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## Surface Characterization of Naturally Degraded Wood-Free Papers by Near Infrared Fourier-Transform Raman Spectroscopy

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Near infrared excited Fourier-transform Raman spectroscopy (NIR-FTR) was applied to non-destructive spectroscopic analysis of the naturally degraded papers. The analytical results reveal that the color of papers was related closely to Raman intensities at  $1600\text{ cm}^{-1}$  band that was assigned to lignin and papermaking additives in the papers. The folding endurances of papers correlated with the intensities at  $1097\text{ cm}^{-1}$  assigned to  $\beta$ -glycosidic linkages of cellulose and hemicellulose and decreased with the increasing storage years. The Raman spectra of the papers illustrate that the  $\alpha$ -glycosidic linkages at  $1126\text{ cm}^{-1}$  of hemicellulose and starch were hydrolyzed faster than  $\beta$ -glycosidic linkages during the storage.

### INTRODUCTION

Compared to permanence of writing paper made hundreds of years ago, modern paper tends to have a much shorter life expectancy, which has been a serious problem for the preservation of books and documents. It has been estimated that approximately one-third of the 19 million books and pamphlets in U. S. Library of Congress are too brittle for circulation. The permanence of paper has therefore become an important property on which many users base for their choice of paper products.

In the previous work (Wu and Tanaka, 1998), we investigated the effects of sizing agents, starch, and other papermaking additives on the natural deterioration of the books stored for 1–32 years using pyrolysis-gas chromatography (Py-GC). To get better understanding of mechanisms of the natural deterioration, it is important to clarify relations between the paper permanence and various paper constituents during storage. Since a destructive means of determining the paper constituents is not suitable for most of the stored books, a non-destructive means is required. The present study dealt with the application of near infrared excited Fourier-transform Raman (NIR-FTR) spectroscopic technique to the non-destructive determining.

Among vibrational techniques that have been applied to the studies on woody materials (Forsskahl and Jason, 1992; Ono *et al.*, 1998), the Raman spectroscopic technique is advantageous since solid or powder samples can be measured directly. However, conventional Raman spectroscopy using the excitation laser of the visible regions causes a fluorescent emission interfering with the Raman measurement, and

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causes sample damage due to high energy of the visible laser. Using near-infrared excitation laser dramatically reduced these problems (Parker, 1991). Near infrared laser does not excite  $\nu$  (O–H) in water much, so that the moisture in sample give little effect on spectra (Edward and Farwill, 1996). Furthermore due to the difference in the selection rule for infrared and Raman spectroscopy,  $\nu$  (C=C) vibration is only active in Raman scattering which is specific for lignin-derived aromatic skeleton (Agarwal and Atalla, 1994).

## MATERIALS AND METHODS

### Materials

The paper samples were taken from the books stored in a shelf at ambient temperature and humidity for 1 to 32 years (Wu and Tanaka, 1998). The samples were taken according to JIS P8110 (Japan Industrial Standard).

### Measurements of paper properties

Folding endurance of papers was measured according to JIS P8115. To avoid influence of ink color, brightness,  $L^*$ ,  $a^*$ , and  $b^*$  values on the unprinted parts of paper samples were measured using a MINOLTA CR-200 photoelectric reflectance photometer.

### Raman analyses

Raman measurements of the papers were carried out using a Perkin–Elmer System 2000 Fourier–transform spectrometer fitted with the standard Perkin–Elmer Raman attachment and a Nd:YAG laser ( $\lambda=1064$  nm). A standard  $180^\circ$  backscatter sampling geometry was used for all of the measurements. The spectra were obtained at a resolution of  $4\text{ cm}^{-1}$ , using an accumulation of 50 scans, over the wavenumber range from  $3600$  to  $400\text{ cm}^{-1}$ . The laser power was  $600\text{ mW}$ .

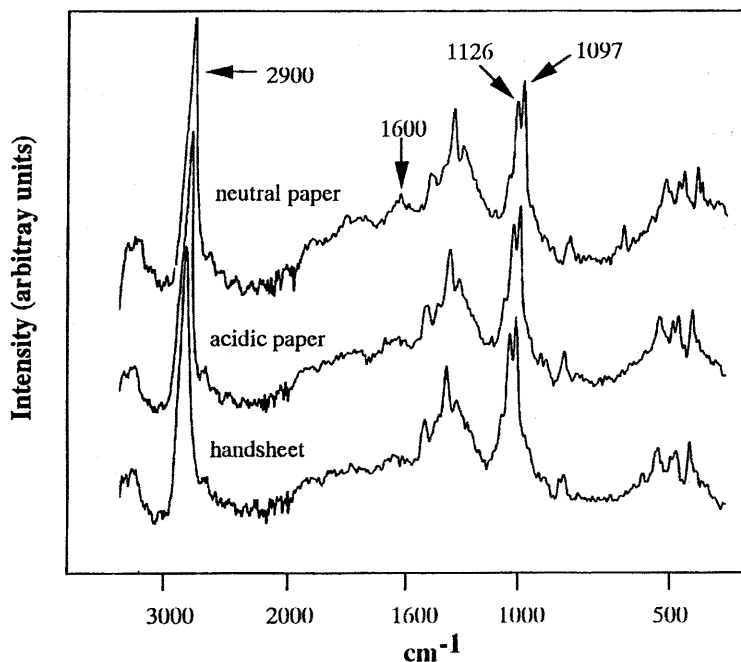
## RESULTS AND DISCUSSION

### Characteristic bands in the Raman spectra of the papers

The Raman spectra of the acidic paper and the neutral paper are shown in Fig. 1, respectively. As a comparison, the spectrum of a handsheet prepared from bleached hardwood kraft pulp without any papermaking additives is also shown in Fig. 1. Though there are not significant differences in the bands of the three Raman spectra, the intensities at  $1600\text{ cm}^{-1}$ ,  $1126\text{ cm}^{-1}$  and  $1097\text{ cm}^{-1}$  are quite different. Based on the model compounds (Wu) and the previous papers (Wiley and Atalla, 1987; Agarwal and Atalla, 1994; Conners and Banejee, 1995; Edward and Farwill, 1996; Takayama *et al.*, 1997), the main wavenumbers and vibrational assignments for the papers are listed in Table 1.

The bands at near  $3300\text{ cm}^{-1}$  are assigned to free and bonded OH groups in the papers. They were weak in the spectra because NIR laser does not excite  $\nu$  (O–H) much. The band at  $2900\text{ cm}^{-1}$  is assigned to stretching vibration of aliphatic  $\text{CH}_2$  in cellulose and hemicellulose. This band was chosen as internal standard because the structure is stable against heat and light (Forsskahl and Jason, 1992). The Raman shifts of unconjugated and conjugated carbonyl groups are in the range from  $1735\text{ cm}^{-1}$  to  $1650\text{ cm}^{-1}$ , and those of

C=C are in the range from  $1650\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$ . The intensity changes at these bands are related closely to color of the papers (Agarwal and Atalla, 1994; Wu and Tanaka, 1997). The strong signals at  $1126\text{ cm}^{-1}$  and  $1097\text{ cm}^{-1}$  are assigned to glycosidic linkages of cellulose, hemicellulose and starch in the papers. The bands at  $788\text{ cm}^{-1}$ ,  $698\text{ cm}^{-1}$  and  $636\text{ cm}^{-1}$  belong to calcium carbonate and clay, respectively.



**Fig. 1.** Raman spectra of a neutral paper, an acidic paper and a handsheet prepared from bleached hardwood kraft pulp.

**Table 1.** Wavenumber and vibrational assignments for the naturally degraded wood-free papers.

Wavenumber ( $\text{cm}^{-1}$ )	Mode	Approximate description of vibration mode
3300	$\nu$ (OH)	free, bonded
2900	$\nu$ ( $\text{CH}_2$ )	holocellulose
1735	$\nu$ (C=O)	unconjugated
1650	$\nu$ (C=O)	conjugated
1600	$\nu$ (C=C)	lignin, papermaking additives
1381	$\delta$ ( $\text{CH}_2$ )	holocellulose
1341	$\delta$ ( $\text{CH}_2$ )	holocellulose, starch
1126	$\nu$ (COC)	$\alpha$ -, $\beta$ -glycosidic linkages
1097	$\nu$ (COC)	$\beta$ -glycosidic linkages
997		alum
788		calcium carbonate
698		calcium carbonate
636		clay

### Bands related to color of the papers

The permanence of paper refers to the retention of significant usage properties, particularly color and folding endurance, over prolonged periods. So the attention in this study was paid on the relations between Raman intensities at the characteristic bands and the two paper properties. It is generally accepted that unconjugated and conjugated carbonyl groups in paper constituents are one of main reasons for discoloration of woody materials (Agarwal and Atalla, 1994; Wu and Tanaka, 1994, 1997). But lignin in the wood-free papers was a minor component (Wu and Tanaka, 1997; 1998), and the Raman spectra of the papers demonstrated that the changes in the range from  $1735\text{ cm}^{-1}$  to  $1650\text{ cm}^{-1}$  were small. These results illustrate that the unconjugated and conjugated groups were not main groups responsible for discoloration of the papers.

It can be seen from the Raman spectra of the papers that the difference in the intensities at  $1600\text{ cm}^{-1}$  is significant. The band assignments in Table 1 show that rosin and papermaking additives such as polyacrylamides in the papers contribute to this band. Therefore, the papermaking additives may be considered to be responsible for discoloration of the papers.

The color of samples from the books stored for 1 to 32 years was investigated in terms of brightness,  $L^*$  (lightness),  $a^*$  (red, green, or gray), and  $b^*$  (yellow, blue, or gray) values. The analytical results showed that the changes in  $L^*$  and  $a^*$  values of the papers were small during the storage, but large losses in the brightnesses and significant increases in the  $b^*$  values of the papers were observed. The statistics demonstrate a smaller brightness (Fig. 2) and a larger  $b^*$  value (Fig. 3) correlated with a larger intensity ratio of  $I_{1600}/I_{2900}$ . These facts revealed that the papermaking additives contributing to the band at  $1600\text{ cm}^{-1}$  would result in large discoloration of the papers during the storage. This is in good agreement with the results determined by Py-GC (Wu and Tanaka, 1998).

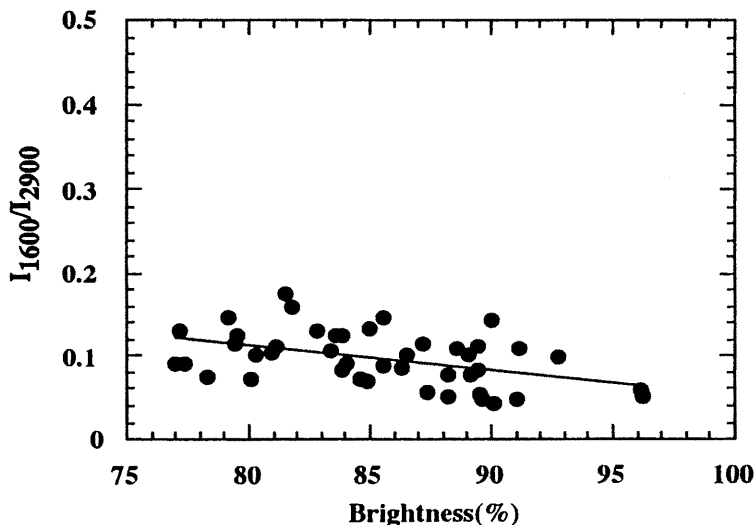


Fig. 2. Relationship between brightnesses of the papers and the Raman intensities at  $1600\text{ cm}^{-1}$ .

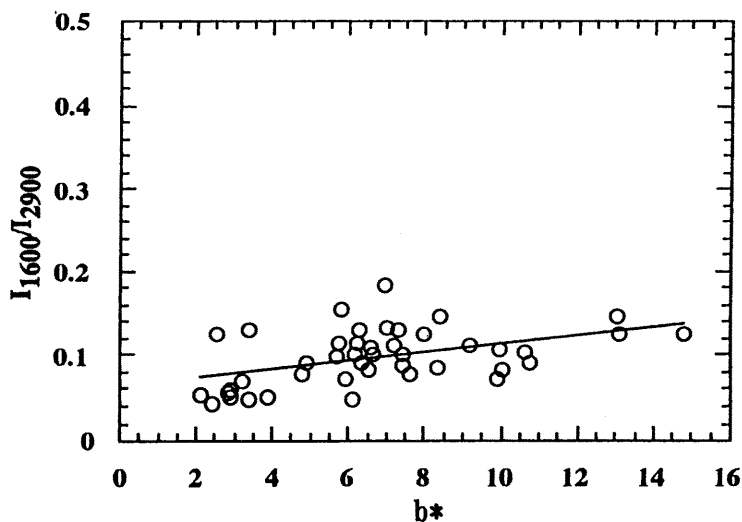


Fig. 3. Relationship between the yellownesses ( $b^*$ ) of the papers and the Raman intensities at  $1600\text{ cm}^{-1}$ .

Our recent study illustrated that rosin and other papermaking additives greatly influenced the color of wood-free papers (Wu and Tanaka, 1997).

#### Changes in glycosidic linkages of the papers during storage

As shown in Fig. 4, the intensities at  $1907\text{ cm}^{-1}$  of the acidic papers decreased gradually with increasing storage years. Since the intensities reflect the polymerization degrees of cellulose on paper surfaces (Agarwal and Atalla, 1994), the decrease in the Raman intensities at  $1907\text{ cm}^{-1}$  illustrates that the cleavage of  $\beta$ -glycosidic linkages on the paper surfaces proceeded gradually during the storage. In the previous paper (Wu and Tanaka, 1998), we reported that the folding endurances of the papers declined with increasing storage years. Thus the Raman spectra suggests that the cleavage of  $\beta$ -glycosidic linkages due to acidic hydrolysis during the storage may be a main reason for the losses in the mechanical property of the acidic papers.

Similar to  $I_{1097}/I_{2900}$ , the intensity ratio of  $I_{1126}/I_{1097}$  also shows a decreasing trend with the increasing storage years (Fig. 4). As shown in Table 1, the band at  $1126\text{ cm}^{-1}$  is assigned to symmetric stretching of  $\alpha$ - and  $\beta$ -glycosidic linkages in carbohydrates. Among the carbohydrates of the wood-free papers, only hemicellulose and starch contain  $\alpha$ -glycosidic linkages in their molecules. The decreases in the intensity ratio of  $I_{1126}/I_{1097}$  with increasing storage years means that both of  $\alpha$ - and  $\beta$ -glycosidic linkages were hydrolyzed gradually due to acid, and the cleavage of  $\alpha$ -glycosidic linkages proceeded faster than that of  $\beta$ -glycosidic linkages during the storage. Luner and Usuda suggested that the hydrolysis of hemicellulose in paper is a more important factor than that of cellulose for the deterioration of paper. The Raman spectra of the papers here demonstrate that the decreases in  $\alpha$ -glycosidic linkages of hemicellulose and starch were

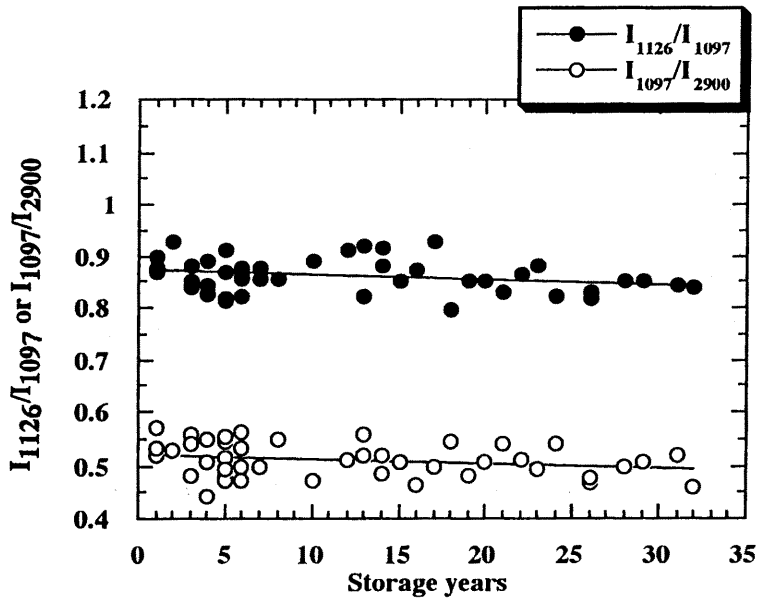


Fig. 4. Relationship between the storage years of the acidic papers and the Raman intensity ratios.

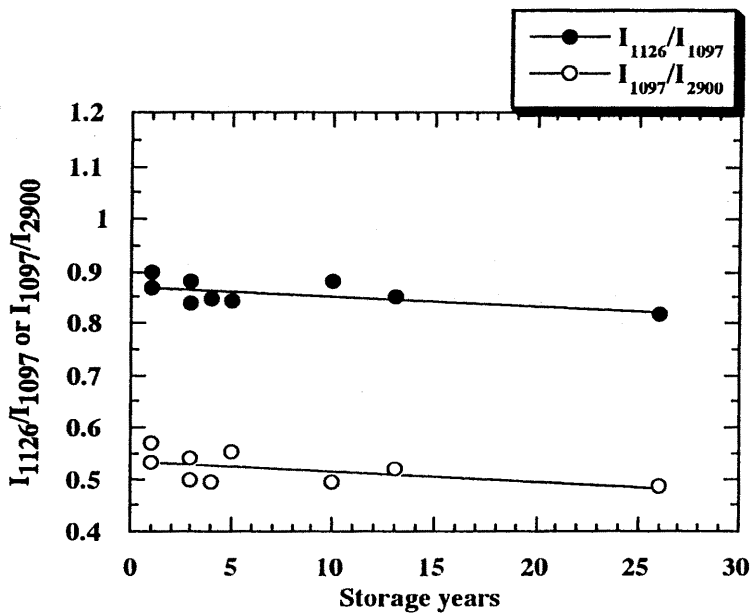


Fig. 5. Relationship between storage years of the neutral-alkaline papers and the Raman intensity ratios.

related deeply to folding endurances of the papers.

It is worthy to note that both intensity ratios of  $I_{1097}/I_{2900}$  and  $I_{1126}/I_{1097}$  in the Raman spectra of neutral-alkaline papers decreased with the increasing storage years (Fig. 5). Based on the statistics between the folding endurances and the intensity ratios as shown in Figs. 4 and 5, it is obvious that the cleavages of  $\alpha$ - and  $\beta$ -glycosidic linkages in the neutral-alkaline papers were as fast as in the acidic papers during the storage. In our knowledge, if a paper is neutral or alkaline, it will have good permanence. But the analysis results in the Raman spectra suggest that chemical additives in neutral-alkaline papers may also cause serious deterioration of the papers.

Besides the bands described above, the band at  $1080\text{ cm}^{-1}$  assigned to oxycellulose, and bands at  $1300$  and  $900\text{ cm}^{-1}$  relate to crystallinity of cellulose were reported to affect the fiber strength (Edward *et al.*, 1996). But there was no clear relationship between these bands and the folding endurance of the papers.

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