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Dyes and Pigments 54 (2002) 173–188

DYES and PIGMENTS

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The stability of offset inks on paper upon ageing

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Received 15 March 2002; received in revised form 19 April 2002; accepted 10 May 2002

Abstract

The standard moist heat (80 °C and 65% relative humidity) and dry heat (105 °C) techniques of accelerated paper ageing were applied in stability investigations of offset ink films printed on alkaline offset paper. The measured characteristics of paper sample evidenced its first-class mechanical properties, large alkali reserve, in addition to high values of brightness and opacity. The pseudoplastic flow behaviour was established for original offset CMYK printing inks by rheological measurements. The results obtained, following application of both ageing procedures, revealed the significant exponential decrease of relative optical density for MAGENTA and YELLOW ink layers. The variance in visible reflectance spectra and in total colour difference ΔE^* ($L^*a^*b^*$ CIE) of ink films evidenced the considerable damage of CYAN and YELLOW ink films, especially upon moist heat treatment. The differences in lightness ΔL^* play the dominant role in ΔE^* values of BLACK ink films upon both ageing procedures. The FT-IR spectroscopy was additionally used in the characterization of paper, inks, as well as ink films on paper before and after ageing.

Keywords: Offset inks; Accelerated ageing; Rheology; Optical density; Colour measurement; FT-IR spectroscopy

1. Introduction

An intensive effort is focused on the methods of preservation and damage inhibition of archival documents [1–3]. The deterioration of paper materials upon ageing is initiated by the irreversible breakage of their mechanical, chemical and optical properties [4]. The significant role in deterioration of historical documents plays chemical composition of paper, ink and ink corrosion [5–7]. The recent investigations are oriented to standardize the printing technologies for printing of permanent documents. The performance requirements of paper material for documents were summarized in the standards STN ISO 9706 and ANSI/NISO Z39.48–1992 [8]. The properties of inks (lightfastness, alkaline resistance, solvent resistance) are characterized with national and international standards [9,10]. The printing inks represent a complex mixture of different components, which are classified by their function in ink matrix, and the ink composition is significantly

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0143-7208/02/$ - see front matter
PII: S0143-7208(02)00045-1

dependent on the printing technology [10–14]. The flow characteristics, drying mechanism, drying time, and polarity of inks are determined predominantly by the liquid vehicle, which includes materials such as oil, solvent and resin. The individual ink colours originate through the combination of dyes and pigments in the inks [13,14]. The selection of suitable inks for permanent printing on alkaline paper remains open to question, and the investigations of ageing stability of ink films are scarce [10–12]. Maraval and Flieder published a detailed study of the stability for black and coloured offset printing inks on alkaline paper upon damp heat ageing (30 days, 90 °C and 65% relative humidity, RH) and light ageing (300 h at 30 °C and 50% RH under 1500-W xenon lamp with radiant energy 70 Wm^{-2}) [10]. Their results demonstrated that black printing inks keep the chemical and visual properties upon accelerated ageing, conversely the tested coloured offset inks showed lower ageing stability especially for magenta and yellow prints [10].

Our study is oriented on the investigations of changes in optical density, visible and FT-IR spectra and in total colour difference of RAPIDA CMYK offset ink films printed on alkaline paper during accelerated ageing procedures (moist heat at 80 °C and 65% RH and dry heat at 105 °C), with the main aim being to decide on the appropriate combination of paper/ink for permanent offset printing.

2. Experimental

2.1. Materials

The investigations were performed using original offset printing inks RAPIDA CYAN (43 F 7000), RAPIDA MAGENTA (42 F 7000), RAPIDA YELLOW (41 F 7000) and RAPIDA BLACK (49 F 7001), produced by Michael Huber, Germany. These printing inks are recommended for offset sheet printing. Standard alkaline offset paper (SCP Ružomberok, Slovak Republic) was applied in all experiments. In accordance with the information from the paper producer, this paper material contains the optical brightening agents.

2.2. Apparatus

The characteristic properties of offset paper samples were measured according to the Slovak Technical Standard (STN) and STN ISO standards using the following instruments: automatically-operated micrometer, automatic analytical balance (Sartorius, precision of 0.001 g), a device for the water absorbency determination according to $Cobb_{60}$, universal apparatus INSTRON 1011 (UK), instrument for the smoothness evaluation according to Beek (Büchel-Van der Korput, Netherlands), and filter photometer ELREPHOMAT DFC-5 used in paper brightness measurements at the wavelength of 457 nm. Paper surface pH values were determined by a WTW pH meter using a combined glass electrode at 25 °C. In accordance with the STN ISO 187 standard, the paper samples were air-conditioned before measurements, which were undertaken under the same conditions. The pH values of the cold aqueous extracts of paper were measured at 25 °C using pH-meter OP-208/1 (Radelkis, Hungary) with a combined glass electrode.

The controlled transfer of the offset inks onto paper was achieved using a TJ-3 print tester (Grafotechna, Czech Republic). The ink was surfaced on the topside of paper in machine direction. The optical density of the prepared ink films was measured in accordance with STN 50 0426 standard, using a reflection densitometer X-Rite 428 (X-Rite, USA).

The rheological behaviour of the offset inks was investigated by means of a Viscotester VT500 (Haake Mess-Technik, Germany) with cone and plate geometry. A 10 mm, 1 degree cone (PK2–1) was applied in the study of the flow behaviour. The standard volume of ink sample (0.130 ml) was placed symmetrically to the centre of the plate. The shear stress was measured during the controlled applied shear rate gradient of 33.3 s^{-1} per minute. The thixotropy of the ink samples was monitored by increasing the shear rate from 0 s^{-1} up to 100 s^{-1} over 2 min, and immediately after reaching the maximal shear rate, decreasing down to 0 s^{-1} during 2 min. The measurements were repeated three times with new sampling undertaken at the constant temperature of 25 °C.

The accelerated ageing of printed paper was studied applying two different techniques in accord with ISO 5630 standard: i) moist heat treatment at 80 °C and 65% relative humidity (climatic chamber FEUTRON, GmbH Greiz, Germany), and ii) dry heat treatment at 105 °C using drying unit WSU 100 (VEB MLW Labortechnik, Illmenau, Germany) during the required time period (0, 3, 6, 12 and 24 days).

Spectrophotometer Spectrolino (GretagMacbeth, Switzerland) was used for the measurements of the reflection spectra of ink layers on paper, and for the determination of specific ink colour components L^*, a^*, b^* before and after accelerated ageing procedures.

The FT-IR spectra were recorded by FT-IR spectrometer Nicolet 740 (Nicolet Instruments Co., USA) using diffuse reflectance infrared Fourier transform (DRIFT) technique for the investigations of paper and inks on paper, before and after ageing procedures. The DRITF spectra were scanned four times on the different sample locations and the averaged IR spectrum was calculated numerically. The FT-IR spectra of the original inks were measured preparing thin ink films on KBr window. The standard FT-IR spectrometer settings were as follows: range 4000–400 cm^{-1}, 1024 scans, resolution 4 cm^{-1}.

Table 1
The mean values of characteristic parameters determined for the original paper

Standard offset paper (SCP Ružomberok, Slovak Republic)		
Grammage ($g\ m^{-2}$)	80.0	
Thickness (μm)	98.9	
Specific weight ($kg\ m^{-3}$)	799	
Brightness (%)	95.6	
Opacity (%)	92.5	
Kappa number	1.3	
pH of cold aqueous extract	9.4	
Alkali reserve ($mol\ kg^{-1}$)	3.5	
Surface pH	8.3	
Smoothness (s)	48[a]	47[b]
Water absorbency by surface ($g\ m^{-2}$)	21.5[a]	22.3[b]
Breaking stress ($kN\ m^{-1}$)	4.4[c]	1.8[d]
Breaking length (km)	5.0[c]	4.2[d]
Breaking index ($N\ m\ g^{-1}$)	49.3[c]	40.7[d]
Tear index ($mN\ m^2\ g^{-1}$)	7.61[c]	6.30[d]
Folding endurance index ($m^2\ g^{-1}$)	0.91[c]	0.24[d]

[a] Topside.
[b] Underside.
[c] Machine direction.
[d] Cross direction.

3. Results and discussion

3.1. Characterization of paper substrates

Table 1 summarizes the evaluated mean values (calculated from 10 measurements) of physico-chemical, optical and mechanical properties of the original paper used in our investigations. The parameters of cellulosic materials were determined in accordance with the corresponding STN ISO standards [8]. The experimental characteristics documented, that this offset paper represents white alkaline paper with mechanical properties of good quality, sufficiently large alkali reserve, as well as high values of brightness and opacity.

3.2. Rheological behaviour of printing inks

The shear stress, τ, versus shear rate, D, flow curves measured for RAPIDA CMYK offset inks are illustrated in Fig. 1a. Almost analogous rheological behaviour was observed for the CYAN and YELLOW inks, as under given experimental conditions flow curves without shear fracture were obtained [15]. In contrast, flow curves for MAGENTA and BLACK inks showed evidence for the shear fracture, caused by samples creeping out of the measuring gap. The analogous rheological profile of various viscous printing inks was studied previously by Chou [16]. Considering the viscoelastic properties of the inks, the analysis of the shear stress versus shear rate dependencies is limited to the shear rate range of $\Delta D = D_{max} - D_{min}$ [15]. The experimental rheological data (shear rate in the region from $D_{min} = 32\ s^{-1}$ up to $D_{max} = 62\ s^{-1}$) of investigated inks were fitted using least square analysis (programme Scientist, MicroMath) by the Ostwald flow model [Eq. (1)] [15]:

$$\tau = A\ D^b \quad (1)$$

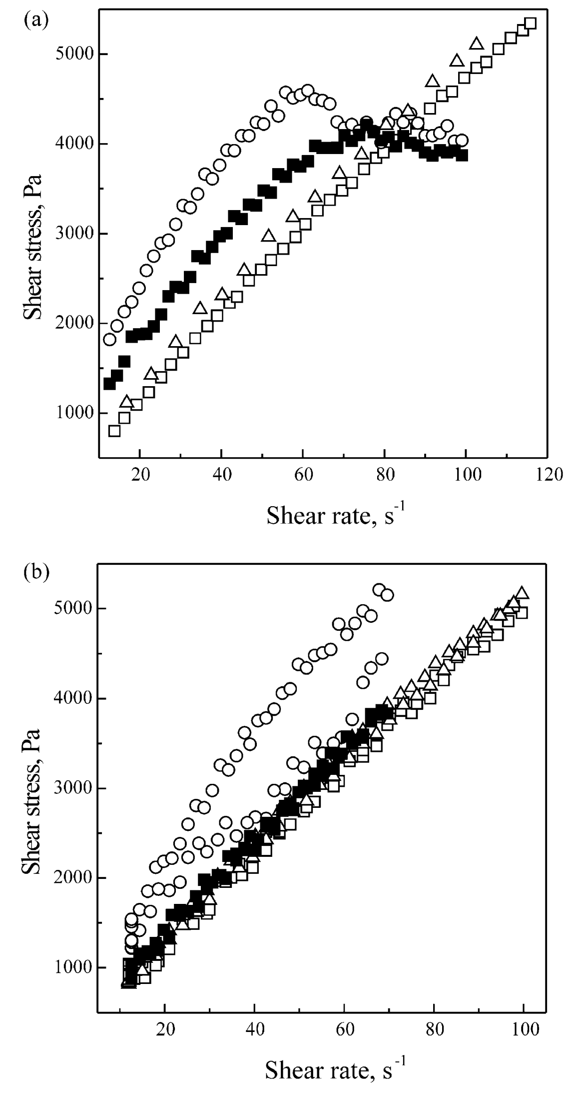

Fig. 1. The shear stress versus shear rate dependencies (a) and the thixotropic flow curves (b) measured for original RAPIDA offset inks ($t = 25$ °C): □ CYAN; ○ MAGENTA; △ YELLOW; ■ BLACK.

where A reflects viscosity and b characterizes the flow behaviour ($b = 1$ Newtonian, $b > 1$ dilatant and $b < 1$ pseudoplastic flow behaviour, respectively).

The results of numerical evaluations by means of the Ostwald rheological model, along with the R-squared of the fittings for RAPIDA CMYK offset inks are summarized in Table 2. The high values of R-squared ($R^2 \geqslant 0.999$) confirmed that a good agreement of the experimental and calculated data was achieved. The evaluated parameters b reflected pseudoplastic flow behaviour ($b < 1$) for RAPIDA CMYK offset inks under study; the highest deviation from Newtonian flow behaviour was obtained for MAGENTA ($b = 0.48$) and BLACK ($b = 0.63$) inks (Fig. 1a). The measurements of thixotropy using offset printing inks RAPIDA CMYK demonstrated only negligible hysteresis loop areas for CYAN, YELLOW and BLACK inks, however a significant thixotropy effect was observed for MAGENTA ink (Fig. 1b).

Table 2
The parameters of the Ostwald rheological model along with the R-squared, calculated using experimental flow curves of the RAPIDA offset inks (shear rate in the range from 32 s^{-1} up to 62 s^{-1})

Ink	Ostwald rheological model $\tau = AD^b$		
	A (Pa s)	b	R-squared
CYAN	78	0.90	0.9999
MAGENTA	640	0.48	0.9997
YELLOW	110	0.82	0.9998
BLACK	290	0.63	0.9997

3.3. Ink transfer on paper

The formation of ink film on the paper in the printing process is substantially influenced by paper—ink interactions, consequently observed optical density of the ink films on paper, i.e. mileage curve, incorporates simultaneously the properties of ink and paper substrates [15].

The dependence of the optical density (OD) on the ink concentration on the paper (y) may be described by the Tollenaar–Ernst equation [17]:

$$OD = OD_{\infty}\ (1\text{-}e^{-my}) \tag{2}$$

where OD_{∞} is the saturation optical density, m is the parameter dependent on pigment distribution in the ink, as well as paper individuality [15].

Fig. 2 shows the experimental data of density curves measured for the original RAPIDA CMYK inks on standard offset paper, along with simulations obtained by non-linear least squares analysis using Tollenaar–Ernst equation [Eq. (2)]. The results of the fitting procedure are summar-

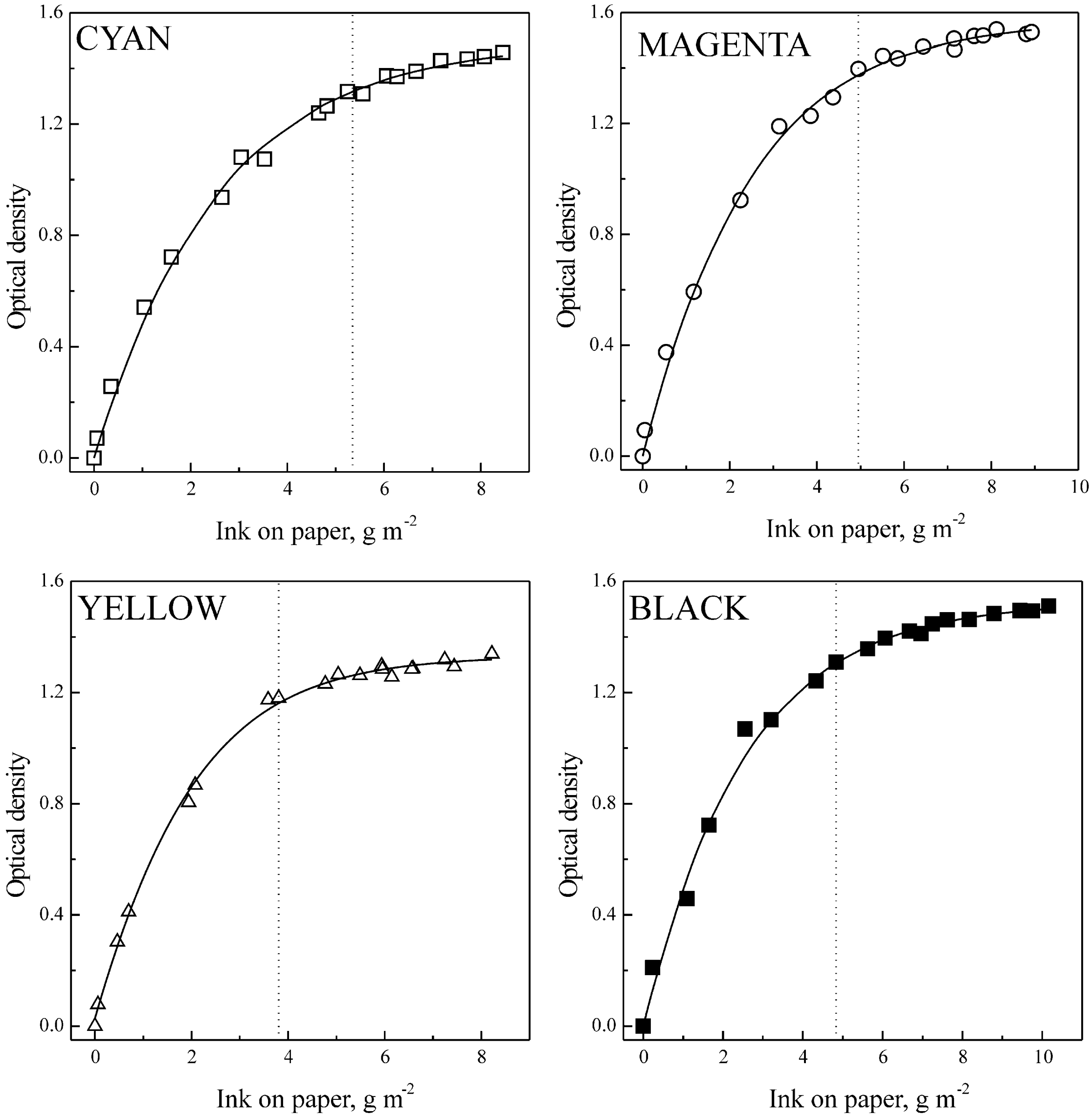

Fig. 2. The ink mileage curves measured using RAPIDA CMYK offset inks on standard offset paper (SCP Ružomberok, Slovak Republic). Solid lines represent the simulations of mileage curves applying Tollenar–Ernst equation (Table 3). Dotted lines illustrate ink concentrations on paper, which correspond to 85% of saturation optical density OD_∞.

ized in Table 3. The calculated values of parameter *m* correlate with the rate at which the saturation density of ink film on paper substrate is achieved. Parameter *m* is decided mainly by the paper characteristics and pigment concentration in the ink. The paper smoothness significantly influences the formation of ink film on the paper surface and the process of saturation density achievement [15]. The highest value of parameter *m* was measured for the YELLOW ink, which on the other hand attained the lower saturation density under given experimental conditions (Fig. 2, Table 3).

The accelerated ageing experiments were performed using paper samples surfaced by ink films with an optical density corresponding to 85% of saturation optical density *OD* (dotted lines in Fig. 2).

Table 3
The parameters of the Tollenaar–Ernst equation along with the *R*-squared, calculated using experimental mileage curves of the RAPIDA offset inks

Ink	Tollenaar–Ernst equation $OD = OD_\infty$ (1-e^{-my})		
	OD_∞	m (m^2 g^{-1})	*R*-squared
CYAN	1.50	0.40	0.9994
MAGENTA	1.58	0.42	0.9995
YELLOW	1.34	0.52	0.9996
BLACK	1.53	0.40	0.9992

3.4. FT-IR spectra of RAPIDA CMYK offset inks

The offset printing inks are manufactured using a variety of substances with different chemical structures [10–13]. Fig. 3 represents the FT-IR spectra measured for the original CYAN, MAGENTA and YELLOW ink films surfaced on KBr window. The presence of absorption bands at 3006, 2925, 2854, 1739, 1462, 1385, 1233, 1163, 1096, 1006 and 727 cm^{-1} is evidence for the presence of alkyd resin [18] in all investigated inks. Additionally, in the infrared spectra were identified representative absorptions peaks for carbonates (1630, 1433, 879, 715 cm^{-1}) and silicates (1032, 1009 cm^{-1}). The recognition of coloured pigments in the inks was based on the comparison of experimental spectral data with a FT-IR spectra database [18]. The CYAN offset ink probably contains copper phthalocyanine pigment with typical infrared absorptions at 2936, 2870, 1607, 1505, 1460, 1419, 1375, 1334, 1288, 1166, 1120, 1091, 998, 900, 786, 778, 726, 571 and 506 cm^{-1} (Fig. 3). The dotted line depicted in Fig. 3 for CYAN ink represents the simulation of experimental FT-IR spectrum fitted as the linear combination of the catalogue FT-IR spectra for alkyd resin, $CaCO_3$ and copper phthalocyanine [18] using a least-squares minimization procedure with the Scientist Programme (MicroMath).

The pigments included in MAGENTA and YELLOW inks were not unambiguously identified by means of FT-IR spectroscopy, since we found no compatible spectra in the FT-IR spectra database.

The FT-IR spectra measured for the RAPIDA BLACK ink confirmed the presence of carbon black, as well as copper phthalocyanine pigment.

3.5. Accelerated ageing of printed paper

The accelerated ageing of printed documents represents complex problems, for during ageing procedure chemical and mechanical properties of the paper materials and the ink components are simultaneously changed. Previously, we applied the dry heat treatment at 105 °C in the investigations of accelerated ageing for different paper samples [19]. The dry heat ageing procedure is very powerful and fast, since three days under these conditions correspond to 25 years of natural paper ageing [8]. On the other hand the moist heat technique of accelerated paper ageing is slower and less effective, but better simulates the natural ageing behaviour of paper materials. Upon accelerated ageing of standard offset paper (SCP Ružomberok, Slovak Republic) we observed the decrease in folding endurance index, breaking stress, breaking length, breaking index, tear index, brightness, cold extract pH, alkali reserve, and changes in water absorbency by surface and smoothness, however in summary this paper indicated good ageing resistance [19].

Fig. 4 illustrates the decrease of paper brightness upon time of accelerated ageing applying moist heat action (80 °C and 65% RH) or dry heat treatment at 105 °C. The experimental data were fitted using least squares analysis by the exponential functions analogous to the formal first-order kinetics (lines in Fig. 4). The loss of brightness (paper yellowing) is more progressive using moist heat treatment, seeing that we found a drop of 9.4% after 24 ageing days, compared with a decrease of 7.9% using dry heat procedure.

The yellowing of paper during the ageing procedure is attributed to the presence of chromophores formed by the degradation of paper components (cellulose, hemicellulose, lignin). The formation of macromolecular hydroperoxides in the cellulose backbone was evidenced previously in the research on paper ageing, and the significant role of the produced radical species was postulated [20]. Newly, the formation of hydroxyl radicals upon accelerated ageing of alkaline cellulose was quantitatively determined using a colourimetric method via *N*,*N*′-(5-nitro,1,3-phenylene)bisglutaramide, and the reasonable correlation between

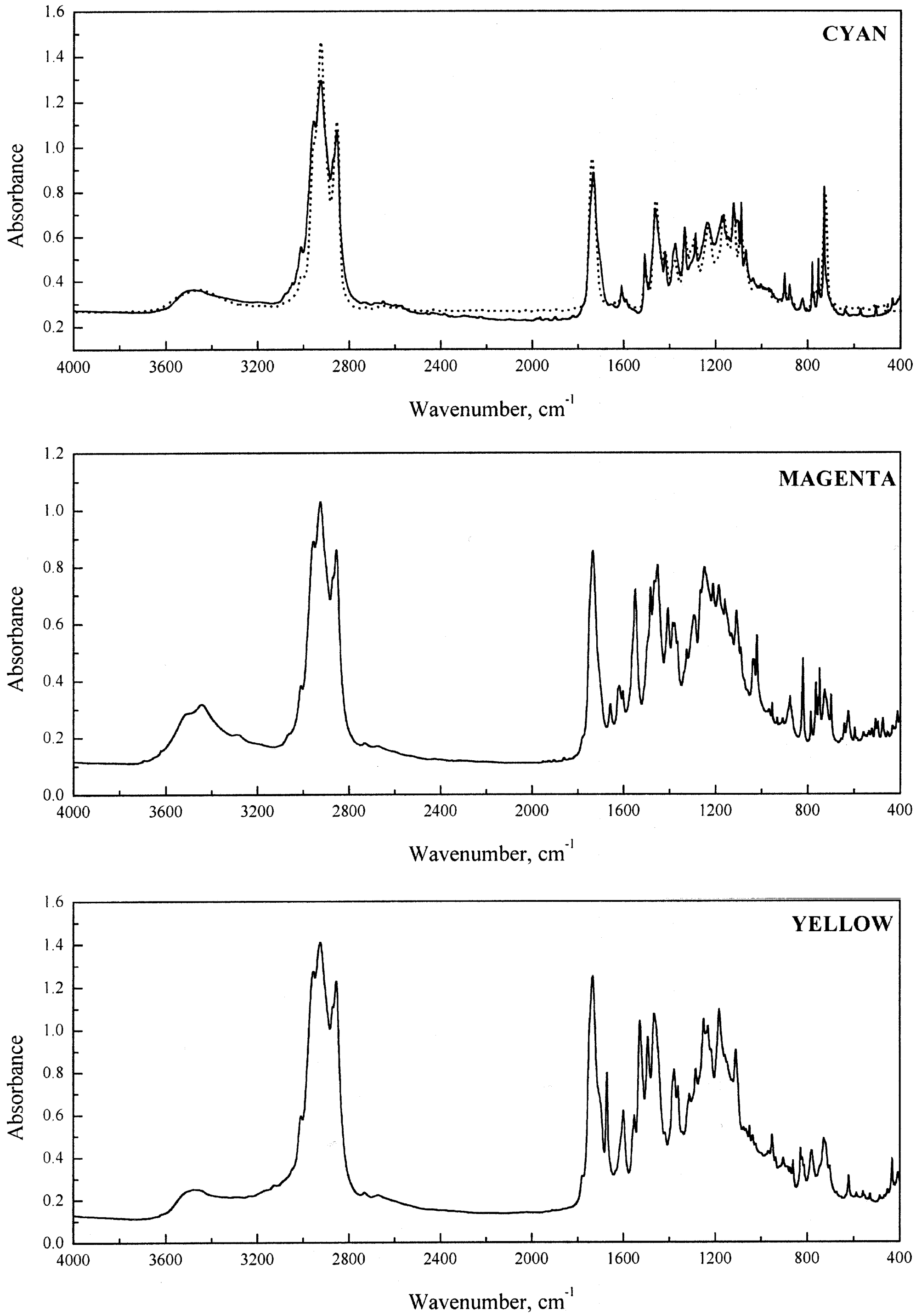

Fig. 3. The FT-IR spectra of original RAPIDA offset inks CYAN, MAGENTA and YELLOW (thin ink films were surfaced on KBr window). The dotted line for CYAN ink represents the simulation of experimental FT-IR spectrum fitted as the linear combination of catalogue FT-IR spectra of alkyd resin, $CaCO_3$ and copper phthalocyanine.

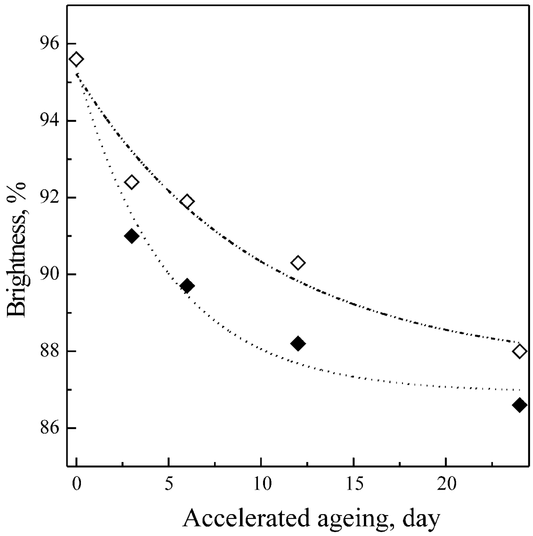

Fig. 4. The dependence of paper brightness on the time of accelerated ageing: ◆ moist heat (80 °C and 65% relative humidity); ◇ dry heat treatment (105 °C). The lines represent the mathematical simulations of experimental data in accord with the formal first-order kinetics.

hydroxyl radicals production and cellulose chain scission was found [21]. Additionally, the presence of metals in paper materials can affect the process of paper yellowing, including a free radical mechanism, in which the metal ions catalyse homolytic cleavage of the cellulose hydroperoxides, and a Lewis mechanism, respectively [22].

Attempting to investigate the changes in the chemical composition of paper caused by accelerated ageing, we measured the FT-IR spectra of original and aged paper samples (Fig. 5). As paper consists mainly of cellulose fibres, the IR absorption bands typical for cellulose [23], dominate in the IR spectrum of the original offset paper, and no considerable changes were monitored in the IR spectra of paper samples aged 24 days (Fig. 5). The difference spectra evaluated by the IR spectra subtraction of original and aged paper samples, confirmed only negligible increase of absorption in the region 1200 – 1000 cm^{-1}, representative for the C–O stretching, ring stretching and C–O–C asymmetric stretching vibrations [3]. The moist heat accelerated paper ageing procedure additionally resulted in the increase of absorptions at 1640 and 2740 cm^{-1}, corresponding to the increase of hydroxyl and aldehydic groups, respectively.

The FT-IR and FT-Raman spectroscopic study of hydrothermally degraded cellulose (100 °C and 100% RH) was performed using different sampling methods (transmission, KBr, ATR), and the obtained results were significantly dependent on the spectroscopic technique applied [24]. The DRIFT FT-IR spectroscopy was applied in the study of cellulose interactions with near-UV, visible and IR pulsed laser light, and the measured FT-IR spectra clearly evidenced the differences between photochemical ($\lambda = 308$ nm) and photothermal ($\lambda = 1064$ nm) degradation of cellulose [3].

FT-IR and near-IR spectroscopy was successfully used in the study of aged cellulosic paper from insulation of electrical transformers. The cellulose crystallinity indices were calculated using ratios of IR spectra absorption bands 1280/690, 1430/900 and 2900/1370, and the results demonstrated that the crystalliny of thermally aged cellulose is higher than that of the original sample [25]. In accordance with this study we evaluated by means of IR spectra, crystallinity indices for the original and aged paper samples; those however showed no clear tendency for cellulose crystallinity change upon accelerated ageing.

The exponential decline of relative optical density for paper samples printed using RAPIDA CMYK inks on the time of accelerated ageing is depicted in Fig. 6. The excellent stability of optical density upon moist heat (80 °C and 65% RH) and dry heat (105 °C) accelerated ageing procedure was observed for CYAN and BLACK inks, as we measured only negligible reduction in the relative optical density whithin the experimental error of the X-Rite 428 densitometer. The layers of MAGENTA and YELLOW inks exhibited lower stability of optical density during both ageing techniques. Upon moist heat treatment the highest drop in optical density was monitored for MAGENTA ink (~11%, Fig. 6a), and on the other hand, the dry heat accelerated ageing method caused the highest decrease of the optical density for the YELLOW ink (~10%, Fig. 6b).

Maraval and Flieder published the analogous behaviour of offset inks upon accelerated ageing (30 days, 90 °C and 65% RH) when the variance

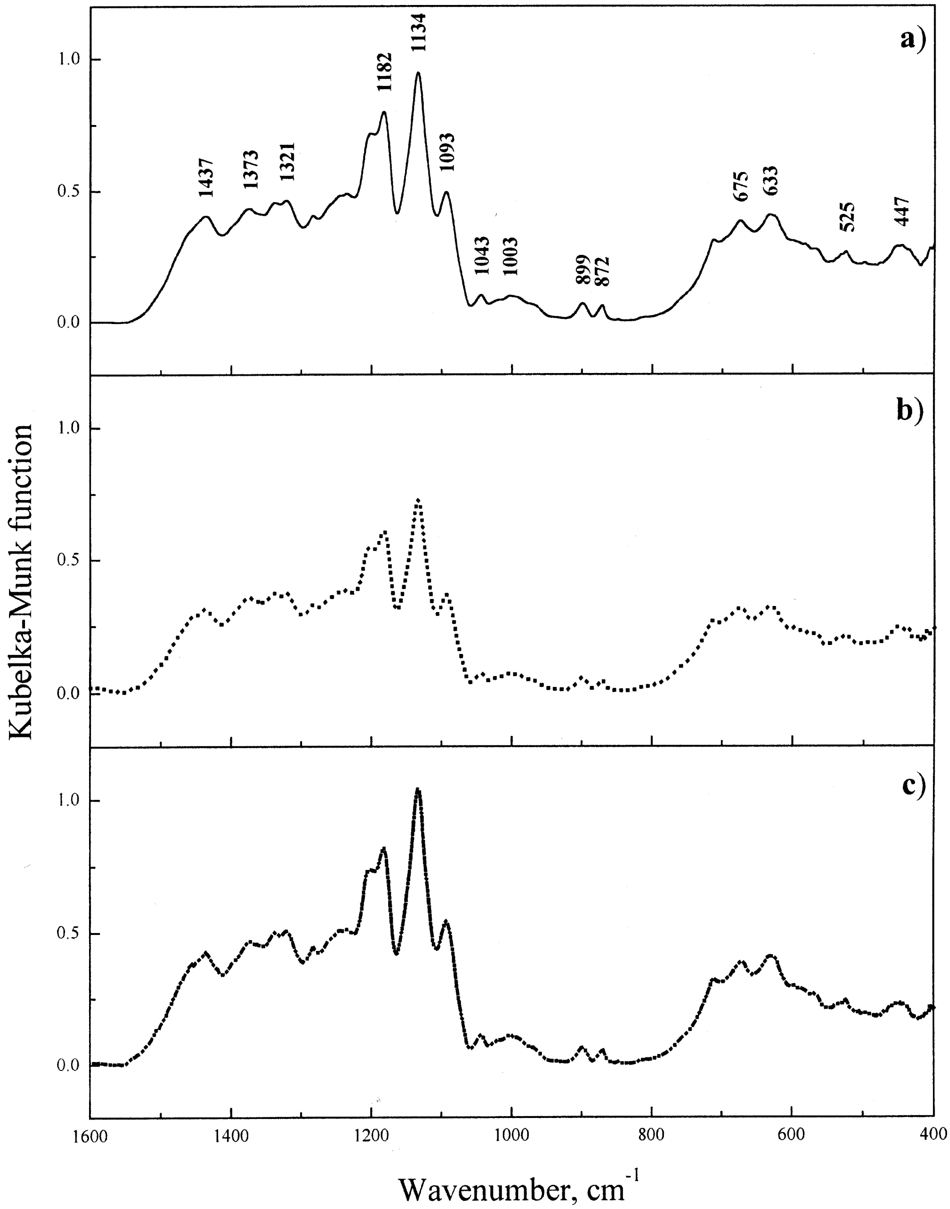

Fig. 5. Diffuse reflectance FT-IR spectra of (a) original offset paper; (b) paper sample after 24 days of moist heat accelerated ageing (80 °C and 65% relative humidity); (c) paper sample after 24 days of dry heat treatment (105 °C).

of optical density for 15 black inks was below 3%, but for magenta and yellow inks it reached a loss of 10% [10].

The reflectance spectra of the original RAPIDA CMYK inks printed on paper, as well as ink layers after 24 days of moist heat (80 °C and 65% RH) and dry heat (105 °C) handling is illustrated in Fig. 7. The original RAPIDA CYAN ink film is characterized with a dominant absorption peak at 470 nm together with a low absorption peak at 400 nm. The application of moist heat caused the formation of a weak absorption band at 396 nm, in addition to the bathochromic shift of the main maximum to 480 nm (Fig. 7). This shift to the

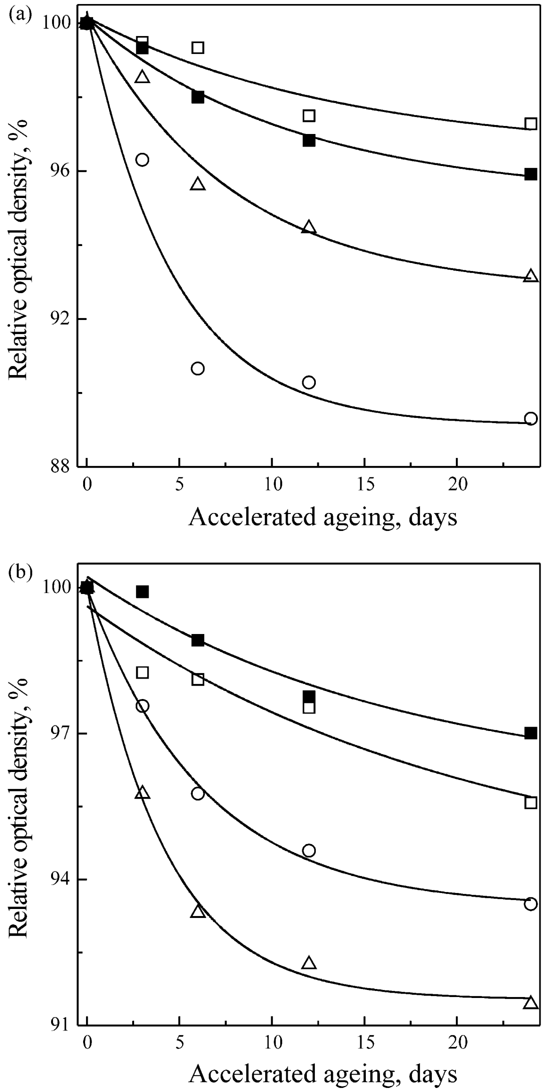

Fig. 6. The dependence of relative optical density on the time of accelerated ageing: □ CYAN; ○ MAGENTA; △ YELLOW; ■ BLACK. (a) Moist heat (80 °C and 65% relative humidity); (b) dry heat (105 °C). The lines represent the mathematical simulations of experimental data in accord with the formal first-order kinetics.

longer wavelengths was observed after 24 days of dry heat treatment, too. Additionally, both ageing methods stimulate the reflectance lowering in the region 410–510 nm.

The MAGENTA ink films exhibited only small reflectance increases after 24 days application of both ageing procedures (Fig. 7).

The layers of YELLOW ink on paper showed only minor variance in the spectral region 380–500 nm. A reflectance decrease in the spectral range of 550–750 nm, as well as the formation of a new absorption band at 690 was measured (Fig. 7).

The reflectance spectra of BLACK ink printed on paper, after both ageing procedures, are characterized by the increased reflectance; however the spectrum shape remained unchanged (Fig. 7).

The colour space $L^*a^*b^*$ (CIE) was applied in the investigations of the RAPIDA CMYK ink layer colour changes upon accelerated ageing (Figs. 8 and 9). Lightness, L^*, is a quantity that measures the percentage of total solar spectral reflectance in relation to a pure white surface; a^* is a measure of the degree red ↔ green; and b^* characterize the quantity yellow ↔ blue [11,12]. The total colour difference ΔE^* was calculated according to Eq. (3):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{3}$$

where $\Delta L^* = L^*(t) - L^*(0)$; $\Delta a^* = a^*(t) - a^*(0)$; $\Delta b^* = b^*(t) - b^*(0)$ are the differences calculated for aged ink films (t) and the original (0) ink layers.

The application of moist heat accelerated ageing method (80 °C and 65% RH) resulted in the insignificant changes of ΔL^* values for CYAN and MAGENTA inks. In contrast, the differences in lightness for YELLOW ink exponentially decreased (darkening of YELLOW ink films) and for BLACK ink increased (bleaching of BLACK ink films) with ageing time, as depicted in Fig. 8.

The differences in a^* values monitored upon moist heat accelerated ageing for ink films on paper were negligible for the BLACK ink, and an exponential reduction was measured for the CYAN and MAGENTA inks. On the other hand, Δa^* values measured during moist heat application for the YELLOW ink films increased (Fig. 8).

The values of Δb^* remained unchanged after 24 days of accelerated moist heat ageing for the MAGENTA ink films, and only a minor decrease was observed for the BLACK ink. However, the Δb^* value of the YELLOW exponentially decreased to the limiting value of minus 8. On the

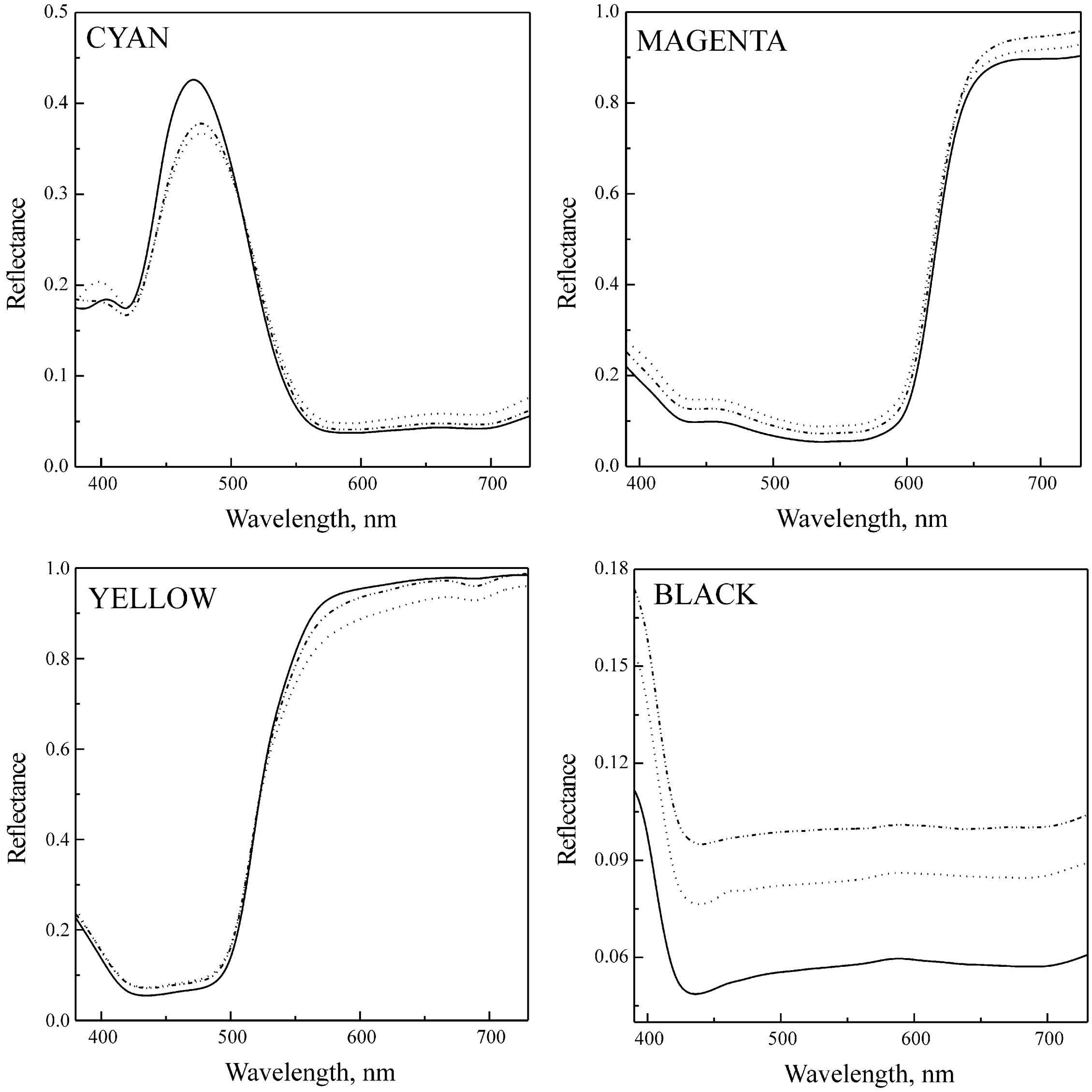

Fig. 7. The reflectance spectra of RAPIDA CMYK inks printed on standard offset paper: — original; · · · · moist heat (80 °C and 65% relative humidity), - · · · - dry heat (105 °C) treatment.

contrary, the values Δb^* of the CYAN ink increased, in accordance with a saturation curve, reaching the saturation value of 8 (Fig. 8).

Summarizing the total colour differences ΔE^* measured for the RAPIDA CMYK offset inks it should be noted, that following 24 days of moist heat accelerated ageing procedure, the best stability was observed for the MAGENTA ($\Delta E^* < 2$) and the BLACK ($\Delta E^* < 6$) ink films on paper. On the other hand, under given experimental conditions (24 days, 80 °C and 65% RH), the CYAN and YELLOW ink layers demonstrated total colour differences over 8, which correspond to the significant change of colour. Whereas the YELLOW ink showed contribution of all ΔL^*, Δa^*, Δb^* parameters in the total colour difference,

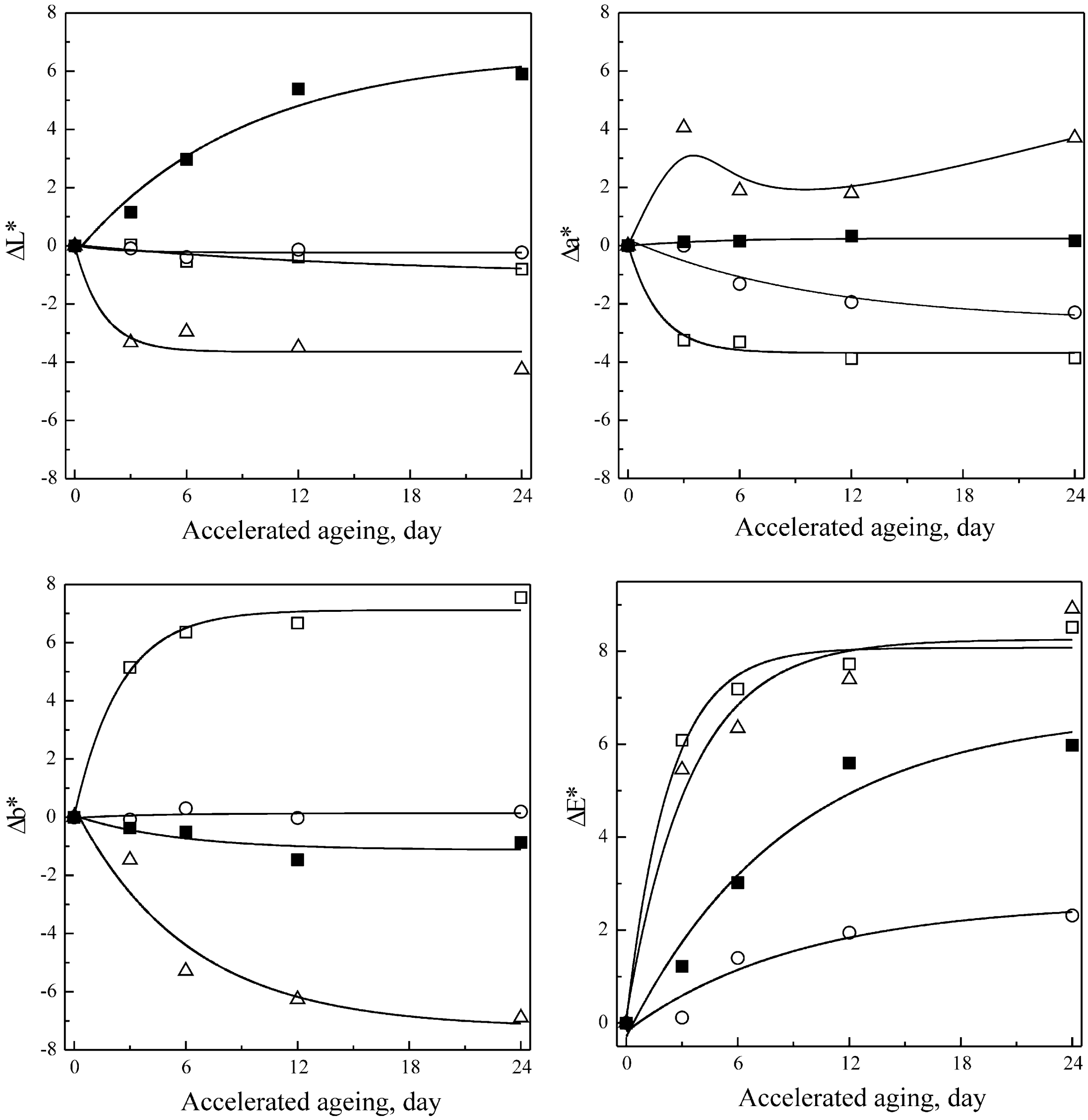

Fig. 8. The changes of ΔL^*, Δa^*, Δb^* and ΔE^* measured during moist heat (80 °C and 65% relative humidity) accelerated ageing of RAPIDA CMYK inks printed on standard offset paper: □ CYAN; ○ MAGENTA; △ YELLOW; ■ BLACK. The solid lines represent the mathematical simulations of experimental data.

upon accelerated moist heat procedure, in the CYAN ink the significant input of Δa^* and Δb^* was evaluated. These ΔE^* alterations are in a good agreement with spectral changes observed for the reflectance spectra of the CYAN and the YELLLOW ink layers on paper upon moist heat ageing (Fig. 7). The differences of lightness played the dominant role in the total colour differences found for the BLACK ink films upon moist heat ageing (Fig. 8).

Fig. 9 summarizes the effect of dry heat (105 °C) accelerated ageing method on the RAPIDA CMYK offset inks colour differences ΔL^*, Δa^* and Δb^*. The MAGENTA and the BLACK ink films displayed quite analogous colour changes upon dry heat treatment as was described above for the application of moist heat ageing (Fig. 8). Additionally, the changes of ΔL^*, Δa^*, Δb^* for the CYAN ink layer are only slightly lower than those observed for moist heat procedure; consequently also at this point the CYAN ink films demonstrated the highest variance of $\Delta E^* \sim 8$ (Fig. 9). The total colour differences of the YELLOW ink films were significantly lower during dry heat treatment (Fig. 9) in comparison with values obtained at 65% relative humidity; especially the ΔL^* and Δb^* decline was twice reduced. Probably, the presence of water during the ageing procedure initiated processes which can lead to the changes of yellow pigment structure [5]. The colour differences ΔL^*, Δa^* and Δb^* monitored upon accelerated ageing procedure reflect the changes in the chemical structure of ink (pigment, vehicle, resin). However, we cannot obtain the

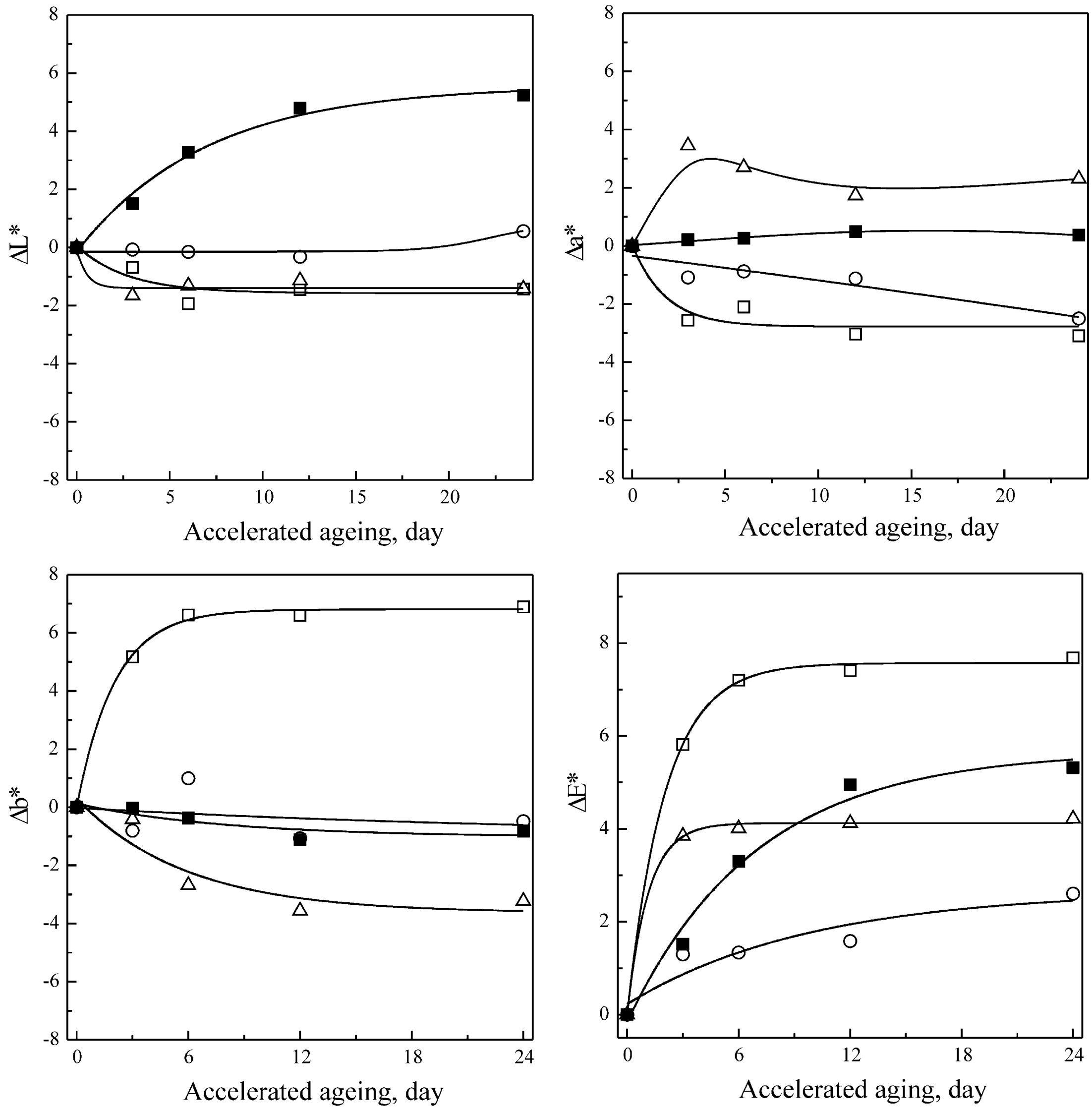

Fig. 9. The changes of ΔL^*, Δa^*, Δb^* and ΔE^* measured during dry heat (105 °C) accelerated ageing of RAPIDA CMYK inks printed on standard offset paper: □ CYAN; ○ MAGENTA; △ YELLOW; ■ BLACK. The solid lines represent the mathematical simulations of experimental data.

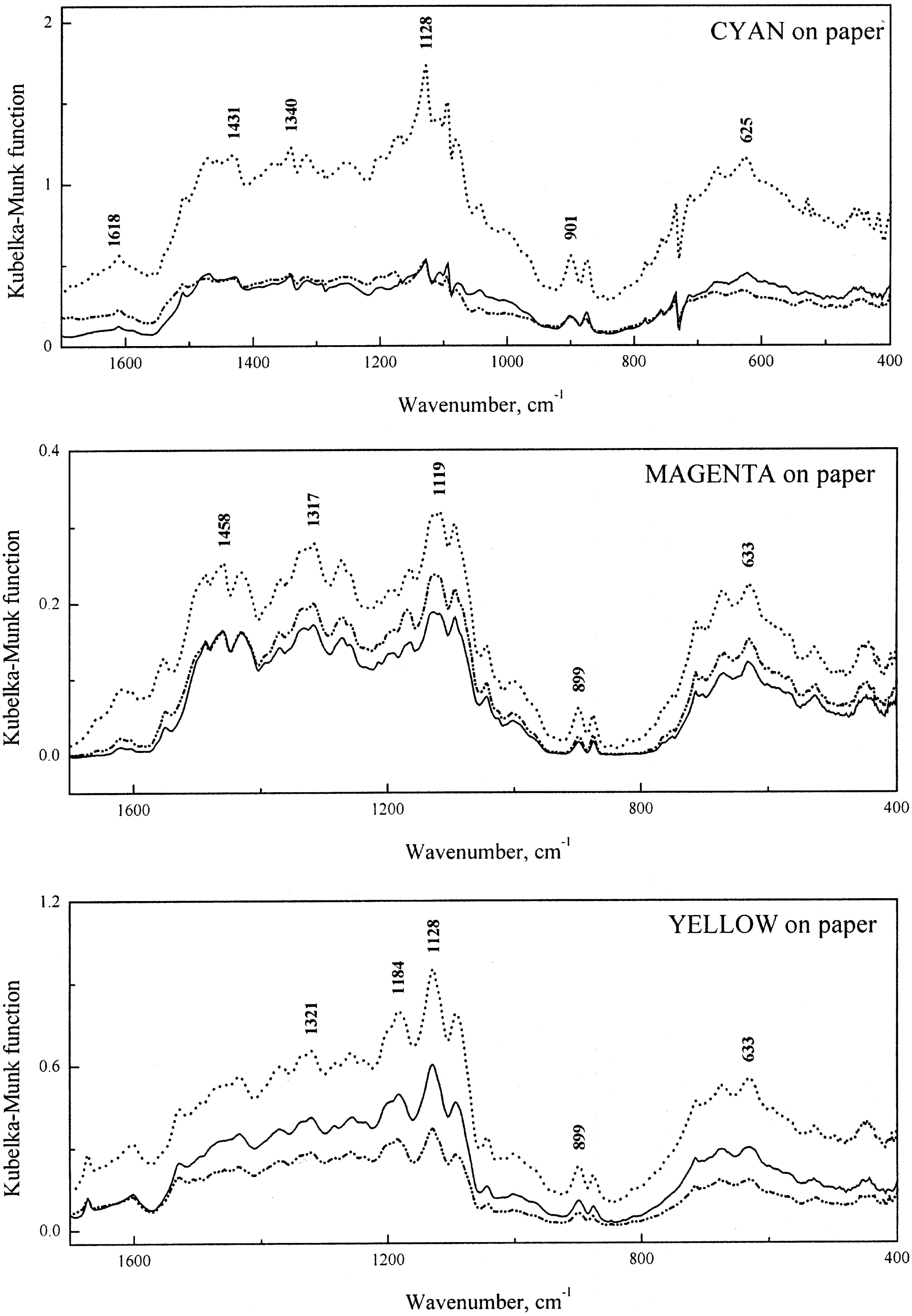

Fig. 10. FT-IR spectra of RAPIDA CMYK inks printed on standard offset paper measured using DRIFT technique: — original; · · · · moist heat (24 days, 80 °C and 65% relative humidity), - · · · - dry heat (24 days 105 °C) treatment.

information on the composition of commercial offset inks used in our study, consequently we are no able to identify the chemical processes initiated by ageing procedures (high temperature, moisture).

The diffuse reflectance FT-IR spectra of the original ink films on paper, as well as of the ink layers after 24 days of accelerated ageing procedures are illustrated in Fig. 10. We observed only negligible changes in FT-IR spectra after dry heat treatment (24 days, 105 °C) for all the RAPIDA CMYK inks. In contrast, application of moist heat (80 °C and 65% RH) reflected the growing absorption in the regions 1600–1100 and 800–400 cm^{-1}, especially in films of the CYAN ink (Fig. 10), corresponding most likely to the simultaneous oxidation of ink and paper components upon ageing in the presence of water.

4. Conclusions

The moist heat (80 °C and 65% RH) and dry heat (105 °C) methods of accelerated ageing were applied in the stability investigations of CMYK ink films printed on alkaline offset paper. The exponential decline of paper brightness (paper yellowing) corresponding to the formal first-order kinetics was measured upon application of both ageing procedures, however only negligible changes were registered in the diffuse reflectance FT-IR spectra of aged paper samples.

The highest variance of relative optical density during ageing was observed for the MAGENTA and the YELLOW ink films on paper. In contrast, the variations in visible reflectance spectra and in total colour difference ΔE^* ($L^*a^*b^*$) evidenced the considerable damage of the CYAN and the YELLOW ink films, especially upon moist heat treatment.

Acknowledgements

We thank J. Hanus and J. Mináriková (Slovak National Archives) for helpful discussions. This study was supported by the Slovak Grant Agency (Project VEGA/1/9146/02).

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