Accelerated Ageing Test of Naturally Aged Paper (Part V)
—Comparison of Predicted Degradation Rate Indicators at Room Temperature by Suspension Method and Sealed Tube Method—

Kang Lee*2 and Masamitsu Inaba
Graduate School of Fine Arts, Tokyo University of the Arts*1

Abstract

Research was conducted to clarify the relationship between natural ageing and accelerated ageing of paper using paper naturally aged for 90 to 130 years. In order to estimate the degradation rate of paper at room temperature, sealed tube method was conducted in four temperature conditions between 60 and 90°C. The degradation rate indicators at room temperature were calculated by Arrhenius plots. With regard to the estimated degradation rate indicators of tear and burst indices of paper samples at room temperature, degradation tended to be faster in sealed tube method than in suspension method.

On the other hand, degradation rate of discolouration showed an opposite result. The correlation of the hydrogen ion concentration before accelerated ageing and the estimated degradation rate indicator of tear index at room temperature showed better relationship than those at uniform higher temperature. Thus, in order to evaluate the permanence of papers, it is desirable to obtain room temperature degradation rate through Arrhenius plot.

Keywords: acidic paper, accelerated ageing, sealed tube method, suspension method, degradation rate indicator, arrhenius plot

1. Introduction

We have been evaluating different kinds of accelerated ageing methods, taking paper samples from volumes of the same periodical published between 1878 and 1923, which means that the samples have already aged for periods of 130 to 90 years. In our first paper3, we studied physical and chemical changes in samples under the suspension method at 80 °C. In the second paper2, we did ageing in other temperatures, 90, 70 and 60°C, beside 80°C, four temperatures in total, humidity being controlled at 65% rh, made Arrhenius plots and determined degradation rate indicators at room temperature.

In the third and fourth papers3, 4, physical and chemical changes in samples under the sealed tube method at 80°C were studied.

In this paper, accelerated ageing by the sealed tube method was carried out at 90, 70 and 60°C, beside 80°C. Degradation rate constants at those temperatures were plotted as the Arrhenius plot, and those at room temperature (23°C) were obtained. Gray (1977) studied the
preservation of paper by the sealed tube method, using the Arrhenius equation, and reported his method was better than those based on only one temperature. Though ours was a follow-up study with different samples, the result was compared with that by the suspension method, which had been reported before. Furthermore, hydrogen ion concentration before accelerated ageing, which was a contributing factor for acid hydrolysis, was interested and its effect on paper preservation was discussed at 80°C as well as at room temperature.

2. Experiment

2.1 Samples
We took aged paper samples from a periodical, the Journal of the Chemical Society (abbreviated as JCS) published from 1878 to 1923 in Britain. The journals published in each year were bound in a book and stored, and 11 books were selected out as samples. As in our preceding papers, the samples from 1878 to 1897 that consisted of esparto, cotton rag and hemp pulp were abbreviated as ECL. Those from 1902 to 1913 that consisted of esparto and softwood pulp were abbreviated as ES. Those from 1918 to 1923 that consisted of softwood pulp were abbreviated as S.

2.2 Accelerated ageing test
The sealed tube method (ISO 5630-5:2008) was used. The ageing was done at four different temperatures, 90, 70 and 60°C in addition to 80°C which was used in our third paper.

2.3 Procedure of experiment
Tear index, burst index, colour, quantitative analysis of organic acids, pH, the degree of polymerization and the degree of oxidation were determined as in our preceding paper.

3. Result and Discussion

3.1 Degradation rate constants of physical properties at room temperature under the sealed tube method at 80°C
An Arrhenius plot was made, using degradation rate constants at four different temperatures, 90, 70 and 60°C, and 80°C which was cited from our third paper, and the degradation rate constant at room temperature (23°C) was determined for various properties.

Fig. 1 summarizes tear index values against ageing periods under different temperatures, 90, 80, 70 and 60°C, by the sealed tube method. The tear index decreased as the ageing time prolonged, and the higher was the temperature, the larger was the degree of degradation. In the early stage of degradation, tear index values at each temperature fitted to its own exponential function. As ageing went, the rate of decrease declined and values tended to be off from the line. As we did in our first paper on the suspension method, a degradation rate constant k at a certain temperature was determined using data in the early stage of its degradation which could be well approximated to the equation, \( S = S_0 \exp (-kt) \), \( S_0 \) being the value before accelerated ageing. The same procedure was applied to burst index and the degree of polymerization to determine their degradation rate constants.

Regarding colour, on the other hand, as will be mentioned in 3.2, using \( \Delta E^{*ab} \), initial colour before ageing could be theoretically calculated with \( \Delta L^*, \Delta a^* \) and \( \Delta b^* \), using their discolouration rate constants at room temperature. \( \Delta a^* \), however, was scattered around, and could not be kinetically treated. So, we used \( \Delta L^* \) instead, which was most influential to the ageing of our JCS samples, and discussed initial colour and discolouration rate constant. As in Fig. 2, \( \Delta L^* \) was plotted against the square root of ageing period. As there was a linear approximation, its inclination was regarded as a discolouration rate. Using the equation \( \Delta L^* = -k \sqrt{t} \), the discolouration rate constant k was determined. Data by the sealed tube method behaved like those by the suspension method, and the discolouration rate constant was calculated at every temperature.

Using these degradation rate constants for each physical property of paper, a set of Arrhenius plot was prepared. Fig. 3 is an example of Arrhenius plots for tear index of paper, acceleratory aged in the sealed tube method. Each sample, eleven in total, showed a high linearity between 60 and 90°C, with the coefficient of correlation of more than 0.97. The same high correlation coefficient was obtained with burst index (\( r^2 \) : over 0.96) as well as with the degree of polymerization (\( r^2 \) : more...
than 0.97), aged in the sealed tube method. Colour ($\Delta L^*$) also behaved with high correlation coefficients of more than 0.98. $S_0$, the sealed tube method demonstrated that Arrhenius plots for four physical properties of paper worked as fine as the suspension method did. It was noticed that the inclination of the line was not the same for all samples, even taking one specific property, suggesting that each basic reactions would not be evenly contributing.

3.2 Predicting initial values of physical properties in the sealed tube method

To study ageing at room temperature, we were going to use degradation rate indicators, as in our second paper instead of degradation rate constants at room temperature. To do that, we needed to have an initial value before ageing for each physical property. Our method is depicted in Fig. 4. Using a degradation rate constant at room temperature calculated by Arrhenius plot, current physical value $S_i$ and ageing period $t$ (we assumed that a sample was manufactured at the year when a journal was published), the initial value $S_0$ would be predicted by the equation used to calculate degradation rate constant. Regarding colour, its initial value $L_0^*$ was predicted with the equation $L_0^* = L^* + k \sqrt{t}$ which represented the lightness change during accelerated ageing.

To verify how predicted initial values of physical as well as chemical properties are close to each other in spite of different published years and how predicted values, though present values are different each other, are similar each other as a whole, their values by the sealed tube method and the suspension method (some of the data cited before) are summarized in Figs. 5, 6, 7 and 8.

Regarding tear index, ECL samples, S samples and one published in 1913 which contained a large portion of softwood pulp, the predicted values seemed to be close enough each other except the 1897 sample aged by the suspension method. On the other hand, ES samples which degraded heavily gave considerably high initial values in the sealed tube method. Similar features were found with burst index (Fig. 6). As shown in Fig. 9, which depicted degradation curves against ageing time, a sample having a degradation rate constant of more than a certain value tended to have an extremely high predicted initial value, due to the nature of an exponential function used as a degradation rate equation. Excluding those cases, the predicted initial values, including the degree of polymerization (Fig. 7) and lightness (Fig. 8), were fairly corresponding each other between the sealed tube method and the suspension method, though not the

![Figure 3](image_url) Arrhenius plots against the degradation rate constant (k) of tear index
Fig. 4  Diagram of natural ageing curve of tear index

Fig. 5  Predicted initial tear index ($T_0$)

Fig. 6  Predicted initial burst index ($B_0$)

Fig. 7  Predicted initial viscosity average degree of polymerization ($DP_{v0}$)

Fig. 8  Predicted initial brightness ($L_0^*$)

Fig. 9  Predicted initial tear index ($T_0$) curve of ES samples
same and some exceptional cases there were.

3.3 Predicted degradation rate indicators of physical properties at room temperature

We proposed, in our first paper\textsuperscript{1}, to use degradation rate indicators which were obtained by dividing degradation rate constants with corresponding current values before accelerated ageing instead of using degradation rate constants, which tended to be larger in samples having high initial values. Likewise, as some predicted initial values tended to be too big, we defined predicted degradation rate indicators by dividing the degradation rate constant with its current value before accelerated ageing, not with its predicted initial value. Regarding discolouration, we used discolouration rate constants just as in the case of 80℃.

Degradation rate indicators of physical properties of paper at room temperature were compared each other between the suspension method and the sealed tube method. The case for tear index is shown in Fig. 10. The behaviors of the values were corresponding each other on an individual sample, though their absolute values were different. The sealed tube method gave larger values than the suspension method on all samples. Especially with ES samples, the value by the sealed tube method was twice as large as that by the suspension method. We had reported in our first paper on the study at 80℃\textsuperscript{1} that samples which had already had a large amount of organic acids during normal ageing gave larger degradation rate indicators on their physical properties by accelerated ageing.

We had reasoned that in a closed condition of the sealed tube method, organic acids could be kept in the tube, without dispersion, increased acidity of paper, promoted acid hydrolysis and degraded physical properties. The same phenomenon occurred at room temperature, and samples containing a large amount of organic acids increased degradation rate indicators in a great degree at room temperature. The effect was observed in burst index (Fig. 11) as well which degraded faster in the sealed tube method, compared by degradation rate constants at room temperature.

Discolouration rate constants at room temperature in the suspension method were compared with those of the sealed tube method in Fig. 12. Though their absolute values were different from their counterparts, the way of change in the rate of discolouration behaved similarly to those of physical properties. The suspension method, however, gave larger values than the sealed tube method, which was contrary to the result at 80℃. One hypothesis is that the volume of oxygen available would

\textbf{Fig. 10} Predicted degradation rate indicator of tear index ($I_{cT}$) at room temperature (23℃)

\textbf{Fig. 11} Predicted degradation rate indicator of burst index ($I_{cB}$) at room temperature (23℃)

\textbf{Fig. 12} Predicted discolouration rate ($k_{\Delta L^*}$) at room temperature (23℃)
be influential to discolouration and the suspension method could supply sufficient oxygen while available oxygen volume would become less in the sealed tube method as ageing period goes on. The fact that the discolouration in the sealed tube method at 80°C was large in spite of limited oxygen volume than that in the suspension method seemed to be contradictory to the hypothesis. We believe that the degradation of cellulose by acid hydrolysis would be more enhanced in the sealed tube method of high temperature, and components contributing to discolouration, directly or indirectly, would be produced in a large amount which would be more than compensating limited oxygen volume.

3.4 Relationship between degradation rate indicators and hydrogen ion concentration, the degree of oxidation and organic acid contents at room temperature

Every predicted degradation rate indicator of tear index at room temperature was plotted against its hydrogen ion concentration (Fig. 13 (A)) and the degree of oxidation (Fig. 14 (A)), both before accelerated ageing. The same kind of result in the accelerated ageing at 80°C was also depicted in Fig. 13 (B) and Fig. 14 (B) respectively. It turned out that the relationship that the degradation proceeded faster in samples of higher hydrogen ion concentration was more positively demonstrated with better correlation in room temperature (23°C), as shown in (A), than in accelerated ageing as shown in (B). Regarding the degree of oxidation, the result was not conclusive.

We studied why the relationship between hydrogen ion concentration and degradation rate indicator of tear index was differently dependent of temperatures, 23 and 80°C. Fig. 15 shows Arrhenius plots of tear index for two ES samples, 1902 and 1909. Two regression lines had different inclinations, which meant that they had different
activation energies, 109 kJ/mol for the 1902 sample and 94 kJ/mol for the 1909 sample. It suggested that some specific fundamental reaction differently contributed to its total, depending on temperature. Fig. 16 shows the relationship between organic acid content before accelerated ageing and predicted degradation rate indicator of tear index. The 1902 sample had more amount of organic acid than the 1909 sample. In the graph (B), 80℃, the 1902 sample had a larger degradation rate indicator of tear index than the 1909 sample. The result in the graph (A), 23℃, was contrary. It suggested that some specific fundamental reaction relating to producing organic acids worked more contributory in 80℃ than in 23℃.

4. Conclusion

Using naturally aged paper samples, it was interesting to predict how their ageing would proceed in room temperature. Accelerated ageing was carried out at 90, 70 and 60℃, beside 80℃. The features at room temperature were predicted, and they were compared with those at 80℃. Then, the effect of temperature on the method of evaluating paper preservation was discussed.

With JCS samples of different ages, the initial values of tear and burst indices were predicted. With paper samples which degraded much in the sealed tube method, the predicted initial values turned out to be extremely large, as an exponential function was used as an approximation to predict it. Except them, the predicted initial values in the suspension method were corresponding to those of the sealed tube method, though they were not the same values. Therefore, we used current values before accelerated ageing, instead of predicted initial values, to calculate degradation rate indicators at room temperature. Taking tear index and burst index, the degradation rate indicators at room temperature, predicted by accelerated ageing, were compared between the two methods. The sealed tube method tended to cause degradation faster than the suspension method.

Regarding lightness, on the other hand, the suspension method discoloured faster as shown in its discolouration rate constants. As organic acids produced in a sample were retained in the tube and increased acidity, its physical properties would likely be degraded worse in the sealed tube method. As for discolouration, the volume of oxygen available might be determining. In the suspension method, enough oxygen was supplied, while it was limited in the sealed tube method. One exception was at 80℃ where the sealed tube method discoloured more than the suspension method. We reasoned that acid hydrolysis would be more influential at 80℃. As a method...
of evaluating the preservation of books, the sealed tube method in which organic acids produced inside could be retained and the effect of oxygen outside was less influential would simulate ageing better than the suspension method.

The relationship between the degradation rate indicator of tear index and hydrogen ion concentration before accelerated ageing was better maintained than in a single accelerated ageing. As the effect of acid hydrolysis affecting degradation was dependent of ageing temperature, it would be preferable to calculate degradation rate indicators at room temperature by Arrhenius plot or to test at temperature as close as to room temperature.

References

(Manuscript accepted 30 March, 2017)