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DIFFICULTIES IN THE APPLICATION OF THE ARRHENIUS MODEL TO PREDICT THERMAL PRINTING LIFETIME

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ABSTRACT

The Arrhenius model is widely used in accelerated aging studies to predict the durability of the properties of both paper and ink. In other words, this model intends to simulate the real-time aging. The Arrhenius model assumes that the rate of chemical reactions (k) depends exclusively on the temperature at which they occur, being expected a linear relation between the reaction rate and the inverse of the absolute temperature (T). This study demonstrates that the application of this model should not be done indiscriminately, and that there are several restrictions in some cases. In this study, the Arrhenius model was used to predict the durability of printing made with thermal transfer ribbon and on thermal sensitive paper. The parameter used to monitor the accelerated aging was the optical density of the printed areas. In the case of the printing made with thermal transfer ribbon, it was observed, at high temperatures, the degradation of the material that comes from the ribbon. This degradation occurs due to side reactions that are not observed under natural conditions of aging. In the case of printing on thermal sensitive paper, the Arrhenius model was not applicable as well, due to the restriction to high temperatures. Two indispensable factors for performing accelerated aging tests using Arrhenius model were confirmed in this study: the choice of test temperatures and the definition of acceptable yield loss for the focused property.

Keywords: Accelerated aging, Arrhenius model, thermal printing, thermal sensitive paper

INTRODUCTION

Accelerated aging tests have been used to simulate, in a short period of time, physical or chemical changes that naturally occur in a material, enabling the prediction of the material lifetime or its behavior in relation to a defined parameter (Zou *et al.*, 1996a). These tests are based on exposure of the object of study to high levels of heat, radiation, humidity, voltage, pressure and other actions (Kececioglu and Jacks, 1984).

There are many theoretical models constructed to explain the behavior of a material from the results obtained in accelerated aging tests, such as the Arrhenius, the Eyring and the Inverse Power Law models (Kececioglu and Jacks, 1984). The choice of the most appropriate model depends on the studied material and on the stress condition to be employed in the test. In the case of paper, it is common to use the temperature as a stress factor. Thus, based on the temperature, the Arrhenius model is the recommended one (Zou *et al.*, 1996a; Pork, 2000; Zou *et al.*, 1996b).

The Arrhenius model was proposed in the 1890s by Svante Arrhenius. This model assumes that the rate of chemical reactions (k) is inversely proportional to the absolute temperature at which the reaction occurs, as shown in **Equation 1** (Kececioglu and Jacks, 1984; ISO 18924, 2000),

$$k = A\,exp\left(\frac{-E_a}{RT}\right) \quad \text{or} \quad \log k = \log A + \left(\frac{-E_a}{2.3RT}\right) \qquad \textbf{Equation 1}$$

where **k** is the reaction rate, **A** is the pre-exponential factor (a constant that depends on the characteristics of the reaction), $\mathbf{E_a}$ is the activation energy in $J.mol^{-1}$, **R** is the universal gas constant (8.314 J/mol.K), **T** is the absolute temperature in Kelvin (Celina *et al.*, 2005).

From Equation 1**,** it is possible to obtain a graphic of the logarithm of the reaction rate (k) or of the degradation time (1/k) *versus* the inverse of temperature (1/T) that is known as the Arrhenius plot (log k x 1/T). If a linear relation is obtained, the line can be extrapolated to lower temperatures, thus obtaining an estimative of the real time required for the variation observed in high temperature to occur in the lower temperature, usually room temperature (ISO 18924, 2000).

To build up an Arrhenius plot, it is necessary to perform the accelerated aging tests at least at three different temperatures. These temperatures are defined by who is performing the test, who also should consider the characteristics of the material being tested. Whenever possible, high temperatures should be chosen to reduce the time required to complete the essay. However, at very high temperatures, degradation side reactions may occur, affecting the final results (such as causing deviation of the Arrhenius plot from

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linearity) or even preventing to get to them (ISO 18924, 2000). It is recommended to investigate the correlation between the results of accelerated aging tests and the results of natural or real aging (ISO 18924, 2000; ASTM F 1980-07, 2009).

In this study, accelerated aging was applied to papers printed by thermal processes in two different ways: using thermal transfer ribbon and using thermosensitive paper. High temperature was used as stress factor; optical density of the printed areas as the measured parameter, and Arrhenius model to predict the lifetime of printed areas.

MATERIALS AND METHODS

Samples

The paper printed with a thermal transfer ribbon ("Paper A") was an 80g/m^2 coated paper. The thermal transfer ribbon was an ink ribbon with a thermal transfer layer, comprising a colored layer containing a wax-like substance as a main component and a thermoplastic adhesive layer. In the thermal printer, portions of this layer were selectively softened or melted and transferred to the paper surface. The printed area used for the measurements had 1cm x 1cm (**Figure 1**).

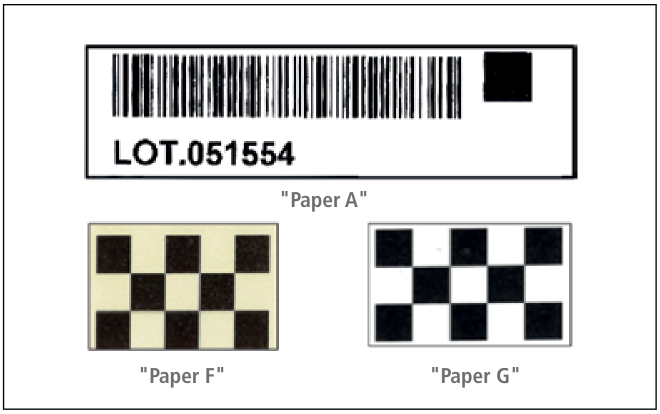

Figure 1. Test pieces of papers A, F and G

The thermosensitive paper was a coated paper, in which the coating composition comprised a thermosensitive dye. In the thermal printer, the thermal head was heated by an electrical pulse current, and the heat was transferred to the thermosensitive paper. During heating, the thermosensitive paper and the thermal head are kept in contact with each other, and some of the agents of the thermosensitive composition are in molten state. These molten agents solidify with the removal of the thermal head from the thermosensitive paper and, as a result, the printing appears. Two thermosensitive papers available in the market were used. They were denominated "Paper F" and "Paper G". In both cases, areas of 1cm x 1cm were printed (Figure 1) using the thermal printer Atlantek model 400, operating with energy density of 13.2 mJ/mm^2. For "Paper F", areas were also printed using nine different energy densities: (3.2; 4.6; 6.1; 7.5; 8.9; 10.3; 11.7; 14.6 and 16.0) mJ/mm^2 (Atlantek, 2003).

Aging

The accelerated aging tests were carried out according to the technical standard ISO 18924:2000: Imaging materials – Test method for Arrhenius-type predictions (ISO 18924, 2000).

Test pieces of the printed papers were submitted to dry heat in ovens. The temperatures and periods of exposure are shown in **Table 1** for the paper printed with thermal transfer ribbon, and **Table 2** for the paper printed with thermal sensitive dye.

Table 1. Accelerated aging conditions - thermal transfer ribbon

Temperature (°C)	Time (hours)
40 ± 5	1430
60 ± 2	1360
80 ± 2	578
100 ± 2	49

Table 2. Accelerated aging conditions - thermosensitive paper

Temperature (°C)	Time (hours)
40 ± 2	672
50 ± 2	672
60 ± 2	1375

For black and white printing, the measurement parameter is usually the optical density (OD). So, in this case, the evaluation of the aging of the printed areas was done by this measurement.

The optical density (OD) was determined according to the technical standard ASTM F 2036-05:2007 – Standard Test Method for Evaluation of Larger Area Density and Background on Electrophotographic Printers (ASTM F2036-05, 2007), using a spectrodensitometer X-Rite, model SpectroEye. The optical density value corresponds to the average of five determinations for the paper printed with thermal transfer ribbon and nine determinations for the paper printed with thermal sensitive dye.

RESULTS AND DISCUSSION

Paper printed with thermal transfer ribbon

Figure 2 shows the printed areas before and after the total period of exposure at 40°C, 60°C, 80°C and 100°C. For temperatures higher than 80°C, changes, as fade and loss of gloss, are visible on the printed areas.

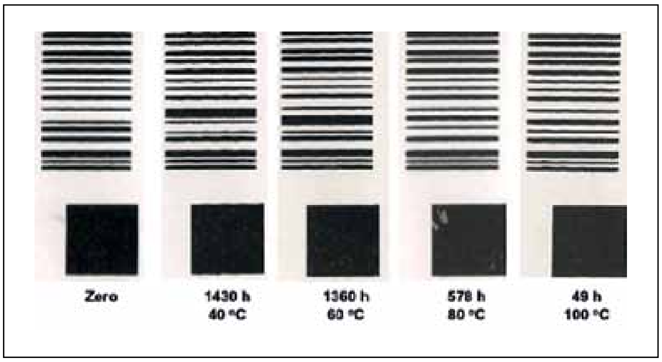

Figure 2. Thermal transfer ribbon printed areas before and after exposure at high temperatures

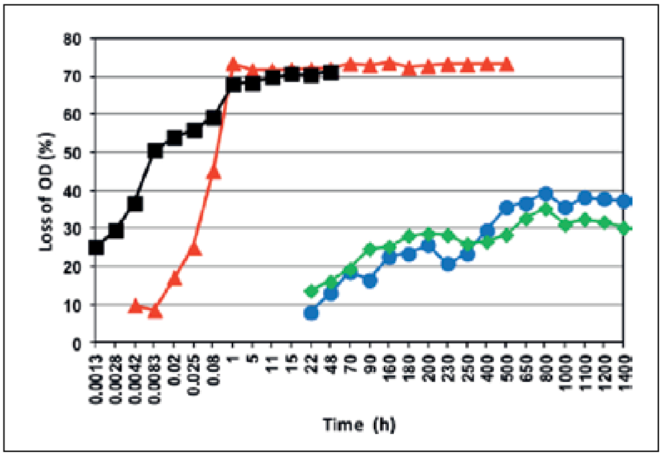

Figure 3. Loss of optical density *versus* time at heat exposure: (-●-) 40ºC; (-◆-) 60ºC, (-▲-) 80ºC and (-■-) 100ºC

Figure 3 shows a graphic of optical density (OD) loss *versus* the time of exposure to dry heat at 40ºC, 60ºC, 80ºC and 100ºC. Two groups are clearly visualized: one formed by lower temperatures (40ºC and 60ºC) and the other formed by higher temperatures (80ºC and 100ºC). For the lower temperatures group, the maximum loss of OD - which was around 30% - was achieved after a 410 hour-exposure at 40°C and after a 200 hour-exposure at 60°C. For the higher temperatures group, the maximum loss of OD - which was around 70% - was achieved after a 1-hour exposure at both 80°C and 100°C. It may be said that, for both groups, the OD value remained steady after the maximum loss of OD occurred.

To build up the Arrhenius plot, it would be necessary to know which value of OD would correspond to the situation where readability of printed information is lost. Once this information is not available, one value of OD should be chosen. It was chosen a point presented in the four curves, the one equivalent to 25% of OD loss, considering that the loss of OD becomes constant after a period of heat exposure.

Figure 4A shows the Arrhenius plot (1/T x log t) built up with the data corresponding to a 25% of OD loss, considering the four temperatures. It is possible to verify that the aging rate of the printed areas do not increase proportionally with temperature. There is no linear correlation between the temperatures and the time of reaction, as shown by the low value of the correlation constant obtained ($R^2 = 0.8462$). Even when the plot is built up only with data from 40°C, 80°C and 100°C temperatures (**Figure 4B**), the correlation constant obtained is low ($R^2 = 0.9173$).

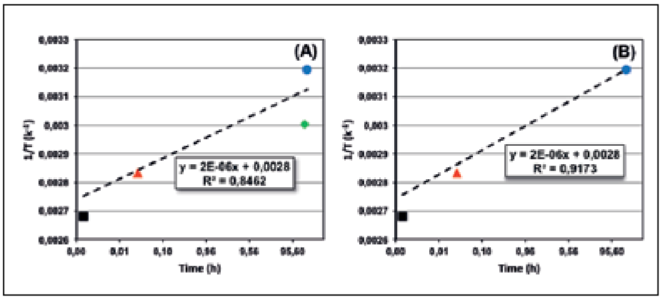

Figure 4. (A) Arrhenius plot considering 25% loss of OD for the four temperatures investigated; (B) Arrhenius graphic without the 60ºC data

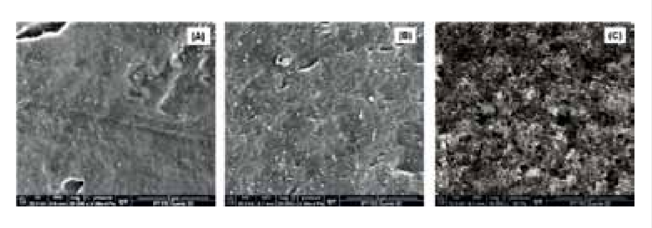

Figure 5. Images of scanning electron microscopy from printed areas (A) after being exposed by 1430 h to heat of 40ºC, (B) after being exposed by 1363 h to heat of 60ºC, and (C), after being exposed by 1 h to heat of 80ºC

For temperatures higher than 80°C, it was very easy to remove the ink by rubbing it with the tip of a finger. **Figure 5** presents scanning electronic microscopy (SEM) images from the printed areas before and after exposure at 40ºC, 60ºC and 80ºC. These images were made using a field-emission scanning electron microscope (FEI, model QUANTA 400) having a Penta FET x3 detector.

Observing Figure 5, it is possible to verify that exposure at 40ºC (**Figure 5A**) and at 60ºC (**Figure 5B**) do not have a great effect on the surface of the printed area when compared to the exposure at 80ºC (**Figure 5C**), which leads to the formation of a rougher surface in comparison to the other ones.

In order to find an explanation for the occurrence, FTIR spectra of the printed areas before and after exposure at 80ºC were made using a spectrometer Nicolet iS10. The bands correlated to the stretch of aliphatic C-H at 2853 cm^{-1} and 2919 cm^{-1} decreased after the exposure to heat. The SEM and FTIR results suggest that the loss of adhesion observed after exposure to higher temperature - by rubbing the surface with the tip of a finger -, is due to the degradation of the wax used in the manufacture of the thermal transfer ribbon.

The degradation of the wax probably affected also the gloss of the printed surface. The decrease of the gloss of the printed surface can influence the determination of the optical density, since it is obtained by light reflection.

The deviation of the Arrhenius plot from linearity is probably a result of the influence of at least two processes: degradation of the colored pigment and degradation of the wax.

The obtained results highlight the importance of knowing well the material that will be submitted to accelerated aging and the importance of choosing the aging temperatures. When performing the aging tests, high temperatures are better; because the higher the temperature the faster the aging reaction rate is, but it must be ensured that the chosen temperature will not catalyze reactions that would not occur in the real life aging.

When higher temperatures are not applicable, and the used temperatures are close to the environment ones, the aging test will take almost as long as the real aging time.

The Arrhenius model was not applicable in the studied case, thus being impossible to predict the lifetime of the printed areas by this model.

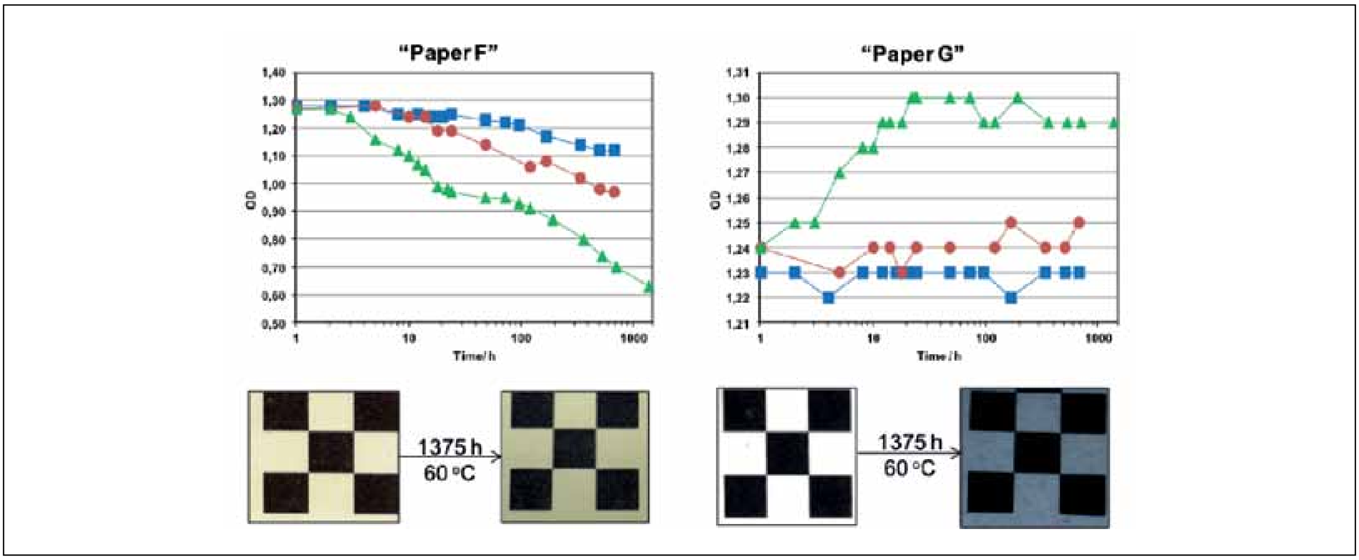

Figure 6. OD *versus* time of exposure at: (-■-) 40ºC, (-●-) 50ºC and (-▲-) 60ºC, and pictures before and after the total exposure time at 60°C

Thermosensitive paper

Figure 6 shows the OD values *versus* the time of exposure to dry heat at 40ºC, 50ºC and 60ºC for "Paper F" and "Paper G". Each one of the studied thermosensitive papers shows a different behavior when exposed to heat. For "Paper F", the OD decreases with the increase of both the temperature and the exposure time. For "Paper G", at 40ºC and 50ºC, the OD value is almost constant, but at 60ºC an increase in OD is observed with the increase of the exposure time. Figure 6 also shows the aspect of the papers after the total exposure period at 60°C.

The different behaviors observed between the two studied papers are due to the difference in their coating composition. The coating layer of the thermosensitive paper has different classes of compounds and, in each class, there is a long list of chemical substances that can be used. So, it is uncommon to find two thermosensitive papers from different manufacturers with same behavior.

In Figure 6**,** it is clear that the Arrhenius model could not be applied to "Paper G", because the aging reaction does not follow the same kinetics on the three temperatures used. Moreover, the exposure to temperatures higher than the environment ones contributes to the OD increase instead of causing its loss. One possible explanation is that the thermal dye is present in the coating in high concentration, and the heat used to print the thermal paper is not enough to sensitize all the dye. In this case, the exceeding dye will be revealed by the heat exposure.

For "Paper F", the Arrhenius model is not useful as well, for the reasons that follow:

- to build up the Arrhenius plot, the same OD loss must be considered for all three temperatures;
- if considered the time to achieve an OD equal to 1,0 - which is the lowest value permitted by the Brazilian government (Ato COTEPE/ICMS nº4, 2010) for printed area from thermosensitive papers used for invoice -, than it took 18 hours of exposure at 60°C and 504 hours of exposure at 50°C to decrease to a value of 1,00;
- the graphic for 40°C shows a smaller slope when compared to the other temperatures and, probably, the time required to get to the OD equal to 1,00 would be too long.

It is important to point out that the printing lifetime of thermosensitive paper is affected by the energy used to print the paper. **Figure 7A** shows the curve of OD *versus* energy density for

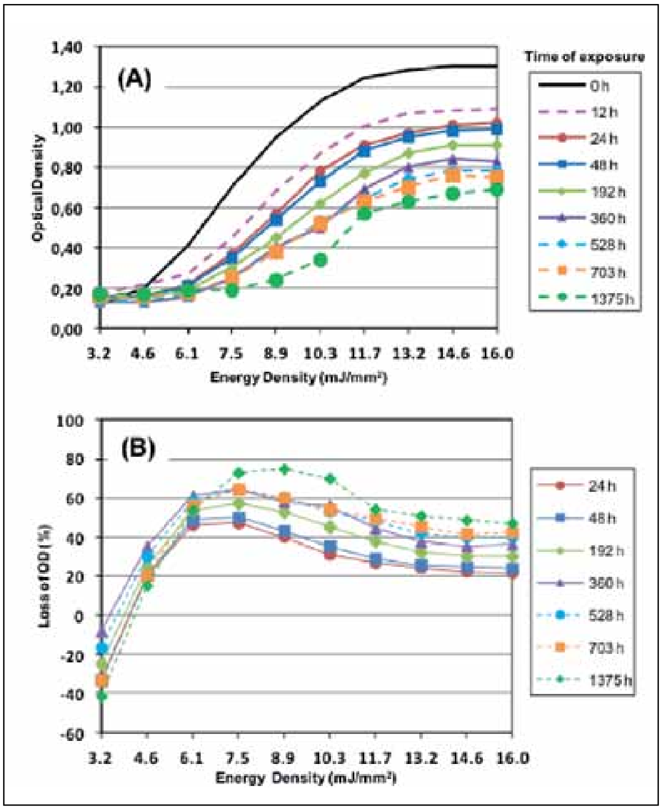

Figure 7. Exposure of "Paper F" at 60°C: (A) OD *versus* energy density; (B) Loss of OD *versus* energy density

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"Paper F" before and after exposure at 60°C during different periods of time, and **Figure 7B** shows the observed loss of OD.

In Figure 7A, the curves are of sigmoidal shape. For energy density lower than 6.1 mJ/mm^2 and higher than 13.2 mJ/mm^2 the OD is basically constant. But between these values of energy density the OD increases.

Figure 7B shows that the areas printed with energy density between 6.1 mJ/mm^2 and 8.9 mJ/mm^2 are the most sensible to heat and present the greatest losses of OD.

The difficulty of applying the Arrhenius model to predict printing lifetime on thermosensitive paper lies on the fact that the stress factor employed for the accelerated aging study (high temperature) is the same used to sensitize the color dye on the paper. So, during the aging test, there are, at least, two reactions occurring: formation of colored compounds and degradation of the colored compounds. The principle of the Arrhenius model is that the studied reaction depends only on one variable. In the case of this study, the parameter used to test the reaction rate (OD) depends on more than one variable, and the Arrhenius model cannot be applied.

CONCLUSIONS

Thermal printing is a complex process, and the study of accelerated aging of printed areas is not a simple task for the type of material studied.

In the aging of printings made with thermal transfer ribbon applying heat, side reactions can occur due to the influence of heat over the wax. In the aging of printings made on thermosensitive papers applying heat, the temperature may act as a degradation agent as well as a sensitizer agent. In both cases there is not a simple relation with the temperature, and the application of Arrhenius model is not possible, once this model assumes that the reaction rate depends on only one parameter, the temperature. ■

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