INVESTIGATION ON THE KINETICS
OF COATED PAPER THERMAL AGING

Dimitrina Todorova, Veska Lasheva, Greta Radeva, Radostina Cenkova

ABSTRACT

The paper aging is primarily attributed to the presence of carbonyl groups formed as a result of the oxidation of the hydroxyl groups at the second and third carbon atom in the elementary unit of the cellulose macromolecule and the presence of both aldehyde and carboxyl groups in the cellulose materials. Reduction of paper whiteness degree is mainly connected with the presence of lignin, hemicelluloses, the presence of metals and the sizing agent type.

The paper as an elasto-plastic, capillary porous material quickly breaks down at an elevated temperature. The latter accelerates the chemical reactions that occur in paper in the course of aging. The depth of the paper change depends not only on the temperature but also on the duration of the impact. For different paper types differing in composition the reaction rate constant is different. Its temperature dependence is described by the Arrhenius equation.

The aim of this work is to carry out a kinetic analysis of the influence of the temperature increase on the ageing of coated paper used for book covers. The accelerated thermal aging is conducted at three different temperatures – 90°C, 105°C and 120°C with duration of 6 h, 12 h, 18 h, 36 h and 48 h. In order to examine the kinetics of the process the level of whiteness is determined. The data obtained from the thermal aging of the paper are treated using the laws of polychrome kinetics.

Keywords: coated paper, kinetics, thermal aging, degree of brightness.

INTRODUCTION

A typical external sign of aging of paper refers to the decrease of its degree of brightness and the deterioration of the paper physical and mechanical properties. The paper aging is primarily attributed to the presence of carbonyl groups formed as a result of oxidation of the hydroxyl groups at the second and the third carbon atom of the elementary unit of the cellulose macromolecule and the presence of both aldehyde and carboxyl groups in the cellulose materials. The decrease of the paper whiteness degree is mainly connected with the presence of lignin, hemicelluloses, the presence of metals and the sizing agent type [1 - 3].

The investigation of the kinetics of accelerated thermal ageing of different paper types provides data on the progress of the ageing process which may facilitate the elucidation of its mechanism with advantage of the methods of treatment and storage. Ageing is a complex process which does not obey formal kinetic principles. Some authors describe the degradation reactions of the cellulose chains due to the ageing processes as reactions of a first or a second order [4 - 7]. But the equations derived consider the processes discussed as taking place on a homogeneous surface. It is worth noting that the influence of the physical structure of the surface has to be taken into account [8] in a real heterogeneous system. In addition, the correlations between the kinetics of cellulose degradation and the changes in a wide range of macroscopic properties such as brightness, P<sub>c</sub> number or tensile strength [8, 9] have also to be taken into account.

The aim of this work is to carry out a kinetic analysis of the temperature increase effect on the ageing of coated paper used for book covers. The analysis accounts the complex influence of the heterogeneous nature of the system focusing to explain the mechanism of the process.
EXPERIMENTAL

The degree of brightness was determined as % reflectance of light in the blue Brightness R457 region according to ISO 2470:2002. Elrepho apparatus [3] was used. The coated paper investigated had a mass of 128 g/m². The microscopic analysis (Fig. 1) of its composition showed that it consisted of a secondary fibrous material of bleached softwood pulp from spruce wood and a hardwood pulp from poplar wood.

The accelerated thermal aging was conducted at three different temperature values – 90°C, 105°C and 120°C with duration of 6 h, 12 h, 18 h, 36 h and 48 h. The degree of whiteness was followed. The data obtained was treated with the application of the laws of polychrome kinetics.

RESULTS AND DISCUSSION

The accelerated aging deals with the chemical stability or resistance of specific materials. These chemical changes are ultimately responsible for the physical disintegration and the materials failure. Changes of the properties with time are most often envisioned on a linear scale in terms of the hours of exposure in a Fade-ometer or hours of heating at an elevated temperature [10].

The effect of ageing is followed on the ground of the changes of samples brightness ($W$). The brightness reversion observed in the course of the process is followed at a function of the temperature studied. The values obtained are summarized in Table 1.

The comparative consideration of the characteristics of the thermal ageing kinetics is done with the introduction of the kinetic variable, $\alpha$ (1):

$$\alpha = \frac{W_0 - W}{W_0}$$

where $W_0$ is the initial brightness value in % (ISO), while $W$ % (ISO) is the current value connected with the time of the treatment. The variable $\alpha$ can be also considered as an extent of ageing proceeding or as a decrease of the degree of brightness in the course of the process.

The kinetic curves of the change of $\alpha$ with time (h) obtained are presented in Fig. 2.

As Fig. 2 shows $\alpha$ increases with time and temperature increase. This corresponds to the increase of the extent of the process of thermal ageing, i.e. to the corresponding brightness reversion.

Various kinetic equations describing the kinetics of processes taking place on homogeneous and heterogeneous surfaces [11 - 12] have been applied aiming to elucidate the specifics of the process. The results show that the process is best described by the exponential

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Table 1. Values of the degree of brightness, $W$ (%) of the book covers, in the course of the process of ageing (h) at the temperature values studied (T°C).

<table>
<thead>
<tr>
<th>Brightness, $W$ %</th>
<th>0</th>
<th>6</th>
<th>12</th>
<th>18</th>
<th>24</th>
<th>36</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=90°C</td>
<td>108.86</td>
<td>106.53</td>
<td>105.30</td>
<td>105.20</td>
<td>103.92</td>
<td>130.40</td>
<td>13.14</td>
</tr>
<tr>
<td>T=105°C</td>
<td>101.52</td>
<td>94.50</td>
<td>90.68</td>
<td>88.50</td>
<td>87.41</td>
<td>84.64</td>
<td>82.20</td>
</tr>
<tr>
<td>T=120°C</td>
<td>101.19</td>
<td>86.70</td>
<td>81.27</td>
<td>77.70</td>
<td>75.61</td>
<td>73.75</td>
<td>69.33</td>
</tr>
</tbody>
</table>
equation (2) valid for heterogeneous processes taking place on uniformly inhomogeneous surfaces:

\[ v = v_0 e^{-a \alpha} \]  

(2)

where the current and the initial rate of the ageing process are designated by \( v = \frac{d \alpha}{dt} \) and \( v_0 \), correspondingly. In accord with the model of uniformly inhomogeneous surfaces \[11 - 12\] the active centres on the surface are distributed linearly in correspondence with their energy. For this type of surfaces the rate of the reactions decreases exponentially with \( \alpha \) increase. The kinetic coefficient of inhomogeneity \( a \) accounts for the energy and entropy inhomogeneity of the system.

All kinetic curves are linearized in coordinates \( \alpha - \ln t \) in correspondence with the approximate integral form of the exponential kinetic equation (3):

\[ \alpha = \frac{1}{a} \ln (v_0 a) + \frac{1}{a} \ln t \]  

(3)

where \( t \) is time, h.

The linear dependences obtained in correspondence with Eq. 3 are presented in Fig. 3.

The value of the slope of the lines obtained (Fig. 3) provides the determination of \( a \) (Eq. 4). The values of the latter are presented in Table 2. It is seen that the coefficient of inhomogeneity decreases with temperature increase. The temperature dependence of \( a \) can be described by:

\[ a = \frac{B}{R T} - a_0 \]  

(4)

Constant \( B = 604.43 \text{ (kJ/mol)} \) stands for the interval of energy inhomogeneity and takes account of the active centres of different energy, while coefficient \( a_0 = 172.7 \) stands for the interval of entropy inhomogeneity and is connected with the number of the active centres, their disposition and availability. The rest of the symbols have their conventional meaning.

The integral form of the exponential kinetic equation (Eq. 3) can be used for the determination of the initial rate, \( v_0 \), of the process of thermal ageing at \( \alpha \rightarrow 0 \) (Table 2). The current rate of the process, \( v \), at different time and temperature values is estimated on the ground of Eq. 5 at a constant value of the extent of the process proceeding (\( \alpha = \text{const} \)):

\[ v = \frac{1}{a t} \]  

(5)

The values of the current rate are given in Table 3. The latter shows that the rate of ageing decreases with \( \alpha \) increase, but increases with temperature increase.

The temperature effect on the process parameters can be followed through the investigation of the temperature dependence of the rate on the ground of the Arrhenius equation presented by Eqs. (6) and (7):

\[ \ln v_0 = \ln A_0 - \frac{E_0}{R T} \]  

(6)
where \( E_0 \) (kJ/mol) and \( E \) (kJ/mol) are the activation energies of the process at \( \alpha \rightarrow 0 \) and at different constant values of \( \alpha \), correspondingly, while \( A \) and \( A_0 \) are the respective pre-exponential factors. The values of the activation energy and the pre-exponential factor as well as their change at different values of \( \alpha \) are summarized in Table 4 and Fig. 4. As Fig. 4 shows that the linear dependences obtained have different slopes, i.e. the values of the activation energy and the pre-exponential factor increase with \( \alpha \) increase. This means that the surface is energy and entropy heterogeneous. Furthermore, the pre-exponential factor increase in the course of the process indicates that the number of the chromophore groups responsible for the brightness reversion increases.

The increase of the activation energy slows down the ageing process but this cannot compensate the increase of the number of the chromophore groups responsible for the brightness reversion. It is characterized by a simultaneous increase of the activation energy and the pre-exponential factor and is not affected by the increase of temperature and the reaction duration. These results are grounded on the kinetic specifics studied.

**CONCLUSIONS**

The accelerated aging deals with the chemical stability or resistance of specific materials. The kinetics of the process is best described by an exponential kinetic equation valid for heterogeneous process taking place on uniformly inhomogeneous surfaces. The initial and the current rates of the process are determined. It is found that they decrease with increase of the extent of the process proceeding. The temperature dependence of the rate is followed and the values of the activation energy and the pre-exponential factor of the Arrhenius equation are estimated.

**REFERENCES**