Review article

Dose–response functions for historic paper

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ABSTRACT

Paper degradation has been studied extensively over the past few decades from both the conservation and the material science perspectives. This review focuses on the quantifiable impacts of the environment and material composition, from the viewpoint of long-term storage of historic paper-based collections. Therefore, temperature, relative humidity and their variation, and pollution are of major interest while photoinitiated processes are covered only briefly.

New experiments comparing the effects of the most abundant indoor pollutants (NO_2, acetic acid and formaldehyde) and the effects of fluctuating temperature and relative humidity are also presented as part of the discussion. This work highlights the need for revision of the existing dose–response (damage) functions for paper and their further development.

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1. Historic paper

Despite the ubiquity of electronic media, paper is still the most generally readable carrier of information. In heritage institutions, collections of documents of the past are being preserved for posterity. It has been estimated that in a typical Western repository, 70–80% of these documents [1] are likely to be acidic and therefore prone to rapid deterioration, their useful lifetime being about a century, a couple at best. This is in a stark contrast to paper produced before ca. 1850, the lifetime of which may be longer for at least a factor of 10 [1]. For curators of these collections, interventive conservation is an option, although the throughput of even mass treatments [2] is not sufficient to address the scale of the problem and the resources are too limited.

In many cases, preventive conservation is therefore the preferred option. However, environmental managers may struggle with the abundance of literature available on environmental effects on paper degradation and the surprisingly scarce data that is well quantified and relevant not only to the scientist but to the user as well. Unlike a recent comprehensive review of the basic mechanistic and thermodynamic concepts [3], the focus of the present review is to provide an overview of dose response functions, based on which environmental management in paper-based collections could be optimised to minimise degradation while optimising resource use.

The main structural component of paper is cellulose. As a linear homopolymer, it is composed of identical monomers and scission of inter-monomer bonds leads to its degradation [4]. It is well known that apart from temperature, water (humidity) and acidity in paper are important factors in its degradation [5–7]. Acid-catalysed hydrolysis is a major cause of paper strength loss [5,7], although other mechanisms may take place as well, such as oxidation and thermal degradation [7,8], depending on the experimental conditions. The effect of oxygen on the hydrolytic pathway should not be neglected, as differences between accelerated ageing in argon and air [8] and nitrogen and air have been observed [9]. Paper degradation should be regarded as a complex process, in which hydrolysis may be the fastest degradation mechanism [10], but not the only relevant one.

For the end user the most important properties of paper are those related to its usability, such as mechanical strength, and its visual appearance, related to text readability or image contrast. This dictates the choice of analytical techniques to measure changes in paper properties.

Mechanical properties are assessed by tensile strength and zero-span tensile strength measurements, tearing resistance, bursting strength, and folding endurance [11–14] and are affected by fibre strength and interfibre bonding, or both. The relationship between zero-span tensile strength and degree of polymerisation,

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determined by Zou et al. [7] implies that the average chain length of cellulose is one of the key factors for this mechanical property. Conversely, a process that is affected mainly by intermolecular bonding is creep of paper, which occurs when paper is under stress and deforms with time [15].

The scission of intramolecular bonds leads to a decrease in average molecular weight of cellulose, which represents the number of monomers in a cellulose polymer (i.e. DP − degree of polymerisation). It can be measured in several ways, most commonly used are viscometry to obtain the viscometric average DP or the more instrumentally demanding size-exclusion chromatography (SEC) to obtain a distribution of molar masses, number-average and mass-average molar mass [16,17].

To determine the colour of paper the CIE $L^*a^*b^*$ system [18] is mostly used, which takes into account the "standard human eye response". As yellowing often accompanies paper ageing, b^* is often used to evaluate changes in colour.

Among the many agents of deterioration, temperature and relative humidity [15,19−27], light [20,28−32], pollution [20,32−37], biogenic agents [34,38,39] and paper composition [5−7,20,33,34,40−43] have been researched most. Of these, temperature, humidity and pollution are the most important ones for storage in the dark, and are reviewed here.

2. Temperature and relative humidity

In this section, a brief review of the most common concepts used to describe the kinetics and thermodynamics of cellulose degradation are described. In-depth reviews of degradation mechanisms have been published elsewhere [3,44]. The most commonly used approach to studying paper degradation kinetics was established by Ekenstam in 1936 [45]. He derived:

$$kt = \frac{1}{DP} - \frac{1}{DP^0},\tag{1}$$

where DP represents the number of monomers in a chain at time t and DP^0 at the beginning of the experiment. The temperature dependence of degradation rate constants is described by the Arrhenius equation:

$$k = Ae^{\frac{E}{RT}},\tag{2}$$

where A is the frequency factor, E is activation energy, R is the gas constant and T is the absolute temperature [5,43]. The activation energy represents a measure of sensitivity of the degradation rate to temperature changes, while the constant A represents all other experimental parameters, such as humidity, acidity, exposure to pollutants and light, and physical structure of paper [6,43]. It should be noted, thus, that the pre-exponential factor may depend on a number of environmental parameters and material properties.

Calvini and Gorassini [6] suggest including LODP (levelling-off degree of polymerisation), rather than glucose, as the asymptotic limit in kinetic equations:

$$\frac{DP^0}{DP} - 1 = \left(\frac{DP^0}{LODP} - 1\right)\left(1 - e^{-kt}\right),\tag{3}$$

and always performing accelerated degradation experiments at least until LODP is reached [6]. This approach might not be practical for historic documents, as the LODP is lower than the DP value of paper at which it can still be safely used.

The remaining lifetime of paper is a concept involving the decision as to when paper reaches the end of useful lifetime. The relative lifetime was first defined by Shahani et al. as the time required for fold endurance to decrease to an eighth of the initial

value [19]. Another possibility proposed was to calculate the 'time to 50% property loss' ($PL_{50\%}$) [43]. Both give little idea of the actual lifetime, as they are defined relative to the initial paper properties. Lifetime could however be calculated from the Ekenstam equation as the time needed for the DP to decrease to some value, regarded as the lower limit of usability (typically 250−400) [17,46,47]. This was also defined for iron gall ink containing documents [48], where one can calculate the time needed for an ink line to become fragile. The point of risk of failure for ink lines was determined at $DP_i = 400$, where the index i indicates the DP of paper with ink application.

A very well received attempt to describe the relative useful life expectancy of paper-based collections was introduced by Sebera [21]. The isoperm method quantifies the effect of temperature and relative humidity upon the anticipated useful life expectancy of paper-based collections in relative terms (relative to paper permanence at 20 °C, 50% RH) and substitutes rates of deterioration with relative permanence, which is the inverse of the ratio of deterioration rates [21].

Sebera suggested a linear relationship between the rate of degradation and RH, while it is in fact known that the proportionality is exponential for acidic papers and hyperbolic for alkaline papers with the maximum rate at about 60% RH [49]. Sebera describes temperature dependence using the Arrhenius equation and employing relative permanence:

$$\frac{P_2}{P_1} = \frac{r_1}{r_2} = \frac{RH_1}{RH_2}\frac{T_1}{T_2}e^{\frac{E}{R}(\frac{1}{T_1} - \frac{1}{T_2})}.\tag{4}$$

where P represents permanence and r deterioration rate, E is the energy of activation in J/mol, R is the gas constant and T is in K.

The isoperm is constructed so that points at which the permanence of paper is equal are linked: if RH is increased, the T needs to be reduced by exactly the right amount to keep the deterioration rate constant. A line of constant permanence ('isopermanence') is defined as the isoperm [21]. According to the author the concept is not supposed to be applied to extreme conditions, such as sub-zero temperatures [21], and it is equally not valid at the extremes of RH, i.e. above 80% and below 20%.

Isoperms were recently revised by Strang and Grattan [22], arguing that it is the concentration of water in the cell wall rather than the concentration of water vapour in the atmosphere (the RH), which has a direct effect on the rate of degradation of paper. To account for the non-linear relationship between RH and moisture content they introduced the Guggenheim−Anderson−deBoer equation (GAB), which describes paper moisture sorption.

However, other research shows an exponential dependence of the rate of degradation on relative humidity, at least at elevated temperatures [49]. Additionally, there is evidence that the degradation of acidic papers depends on pH and possibly RH, differently to alkaline papers. If this is so, then isoperms are in need of revision and need to reflect differences in paper composition.

Moisture in paper not only represents a reactant, but also the reaction medium for hydrolysis and is also an additional source of radicals (e.g. OH·) [20], so the degradation is generally slower in dry environments [50]. Unfortunately, low moisture content of paper leads to decreased flexibility which can lead to physical damage during handling, as brittleness is increased [23,24]. The reason is that water forms intermolecular H-bonds with cellulose and acts as a plasticizer, which increases material flexibility [51]. Stiffening of the polymer structure due to drying or water removal is referred to as 'hornification' [52,53]. Hornification has frequently been associated with the formation of irreversible intra-fibre hydrogen bonding [53], but has recently been described as the particular case of lactone bridge formation in lignocellulosic materials [52]. On the other hand, paper loses elasticity under high humidity conditions