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Water-reducible flexographic printing inks—rheological behaviour and interaction with paper substrates

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The rheological behaviour of 5 water-reducible flexographic printing inks was tested using viscometer with the cone and plate geometry. The obtained shear stress *versus* shear rate curves for the original inks, and additionally, for the mixtures with various amount of added water, exhibit pseudoplastic behaviour, and were successfully fitted by Ostwald and Casson models. The viscosity of printing inks after addition of water was tested also by means of outflow funnel. The transfer of flexographic inks on the different paper substrates was examined by optical density measurements. The density curves confirmed that the ink concentration above 50 wt % is sufficient to obtain the constant value of optical density. The best ink transfer to the investigated paper substrates was observed for folding carton characterized by the high value of smoothness. © *1999 Kluwer Academic Publishers*

1. Introduction

Flexography, a progressing printing technology, is fundamentally direct rotary printing using flexible raised image printing plates and rapid drying fluid inks. The flexographic printing technology is accelerated now, as it is suitable for printing on coated and uncoated paper materials, non-porous substrates including metallized and paper foils, and plastic films, used especially in the packaging industry. This printing technology requires the low-viscosity inks (viscosity of 0.1–0.25 Pa·s) [1–3]. The attention in the industry is at this time focused on the production of water-based and water-reducible, low toxicity flexographic printing inks, in order to minimize the presence of organic vapours and liquids in the work area [1, 2].

Previously, the rheological measurements were done in the attempt to predict ink performance on the press [4–9]. However, these investigations were focused on the rheology of high-viscosity offset inks and ink emulsions [10–13].

The main aim of our work was to study the rheological behaviour of low-viscosity, water-reducible flexographic printing inks, and additionally, to monitor the process of the ink transfer to the individual paper substrates.

2. Experimental procedure

2.1. Materials

The investigated water-reducible flexographic printing inks were purchased from COLORPRINT S.P.A. (Italy): Base Idroflex B210 (yellow), Base Idroflex B 265 (black), Base Idroflex SL 3320 (red), Idroslotter C 380 (brown) and Idroflex B 072 (blue).

The coated and uncoated paper substrates for the packaging industry from SURPACK (Slovak Republic) were used: duplex liner, one-side whiten (D1); duplex liner, one-side whiten (D2); offset paper (OP); mixture fluting (F) and folding carton, one-side coated (FC).

The deionized water was used for the preparation of ink solutions.

2.2. Apparatus

The characteristic properties of the paper substrates were measured according to the STN and STN ISO norms using the following instruments: automatically-operated micrometer, automatic analytical balance (Sartorius, precision of 0.001 g), apparatus for the bursting strength measurements according to *Mullen* BURST-O-MATIC (Lorentzen & Wettre, Sweden), device for the water absorbency determination according to *Cobb*, universal apparatus INSTRON 1011 (England), permeameter (Frank, Germany) for the air permeance determination according to *Bendtsen*, apparatus for the smoothness evaluation (Büchel-Van der Korput, Netherlands) according to *Beek*, filter photometer ELREPHOMAT DFC-5.

The pH values of the paper substrates were measured using a combined glass electrode at 25 °C.

In accordance with the STN ISO 187 norm the paper samples were air-conditioned before measurements,

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which were carried out under the same conditions. The transfer of the flexographic inks to the paper materials was determined using K-hand coater (Lorentzen & Wettre, Sweden) and reflection densitometer (X-RITE 428, USA). The ink film (12 and 24 μm) was coated on the paper substrates at 20 °C, and the optical density was monitored after 24 hours.

The rheological behaviour of inks and inks solutions was investigated by means of Viscotester VT500 (Haake Mess-Technik, Germany) with the cone and plate geometry. A 28 mm, 0.5 deg cone was applied to study the flow behaviour. The solutions of flexographic printing inks were prepared by the addition of the calculated amount of water to obtain the required concentration of ink in the mixture. The water was added dropwise to the ink upon continuous stirring and the resulting mixture was stirred for further 5 min. The standard volume of sample (0.1 ml) was placed symmetrically in the centre of plate. The shear stress was measured during the controlled applied shear rate increasing from 0 s^{-1} up to 5000 s^{-1} in 1 min. The measurements were repeated 5 times with new sampling at 25 or 30 °C.

The rheological characteristics of the flexographic printing inks were specified additionally by the outflow time in the outflow funnel (volume 100 ml, outlet diameter of 4 mm, Dioptra, Czech Republic) according to STN ISO 67 3013. The outflow times were determined for solutions with various concentrations of inks. The ink solutions were prepared by the dropwise addition of calculated weight of water to the ink upon continuous stirring. The measurements were performed at 20 °C immediately, and 5 min standing after 5 min of mixing, respectively. Under given experimental conditions the results obtained in both measurements coincide (relative error less than 3%).

3. Results and discussion

3.1. Characterization of paper substrates

Tables I and II represent the paper substrates properties characterized by the mean values and their standard deviation (SD), evaluated from 10 measurements. If necessary, the measurements were performed on both sides of materials (brown or white for D1 and D2, wire or felt for OP and F, coated or uncoated for FC) according to the character of paper substrates. The properties and behaviour of the surface being printed by the flexographic procedure, determine the selection of the suitable printing ink to obtain the best printing efficiency and quality in the printing and packaging industry. The smoothness and water absorbency by paper surface are especially important parameters applying water-reducible flexographic printing ink.

3.2. Rheological behaviour of the flexographic printing inks

The flexographic printing technology requires quick-setting, low-viscosity printing inks (viscosity from 0.1 to 0.25 Pa·s) [1, 2]. The shear stress *versus* shear rate flow curves measured using 5 different original flexographic printing inks are shown in Fig. 1.

The obtained dependencies may be analyzed applying the following models [14]:

Linear:

$$\tau = \tau_0 + \eta D \tag{1}$$

where τ_0 is yield stress and η is viscosity;

Ostwald:

$$\tau = AD^b \tag{2}$$

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

Casson:

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta D} \tag{3}$$

where τ_0 is Casson yield stress and η is Casson viscosity;

Herschel-Bulkley:

$$\tau = \tau_0 + AD^b \tag{4}$$

where A, b are analogous to Ostwald model and τ_0 is yield stress analogous to Casson [14].

TABLE I The mean values and standard deviations of mean values (SD) of thickness, grammage, bursting strength and ring crush test for the paper substrates used in our study along with the norm specification used for the evaluation

	Paper substrate								
Parameter	D1		D2		OP	F	FC		NORM
Thickness (μm)	232		317		176	163	427		STN ISO 534
SD (μm)	6		11		5	6	4		
Grammage (g m^{-2})	149.6		196.4		139	99.1	274.9		STN ISO 536
SD (g m^{-2})	0.5		0.6		1	0.4	0.8		
Bursting strength (kPa) *according to Mullen*	585[a]	520[b]	680[a]	600[b]	230	280	640[c]	660[d]	STN ISO 2759
SD (kPa)	40	30	50	40	20	20	40	30	
Ring crush test (N)	200		310		100	150	330		STN 50 0362
SD (N)	10		30		10	10	40		

[a] Brown side.
[b] White side.
[c] Coated side.
[d] Uncoated side.

TABLE II The mean values and standard deviations of mean values (SD) of smoothness, water absorbency by surface, surface pH, brightness, air permeance and picking-resistance determined by *Dennison's* waxes procedure for the paper substrates used in our study along with the norm specification used for the evaluation

	Paper substrate							
Parameter	D1	D2	OP		F		FC	NORM
Smoothness (s) *according to Bekk*	6.3	5	35[a]	17[b]	3.9[a]	2.7[b]	86	STN ISO 5627
SD (s)	0.8	1	4	3	0.2	0.2	4	
Water absorbency by surface (g m^{-2}) *according to Cobb*	26	24	36[a]	35[b]	—		29.0	STN ISO 535
SD (g m^{-2})	1	1	2	2			0.5	
Picking-resistance *according to Dennison waxes* [c]	16	18	12[a]	14[b]	14[a]	11[b]	8	STN 50 0361
Surface pH (25 °C)	5.8	5.6	6.9[a]	6.6[b]	5.6[a]	5.4[b]	5.8	STN 50 0374
SD	0.3	0.3	0.5	0.5	0.4	0.4	0.3	
Brightness (%)	61	66	92[a]	92[b]	—		84	STN ISO 2470
SD (%)	1	3	0.4	0.2			0.1	
Air permeance (μm (Pa·s)$^{-1}$) *according to Bendtsen*	2.3	1.7	1.6		1.5		—	STN ISO 5636-3
SD (μm (Pa·s)$^{-1}$)	0.1	0.2	0.2		0.1			

[a] Wire side.

[b] Felt side.

[c] Dennison wax number.

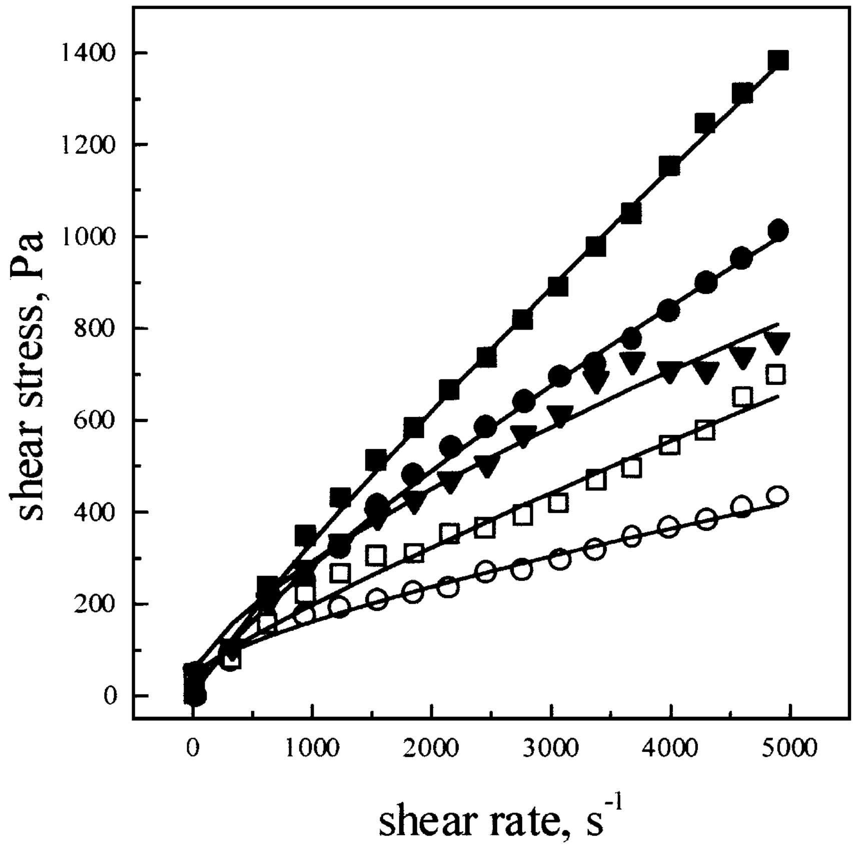


Figure 1 The shear stress *versus* shear rate dependencies measured for 5 original flexographic printing inks ($t = 25$ °C). ■ yellow; ● blue; ▼ red; ☐ brown; ○ black. All experimental points are fitted by Ostwald model (Table III).

The flow curves depicted in Fig. 1 were fitted by the theoretical models of Equations 1–4 using least square analysis (programme Scientist, MicroMath). We test all the regression models and choose the best fit based on the statistical parameters of the fitting [14].

Our evaluation procedure confirmed that the best compatibility of the experimental results and fitting curves was obtained for Ostwald and Casson models. The parameters A, b (Equation 2) and τ_0, η (Equation 3) along with the R-squared of the fittings for 5 original

TABLE III The parameters of the Ostwald and Casson models along with the R-squared of the fitting calculated for the flow curves of the original flexographic printing inks

	Ostwald parameters			Casson parameter		
Ink	A (Pa·s)	b	R-squared	τ_0 (Pa)	η (Pa·s)	R-squared
Yellow	0.94	0.85	0.999	14	0.21	0.999
Blue	1.2	0.80	0.999	20	0.15	0.998
Red	2.0	0.71	0.996	30	0.11	0.994
Brown	0.40	0.87	0.996	5	0.11	0.996
Black	0.8	0.73	0.999	14	0.05	0.996

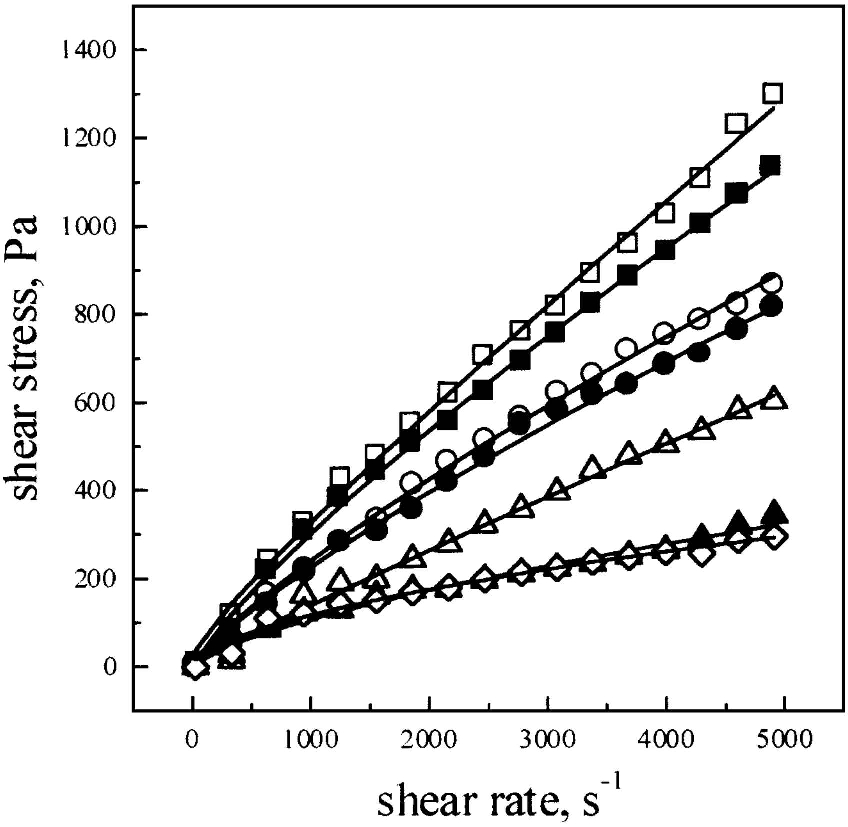


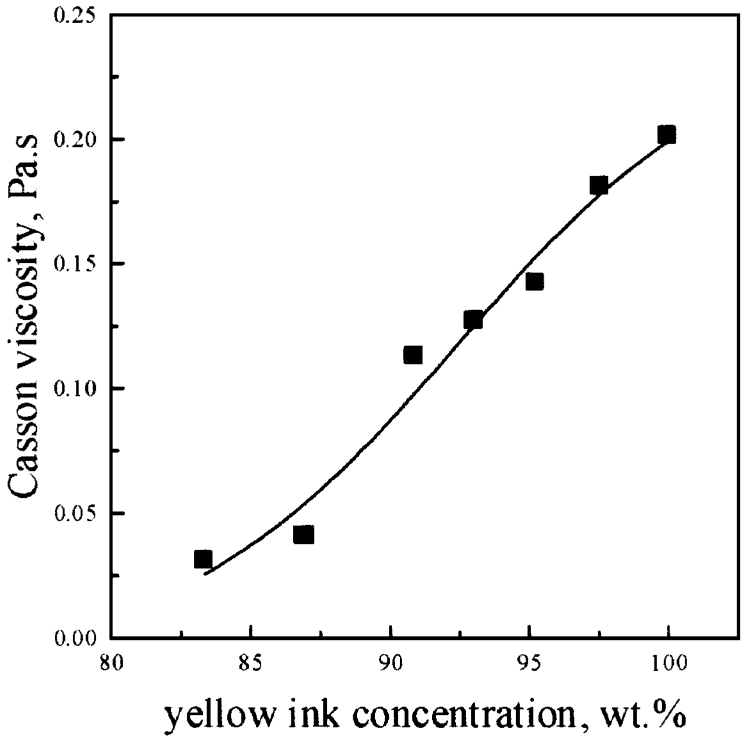
Figure 2 The shear stress *versus* shear rate dependencies obtained for yellow flexographic printing ink after addition of water (t = 25 °C). Ink concentration (wt %): □ 100; ■ 97.6; ○ 95.2; ● 93.0; △ 90.9; ▲ 86.9; ◇ 83.3. All experimental points are fitted by Ostwald model.

flexographic printing inks flow curves are summarized in Table III.

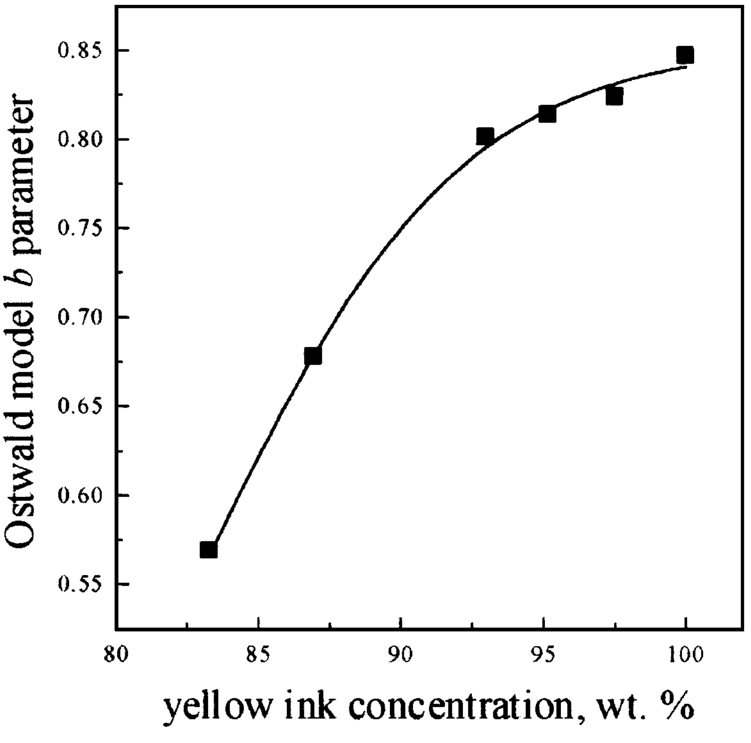
According to the Ostwald model (Equation 2) pseudoplastic flow behaviour expressed by $b < 1$ is characteristic for all 5 original inks (Table III). The calculated values of Casson viscosity (Equation 3) for yellow, blue, red and brown inks correlate with viscosity requirements for the flexographic printing technology. Moreover, our measurements confirmed too low viscosity of the original black ink ($\eta_{\mathrm{Casson}} = 0.05$ Pa·s).

The original printing inks were diluted by water and the flow behaviour of the prepared mixtures was investigated. Fig. 2 illustrates the dependencies of the shear stress on the applied shear rate for the yellow ink after addition of various amounts of water. The analogous sets of experimental flow curves were measured for the other inks, too. All flow curves were fitted by Ostwald and Casson models and the parameters of these calculations were evaluated. As shown Figs 3a and b, Casson viscosity and Ostwald b parameter are significantly dependent on the ink concentration. The increasing amount of added water caused the decrease of Casson viscosity, as depicted in Fig. 3a. It is interesting that this decrease of viscosity is not reflected in the convergence of ink flow behaviour to the Newtonian flow ($b = 1$). The Ostwald b parameter decreases, representing the pseudoplastic flow after addition of water to the yellow ink (Fig. 3b). This flow behaviour, which is probably related to the internal structure of inks after addition of water, was observed for all investigated inks.

It should be noted here that all original flexographic inks, as well as inks diluted by water exhibit rheopectic behaviour, as illustrated in Fig. 4 for the original yellow ink. The increasing viscosity with time associated with rheopectic behaviour may reflect the shear-induced formation of internal structure or the change in the ink composition [15]. As the temperature increase



(a)



(b)

Figure 3 (a) Casson viscosity *versus* yellow ink concentration; (b) Ostwald model *b* parameter *versus* yellow ink concentration. The parameters were evaluated from the experimental flow curves depicted in Fig. 2.

from 25 to 30 °C caused a significant increase of the loop area (Fig. 4), the latter seems to be more likely the reason of the rheopectic behaviour. The evaporation of solvent from the original yellow ink during the measurements probably caused the changes in the ink composition. The presence of water in the water-diluted inks may modify the solvent evaporation, as the loop area decrease is proportional to the reduction of ink concentration.

In addition, the viscosities of the flexographic printing inks after addition of various amounts of water were tested using the outflow funnel. Fig. 5 unambiguously demonstrates that the decrease in yellow ink concentration from 100 to 95 wt % twice reduces the outflow

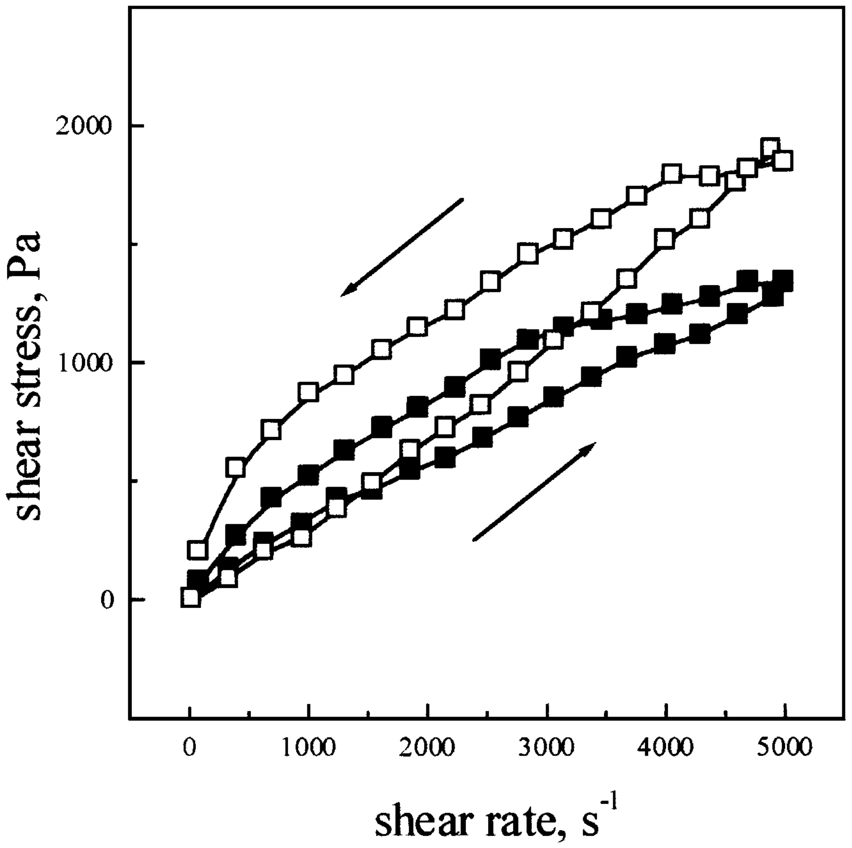


Figure 4 Rheopectic flow curves of the original yellow ink. ■ 25 °C; □ 30 °C.

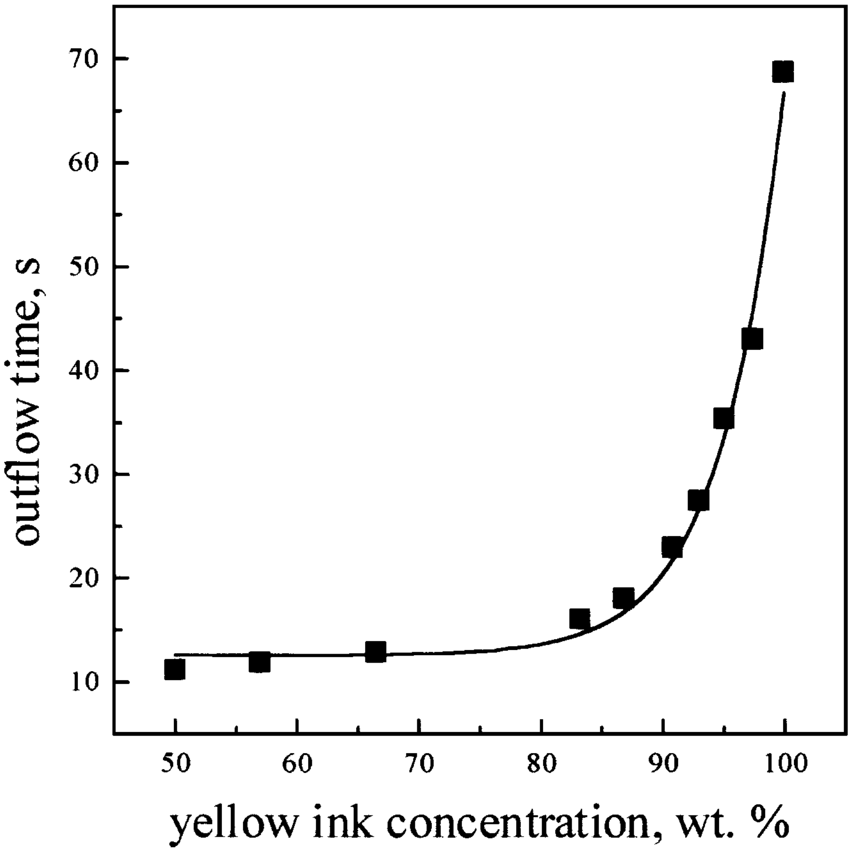


Figure 5 The dependence of the outflow time on the concentration of yellow ink ($t = 20$ °C).

time. According to the literature data, inking of the flexographic inks to the anilox-roller requires the outflow times 18–35 s (outlet diameter of 4 mm) [1, 2]. Consequently, the concentration of the investigated yellow ink under 85% is unsuitable for the flexographic printing technology. Simultaneously, the addition of water solvent over 15–20% can destroy the pigment distribution in the ink [2].

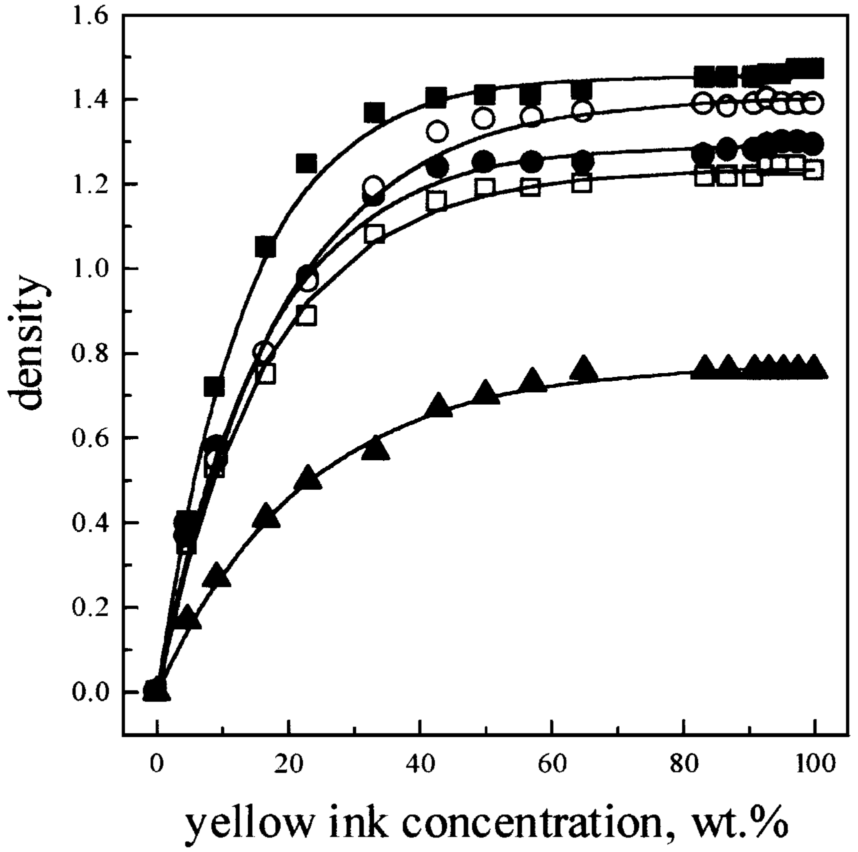


Figure 6 The dependence of the optical density on the concentration of yellow ink for the 12 μm films coated on the different paper substrates. ■ FC coated side; ○ OP wire side; ● D2; □ D1; ▲ F felt side.

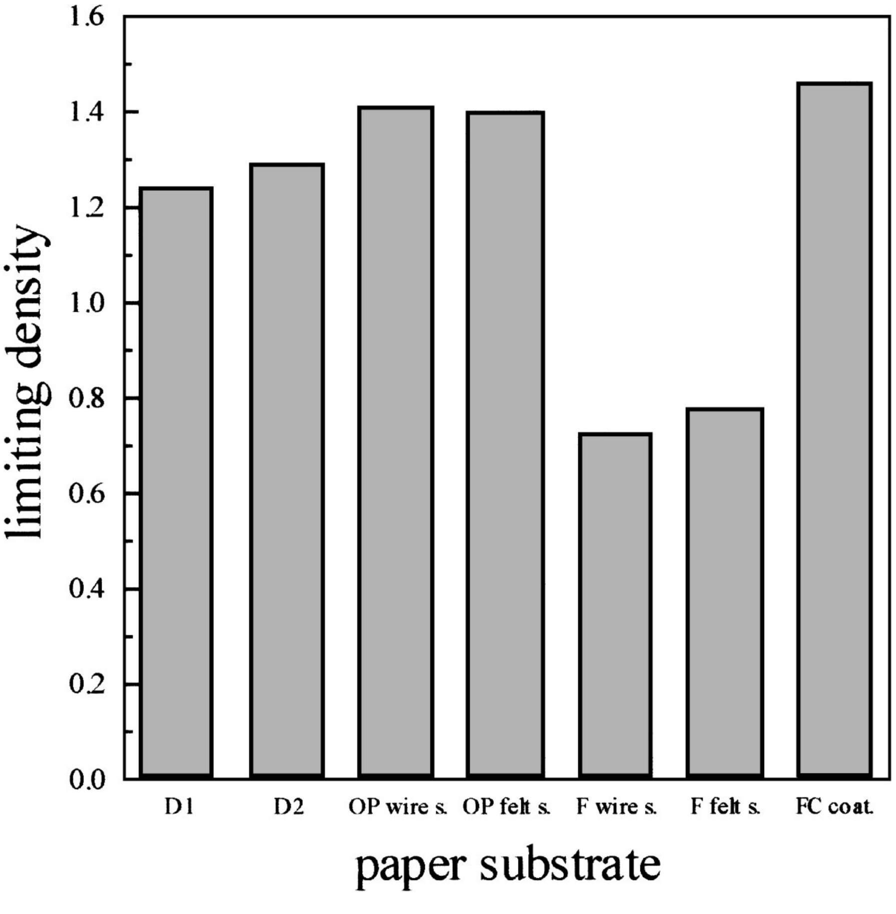


Figure 7 The calculated values of limiting density (yellow water-reducible flexographic printing ink) for the investigated paper substrates.

3.3. Transfer of the flexographic printing inks on the paper substrates

The properties of printing inks, as well as the characteristics of materials to be printed using flexographic printing technology, significantly influenced the quality of final products. The content of water in the water-reducible flexographic printing inks changes ink viscosity and pigment distribution and can directly influence the printing process [1–3]. Moreover, water has strong effect on the drying of the ink film on the individual paper substrate. Consequently, the observed optical density of the ink films reflects the properties of inks and paper substrates. Fig. 6 shows the dependence of the optical density (film thickness of 12 μm) on the concentration of yellow ink measured on the different paper substrates.

The dependence of density, D, on the ink concentration, y, may be described by the following equation

$$D = D_\infty(1 - \exp(-my)) \qquad (5)$$

where D_∞ is limiting density and m is parameter dependent on the ink pigment distribution and on the characteristics of paper substrates (e.g., smoothness, water absorbency) [16].

The yellow ink density curves depicted in Fig. 6 were successfully fitted using non-linear least-squares analysis by Equation 5, and the parameters D_∞ and m were evaluated (R-squared over 0.9995). Fig. 7 illustrates the values of limiting density of the yellow flexographic ink calculated for the investigated paper substrates. Using this ink, the highest densities were measured for the folding carton (coated side). This finding correlates with the large value of smoothness measured for this paper substrate (Table II). The corresponding density was observed in experiments with yellow ink for offset paper and mixture fluting wire and felt sides, respectively (Fig. 7). The density curves confirmed the excellent pigment distribution in the yellow water-reducible flexographic printing ink, as ink concentration above 50 wt % is sufficient to achieve the constant values of density on different paper substrates (Fig. 6). The analogous results were obtained for 24 μm thick yellow ink films on paper substrates, too.

4. Conclusions

1. The shear stress *versus* shear rate curves for the 5 different flexographic printing inks with various amounts of added water were measured and evaluated using Ostwald and Casson models. The fluids exhibited pseudoplastic flow behaviour. The Ostwald and Casson parameters calculated were significantly dependent on the ink concentration. The rheopectic behaviour of the investigated inks reflect probably the changes in the ink composition by solvent evaporation during measurements.

2. The optical density of the ink films coated on the paper substrates with different characteristics was monitored for the printing inks with various amounts of water. The reduction of ink concentrations up to 50 wt % has no influence on the optical density measured on the paper substrates. However, the viscosity of the 50 wt % yellow ink is too low for the flexographic printing technology. The highest values of optical density agree with the smoothness of the paper substrates.

Acknowledgements

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