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Case study

Chemical characteristics of degraded beeswax in the waxed volume of the *annals of King Sejong* in the Joseon Dynasty

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ABSTRACT

The chemical characteristics of degraded beeswax in the wax treated volumes of the *annals of King Sejong* in the Joseon Dynasty of Korea were investigated and compared with a standard beeswax sample. The oxidation index of the artificially thermally aged beeswax was similar to that of the beeswax in the waxed volumes of the annals of King Sejong. The beeswax in the waxed volumes had gradually degraded in molecular weight over about 400 years. Two low molecules free fatty acid (tetradecanoic acid and lauric acid) were detected in the beeswaxes on the *Annals of King Sejong* and artificially aged beeswax. These fatty acids should be generated from ester compound of the beeswax by oxidative and hydrolytic degradation. Therefore, it can be concluded that the beeswax in the waxed volume of King Sejong should be oxidized and hydrolyzed gradually for a long time progressed.

1. Introduction

There is so many documentary heritage on paper in Korea because the *Hanji* (Korean traditional paper made of mulberry bark fiber) has a very high durability and mechanical strength [1]. Among the various papers on documentary heritage, "*The annals of the Joseon Dynasty (A.D. 1392–1863)*" is a representative one. It is designated as Korea National Treasure No. 151 and also listed as a UNESCO Memory of the World Register.

Five hundred and seventy-seven books of the annals, out of a total 2077 books, were coated with beeswax on every page. The beeswax coating on the paper of the annals was performed at early period in the Joseon Dynasty. There is no any other case of lettered paper with treated beeswax in world documentary history. The purpose of beeswax treatment of paper could have been to increase the permanence and elegance of the annals. But today, compared to untreated books, some of the waxed volumes of the annals are seriously damaged, such as pages being cracked, adhered together, and discolored to brown or red, and partially degraded. As the amount of coated wax increased, the total damage increased. Among the beeswax coated volumes, "*The volumes of the annals of King Sejong* (reigned over the Joseon Dynasty from A.D. 1418 to 1450)" was the most damaged [2,3].

The wax is a mixture of organic substances, usually long chain molecules. They are composed of hydrocarbons, esters of fatty acids, long chain alcohols, and so on. Their chemical compositions depend on mainly the origin of it, like as animal, vegetal or mineral [4,5].

The mechanisms of degradation of the waxed volume in the annals of the Joseon dynasty might be understood by understanding the chemical change of the beeswax that occurred over 500 years.

In this paper, the chemical characteristics of the degraded beeswax in the wax treated volumes of the *Annals of King Sejong* in the Joseon Dynasty were investigated and compared with a beeswax sample.

2. Materials and methods

2.1. Materials

Three small pieces of beeswax paper debris from the wax treated book of the annals of King Sejong of the Joseon Dynasty were offered by the NRICH (National Research Institute of Cultural Heritage) in Republic of Korea. And the reference beeswax sample was treated artificially aging at 150 °C during 15 and 30 days. Origin of beeswax samples are shown in Table 1.

2.2. Methods

The melted Korean beeswax (90 °C) was brushed onto the Hanji [7]. The beeswax coated Hanji was kept in a dry oven (150 °C) for

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Table 1
Origin of beeswax samples from the *Annals of King Sejong* and the reference beeswax samples.

Sample name	Origin of beeswax	Sample name	Origin of beeswax
154-4B	Book No. 154-4 (brown stain)	B-K	Korean beeswax (150 °C aging: 15, 30 days)
154-9R	Book No. 154-9 (red stain)		
154-17 W	Book No. 154-17 (white stain)		

30 days for aging. The beeswax was extracted from the beeswax paper debris of the annals of the King Sejong and from the artificially aged beeswax coated Hanji with 200 mL of solvent (ethanol: benzene = 1: 2, v/v), three times. The solvent extract was filtrated with glass fiber filter paper, the solvent was evaporated using a rotary evaporator and dried on a silica gel [8,9].

IR analysis of extracted beeswax samples (solvent: dichloromethane) from the beeswax paper debris and beeswax coated Hanji's surface were performed with the ATR-IR (ALPHA-P model, Bruker Optics Co., Germany). The oxidation index for each sample was calculated as methods of Tasker et al. [10] and Łojewska et al. [11].

The same amount of beeswax samples was dissolved in 100 μL tetrahydrofuran (THF) and the molecular weight distributions were measured with GPC (Waters, Alliance GPCV2000).

About 2 mg of beeswaxes were solved to 10 mL of HPLC grade cyclohexane and evaporated with a rotary evaporator until dry. The syrup was solved in 50 μL BSTFA, *N,O*-bis(trimethylsilyl) trifluoroacetamide and kept in a water bath at 70 °C for 30 minutes for trimethylsilylation. The trimethylsilylated samples were analyzed with HTGC (Hewlett-Packard 6890, Agilent) and HTGC/MS (Hewlett-Packard 7890A, Inert XL MSD, Agilent) by methods of Regert et al. [12].

3. Results and discussions

As shown in Fig. 1, the oxidation index of the Korean beeswax is 0.07, but it increased to 0.6 by forced thermal degradation. This means beeswax is oxidized and amount of carbonyl group in the beeswax is increased. The oxidation index of the thermally aged beeswax is similar to that of the beeswax (over 0.5) on the waxed volume of the *Annals of King Sejong*. Therefore, the beeswax in waxed volume of the *Annals of King Sejong* was oxidized considerably over a long period.

On the other hand, when you look in detail at the carbonyl peak (Fig. 2), the intensity of the C=O peak derived from the free carboxyl group (–COOH, 1715 cm^{-1}) of the Korean beeswax (reference sample) which was artificially aged (30 days, 150 °C), becomes

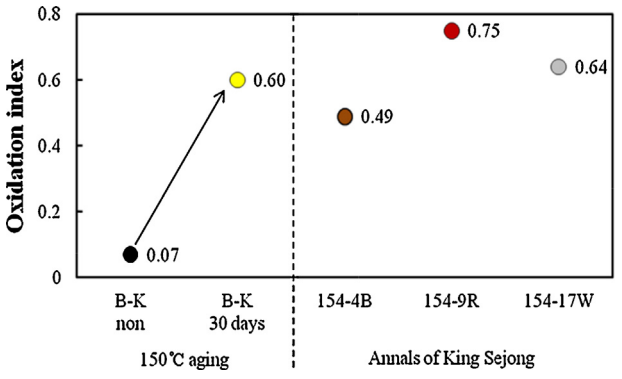

Fig. 1. Oxidation index of wax extracted from historical fragments and artificially aged reference samples.

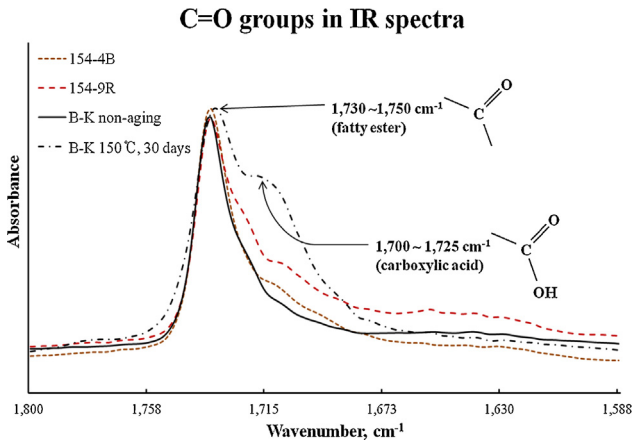

Fig. 2. Comparisons of the carbonyl groups in the IR spectra of the beeswaxes.

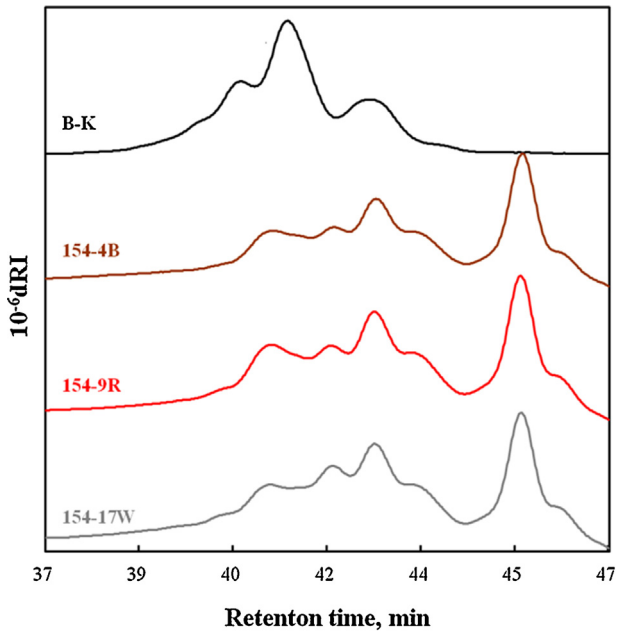

Fig. 3. Molecular weight distributions of the beeswaxes.

relatively strong compared to C=O peak derived from the ester (1730 cm^{-1}) [10]. This is also the same for the beeswax on the paper debris from the *Annals of King Sejong*. Accordingly, it could be assumed that the free carboxyl group in the beeswax applied to the paper increased from the hydrolytic degradation of ester of fatty acids and long chain alcohols during the several hundred years.

The result of GPC is shown in Fig. 3. The main peak (retention time 41 minutes) of the Korean beeswax corresponds to a molecular weight about the 3000 g/mol. However, the 41 minutes peak of the beeswax extracted from the *Annals of King Sejong* is reduced considerably and the intensity of the at 43 minutes retention time increased. The peak with 45 minutes retention time (Mw = 1060 g/mol) becomes the main peak of the beeswax in *Annals of King Sejong*. It can be concluded that the beeswax coated on the *Annals of the Joseon dynasty of Korea* in order to enhance the durability and elegance had gradually degraded in molecular weight over several hundred years. Decomposition of the beeswax from the waxed volume of the *Annals of King Sejong* could be due to hydrolytic and oxidative degradation of the beeswax.

The HTGC chromatogram and the mass spectra of the beeswax are shown in Fig. 4. The three samples of extracted beeswax from