

## TECHNICAL NOTE

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### Comments on the Accelerated Aging of Ink

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**ABSTRACT:** Several conditions are determined for relating aging curves of the same ink on the same paper obtained at two different temperatures.

**KEYWORDS:** questioned documents, inks, papers, aging, ink aging, paper aging, accelerated aging, solvent extraction, process kinetics, Arrhenius equation

Questions on the natural and artificial (accelerated) aging of documents are becoming more frequent in courts of law, particularly in cases where no backdating fraud is detected by traditional ink and paper examinations. Often cited is the extensive work done in the area of paper aging which includes studies on the causes and prevention of aging and the relation between artificial and natural aging [1, 2]. Because of such vast research, there are now empirical equations describing the effects of temperature on paper aging and several formal analytical treatments for measuring paper aging.

Studies on ink aging are much more limited [3, 4]. The most recent advances include the use of analytical tools to quantify the aging process—natural and artificial. However, little to no work has been done in establishing relationships between artificial and natural ink aging. This paper shows that much of the formal treatment that applies for paper also applies for ink. A key difference is that the aging of ink on paper involves the interrelated aging of the ink and of the paper.

#### The Ink Aging Process

The changes in the physical and chemical properties of an ink as it ages on paper are amenable to analytical treatment. Some of the *aging properties* recently evaluated [4] include the evaporation of volatile solvents, the change of extraction efficiencies of dyes into weak solvents, and the change in the ink's infrared (IR) spectral characteristics.

Each of these aging properties can be measured by one or more parameters which are called *aging parameters*. These should be independent of the amount of ink sampled (mass invariant measurements). The plot of these parameters versus age produces an *aging curve*.

An aging curve can be obtained under normal or elevated temperature conditions. The question then is to determine if the two curves can be related so that *one curve can predict*

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*the other.* In this paper, conditions under which these two curves can be so related are determined. These conditions are based on work involving the accelerated aging of paper [1,2]. Since accelerated aging was used in studying extraction efficiencies of inks [3], this example will be used for illustration.

### Ink Aging Parameters

The ink aging observation most studied to date involves the extraction efficiency of ink into a given weak solvent [3,4]. This efficiency can be characterized by the rate and extent of extraction. There are two parameters that characterize the rates of extraction and one that measures extents of extractions. All three parameters are independent on the amount of ink sampled (mass invariant).

The two parameters that characterize the rates of extraction are:

The  $R$  ratio—the amount of ink extracted after  $t_1$  min as a fraction of that extractable from the paper after a longer period,  $t_f$  min, of extraction. The time  $t_f$  is any time after  $t_1$ , but the normal choice is that time after which no more ink can be extracted from the paper.  $R$  normally decreases with age as expected; however, increases have been observed.

The  $L$ th extraction time  $t_L$ —the time it takes to extract  $L \times 100\%$  ( $0 < L < 1$ ) of the ink extractable from the paper after  $t_f$  min of extraction. It normally increases with age as expected; however, decreases have been observed. The time  $t_L$  is really an inverse, rather than direct, measure of the rate of extraction. The inverse of this time, that is,  $1/t_L$ , is a direct probe of the rate of extraction; it normally decreases with age as expected.

The extent of extraction can be measured by the following parameter: the percent of extraction  $P$ —the percent of the total amount of ink deposited on the paper that can be extracted after  $t_f$  min. It decreases with age and increases have not been observed.  $P$  can be obtained by the sequential solvent extraction procedure where a strong second solvent extracts what remains in the residue after the first extraction. The total amount of ink deposited is the sum of these two extracts. If one tries to obtain approximately the same amount of sample in a comparative examination of inks, the concentration of the first extract would be proportional to  $P$  because the total amount of ink deposited is presumably kept constant [4].

The anomalies observed with the two rate characterizing parameters  $R$  and  $t_L$  can be due to the fact that the extracts are not of a single dye but of several dyes which may have widely different extraction efficiencies. Separating the dyes and measuring their extraction efficiencies has been suggested as a way to avoid these unexpected (reversed) trends [3,4].

Note that if *the extraction curve is exponential* and its rate constant is denoted by  $\beta$ , the two rate characterizing parameters,  $R$  and  $t_L$ , are related to  $\beta$  by

$$\beta = \frac{-\ln(1-L)}{t_L} = \frac{-\ln(1-R)}{t_1} \quad (1)$$

In obtaining  $R$  and  $t_L$ ,  $t_f$  is taken to be the time after which no more ink can be extracted from the paper. For  $t_f'$  less than  $t_f$ ,  $L$  and  $R$  in Eq 1 are multiplied (attenuated) by an  $R$  ratio with  $t_1 = t_f'$  and  $t_f$  as above.

### Ink Aging Curves

Consider the case where lines from a single formula of ink have been placed periodically on a piece of paper over a given period of time and this document had been stored during this time under controlled environmental conditions (for example, under constant temperature, humidity, and light conditions). The extraction efficiencies of the inks should increase with the order in which they were placed on the document.

Each of the aging parameters studied so far is found experimentally to change monotonically with age and levels off to a horizontal asymptote. In this study, only aging parameters that *decrease* monotonically with age shall be considered. Those parameters that increase monotonically can always be arranged to decrease monotonically with age.

Let  $f(T; \theta)$  represent an aging curve of a given aging parameter for inks aged at a constant temperature  $\theta$ . This can be expressed analytically as

$$f(T; \theta) = [f(0; \theta) - f(\infty; \theta)] Y(T; \theta) + f(\infty; \theta) \quad (2)$$

where  $f(0; \theta)$  is the aging of ink freshly placed on paper,

$$Y(T; \theta) = \begin{array}{l} \text{a function that is 1 at } T = 0, \\ \text{decreases monotonically with age} \\ \text{and levels off to a 0 asymptote} \end{array} \quad (3)$$

and

$$f(\infty; \theta) = \begin{array}{l} \text{the horizontal asymptote or the} \\ \text{value to which } f(T; \theta) \text{ levels} \\ \text{off with aging} \end{array} \quad (4)$$

$Y(T; \theta)$  shall be referred to as the *core aging curve*. It, like  $f(T; \theta)$ , is dependent on the ink formula, the paper on which the ink is placed, and on the method of analysis used.

Some properties of  $f(T; \theta)$  and  $Y(T; \theta)$  are:

1. Two aging curves obtained at two different temperatures begin at the same point and may level off to the same asymptote. They have the same beginning value since aging has not occurred here. Consequently,  $f(0; \theta)$  is independent of temperature.

2. When the two aging curves level off to the same asymptote, the corresponding temperatures are said to be within the *acceptable temperature range*. Consequently, within this range  $f(\infty; \theta)$  is constant and thus independent of temperature.

3. When aging parameters obtained at different temperatures disappear with age, for example, those that measure the evaporation of volatile components, then  $f(\infty; \theta) = 0$  for all temperatures.

4. Within the acceptable temperature range, the temperature derivative of Eq 2 shows that the derivatives of two curves are proportional. (Here recall that the temperature derivative of  $f(\infty; \theta)$  is zero). Consequently,  $Y(T; \theta)$  represents the aging characteristics of  $f(T; \theta)$ .

5. Within the acceptable temperature range, the core aging curve is thus a normalized representation of the aging curve; in this form it is simpler to use and more manageable.

The size of the acceptable temperature range can only be determined experimentally. Each temperature is tested by checking the asymptote of the aging parameter at that temperature. Within this range, the changes in paper caused by paper aging are not sufficient to affect how ink aging levels off.

## Scaling and Linearization

### Scaling

Let  $\theta$  be a natural aging temperature and  $\theta'$  be an accelerated aging temperature. The corresponding core aging curves  $Y(T; \theta)$  and  $Y(T; \theta')$  are said to be *equivalent by scaling* if

they become coincident by changing (expanding or contracting) the aging scale of one. That is, there exists a scaling factor  $n(\theta'; \theta)$  such that when

$$T' = n(\theta'; \theta)T \quad (5)$$

one has

$$Y(T; \theta') = Y(T'; \theta) \quad (6)$$

Note that  $T$  and  $T'$  must be in the same units which makes  $n(\theta'; \theta) = T'/T$  unitless. However, it can be expressed in terms of ratios of different time units when conversion factors are used. For example,  $n(\theta'; \theta) = 57\,600$  can be written as  $[(120 \text{ days}) \times (24 \text{ h/day}) \times (60 \text{ min/h})]/3 \text{ min}$  which means that  $T' = 120$  days of natural aging at some normal room temperature (for example,  $\theta = 22^\circ\text{C}$ ) is equivalent to  $T = 3$  min of artificial aging at some elevated temperature (for example,  $\theta' = 100^\circ\text{C}$ ).

Until proven otherwise, it shall be assumed that the scaling factor is dependent on the formula of ink and the paper just as  $f(T; \theta)$  and  $Y(T; \theta)$  are. It shall be *conjectured* that the equivalence is valid for all the aging parameters that measure aspects of the same aging property.

For the extraction efficiencies, the efficiencies for extracting the total ink (unseparated dyes) can be widely different, as has been observed [3] from the corresponding efficiencies for extracting individual dyes. Since the efficiency of the total ink is not necessarily related to the sum of the individual dye efficiencies, it is *conjectured* that these efficiencies (of unseparated and individual dyes) should perhaps be treated as two separate aging properties even though they both involve extraction efficiencies.

### Linearization

According to Eq 3, the core function resembles an exponential function. In the special case where the core function is *exponential* with rate constant  $k(\theta)$ ,

$$Y(T; \theta) = \exp[-k(\theta)T] \quad (7)$$

then the plot of  $\ln Y$  versus  $T$  is linear with slope  $-k(\theta)$ . For this case, the aging process is said to follow first order "property kinetics" as opposed to chemical kinetics [2]. When this holds, scaling is guaranteed and is given by

$$n(\theta'; \theta) = k(\theta')/k(\theta) \quad (8)$$

If  $Y(T; \theta)$  is *not exponential*, then the function that linearizes  $Y(T; \theta)$  is not the natural logarithmic function but one that can do a similar function: it takes the graph of  $Y(T; \theta)$ , brings it down to begin at the origin, and "stretches" the ordinate in the negative direction so that the leveling off behavior becomes linear with slope  $-m(\theta)$ ,

$$\text{Linearization of } Y(T; \theta) = -m(\theta)T \quad (9)$$

When the linearization here is the logarithmic function,  $\ln$ , the slope  $m(\theta)$  is represented by  $k(\theta)$ .

If two core aging curves can be made coincident by scaling, then, by Eqs 5 and 6, they can be linearized by the *same linearizing function*, and furthermore, the ratio of the slopes of the two linearized graphs becomes the scaling factor according to the equation

$$n(\theta'; \theta) = m(\theta')/m(\theta) \quad (10)$$

### Activation Energy

Since an increase in temperature accelerates aging, the slope  $m(\theta)$  increases with increasing temperature. Just how this increases is found in the thermodynamic treatment of chemical kinetics.

If the plot of  $\ln m(\theta)$  versus  $1/\hat{\theta}$  ( $\hat{\theta}$  = absolute temperature) is linear, then the Arrhenius equation holds,

$$m(\theta) = \text{constant} \times \exp[-E^\ddagger/R\hat{\theta}] \quad (11)$$

where  $E^\ddagger$  is the activation energy and  $-E^\ddagger/R$  is the slope of the plot ( $R$  = gas constant). In this case, the scaling factor  $n(\theta'; \theta)$  has an analytical form and can thus be predicted from  $E^\ddagger$ .

$$n(\theta'; \theta) = \exp\left[(E^\ddagger/R)\left(\frac{1}{\hat{\theta}} - \frac{1}{\hat{\theta}'}\right)\right] \quad (12)$$

This shows that besides the two temperatures  $\theta'$  and  $\theta$ ,  $n(\theta'; \theta)$  is solely dependent on  $E^\ddagger$ . Any dependence on the ink formula, paper, and method of analysis used is incorporated into  $E^\ddagger$ . Since  $E^\ddagger$  is the activation energy for the aging process corresponding to a given aging property, there is support for the conjecture stated above that  $n(\theta'; \theta)$  is independent of the various parameters that measure different aspects of the same aging property. The actual proof of the conjecture, which theoretically appears to be valid, can only be made by experimental evidence. Currently, this has not been done.

### Experimental Results

The aging of Fisher pressurized black ballpoint ink on Nashua (photocopy) paper has been studied and reported [3]. Various experiments were performed to test several major theoretical hypotheses of ink aging. Since the Fisher ink contains a fluorescent rhodamine dye among its dye components, one experiment measured, using fluorescence spectroscopy, the percent of extraction of this dye as it extracts into aqueous methanol solutions of increasing strength. The sequential solvent extraction procedure, with pure methanol as the second (strong) solvent, was used to obtain the percents of extraction. Percent extraction aging curves were obtained for inks artificially aged at 100°C.

For inks of the same formula naturally aged at 25°C on the same paper, several points of the percent extraction curve were obtained, including one around the asymptote. Here, the rhodamine dye was extracted into a 25% methanol solution. In comparing these few points with those from the artificial aging curve, attempts were made to determine if scaling was possible to make them equivalent.

The aging curves could not be linearized using the logarithmic function and so Eqs 7 and 8 could not be used to obtain the scaling factor. A linearizing function common to both curves was found by trial and error. The asymptotes coincided so the two temperatures were in the acceptable range. The resulting scaling factor indicates that 90 days (3 months) of natural aging at 25°C is equivalent to 4 min of artificially aging at 100°C. The accuracy of the scaling factor may suffer because of the limited number of points available for comparison.

The scaling factor obtained applies at least to the Fisher ink on the Nashua paper and for the method used for measuring the percent extraction. If the conjectures stated above are valid, this same scaling factor should result from the other parameters, that is, the two rate parameters that measure other aspects of the same aging property, namely, the extraction efficiency of the single dye rhodamine.

## Discussion and Conclusions

Recalling that throughout this paper aging curves refer to inks of the same formula on the same paper, the following has been established.

1. All aging curves begin at the same point.
2. If two aging curves obtained at two different selected temperatures have a common asymptote, that is, the temperatures are within the acceptable range, then their normalized form, the core aging curves, can be substituted for them.
3. If the corresponding core aging curves can be made coincident by using a scaling factor, then there is a single linearizing function that linearizes these curves.

The algebraic properties of the linearized core aging curves provide some useful rules for obtaining scaling factors.

1. Begin by determining the two extreme values of an aging curve,  $f(0; \theta)$  and  $f(\infty; \theta)$ . This serves to convert values from the aging curve to the core aging curve, and vice versa, by use of Eq 2.

2. A single point on an aging curve—the value of the aging parameter  $f(T; \theta)$  at a given age  $T$ —determines the slope  $m(\theta)$  in Eq 9. This is done by first using Eq 2 to convert the value to a core aging value

$$f(T; \theta) \rightarrow Y(T; \theta) = \frac{f(T; \theta) - f(\infty; \theta)}{f(0; \theta) - f(\infty; \theta)} \quad (13)$$

and then applying the linearizing function and Eq 9.

3. Consequently, only one point from each of the two aging curves is needed to obtain the scaling factor. This follows since the two points identify the slopes needed for computing the scaling factor according to Eq 10.

4. An obvious consequence results from Eqs 5 and 6. If the two points have the same value of the aging parameter (ordinate), then the scaling factor becomes the ratio of the corresponding ages,  $T'/T$  as in Eq 5.

The discussion so far involves aging curves obtained at two different selected temperatures and what can be done if they are linearized by a single linearizing function. If ink aging is truly a kinetic process, this same linearizing function should linearize aging curves obtained at any temperature and not only the selected two. Arney and Chapelaine [2] discuss the concept of "property kinetics" as it applies to paper and how it is related to chemical kinetics. Much of what they say is applicable to inks and this lends support to a single function linearizing aging curves of different temperatures in general.

In the case where the Arrhenius equation holds, Eq 11, the rate of change of the linearized core aging curve with respect to temperature, is given by

$$\frac{d[\text{linearized } Y(T; \theta)]}{d\theta} = - \frac{E^\ddagger}{R\theta^2} \times T \times m(\theta) \quad (14)$$

This shows that the rate is negative and as a negative rate it increases as the absolute temperature increases. Also this increase becomes more gradual as the activation energy increases. Since most kinetic processes usually follow the Arrhenius equation, it is conjectured that the Arrhenius case is a first approximation to "property kinetics," that is, "property kinetic" processes tend to follow the Arrhenius equation. If this is valid—and only experimental results can verify this—the conjecture proposed earlier regarding the existence of a common scaling factor for parameters measuring several aspects of a given aging property is further supported.

Since this work borrowed ideas from the extensive work that has been done in paper aging, it is proper to mention some of their results. The folding endurance test is one of several tests of physical properties that is affected by paper aging. Aging of paper can be measured by the folding enduring test. According to Roberson [1], the plot of the  $\ln$  of folding endurance of book paper versus age is linear (folding endurance is exponential—see Eq 7), and the Arrhenius relation also holds with  $E^* = 25.3$  kcal/mole (see Eq 11). The scaling factor of 8247 translated into 3 days of aging paper at 100°C is equivalent to 68 years of natural aging at 22°C. This equivalence is true at least for this paper and this test. Other tests that have different scaling factors are tensile strength and reflectance or brightness (reduced by “yellowing”) [2].

A closing remark should be made regarding relating aging curves obtained under conditions other than different temperatures. The temperature variable  $\theta$  can be replaced by other factors such as paper or ink formula which so far have been kept constant. When one of these is chosen as the variable, the others have to be kept constant to retain a two-variable aging function. One can then develop criteria, in a manner similar to that used in this paper, to determine scaling factors that relate aging curves for inks on different paper or inks of different formula. In this case, unlike the case of temperature differences, the extreme values,  $f(0; \theta)$  and  $f(\infty; \theta)$ , are more likely to be different for different paper or ink formula. Recall also that these variables are more difficult to change continuously as temperature is. These determinations serve in the dating of inks found on different paper [3] or even of inks of different formulas.

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