Extending the useful life of paper - evaluation of the effect of various preservation actions

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Abstract

Environmental influences, such as temperature, relative humidity and volatile organic compounds in the atmosphere surrounding an artefact often play a key role in its deterioration. Yet the effects of these parameters are seldom quantified, leading to difficulties in the development of suitable preservation programmes. A recent project, PaperTreat, co-funded by the European Commission's 6th Framework Programme, addresses these issues with respect to paper-based cultural heritage.

Using the Arrhenius approach, data on the extension of the useful life of paper, as achieved by Bookkeeper mass deacidification, cool and cold storage, were obtained. It is demonstrated that deacidified paper is 3.5 times more stable than untreated (pH 6.2), while a decrease of storage temperature by 5 °C increases the longevity of paper by a factor of 2.

Introduction

The memory of civilisation is inherently linked to the written word which, written on durable materials, has withstood the test of time. For more than five centuries, paper has been the predominant carrier of information and numerous medieval manuscripts bear witness to its durability. However, increasing demand for paper led to several changes in its production in the 19th century. High quality rag fibres were replaced by inferior wood-derived ones. Acid manufacturing technology was introduced which, due to its simplicity and low cost, continued to be used until the end of the 20th century. Otherwise stable paper rapidly degrades in the presence of acids and its decay is further promoted by poor storage conditions and environmental pollutants. As a result, the amount of degraded paper in libraries, archives and museums is reaching enormous proportions.

In order to prolong the usable time of the vast quantities of original materials, paper collections may be treated with alkalis (i.e. deacidified) and/or stored at lower temperatures. While preservation options are known, the lack of well-controlled comparative studies leaves collection keepers hesitant to use them.

Within the PaperTreat project, several European libraries and archives have joined forces with research laboratories to provide information on the extension of the usable life of paper, as achieved by various preservation options. This is a challenging task. Degradation of paper at room temperature is a slow process and although numerous analytical techniques have been used to study the degradation of paper, none is sensitive enough to observe the processes under ambient conditions. In order to estimate the longevity of paper at room temperature, we thus have to resort to determinations of the degradation rate at higher temperatures.

The rate of chemical reaction at a given temperature can be experimentally determined using viscometry by the Ekenstam equation (eq. 1)[1], where *t* is time and *k* is the rate constant in $mol_{bonds}\ mol_{monomers}^{-1}\ s^{-1}$:

$$\frac{1}{DP_t} - \frac{1}{DP_0} = k \cdot t \qquad \text{(eq. 1)}$$

Interested reader may obtain further information about the Ekenstam equation from readily available works, such as the recently published book 'Ageing and degradation of paper' by Strlič et al. [3]

The rate of degradation under ambient conditions is then obtained by extrapolation of the data to room temperature using the Arrhenius equation (eq. 2), where the rate constant depends on a pre-exponential factor *A*, activation energy E_a, universal gas constant *R* (8.314 J mol^{-1} K^{-1}) and temperature (*T*).

$$k = A \cdot e^{\frac{-E_a}{R \cdot T}} \qquad \text{(eq. 2)}$$

The approach was experimentally confirmed by Zou et al. for a number of slightly acidic bleached cellulose pulps[2]. The authors showed that the rates predicted from (eq. 2) are in comparatively good agreement with the rates of degradation observed during 22 years of natural ageing. In another experiment, the validity of the Arrhenius equation for oxidation of a bleached sulphate pulp

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(pH 7.2) in dry air in a wide temperature interval was demonstrated[3].

This approach is used in the present paper to evaluate and compare the effects of deacidification and storage at lower temperatures on the useful life of paper made from bleached chemical pulp.

Experimental

The paper used in the study was Wifsta Office paper, used previously in a EU co-funded STEP project, CT-90-0100. It is composed of 40% softwood, 60% hardwood fibres, is alum-rosin sized and has a pH of 6.2. The paper was deacidified during the STEP project using the Bookkeeper system (Preservation Technologies, L.P., Cranberry Township PA, USA). The deacidification is based on a liquid-phase process using magnesium oxide (MgO) particles suspended in an organic solvent (perfluoro heptane).

Samples were aged between 90 and 60 °C, at 65% RH, in a Vötsch VC 0020 ageing oven.

Viscometric determinations of the degree of polymerisation (DP) were performed according to the standard procedure[4], using cupriethylenediamine solvent (Carlo Erba). Degree of polymerisation (DP) was calculated from the intrinsic viscosity [η] using the equation 3.[5]

$$DP^{0.85} = 1.1\times[\eta] \qquad \text{(eq. 3)}$$

Results

Degradation rate constants at room temperature, obtained by extrapolation of data from experiments undertaken at higher temperatures, are associated with considerable error. To improve the quality of predictions, accelerated ageing experiments were performed at seven temperatures. In determinations of degradation rate constants (*k*), linear correlation coefficients were between 0.976 and 0.998.

	Factor of stabilization
Storage at 15°C	1.9 ± 0.8
Storage at 5°C	8 ± 4
Deacidification and storage at 20°C	3.3 ± 0.9
Deacidification and storage at 15°C	7 ± 3
Deacidification and storage at 5 °C	30 ± 17

Table 1. Factor of stabilisation due to deacidification with Bookkeeper (BK) and/or storage at lower temperature, with respect to untreated paper, stored at 20 °C.

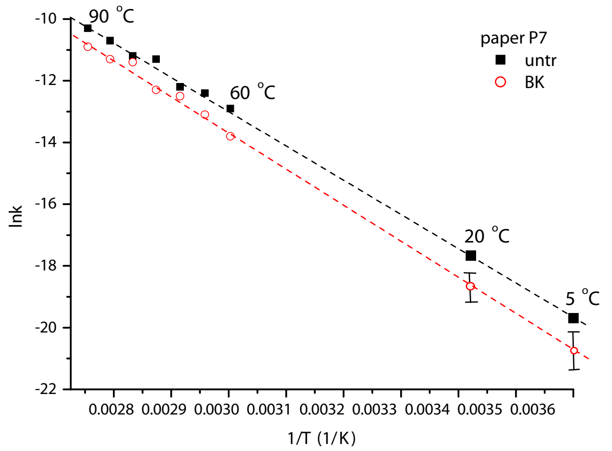

Figure 1. Extrapolation of ln(k)k to 20 °C: ageing of paper P7, either untreated (untr) or deacidified using Bookkeeper (BK) in air at seven temperatures in the interval 60-90 °C. Each of the seven rates of degradation was obtained experimentally by applying the Ekenstam equation to a number of points (DP) determined during an experiment, while the predicted ones (20 and 5 °C) were calculated from the regression parameters. The regression parameters are as follows: untreated; $y = (18 \pm 2) - (1.05 \pm 0.07)\cdot 10^5\cdot x$, $R = 0.989$ BK; $y = (21 \pm 2) - (1.16 \pm 0.08)\cdot 10^5\cdot x$, $R = 0.988$

As observed from Figure 1, a reasonably good correlation was obtained between ln(*k*) and 1/*T*, which allowed us to observe significant differences between predicted degradation rate constants of untreated and of deacidified paper at 20 °C. The ratio of degradation rate constants of deacidified paper and of untreated paper at 20 ºC provides a factor of stabilisation, which enables us to establish the efficiency of deacidification compared with storage at lower temperatures (Table 1). It can be observed that the deacidified paper is 3.3 times more stable than the untreated one (pH 6.2), while a decrease of storage temperature by 5 °C increases the longevity of paper by a factor of 1.9. A combined approach, deacidification and storage at low temperature (5 °C), enhanced the stability of paper by a factor of 30.

Conclusion

Using the Arrhenius approach, predictions of the extension of the useful life of paper, as achieved by mass deacidification, cool and cold storage were obtained. In the following year, the study will be expanded to include several other papers and other mass deacidification techniques. The results will enable development of the most cost-effective preservation strategies for the decaying collections, and thus contribute to safekeeping and long term access to the endangered written cultural heritage.

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References

1 A. Ekenstam: "Über das Verhalten der Cellulose in Mineralsäure-Lösungen, II Mitteil: Kinetisches Studium des Abbaus der Cellulose in Säure-Lösungen", Ber., 69 (1936) 553-559.
2 X. Zou, T. Uesaka, N. Gurnagul: "Prediction of paper permanence by accelerated aging I. Kinetic analysis of the aging process", Cellulose, 3 (1996) 243-267.
3 M. Strlič, J. Kolar, B. Pihlar: "Methodology and analytical techniques in paper stability studies", in: M. Strlič, J. Kolar (eds.), "Ageing and Stabilisation of Paper", National and University Library, Ljubljana, Slovenia, 2005.
4 ISO 5351/1: "Cellulose in dilute solutions-Determination of limiting viscosity number. Part 1: Method in cupri-ethylene-diamine (CED) solution."
5 R. Evans, A. F. A. Wallis, "Comparison of Cellulose Molecular Weights Determined by High Performance Size Exclusion Chromatography and Viscometry", in: 4th Int. Symp. Wood Chem., (1987) 201-205.