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DIFFICULT OF APPLYING THE ARRHENIUS MODEL TO PREDICT THERMAL PRINTING LIFETIME

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ABSTRACT

The Arrhenius model is widely used in the 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 relations between the reaction rate and the inverse absolute temperature (T). This study demonstrates that the application of this model should not be done indiscriminately and 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 because of side reactions that are not observed under natural conditions of aging. In the case of printing on thermal sensitive paper the application off the Arrhenius model was also not applicable due to the restriction to high temperatures. Two critical factors for performing accelerated aging tests were identified in this study: the choice of test temperatures and the definition of acceptable yield loss for the focused property.

Keywords: *Arrhenius model; accelerated aging; thermal printing*

1. INTRODUCTION

Accelerated aging tests have been used to simulate, in a short period of time, physical or chemical changes that occur naturally in a material, enabling the prediction of the material lifetime or its behavior in relation to a defined parameter [1]. These tests are based on exposure of the object of study to high levels of heat, radiation, humidity, voltage, pressure and others[2].

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, Eyring and Inverse Power Law models[2]. The choice of the most appropriate model depends on the studied material and on the stress condition employed in the test. In the case of paper, it is common to use the temperature as a stress factor. Thus, in this case, the Arrhenius model is the recommended one[1,3,4].

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**[2, 5].

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

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 (K)[6].

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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 [5].

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 linearity), or even preventing to get them[5]. It is recommended to investigate the correlation between the results of accelerated aging and the results of natural or real aging[5, 7].

In this study, accelerated aging was applied to papers printed by thermal processes in two different ways: using thermal transfer ribbon and using thermo sensitive 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.

2. METHODS

Samples

The paper printed with a thermal transfer ribbon (“Paper A”) was a 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 a 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 1 cm X 1 cm (**Figure 1**).

The thermo sensitive paper was a coated paper, whose coating composition comprised a thermo sensitive dye. In a thermal printer, the thermal head was heated by an electrical pulse current and the heat transferred to the thermo sensitive paper. During heating, the thermo sensitive recording paper and the thermal head are kept in contact with each other and some of the ingredients of the thermo sensitive composition are in molten state. The molten ingredients solidify when removal of the thermal head from the thermo sensitive recording paper is to take place. Two thermal sensitive papers available in the market were used. They were denominated “Paper F” and “Paper G”. In both cases were printed areas of 1cm x 1cm (**Figure 1**) using the thermal printer Atlantek model 400, operating with energy density of 13.2 mJ/mm^2. For “Paper F” it was also printed areas 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. [8]

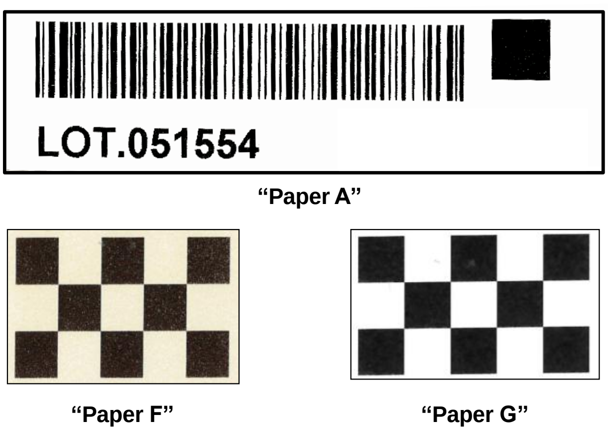

Figure 1 –Test piece of paper A, F and G

Aging

The accelerated aging tests were carried out according to the technical standard ISO 18924:2000 – Imaging materials – Test method for Arrhenius-type predictions [5].

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	1 430
60 ± 2	1 360
80 ± 2	578
100 ± 2	49

Table 2. Accelerated aging conditions - thermal sensitive paper

Temperature (°C)	Time (hours)
40 ± 2	672
50 ± 2	672
60 ± 2	1 375

For black and white printing the measurement parameter is usually the optical density (OD), so in this case the evaluation of 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 [9], using a spectrodensitometer X-Rite, model SpectroEye. The optical density value corresponds to the average of five determinations to the paper printed with thermal transfer ribbon and nine determinations to the paper printed with thermal sensitive dye.

3. RESULTS AND DISCUSSION

3.1. 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 temperature higher than 80°C, changes, as fade and loss of gloss, are visible on the printed areas.

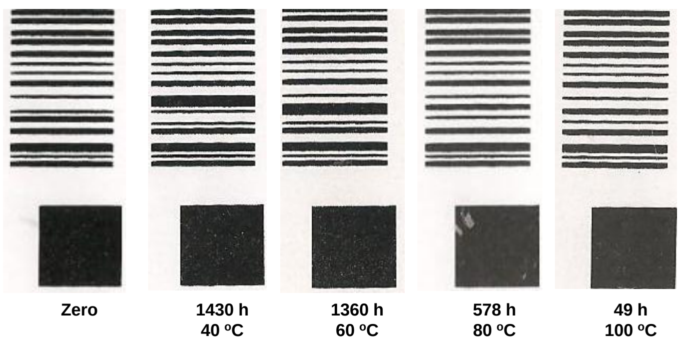

Figure 2. Thermal transfer ribbon printed areas before and after exposure at high temperatures

Figure 3 shows a graphic of optical density (OD) loss versus the time of exposure to dry heat at 40 °C, 60 °C, 80 °C and 100 °C. Two groups are clearly visualized, one formed by the lower temperatures (40 °C and 60 °C) and the other formed by the higher temperatures (80 °C and 100 °C). For the lower temperatures group, the maximum loss of OD, which was around 30 %, was achieved after 410 h exposure a 40°C and after 200 h exposure at 60°C. For the higher temperatures group the maximum loss of OD, which was around 70 %, was achieved after 1 h of 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.

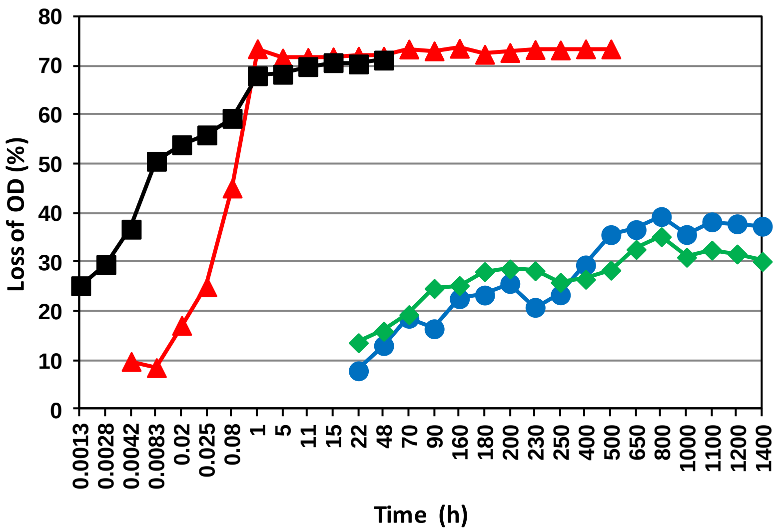

Figure 3. Loss of optical density versus time at heat exposure: (-•-) 40 °C; (-◆-) 60 °C, (-▲-) 80 °C and (-■-) 100 °C.

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% 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 % 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 time of reaction, as can be seen 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 obtained correlation constant is low (R^2 = 0.9173).

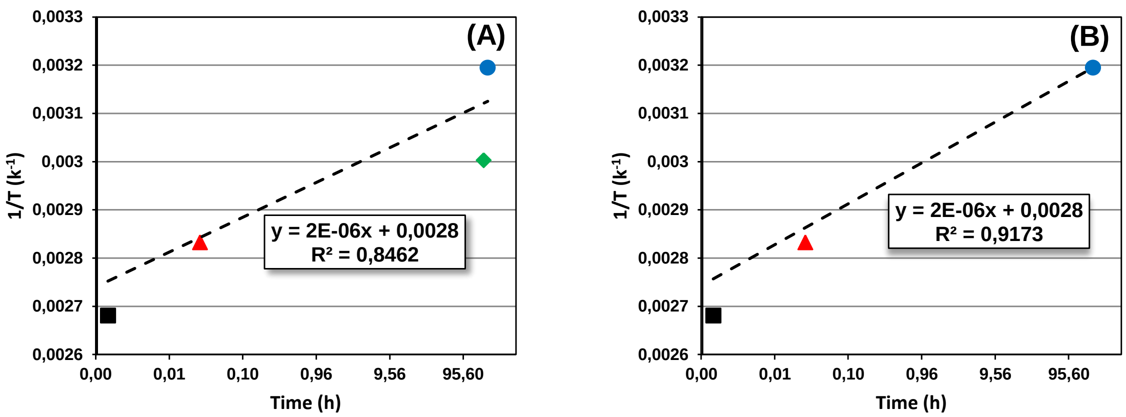

Figure 4. (A) Arrhenius plot considering 25% loss of OD for the four temperatures investigated; (B) Arrhenius graphic without the 60 °C data

It was also observed, for temperatures higher than 80°C, that 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 40 ^oC, 60 ^oC and 80 ^oC. These images were made using a field-emission scanning electron microscope (FEI, model QUANTA 400) having a Penta FET x3 detector.

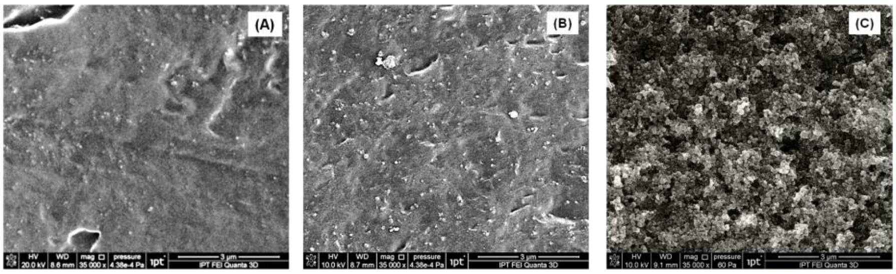

Figure 5. Images of scanning electron microscopy from printed areas (A) after being exposed by 1430 h to heat of 40 ^oC; (B) after being exposed by 1363 h to heat of 60 ^oC and (C) after being exposed by 1 h to heat of 80 ^oC.

Observing **Figure 5** it is possible to verify that exposure at 40 ^oC (**Figure 5A**) and at 60 ^oC (**Figure 5B**) do not have a great effect on the surface of the printed area when compared to the exposure at 80 ^oC (**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 80 ^oC were obtained using a spectrometer Nicolet iS10. It was observed that 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 the gloss of the printed surface too. 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 results obtained highlight the importance of knowing well the system that will be submitted to accelerated aging and the importance of choice the temperatures. High temperatures are desired when aging tests are performed 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 the system does not permit the use of higher temperatures, and the temperatures applied are close to the environment ones, the aging test will take almost as long time as the aging real 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.

3.2. Thermal sensitive paper

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

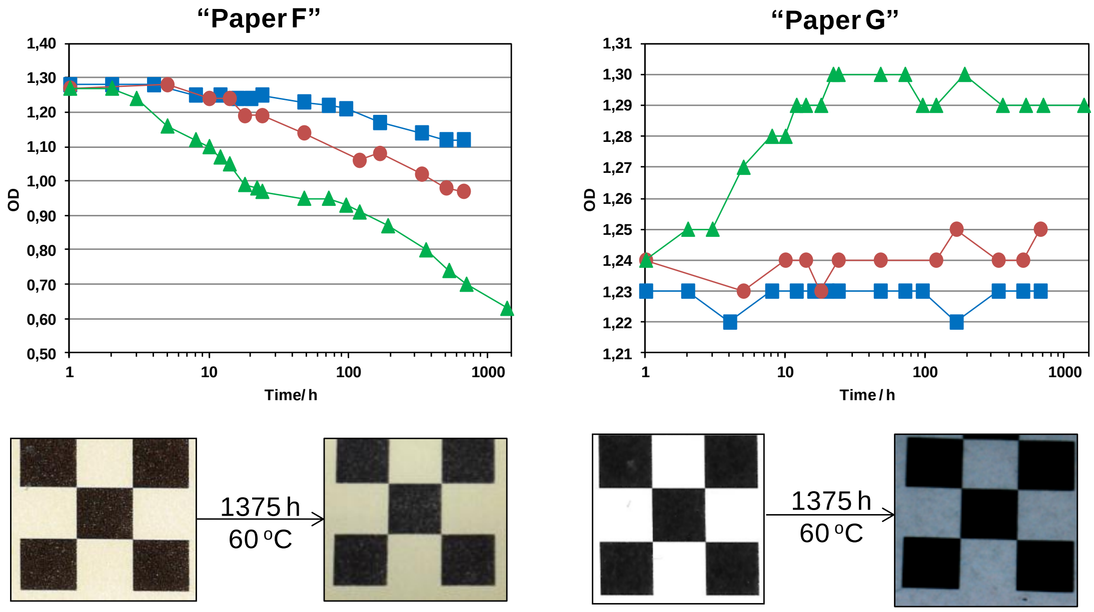

Figure 6. OD versus time of exposure at: (-■-) 40 °C, (-●-) 50 °C and (-▲-) 60 °C and pictures before and after the total exposure time at 60°C

The different behaviors observed between the two studied papers is due to the differences on their coating composition. The coating layer of the thermal sensitive 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 thermal sensitive papers from different manufacturers with the same behavior.

From **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 on 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 too, for the reasons given bellow:

- to build up the Arrhenius plot, a same OD loss must be considered for all three temperatures;
- if the considered the time to achieve an OD is equal to 1,0, which is the lowest value permitted by the Brazilian Government [10] for printed area from thermal sensitive papers used for invoice, than it took 18 hours of exposure at a 60°C temperature to decrease to a value of 1,00, and 504 hours of exposure at a 50°C temperature;
- 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 that the printing lifetime of thermal sensitive paper is affected by the energy used to print the paper. **Figure 7A** shows the curve of OD versus energy density for "Paper F" before and after exposure at 60°C during different periods and **Figure 7B** shows the loss of OD observed.

In **Figure 7A,** the curves are of sigmoidal shape. For energy density lower than 6.1 mJ/mm^2 and higher than13.2 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 ones more sensible to heat, and present the greatest losses of OD.

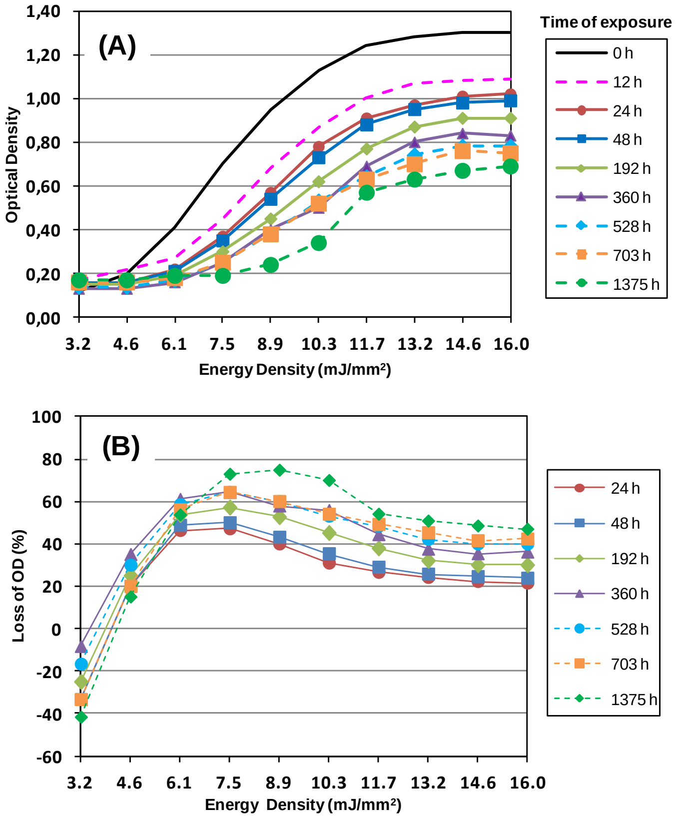

Figure 7. Exposure of "Paper F" at 60°C: (A) OD versus energy density;(B) Loss of OD versus energy density

The difficult of applying the Arrhenius model to predict printing lifetime on thermal sensitive paper lies on the fact that the stress factor employed for the accelerated aging study (high temperature) is the same one 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.

4. CONCLUSIONS

Thermal printing is a complex process and the study of accelerated aging of printed areas is not a simple task in this type of system.

In the aging of printings made with thermal transfer ribbon using heat side reactions can occur due to the influence of heat over the wax. In the aging of printings made on thermo sensitive papers using 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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