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Yellowing of Chemical Pulp by Glucuronoxylan

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ABSTRACT

Xylan in hemicellulose has been reported as one of the reasons of the yellowing of chemical pulp and paper. But little relevant information is available in literature.
In this study, we examined into the influence that glucuronoxylan or glucomannan and metallic ion(Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}) residued in pulp get each or when mixed at yellowing. Filter paper was treated with each metallic ion, glucuronoxylan and the mixture of glucuronoxylan and metal ions, and brightness and CIE $L^*a^*b^*$ was measured after accelerated aging. As the results of measurements, the filter paper processed by 10% glucuronoxylan was dropped 2~3% on the brightness after accelerated aging for 24 hours. Also, the filter paper treated with glucuronoxylan and Fe^{2+} was dropped 7% on the brightness.

Kewords *: yellowing, glucuronoxylan, brightness, accelerated aging, metal ions*

1. Introduction

The paper causes aging (or deterioration) according as microorganism, ash, heat, light (ultraviolet rays), temperature, water, air (SO_2, O_2, NO_2) and folding etc. Specially, the book and documents made by acid-free paper as well as acidic paper keeping in long term are aged by light, moisture, microorganism and are fallen the strength. Also, according as time passages, it becomes in state that interpretation of information is impossible and can not keep by strength's decline. According to reports, the acidic paper that passes in about 50 years is damaged about 96% of original folding endurance of paper (1-3). Lots of paper have been focused on the acid in paper which affect in aging directly and the aging preventive method.

Yellowing is considered as one of early phenomenon of paper aging. According to kind of paper and storage conditions, yellowing happens in beginning and paper breaks because strength decline of paper is continued as time goes by. Yellowing can be explained by existence of color reversion materials such as degradations of lignin, low-molecule hemicellulose and cellulose that exist in paper.

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The research for yellowing during paper aging have limited to mechanical pulp that lignin is rich until present, but the study about yellowing of chemical pulp has recently been proceeded on.

The hemicellulose is consist of short side chain and mixtures of polysaccharide that has lower the degree of polymerization than cellulose, and the paper that have hemicellulose happens more yellowing because of faster oxidation reaction than cellulose (5-7).

Glucuronoxylan in hemicellulose included in hardwood is highly included in bleaching pulp too. Sevastyanova reported that the content of hexenuronic acid groups or glucuronic acid groups attached to glucuronoxylan is proportional to the yellowing tendency of kraft pulps. This also showed that the brightness reduction of pulp is accompanied by successive degradation of hexenuronic acid groups or glucuronic acid groups. In previous research it was also demonstrated that hexenuronic acid, glucuronic acid and other chemical compound of carbohydrate origin with conjugated double bonds and carbonyl groups as structural fragments, play an important role in the yellowing process (4,12).

Metal materials such as iron or copper, manganese are presented in pulp (8-9). There are known that the metal acts as catalyzer at pulp bleaching by oxygen or hydrogen peroxide, and then promotes dissolution of cellulose, hemicellulose (6). In resent research, it was showed that the metal materials affect at the paper aging made by mechanical pulp (11) but, there are little systematic study that the metal material causes some effect in dissolution of cellulose or hemicellulose and in yellowing up to now.

This study was carried out in order to investigate about the influence that glucuronoxylan and glucomannan residued main ingredients of hemicellulose in chemical pulps and each metallic ion (Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}) get at yellowing of paper

2. Materials and Methods

2.1 Materials

2.1.1 Holocellulose

45 g of $NaClO_2$ were dissolved in 1 L of H_2O and pH of solution set to 4.5 using CH_3COOH, and 50 g of wood meal unextracted with organic solvent was put into the mixture solution and sealed. After agitating for 24 hr, the mixture was filtered. The same procedures were repeated 4 to 5 times.

Table 1. A species of wood

Species		Year	Diameter (cm)
Softwood	*Pinus koraiensis*	22	42
Hardwood	*Quercus variabilis*	23	44

Table 2. Specification of reagents

Reagents	Mw	Assay, %	Mw(ion)	Manufacturer
$MnSO_4 \cdot H_2O$	169.02	98.0	54.948	Oriental Chemical Industries
$CuSO_4$(Anhydrous)	159.10	97.5	63.546	Kanto Chemical Co., Inc
$FeCl_2 \cdot nH_2O$	126.75	99.5	55.847	Katayama Chemical
$FeCl_3 \cdot 6H_2O$	270.30	97.0	55.847	Showa Chemicals Inc.

2.1.2 Metallic ion

Table 2 shows reagents to make metallic ion solution to search the influence of metallic ion in acceleration aging of paper.

2.2 Methods

2.2.1 Glucuronoxylan and glucomannan isolation

1) 50 g of holocellulose was added to 1 L of 24% KOH solution and the mixture was agitated, and the mixture was allowed to stand in a stream of nitrogen at room temperature for 24 hr. And it was filtered through unfold gauze of 2 on Büchner funnel to acetic acid involving 10 g of ice. And filtrate solution united with washed solution neutralized by pH 5.5 by acetic acid, and glucuronoxylan was isolated by 1/10 concentrating under pressure at 60-70℃.

2) Glucuronoxylan free sediments was put into 1.5 L of H_2O and 24% NaOH(14.48 g) and then 4% H_3BO_3(3.72 g) were added. And this mixture was extracted by agitating in a stream of nitrogen for 8 hr and filtered in press into acetic acid with 10 g of ice. According to 1), glucomannan was isolated.

2.2.2 Accelerated aging of paper and brightness

1) Filter paper was treated with each 5%, 10%, 20% of glucuronoxylan and glucomannan per weight, and filter paper was dried in desiccator for 24 hours.

2) The amounts of iron, copper and manganese ions in the filter paper were treated to 35.0 ppm, 1.30 ppm, and 19.6 ppm, respectively. And these were dried in desiccator under vacuum for 30 minutes.

3) After mixing or treating each metallic ion (Cu^{2+}, Fe^{2+}, Fe^{3+} and Mn^{2+}) to 10% glucuronoxylan and 10% glucomannan, it was dried in desiccator.

4) Filter paper was then aged under the 500 W mercury-tungsten lamp on a Light-fastness tester by Microscal Ltd.

5) Brightness and CIE $L^*a^*b^*$ were measured with Elrepho 3300(Datacolcor International Co.). Each yellowing degree by glucuronoxylan or glucomannan, metal ions and their mixture was measured.

3. Results and Discussion

3.1 Brightness change by aging of filter paper treated with hemicellulose

When the paper is aged artificially, the paper decreases in its brightness as well as strength. We need to investigate these decrease degree according to hemicellulose's kind in chemistry pulp and to know method about ageing-prevention. Brightness is one of the methods that can confirm easily aging degree of paper with naked eye.

There are various kinds of element affecting in paper aging. So, we investigated aging degree by throughput of glucuronoxylan and glucomannan isolated from hemicellulose.

As a result of this experiment, we could confirm that brightness becomes low as glucuronoxylan's throughput increases while glucomannan was no big change even if

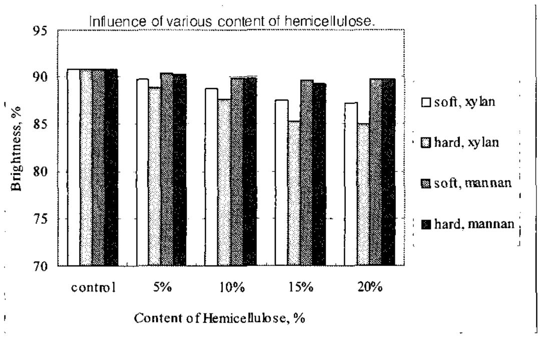

Fig. 1. Influence of various content of hemicellulose.

throughput increases (Fig. 1).

Usually, hemicellulose's content in chemical pulp is about 5 - 18%. Therefore, there were treated with 5 - 20% of glucuronoxylan or glucomannan and investigated brightness' change by acceleration aging times.

In the case of glucuronoxylan, we can see that brightness decreases about 2 - 3% according to aging times. On the other hand, it is not influence greatly to brightness in glucomannan's occasion. Therefore, we can know that glucuronoxylan among hemicelluloses has influences on aging as shown in Fig. 2. Also, glucuronoxylan isolated in hardwood is influenced much more in aging than glucuronoxylan extracted in softwood.

3.2 Brightness influence by addition of metallic ion

Fig. 3 shows that brightness change is occurred when treated with Cu^{2+}, Mn^{2+}, Fe^{2+} or Fe^{3+} to filter paper. Brightness is greatly decreased by Fe^{2+}. Yellowing happens as soon as the paper treated with Fe^{2+} because Fe^{2+} itself changes into Fe^{3+} easily by automatic oxidation while Cu^{2+}, Mn^{2+}, Fe^{3+} are stable in oxidation(11). Also, the filter paper aged accelerating after Fe^{2+} processing is dropped

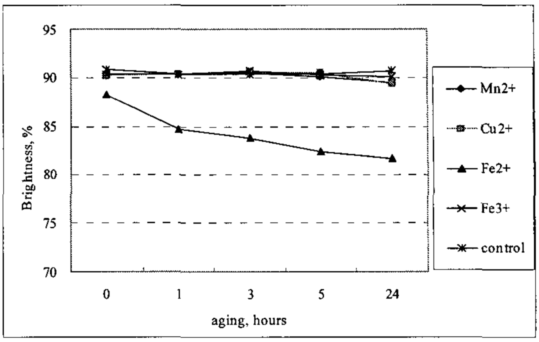

Fig. 3. Influence of metal ions on brightness during aging.

5% on the brightness.

3.3 Brightness influence by addition of hemicellulose and metal ions

Filter paper was treated with glucuronoxylan or glucomannan by throughput 10% per filter paper weight and each metallic ion (Cu^{2+}=1.30 ppm, Mn^{2+}=19.6 ppm, Fe^{2+}=35.0 ppm, Fe^{3+}=35.0 ppm) respectively, and measured brightness after accelerated aging.

Specially, glucuronoxylan were decreased brightness to 7% by Fe^{2+}(Fig. 4). It is thought that glucuronoxylan combined glucuronic acid is oxidized by 2-furancarboxylic acid, 5-formyl-2-furancarboxylic acid and 2,3-dihydroxy-2-

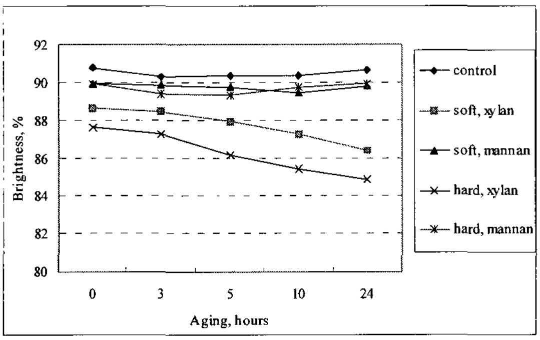

Fig. 2. Influence of 10% glucuronoxylan and 10% glucomannan on brightness during aging.

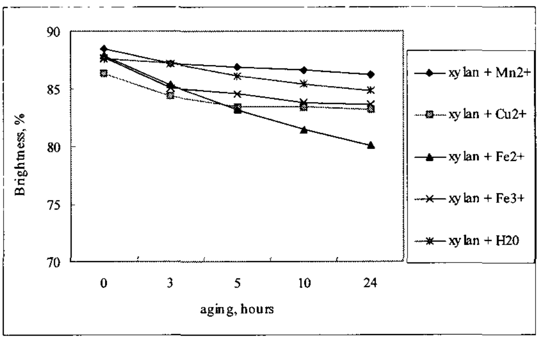

Fig. 4. Influence of 10% glucuronoxylan and metal ions on brightness during aging.

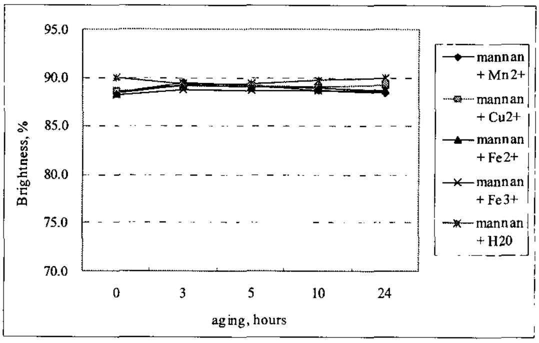

Fig. 5. Influenceof 10% glucomannan and metal ions on brightness during aging.

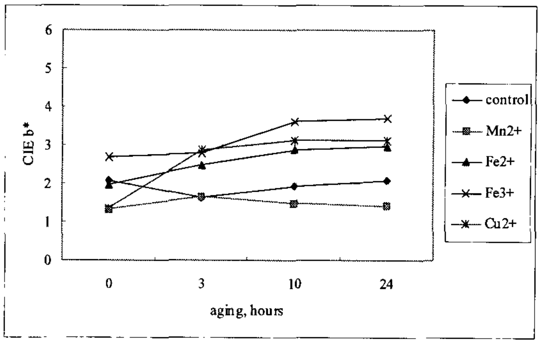

Fig. 7. CIE b* bymetal ions during aging.

cyclopenten-1-one acid and then brightness is decreased .

Even if glucomannan is mixed with metallic ion comparing with glucuronoxylan, brightness did not drop (Fig. 5). It is thought that activation of metallic ion is stopped by that hydroxyl of carbon 2 and 3 positions of glucomannan and iron ion form mannan-metal complexes.

3.4 CIE L*a*b* influence by addition of each hemicellulose, metallic ion or their mixture

CIE $L^*a^*b^*$ to measure yellowing degree of paper was used. Among CIE $L^*a^*b^*$, it means that yellow degree as b^* increases to positive direction.

In the case of glucuronoxylan, b^* value increases according to aging time. In the case of hardwood glucuronoxylan, specially, yellowing degree is bigger (Fig. 6). When treated with metallic ion to filter paper, we could find that b^* values of Fe^{2+}, Fe^{3+} and Cu^{2+} increase according to aging time (Fig. 7).

In occasion of glucuronoxylan and metal ion mixing processing, yellowing degree is higher in general than glucomannan and metal ion mixing processing, except in the case of Mn^{2+} is added. Also, glucuronoxylan and metal ion mixing processing showed higher yellowing degree than glucuronoxylan and metal ion affect in each b^* value (Fig. 8).

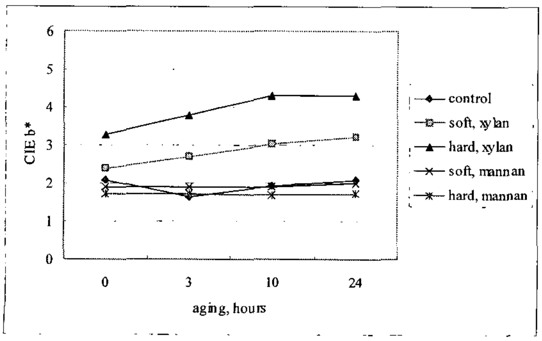

Fig. 6. CIE b* by 10% xylan and mannan during aging.

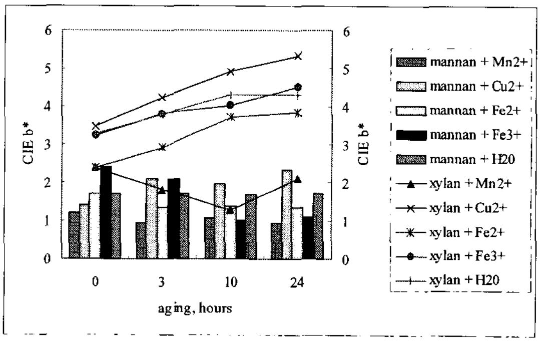

Fig. 8. CIE b* by xylan/metal and mannan/metal mixtures during aging.

4. Conclusions

1. The brightness of chemical pulp was decreased in proportion to glucuronoxylan's content and aging time, and CIE b^* value increased while there was no change by glucomannan after accelerated aging by light and moisture.

2. Fe^{2+} added to filter paper reduced the brightness of paper becoming a Fe^{3+} but there was no significant effect on color reversion by the other metallic ions.

3. Metal ions mixed with glucuronoxylan in filter paper have decreased the brightness except Mn^{2+}, specially, the brightness was reduced 7% by Fe^{2+} and CIE b^* value was appeared highly.

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