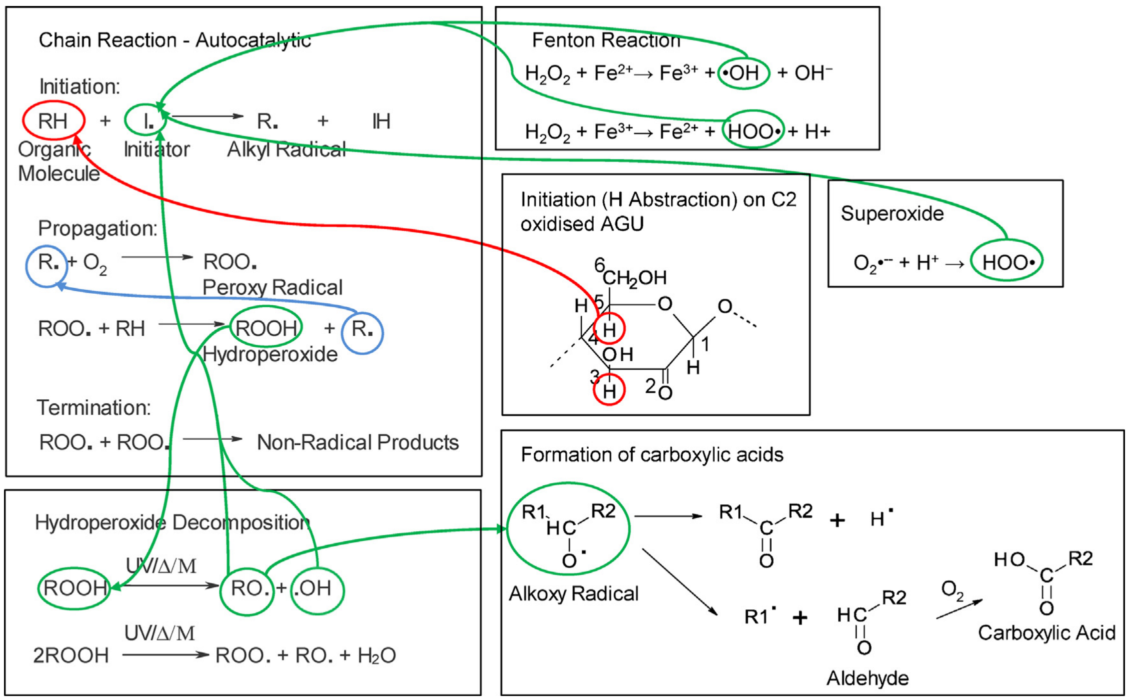

Scheme 1. Autoxidation chain reaction and related free radical reactions. UV = UV catalyzed reaction, *Δ* = thermal reaction, *M* = metal ion catalyzed reaction.

which is in an α-position to a double bond formed after oxidation of the —OH on C2 to a ketone group, and on the tertiary carbon atom C5. The alkyl radical rapidly reacts with oxygen to form a peroxy radical. The peroxy radical abstracts a hydrogen from another molecule and forms a hydroperoxide (R-OOH). Hydroperoxides, the initial products of oxidation, easily decompose to yield peroxy, alkoxy and hydroxyl radicals, which further participate in the free radical chain process, which is therefore also considered autocatalytic (Scott, 1993). Many more complex reactions may take place. In an aqueous environment, Fenton reactions, in which hydrogen peroxide is decomposed in the presence of Fe^{2+}/Fe^{3+}, as well as other transition metal ions such as Cu^{2+}/Cu^{1+}, to yield free radicals, can furthermore play a role (Kolar, 1997; Kolar, Strlič, Novak, & Pihlar, 1998; Walling, 1975). Superoxide radical anion is believed to play a part in aqueous oxidation reactions (Kočar et al., 2005). It is known to be involved in a stepwise one-electron reduction of molecular oxygen leading to the production of hydrogen peroxide (Prousek, 2007).

Antioxidants interfere with free radical oxidation by eliminating reactive species. They can be divided into free radical scavengers, also known as chain-breaking antioxidants, which remove free radicals (Pospíšil & Nespurek, 1995; Scott, 1993), primarily peroxy radicals, and preventive antioxidants, which convert hydroperoxides to their corresponding alcohols (Scott, 1993). Hydroperoxide decomposers are often used in combination with free radical scavengers as they work synergistically.

Antioxidants have been rarely employed in paper. For the most part they have been utilized in attempts to stabilize iron gall ink containing papers, in which oxidation reactions catalyzed by iron ions are believed to play a role. Potassium iodide and other halides (Malešič, Strlič, Kolar, & Polanc, 2005), as well as calcium and magnesium phytate have been studied for this purpose (Kolar et al., 2007; Neevel, 1995). Although the latter have been described as preventive antioxidants in the literature, it appears that their main function is as chelating agents for iron ions to suppress the Fenton reaction. The chelating effects of EDTA, citrate and other compounds have also been studied (Strlič, Kolar, & Pihlar, 2001). Although present at low concentrations, iron and other metal ions may be a factor in the tideline phenomena observed on pure cellulose paper.

Lignin, a common constituent in paper, has been reported to function as an antioxidant although it may also cause discoloration (Schmidt, Rye, & Gurna, 1995). It is structurally similar to phenolic antioxidants. Hindered phenols are powerful chain breaking antioxidants (Pospíšil & Nespurek, 1995). They have the drawback of developing colored transformation products and are therefore not suitable for use in paper. Hindered amine stabilizers (HAS) are powerful free radical scavengers that do not form colored transformation products (Gugumus, 1994). They are oxidized by peroxy radicals to nitroxyl radicals, which are considerably more stable and can be regenerated via a process that involves alkyl radicals and peroxy radicals (Scheme 2). The chemistry of HAS is complex and cannot be done justice in the context of this paper. In this study the effects of the HAS Tinuvin 292 (bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate and methyl 1,2,2,6,6-pentamethyl-4-piperidyl sebacate) were investigated. Preventive antioxidants such as tetrabutylammonium bromide, 1-ethyl-3-methylimidazolium bromide and Irgafos 168 (tris(2,4-ditert-butylphenyl)phosphite), a phosphite with presumably better hydrolytic stability than most phosphites (Tocháček & Sedlář, 1993), were also included in this study (Scheme 2). The molecular structures of the antioxidants can be found in Table 1.

The aim of this research was to further study oxidation reactions occurring during tideline experiments. Only the effects of water migration were investigated but it is plausible that exposure to high or fluctuating humidity affects similar reactions. The formation of hydroperoxides and hydroxyl radicals in papers with or without treatment with antioxidants was studied to better understand the oxidation process occurring in the tideline and neighboring areas in the paper. To assess the role of metal ions, Whatman paper was doped with various concentrations of ferrous sulfate (Calvini & Silveira, 2008). Some papers were artificially aged in order to enhance degradation and predict future behavior.

Among the various methods available for quantifying hydroperoxides and hydroxyl radicals, chromatographic methods using triphenylphosphine and terephthalic acid as probes, respectively,