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Permanence of wood-free paper I: Paper-making additives in naturally degraded wood-free papers*

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Abstract Effects of pH, sizing agent, and starch on the natural deterioration of 45 printed wood-free papers stored 1–32 years was investigated in terms of MIT folding endurance, brightness, and L*a*b* values. The neutral and alkaline papers retained their folding endurances well and significantly lost their yellow color (b*) during storage. The folding endurance of the acidic papers stored more than 15 years showed a declining trend with increased storage time. The sizing agent content in the papers stored more than 10 years increased and the amount of starch decreased with increasing storage years. A larger amount of the sizing agents correlated with less folding endurance and more yellow color of the papers. The relation between the starch content and the degree of yellow color of the papers was unclear, and the endurance of the papers increased with the increase in starch content.

Key words Wood-free papers · Permanence · MIT folding endurance · Sizing agents · Paper additives

Introduction

Compared to permanent writing paper made hundreds of years ago, modern writing 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 the U.S. Library of Congress are too brittle for circulation.[1] The permanence of paper has therefore become an important property on which many users base their choice of paper products.

According to the *Dictionary of Paper*,[2] the permanence of paper refers to the retention of significant usage properties, particularly folding endurance and color, over prolonged periods. The permanence of paper is affected by fiber quality, paper-making additives, heat, light, moisture, and gases – alone or in combination. It is well known that the introduction of alum to paper-making about 150 years ago is one of the main causes of the poor permanence of modern writing papers. In recent years, new kinds and larger quantities of chemical agents are used in paper-making processes because of the development of new pulping and bleaching methods, greater use of recycled fibers and other pulps with low quality, the development of new sizing and strength additives, the greater extent of white water circuits, and so forth. It is reasonable to consider that these changes, in addition to the paper-making additives, may greatly influence paper permanence. New studies are therefore required to obtain a better understanding of the effects of the additives on paper permanence.

Papers in wood-free grades are mainly for writing and printing where preservation of the paper is an important consideration. There have been a number of studies on accelerated aging of wood-free papers.[3–5] Dixson and Nelson[3] observed that the structure of the sheets was a determining factor for the permanence of the papers sized with normal rosin-alum. Oye[4] found that the wood-free papers lost more folding endurance than the wood-containing papers under various accelerated aging and recycling conditions. McComb and William[5] reported that the alkaline papers retained their folding endurance well during similar treatments. Recently, Mailly et al.[6] reported that antioxidants and optical brighteners in alkaline wood-free papers were responsible for the yellowing of the papers. There have been relatively few studies, however, on the natural aging of wood-free papers during the last 50 years. In the present study the effects of pH, starch, and sizing agents on the natural deterioration of 45 printed wood-free papers stored 1 to 32 years were investigated in terms of folding endurance, brightness, and the L* (lightness), a* (red, green, or gray), and b* (yellow, blue, or gray) values (see below).

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Materials and methods

Materials

The paper samples were mainly obtained from the abstracts of annual meetings of the Japan Wood Research Society and those from a lignin symposium. The abstracts were stored on a bookshelf at ambient temperature and humidity for 1–32 years. The top 20 pages of the books were taken as samples and conditioned according to Japan Industrial Standard (JIS) P 8111. It was assumed that the papers used were manufactured during the years corresponding to the meetings or symposiums.

Measurement of paper properties

The MIT folding endurance of the papers was measured according to JIS P 8115. The pH values of the papers were determined by a cold extraction method (JIS P 8133). To avoid the influence of ink, the brightness and L*, a*, and b* values on blank parts of the papers were measured with a Minolta CR-200 photoelectric reflectance photometer. Fiber analysis of the papers was carried out using the Graff "C" stain according to Tappi test method T401om-93.

Measurement of paper-making additives

The ash and starch contents in the papers were measured according to Tappi test methods T413om-93 and T419om-91, respectively. The quantity of sizing agents in the papers was determined by pyrolysis-gas chromatography (Py-GC) combined with on-line methylation.[7–9] A vertical microfurnace-type pyrolzer (Shimadzu PYR-4A, Shimadzu, Kyoto, Japan) was attached directly to a gas chromatography apparatus (Shimadzu GC-17A) equipped with a flame ionization detector. About 500 µg of the milled paper sample was placed in a platinum sample cup, and 4 µl of tetramethylammonium hydroxide (TMAH) was added to the cup. A fused silica capillary column (Shimadzu CBP_5-M25-025) was used. The flow rate of carrier gas (He) was reduced from 50 ml/min at the pyrolyzer to 1 ml/min at the capillary column by means of a splitter. The column temperature was initially set at 80°C and then programmed up to 300°C at a rate of 5°C/min.

Results and discussion

Permanence of acidic and neutral/alkaline papers

The analysis of fibers in the papers by Graff "C" stain indicated that no mechanical pulp was present in the papers, and the pyrograms of the papers showed that the amount of lignin in the papers was too small to be detected by Py-GC.[9] These facts proved that the papers used were in wood-free grades. The basic weights (containing inks) of the papers were in the range of 63–72 g/m^2 except for about 85 g/m^2 for six types of paper. The ash contents of the papers changed from 2% to 23% and were independent of the manufacture years. To reduce errors of paper endurance measurements caused by differences on the basis of weight, the six papers with about 85 g/m^2 basic weight were excluded from the discussion on the folding endurance of the papers.

Table 1. Distribution of the papers according to their pH

Storage year	pH 4.2–5.6	pH 6.1–7.6	pH 8.3–8.9	Total
0–5	10(22%)[a]	1(2%)	5(11%)	16(36%)
6–10	6(13%)	1(2%)	0	7(16%)
11–20	11(24%)	0	1(2%)	12(27%)
21–32	9(20%)	1(2%)	0	10(22%)
Total	36(80%)	3(7%)	6(13%)	45(100%)

[a] Percent of total paper samples.

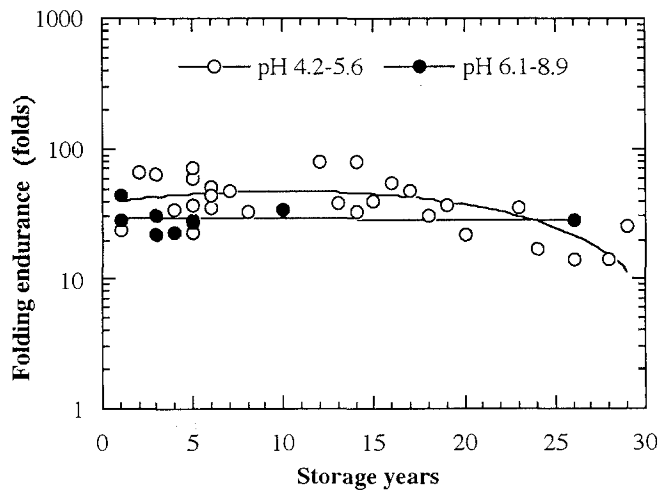


Fig. 1. Relation between storage years and folding endurance of the papers

The data in Table 1 show that the pH values of the 45 printed wood-free papers were in the range of 4.2–8.9. Acidic papers (pH 4.2–5.6), near-neutral and neutral papers (pH 6.1–7.4), and alkaline papers (pH 8.3–8.9) occupied 80%, 7%, and 13% of the total paper samples, respectively. Although 80% of the samples were acidic, the percentage of neutral and alkaline papers increased dramatically from 10% of the papers produced prior to 5 years to 38% of the papers produced during the most recent 5 years. This finding is in agreement with the trend that paper-making conditions have shifted rapidly from acidic to neutral/alkaline in recent years.[10,11]

Considering the fact that paper pH is generally accepted to be a key factor for determining paper permanence,[12–14] we attempted to clarify the relations between the pH values and the folding endurance, brightness, and degree of yellow color (yellowness) of the papers. As shown in Fig. 1, the change in folding endurance of the neutral/alkaline papers

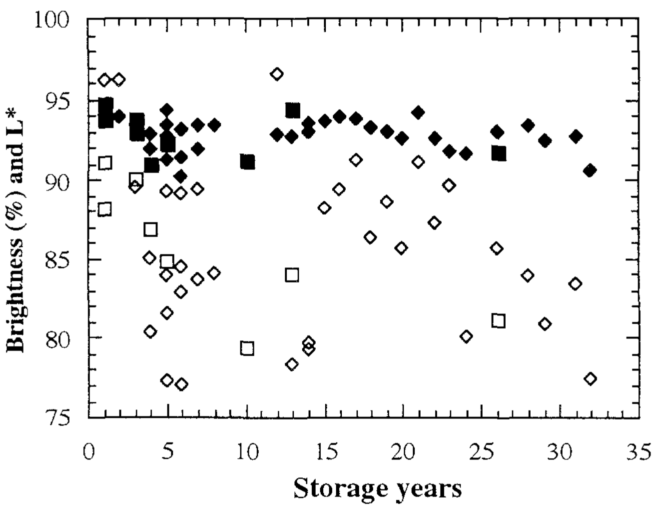


Fig. 2. Relation between storage years and the brightness and L* values of the papers. *Open diamonds*, brightness (pH 4.2–5.6); *filled diamonds*, L* (pH 4.2–5.6); *open squares*, brightness (pH 6.1–8.9); *filled squares*, L* (pH 6.1–8.9)

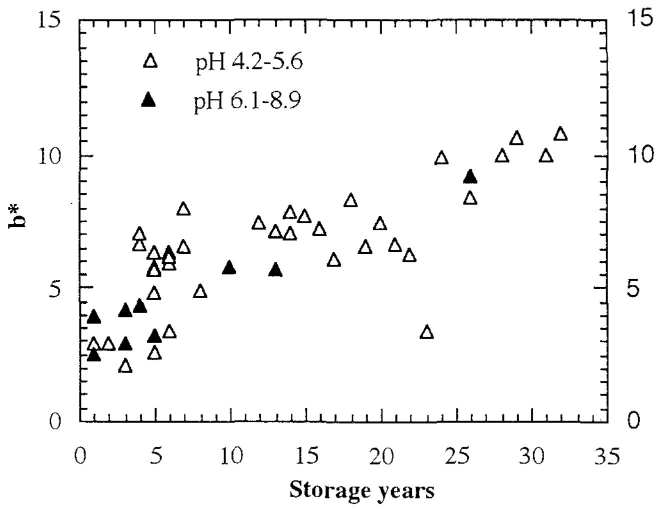
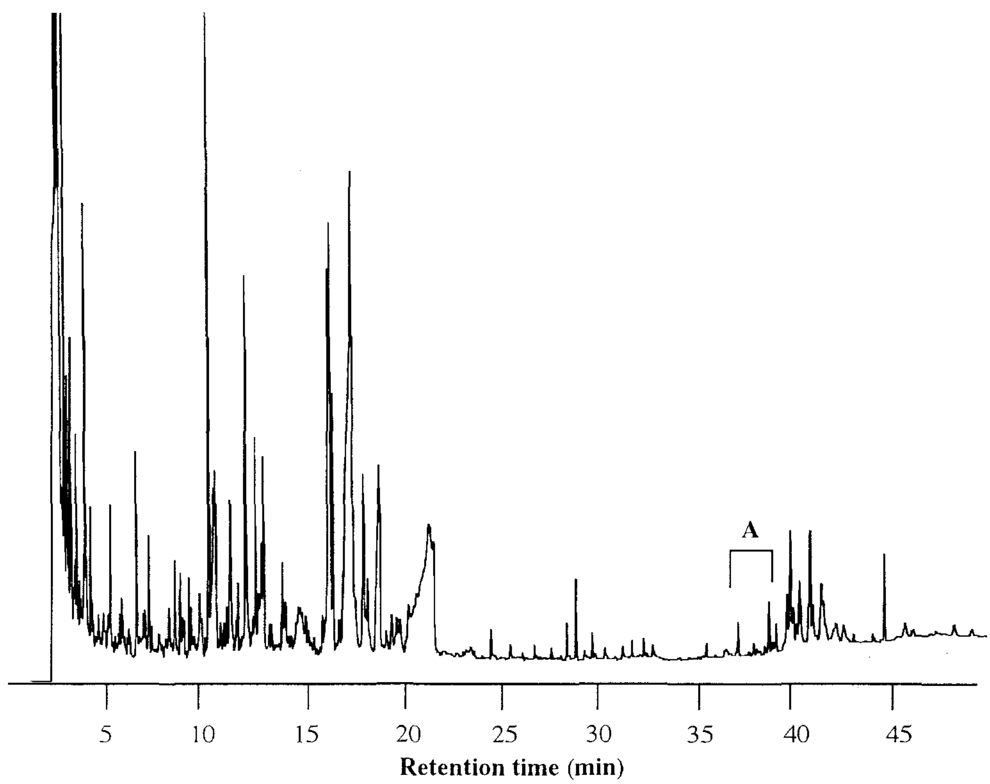


Fig. 3. Relations between storage years and the b* values of the papers

Fig. 4. Pyrogram of an acidic wood-free paper



was small during storage. However, the storage times of the neutral/alkaline papers were shorter than 26 years. Further investigation is required because a recent study noted that the folding endurance of an acidic wood-free paper became zero, and two commercial alkaline wood-free papers lost half of their folding endurance after being heated at 105°C for 10 days.[15]

It is apparent in Fig. 1 that the folding endurance of the acidic papers stored for more than 15 years declined with the increase in storage years despite the different sources of the samples. The results are consistent with the estimation that approximately 90 million books (about 30% of the total) found in American research libraries cannot be used because of brittleness due to acid attack[16]; moreover, they

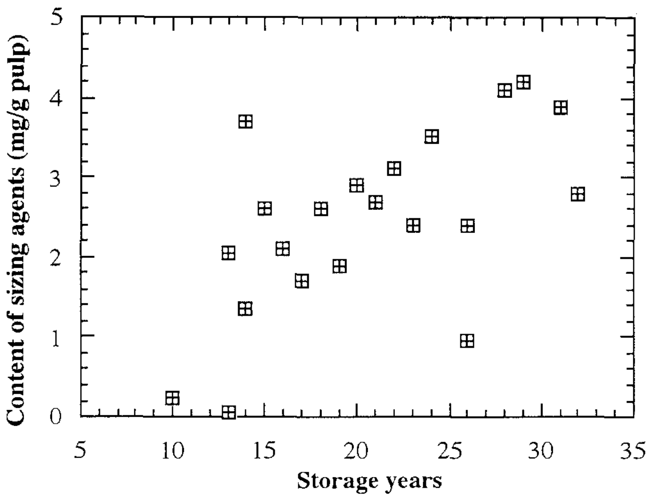


Fig. 5. Relation between storage years and contents of sizing agents in papers stored more than 10 years

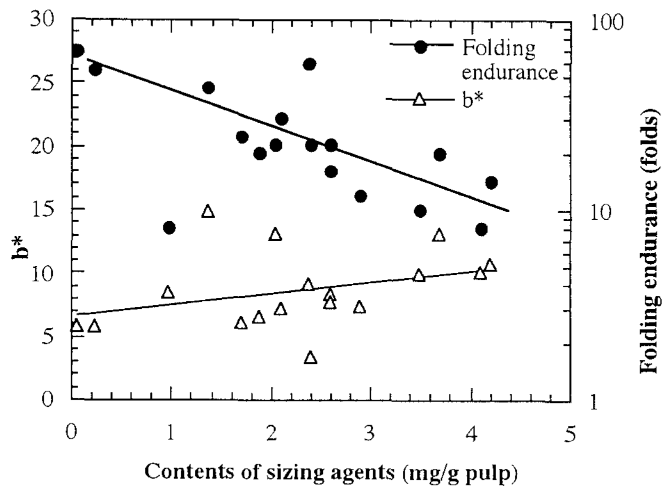


Fig. 6. Relations between contents of the sizing agents and the b* values and folding endurances of the papers stored more than 10 years

illustrate that the pH of paper is an important factor in regard to the stability of the folding endurance of wood-free papers.

The optical properties of book paper have been reported to be sensitive to deterioration of the paper during natural aging.[17] As shown in Fig. 2, the relation between the years of storage and the brightness of the paper was unclear, although the yellowness of the paper showed good correlation with the years of storage (Fig. 3). An explanation may be that fluorescent whitening agents in the paper affect the measurement of paper brightness.[18,19] For this reason, the Commission International de l'Echairage (CIE) 1976 L*a*b* system was introduced to measure the color of the paper. The symbols L*, a*, and b* are used to designate the measured values of three attributes of surface color appearance: L* represents lightness, increasing from 0 for black to 100 for perfect white; a* represents redness when it is plus, greenness when minus, and zero when gray; b* represents yellowness when it is plus, blueness when minus, and zero when gray.[20]

As shown in Fig. 2, the change in the L* values of the papers during storage is small. The b* values of the acidic and neutral/alkaline papers shown in Fig. 3 increase with increasing storage years, indicating that yellowing of the papers proceeded from the start of storage. It is worth noting that the loss in b* value of the neutral/alkaline papers was almost the same as that for the acidic papers, indicating that the effect of pH on the yellowness of the papers was small during storage.

Effects of sizing agents on the permanence of paper

Sizing agents are applied to paper-making to provide paper with resistance to liquid wetting, penetration, and absorption. Rosin with alum is used under acidic conditions, and synthetic sizes such as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) are used for neutral/alkaline paper-making systems. To elucidate the effects of the sizing agents on the natural deterioration of the papers, we measured the quantity of sizing agent in the papers by means of Py-GC.[7–9] Only the papers stored more than 10 years were analyzed because there was a significant reduction in folding endurance in the papers stored more than 15 years, as described above. Figure 4 is a pyrogram of an acidic wood-free paper. The peak retention time at 36–38 min (A) was assigned to the sizing agents.[7–9]

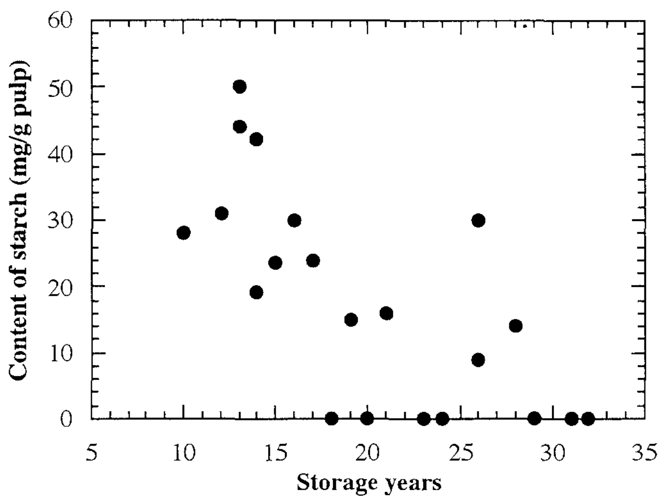


Fig. 7. Relation between storage years and the starch content in the papers stored more than 10 years

The pyrogram of the alkaline paper gave the pattern[7] for ASA whose content was about 0.04 mg/g pulp. As shown in Fig. 5, however, the rosin contents in the acidic and near-neutral papers cover a range of 0.2–4.2 mg/g pulp; a declining trend in the amount of rosin used is apparent. It can be seen from Fig. 6 that the folding endurance decreased with

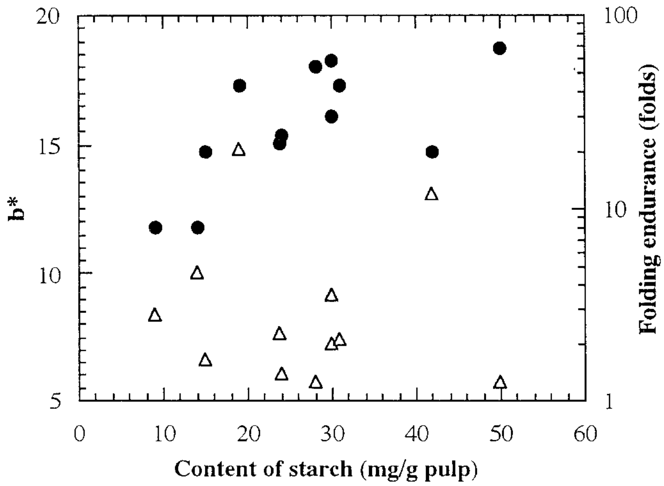


Fig. 8. Relations between the starch content and the b* values and folding endurance of the papers stored more than 10 years. *Triangles*, b*; *circles*, folding endurance

the increase in rosin content in the papers. Because rosin must be used with alum, the larger amount of rosin means that more alum is present in the papers as well, which may be an explanation for the relation. A similar correlation was seen between the rosin content and yellowness of the paper. More yellowness is related to a larger rosin content. These facts indicate that rosin quantity has a deteriorative effect on the permanence of wood-free paper.

Effects of starch on the permanence of paper

Starch is applied to paper-making as a strength agent and a coating binder. Among the 22 paper samples stored for more than 10 years, 7 samples (18–32 of storage years) contained no starch, and the amounts of starch in the other samples changed from 9 to 50 mg/g pulp (Fig. 7). In contrast to the rosin content, there was an increasing trend in the use of starch.

The folding endurance of the papers containing starch increased significantly with the increase in starch content (Fig. 8). However, it is difficult to elucidate the effects of starch on the decrease in folding endurance of the papers during storage because starch has a strengthening effect on the folding endurance of paper. The results in Fig. 8 show that the relation between the starch content and the yellowness of the papers is unclear.

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