



Lack of evidence for an autocatalytic point in the degradation of cellulose acetate



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ABSTRACT

The evidence for the existence of a critical concentration of acetic acid, or autocatalytic point, at which deacetylation of cellulose triacetate film accelerates markedly, is re-examined. It is concluded that in fact deacetylation is autocatalytic at all concentrations of acid, and also that there is no evidence for the existence of an induction period.

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1. Introduction

The slow deacetylation of cellulose triacetate film to give the unmistakable smell of acetic acid is very familiar to those who work in libraries and photographic archives. This hydrolysis is accelerated by temperature and relative humidity and is catalysed by acetic acid. Since acetic acid is one of the products of the reaction it may be described as an autocatalytic reaction. However, some believe that there is a critical or autocatalytic point at which the reaction accelerates markedly, so that as long as the concentration of acetic acid is kept below this critical point the reaction will be slow and the film collection will be reasonably safe.

Conservators will be familiar with illustrations such as Fig. 1, from the Image Permanence Institute's User's Guide for A-D Strips [1]. It shows that free acidity (concentration of hydrogen ions, used as a measure of the amount of deterioration) increases slowly until 0.5 ml of 0.1 M sodium hydroxide is required to neutralise the acid liberated by 1 g of film, i.e. $[\text{H}_3\text{O}^+] = 5 \times 10^{-5} \text{ mol g}^{-1}$. Above this critical or autocatalytic point, the rate of deterioration appears to increase dramatically.

It is interesting to consider the evidence which supports the existence of an autocatalytic point. The degradation of cellulose acetate has been studied by many authors over the years, e.g. Refs. [2–4]. The body of evidence that is most familiar to conservators

comes from an extensive series of tests carried out in the 1990s by the Image Permanence Institute (IPI) on the rate of degradation of cellulose ester film bases [5–10]. The measurements included the decrease in viscosity of a solution of the film, which is related to the degree of polymerisation, and the increase in acidity, which is related to the hydrolysis of the ester bonds, does not affect the degree of polymerisation, and is independent of it. The IPI researchers also measured various mechanical properties of the film such as Young's modulus and breaking stress. Although these are clearly affected by the degree of polymerisation and the degree of deacetylation, there is not necessarily a linear relationship between the molecular properties and the mechanical properties, nor is it possible to say how much chain breaking and deacetylation each contribute to the loss of mechanical properties.

In the hydrolysis experiments, the IPI researchers chose an arbitrary end-point of acidity equivalent to $5 \times 10^{-5} \text{ mol of H}_3\text{O}^+$ per gram of cellulose triacetate film base. This corresponds to a degree of hydrolysis of 1.44% of all the ester bonds in each polymer molecule, assuming that there are three acetyl groups per glucose residue and that each one is identical [see Appendix]. Most of the results are presented in terms of the time taken to reach this degree of hydrolysis, rather than the rate of reaction. However, Fig. 7 of Ref. [5] (Fig. 2), shows how the hydrogen ion concentration of acetate film stored at different temperatures increases over time, from which the rate of reaction can be calculated. It can be seen that at 70 °C, the rate continues to increase over time, while at 80 °C and higher temperatures, the rate increases initially but then starts to decrease. As the authors state, this is probably caused by loss of

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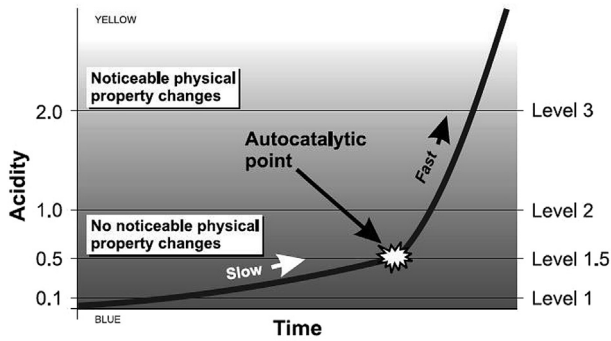


Fig. 1. The autocatalytic point (from Fig. 4 of [1]). Reproduced by kind permission of the Image Permanence Institute.

acetic acid at higher temperatures from the aluminium foil-polyethylene bags used to contain the specimens.

2. The kinetics of autocatalytic reactions

If a reaction $A \rightarrow B$ is catalysed by the product B, the equation for the rate of formation of B is:

$$d[B]/dt = k[A][B]$$

where k is the rate constant, $[A]$ is the concentration of the reactant A (cellulose triacetate in this case) and $[B]$ is the concentration of the product B (hydrogen ions in this case). In the early stages of the reaction, the concentration of cellulose triacetate is much greater than the concentration of hydrogen ions and hardly decreases at all, so $[A]$ can be treated as a constant. The rate equation can then be easily solved:

$$d[B]/[B] = k[A].dt$$

$$\ln[B] = k[A].t \text{ or } [B] = \exp(k[A]t) \tag{1}$$

so a plot of $\ln[B]$ against time should be linear.

For a more accurate description of the progress of the reaction at longer times, we should write:

$$[A]_t = [A]_0 - x \text{ and } [B]_t = [B]_0 + x$$

where $[A]_0$ and $[B]_0$ are the concentrations of A and B at $t = 0$ and x is the extent of the reaction.

The rate equation is then:

$$dx/dt = k([A]_0 - x)([B]_0 + x)$$

The solution of this differential equation is [11]:

$$x = \frac{[A]_0[B]_0(\exp(kt[A]_0 + [B]_0)) - 1}{[A]_0 + [B]_0 \exp(\dots)} \tag{2}$$

If $[A]_0 \gg [B]_0$ then $x = [B]_0 \cdot \exp(k[A]_0 t)$ as in the simple derivation (Equation (1)), but a plot of $\ln x$ vs. t will deviate from linearity at large t .

The IPI Storage Guide for Acetate Film [1] describes the time before the hydrolysis of cellulose triacetate accelerates markedly as being an “induction period”. This is confusing, because the term “induction period” properly applies to the interval seen in certain multi-stage reactions, such as $A \rightarrow B \rightarrow C$, where an intermediate product B is formed before the final product C appears. If the rate of the reaction $A \rightarrow B$ is greater than for the reaction $B \rightarrow C$, the intermediate B accumulates before C is formed and a delay or induction period is observed.

$k_1 \ k_2$

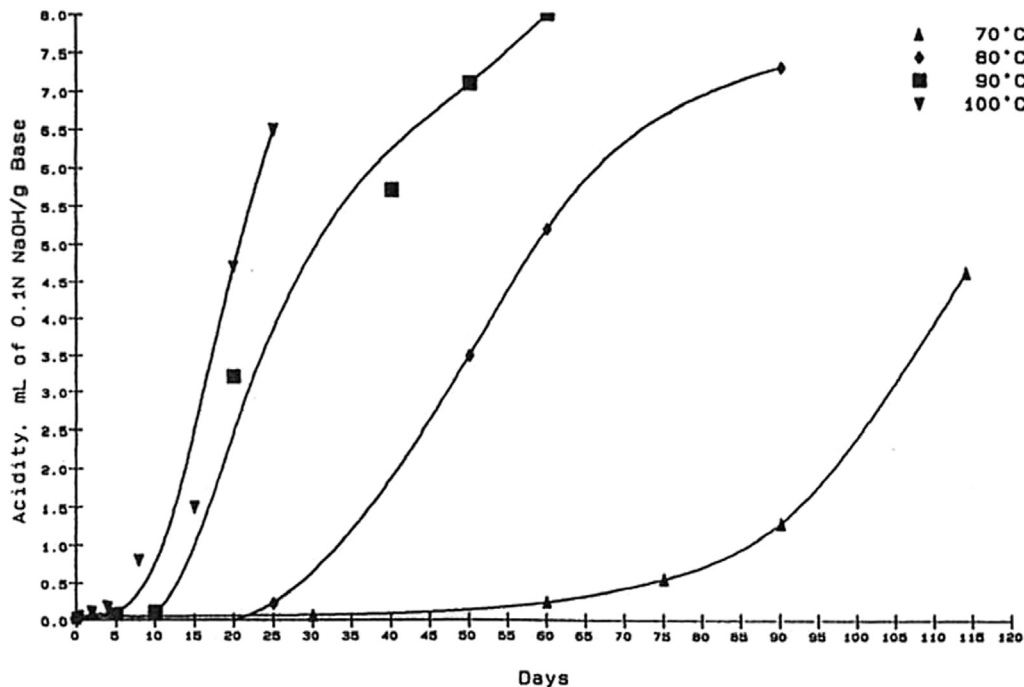


Fig. 2. The rate of increase of acidity of cellulose triacetate film (from Fig. 7 of [5]). Reproduced by kind permission of the Society of Motion Picture and Television Engineers. ©SMPTE 1992.

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