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Effect of dry-heat ageing on label paper quality

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Ageing of paper can be defined as a sum of all irreversible physical and chemical processes which appear in the material during time. Brightness reversion is of importance for high brightness paper producers. Reversion is a result of chromophores generation via condensation reactions.

The impact of dry-heat ageing on strength and optical properties of label paper was studied. Three types of pigment coated label papers were used. Dependence of Pc number on reaction time for three different temperatures was examined. The studies showed that it increases significantly in the paper with denser surface layer. This was determined by the chromophore structures in pigment surface layer. The kinetics of the ageing process was described most precisely by an exponential kinetic equation for all types of sample papers.

Second examination was carried out to determine the color stability of aged digital prints. The label papers were printed by multicolor printing device and artificially aged using the same technique of accelerated ageing. Differences between aged and non-aged papers were analyzed. Their colorimetric characteristics are represented by means of color difference ΔE^*_{ab}.

***Key words**: dry-heat ageing, label paper, exponential kinetic equation, color difference*

INTRODUCTION

The mechanism of ageing involves numerous interactions between substances in the paper and with its surroundings. These could be defined by deterioration in the mechanical strength, loss of chemical stability and deterioration of the optical characteristics of the paper [1]. The term "permanence" describes the ability of paper to remain chemically and physically stable over long periods of time. The durability depends mainly on the physical and mechanical characteristics of the principal raw materials and on contamination by ions from the environment, the action of light, heat, humidity and microorganisms [2,3]. A study of the natural ageing of paper can take several years to register certain paper properties. To solve these problems of hostile environment which are more aggressive than the normal environment conditions are implemented. The first and the most widespread approach is the exposure to elevated temperatures, usually referred to as thermal accelerated ageing. Accelerated ageing tests are often used to determine the changes of the permanence and durability of paper, as well as to predict the long-term effect of a paper usage [4,5]. Heat is one of the most important environmental influences on the stability of papers [6]. In the accelerated ageing method proposed by TAPPI [7], the material is exposed in a climate chamber at extreme temperature for a certain period of time, during which the changes in the material are measured. The reasons for the loss of strength with ageing are not completely understood, but they are presumed to be directly related to changes that occur at molecular level. Consequently, the concept of chemical kinetics in quantifying the effects of aging is applied. In the chemical kinetics approach, the loss of strength property with time is used to characterize the rate of deterioration of the material [8,9]. "ZOU *et al.* [10,11]" conducted a general kinetic analysis to investigate the aging process of paper. The results from their investigation proved the accurate usage of accelerated aging tests for paper permanence prediction.

In case of label papers the permanence is of great importance. This type of paper is used for different products labeling: bottles, containers etc. Each label carries not only important data but also graphical information for the brand. That is why paper`s color characteristics stability over time is important. Moreover the physical and mechanical properties have to satisfy high demands because the labeled product often experiences a lot of different kinds of environments, which can damage or deteriorate its quality. Depending on the product, the label may be exposed to extreme moisture or dryness, elevated heat or cold, physical tortures and other unforeseen circumstances over time.

The aim of the present study is to determine the impact of dry-heating ageing on the quality of label paper properties. This will allow identification of

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the stability of paper when aged under normal conditions of use and handling over time.

The accomplishment of this goal requires estimation of the impact of dry-heat ageing on the strength and optical properties of the label paper. This was done by analyzing the following parameters:

- mechanical properties of the tested papers;
- ageing by means of ISO Brightness (R457 nm) loss and Pc number (post color number);
- kinetics of the ageing process;
- colour differences between aged and non-aged printed images.

EXPERIMENTAL

Three types of pigment coated label papers were examined. Their properties according to the technical data are presented in Table 1. The specimens were put under accelerated ageing in oven with forced ventilation. Experiments were carried out at 85ºC, 105ºC and 125ºC for 4 hours ageing time.

Table 1. Technical data for the three types of label paper

Paper, [№]	Opacity, [%]	Gloss, [%]	ISO Brightness, [%]
1	90±2	72±3	88±2
2	≥ 84	65±5	92±3
3	94	70	87

In order to characterize the paper some important mechanical and strength properties were examined. The research includes experimental data for tensile strength, tearing resistance and bursting strength. The tests for tensile strength were done according to ISO 1924:2008 [12]. The tearing resistance and bursting strength were determined in conformity with ISO 1974:2012 [13] and ISO 2758:2001 [14] respectively. The selected properties of the three types of paper are compared before and after the second and the fourth hour of ageing.

Since the loss of brightness is an index for the yellowing of paper, ISO Brightness values were studied during the accelerated ageing for the three types of paper. Specimens were measured at regular time intervals within four hours. The measurements were carried out according to ISO 2470-1:2009 [15] with Elrepho "Datacolor 2000" spectrophotometer. Behavior of fiber material subjected to ageing was characterized in term of relative variation of Kubelka-Munk (k/s) function using the experimentally obtained brightness values. In order to show the comparison of the magnitude of yellowing for the three label papers a recalculation of Pc number was accomplished. The kinetics of the ageing process, based on the calculated Pc numbers, was examined and applicability of different kinetic equations valid for heterogeneous processes was verified.

Color stability of printed test charts was investigated in order to determine the usability of the label papers for long periods of time. The charts were printed on the three types of paper with 6 channel ink-jet printing device. Since offset printing is the most popular process device linked profile was created to simulate this type of printing. Chart with 452 patches was generated including patches for determining the color densities of CMYK process colors and halftone values. The device link profiles were applied to the test chart according to the paper types and then were printed. The samples were put under accelerated ageing for 8 hours at 105^{0}C. Their colorimetric characteristics were measured with X-Rite Spectroscan spectrophotometer at regular time intervals. The color differences between non-aged and aged prints are represented in terms of ΔE_{ab}.

RESULTS AND DISCUSSION

Mechanical properties

Studies of the ageing influence on tensile length and tear index for the three types of label papers were carried out in machine and cross direction. Figure 1 illustrates the obtained results for tensile strength measured at different temperatures. It can be seen that in the course of ageing at different temperatures the tensile length in both directions increases for the three types of examined papers. It was found that after the second hour of accelerated ageing the tensile length changes for Paper No 1 and Paper No 2 are minimal with respect to the initial values. After the fourth hour of ageing the experiments at 85ºC showed marginal changes in the tensile length. Significant changes were observed in the tensile length measured for Paper No 3. As an exception, the experimental data for Paper No 3 showed correlation between tensile length and temperature of ageing.

The measured values for the tensile length in cross direction for Paper No 3 differ significantly from those for the other types. This can be explained with the denser pigment surface layer. When ageing is carried out at higher temperature cross-linking reaction appears. As a result the fiber bonding in cross direction is getting stronger, which increases the tensile length.

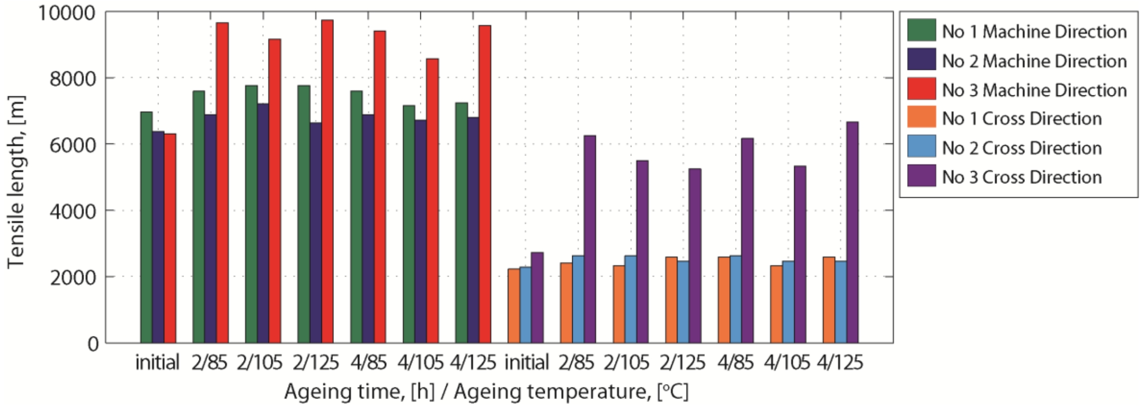

Fig. 1. Effect of ageing time and temperature on tensile length in machine and cross direction for the three types of label paper.

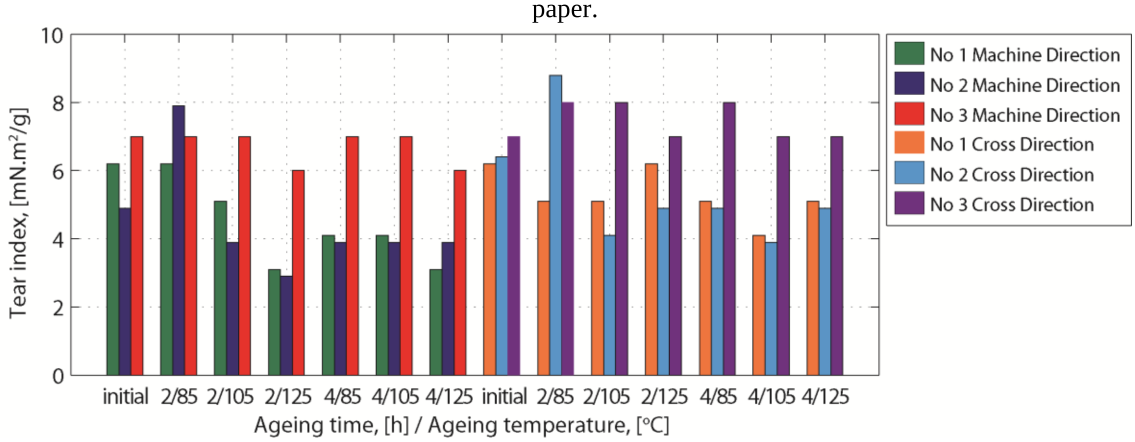

Fig. 2. Effect of ageing time and temperature on tear index in machine and cross directions for the three types of label paper.

The essential chemistry, structure and morphology of the fibers which form the paper as well as their mutual disposition are reflected by the mechanical and strength properties of the paper. The latter also reflect the chemical changes in the paper permanence caused by time. The most commonly used tearing test, measures the internal tearing resistance of paper. Figure 2 shows the obtained results for the tear index measured at different temperatures for the three types of label papers. It is seen that the tear index for Paper No 1 and No 2 decreases with increasing temperature and ageing time. Paper No 3 had slightly different behavior. Its tear index showed correlation to the temperatures used for the experiment rather to the ageing time. The lowest index has been measured at 125°C.

The tear index measured in cross direction for Paper No 1 decreases most significantly after the fourth hour of accelerated ageing at 105°C. Measured values of the tear index for Papers No 2 and No 3 after the second hour of ageing at 85°C increased, while those for Paper No 1 decreased. This experimental data can serve as indicator of the permanence of paper. The results prove that ageing changes the fiber structure, their length and consequently affects the paper permanence.

In support to this conclusion are the results for burst index of the label papers reported in Table 2. This indicator for Paper No 1 and No 2 does not change during the aging process, while increases significantly for Paper No 3. The reason is the polymerization process during ageing which forms a denser surface layer.

Yellowing

Yellowing is reported either as loss of ISO Brightness units or after recalculation as Pc number. The ISO method is used when papers with same ISO Brightness are compared. The main advantage of the approach is the clear understanding of the magnitude of yellowing. The chromophore concentration is not linearly related to the ISO Brightness, but is linked to it via the Kubelka-Munk equation (Eq.1):

$$\frac{k}{s} = \frac{(1-R_{\infty})^2}{2.R_{\infty}} , \tag{1}$$

Table 2. Effect of ageing time and temperature on the burst index for the three types of label paper

Paper, [№]	Burst index of zero sample, [kPa.m^2/g^{-1}]	Ageing time, [h]	Burst index at 85^{0}C [kPa.m^2/g^{-1}]	Burst index at 105^{0}C [kPa.m^2/g^{-1}]	Burst index at 125^{0}C [kPa.m^2/g^{-1}]
1	2.7	2	2.8	2.9	2.9
		4	2.8	2.8	3.1
2	2.5	2	2.4	2.7	2.4
		4	2.3	2.8	2.4
3	2.2	2	3.5	3.6	3.6
		4	3.7	3.5	3.7

Fig.3. Micrographs of polyurethane-keratin membranes: a) keratin salt, b) dialyzed keratin, c) alkaline biofiber solution, d) acid biofiber solution, all of them at 15 wt.% [40].

where k is the absorption coefficient, s is the scattering coefficient and R_∞ is the ISO Brightness. The values for the k/S factors were calculated using the experimentally obtained brightness units for the three types of label papers aged at different temperatures. In order to achieve better accuracy the Pc number was recalculated according to Eq.2.

$$Pc = 100\left[\left(\frac{k}{s}\right)_{afterageing} - \left(\frac{k}{s}\right)_{beforeageing}\right], \quad (2)$$

where the scattering coefficient s is unaffected by the yellowing.

Physical factors affecting yellowing of paper include humidity, temperature and time. One of the major phenomena of paper ageing is the trend for reduced brightness and increased yellowness. Figures 3, 5 and 7 show the brightness reversion versus time of ageing at various temperatures for each of the examined types of label papers. Obviously the brightness decreases with increasing temperature and time of ageing. The figures have inherent shapes indicating stable correlation between the brightness loss and temperature. The yellowing increases as the retention time increases. The measured values are similar for the first and second type of papers. The third type has slightly different behavior due to differences in the pigment and binder used for coating. The experimental data were sufficiently well described by one-term power series model.

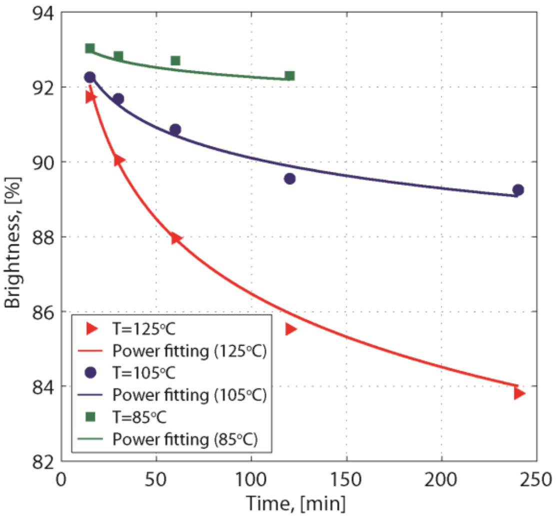

Fig. 3. Brightness dependence on temperatures for paper No 1.

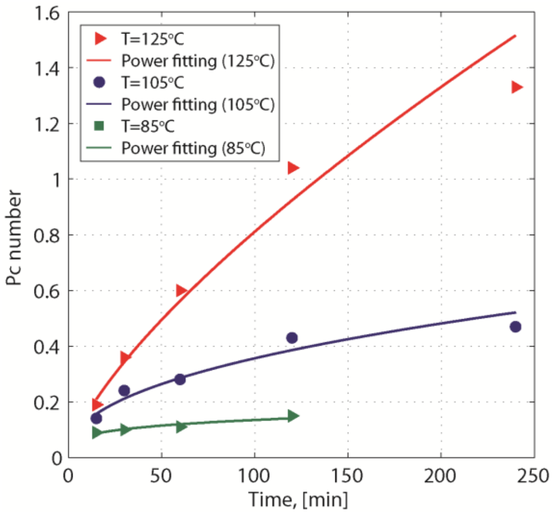

Fig. 4. Pc number dependence on temperatures for paper No 1.

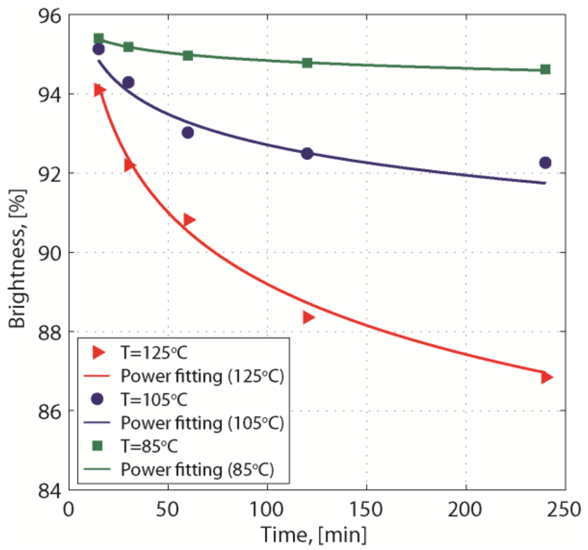

Fig. 5. Brightness dependence on temperatures for paper No 2.

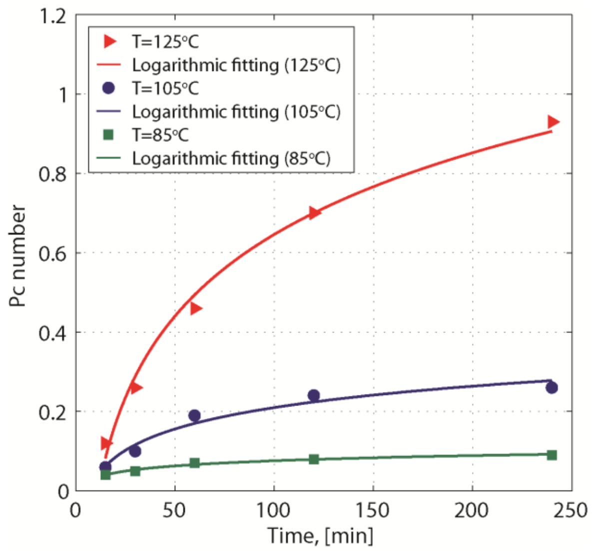

Fig. 6. Pc number dependence on temperatures for paper No 2.

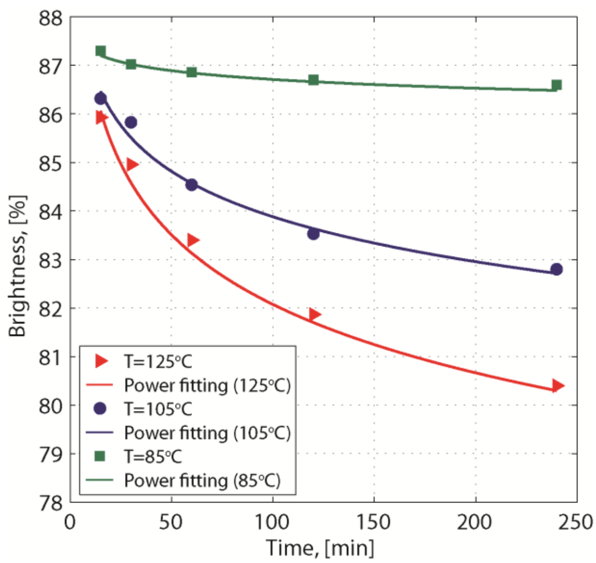

Fig. 7. Brightness dependence on temperatures for paper No 3.

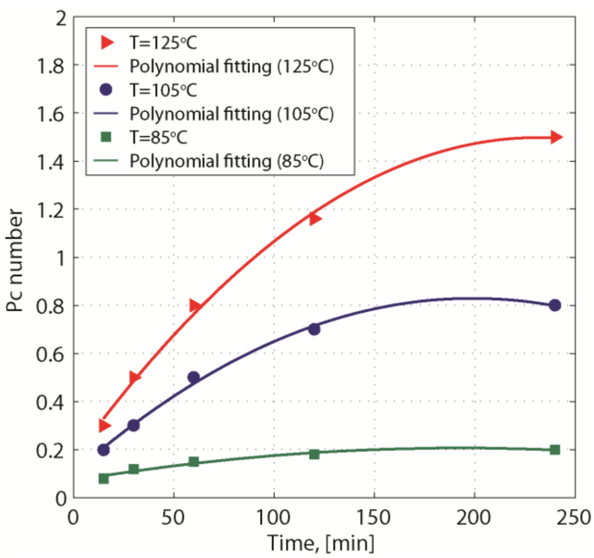

Fig. 8. Pc number dependence on temperatures for paper No 3.

The brightness reversion was also recalculated to Pc number and plotted versus the ageing time. Figures 4, 6 and 8 illustrate the time dependence calculated for the label papers at different temperatures. The figures show good correlation and stability of the ageing process, which proves the general decrease in brightness. The experimental data obtained for Paper No 1 were well described by one-term power series model. Logarithmic equation was used for description of the Pc number data calculated for paper No 2. Second degree polynomial model successfully fitted the calculated data for Paper No 3.

Kinetics of the ageing process

In accordance with Pc number dependences on reaction time kinetic curves were plotted for the three label papers. As already discussed the changes of the Pc number values are with similar characteristics. A representative kinetics of the aging process for Paper No 3 is presented. The experimental data was recalculated in terms of dimensionless quantity α to present the corresponding kinetic curves at different temperature values. The quantity α has a meaning of degree of the ageing and has been used as a kinetic variable. It was calculated in correspondence with equation (Eq. 3):

$$\alpha = \left(\frac{k}{s}\right)_{afterageing} - \left(\frac{k}{s}\right)_{beforeageing}, \qquad (3)$$

where the k/s values changes describe the Pc number values and illustrate the brightness

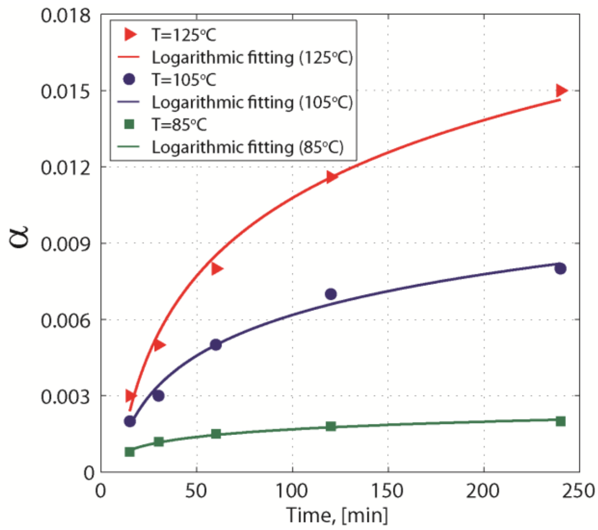

Fig. 9. Described kinetic curves of the ageing at all temperatures for paper No 3.

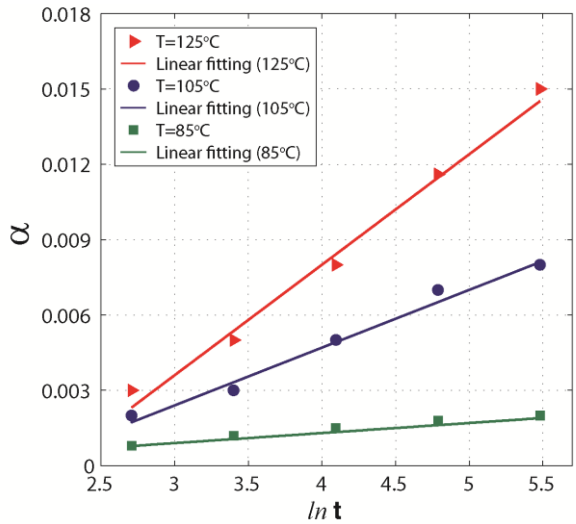

Fig. 10. Linearized kinetic curves of the ageing at all temperatures for paper No 3.

reversion. Figure 9 illustrates α as a function of the ageing time for experimental based recalculations for Paper No 3. As it can be seen the degree of ageing increases with increasing time and temperature.

After verification of applicability of different kinetic equations valid for heterogeneous processes was found that the accelerated ageing process was best described by an exponential kinetic equation. This equation is valid for processes which are taking place on uniformly inhomogeneous surfaces like the label papers surfaces [16]. According to the model of uniformly inhomogeneous surfaces expressed by Eq. 4 the active centers on the surface are distributed linearly referring to their energy and entropy,

$$v = v_0 e^{-a\alpha} \quad (4)$$

where $v = d\alpha/dt$ is the current rate and v_0 is the initial rate of the ageing process. The kinetic coefficient of inhomogeneity α, which is temperature-dependent term, accounts for the energy and the entropy inhomogeneity of the system [17].

Figure 10 shows α values for three temperatures as a linear function of lnt in correspondence with the approximate integral form of the exponential kinetic equation (Eq.5):

$$\alpha = \left(\frac{1}{a}\right)\ln(v_0 a) + \left(\frac{1}{a}\right) lnt \ . \quad (5)$$

The kinetic coefficient of inhomogeneity *a*, which is temperature-dependent term, accounts for the energy and entropy inhomogeneity of the system.

Equations 5 and 4 were used respectively for estimation of the initial rate v_0 and current rates v of the ageing process performed at the three temperature values. Their linearized values in accordance with Equation 4 are presented in Figure 11. It is seen that the current rate decreases in the course of the process.

As a proof of this conclusion the results for linearized process rate values calculated at 105°C ageing temperature for the three types of label papers are presented in Figure 12. It is seen that the current rate decreases in the course of the process with increasing of the ageing degree.

The temperature dependence of ageing rate constants was described by the well-known Arrhenius equation (Eq.6):

$$v = Ae^{-E/RT} \ , \quad (6)$$

where *A* is the pre-exponential factor, *E* is the activation energy (kJmol-l). This dependence was applied for the initial rate and calculations for the initial activation energy and pre-exponential factor were done. In Table 3 are summarized the values calculated for the three types of paper. It can be seen that the differences in the activation energy values are minimal for the examined papers. It was found that the activation energy is a determinant for the decreasing rate of the ageing process. The higher pre-exponential factor value for Paper No 3 could be explained with the different pigment layer of the label paper. The ageing process was localized in the surface layer which is determined by the pigment surface coatings used for the three examined label papers. The initial stage of the process affects more active chromophores. During the ageing process new chromophore groups are generated. This new active centers are with decreasing reactive ability with increasing of the ageing time.

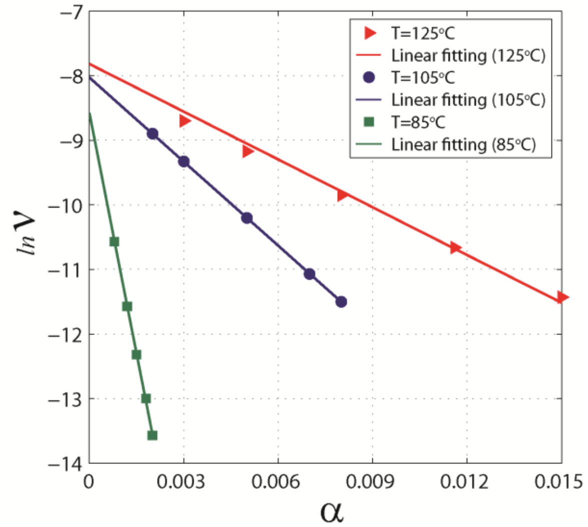

Fig. 11. Linear dependence of process rate vs. ageing degree for paper No 3.

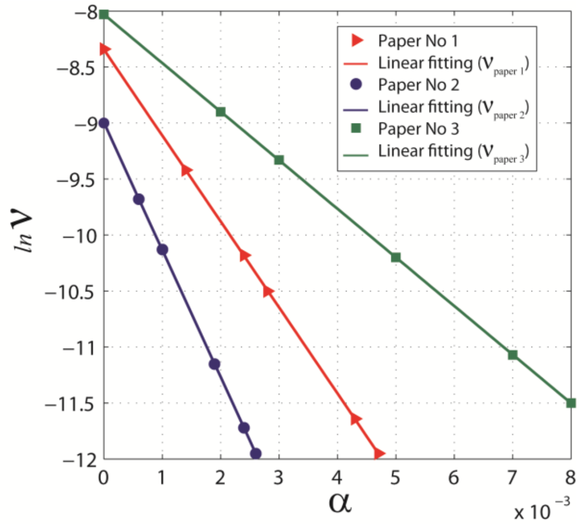

Fig. 12. Linear dependence of process rate vs. ageing degree for all types of paper.

Table 3. Initial activation energy E_0 and pre-exponential factor for all types of paper.

Paper No		2	3
E_0, [kJ/mol]	26.3	26.7	29.7
lnA_0	1.02	0.87	4.06

Colour differences

The permanence of the examined label papers was studied in term of color stability of printed images. Ink-jet system with dye-based inks was used for the printing process. Dye inks are prepared by dissolving of the liquid colored dyes into a fluid carrier. This makes them easy to apply. When they are applied to a paper, the dyes are absorbed very uniformly and reflect light very evenly. During ageing the properties of the paper and ink are simultaneously changing. Hence the durability of the prints depends not only of their chemical composition but also of the physical characteristics of the printed paper.

One of the main quality characteristics of a printed testcharts is the color difference between measured and reference solid process colours. Figure 13 illustrates the obtained colour differences differences were obtained for Paper No 3 due to the denser pigment layer of this paper and its more stable surface structure. The differences are higher at the end of the ageing process.

Figure 14 demonstrates the maximum and averaged colour differences between all ink colours on non-aged samples and aged printouts of the for solid patches of the four process colours on aged papers in relation to the prints on non-aged papers. The color difference was calculated in term of ΔE^*_{ab} in accordance with Equation 7:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}\ , \quad (7)$$

where $\Delta L^* = L^*_2 - L^*_S$, $\Delta a^* = a^*_2 - a^*_S$, $\Delta b^* = b^*_2 - b^*_S$ are the distances between aged and non-aged colour values in the coordinates respectively of L^*, a^* and b^*. The value of ΔE^*_{ab} is perceptually similar to human's visual perception of color difference. The dimensionless values of ΔE^*_{ab} can be roughly classified into three different levels to reflect the degrees of color difference perceived by human. The color difference is hardly perceptible when ΔE^*_{ab} is smaller than 3; is perceptible but still tolerable when ΔE^*_{ab} is between 3 and 6; and not acceptable when ΔE^*_{ab} is larger than 6 [18]. From the results can be seen that all colour shifts are tolerable. Lowest colour

three types of paper. According to the experimental data Paper No 3 is less influenced by the accelerated ageing but all obtained results are tolerable. The averaged differences are hardly perceptible. This manifests that the prints are stable during time.

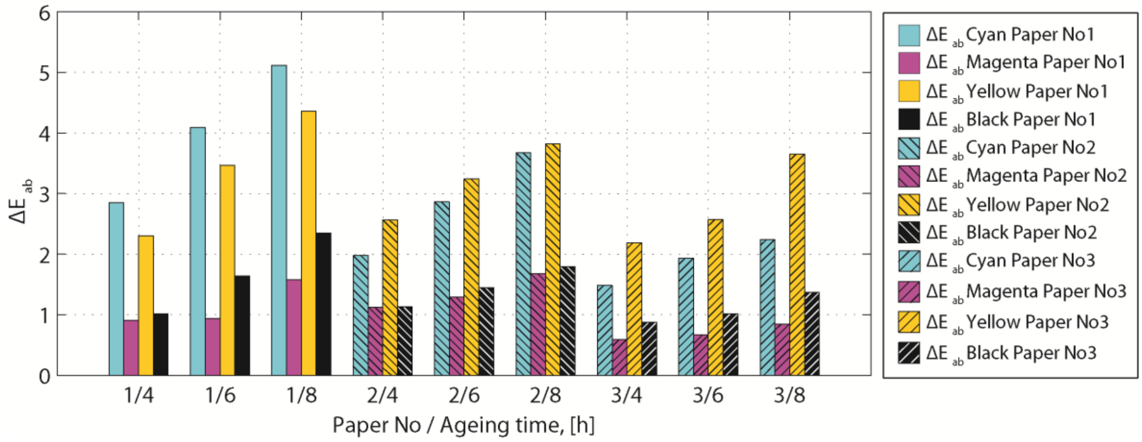

Fig. 13. Ageing influence on color differences for full tone CMYK.

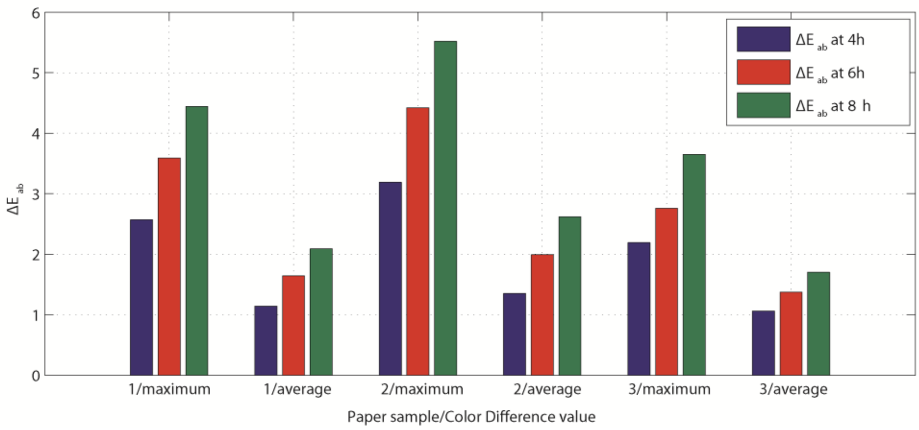

Fig. 14. Ageing influence on color differences of printed testcharts

CONCLUSION

Experimental data showed that paper No 3 has slightly different behavior in respect of brightness reversion compared to other studied label papers. This can be explained with the denser pigment surface layer and different pigment surface coating.

The kinetics of the ageing process was studied. The results indicated that the process takes place at the surface. As the paper surface is uniformly inhomogeneous an exponential kinetic equation valid for this type of processes was successfully applied to describe the experimental kinetic data. The temperature-dependent kinetic coefficient, which takes into account the energy and entropy of the ageing, was determined.

Analysis of the kinetics of the ageing process showed that similar initial activation energies are found for the three types of label papers. The activation energy was found to increase in the course of the ageing process because of the formation of new active centers.

All three types of paper are suitable for labeling applications due to their resistance of mechanical and optical properties to accelerated ageing.

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ВЛИЯНИЕ НА ТЕРМИЧНОТО СТАРЕЕНЕ ВЪРХУ КАЧЕСТВАТА НА ХАРТИЯ ЗА ЕТИКЕТИ

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(Резюме)

Стареенето на хартията може да бъде разгледано като резултат от всички необратими физични и химични процеси, които възникват в материала в течение на времето. Понижаването на белотата е един от тези процеси, които са от значение за производителите на висококачествени бери хартии. Реверсията е в резултат от образуването на хромофорни структури в резултат на реакции на кондензация.

Влиянието на термичното стареене върху механичните и оптични свойства на хартия за етикети е предмет на настоящото изследване. За анализа са използвани три вида пигментно покрита хартия. Изследвана е зависимостта на Pc числото от продължителността на стареене при три различни температури. Резултатите показат значително нарастване при хартията с по-плътен повърхностен слой. Това се определя от хромофорните структури в пигментния повърхностен слой. Кинетиката на процеса на стареене при всички използвани хартии се описва най-точно от експоненциалното кинетично уравнение.

Проведено е допълнително изследване за определяне стабилността на цветовите характеристики на дигитални отпечатъци при термично стареене. Върху хартиите за етикети са направени отпечатъци посредством многоцветно печатащо устройство и подложени на термично стареене, при същите условия. Анализирани са разликите между начални отпечатъци и такива, които са подлагани на стареене. Техните колориметрични характеристики са представени като цветна разлика ΔE^*_{ab}.