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COMPARATIVE STUDY OF PHYSICAL PROPERTIES OF HYBRID AND UV OFFSET INKS

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Hybrid inks represent a type of inks that are cured by two various mechanisms, oxypolymerization and polymerization induced by UV radiation. The printability of offset inks strongly depends on the rheological properties of printing inks, their tack and fountain solution pick-up behaviour. In this work, two process hybrid inks and two UV curable inks were tested. The studied process inks were in both cases cyan and magenta. The tested physical properties were evaluated for unemulsified inks and their emulsions with fountain solution. The emulsions of inks and fountain solution were characterised by the amount and rate of fountain solution pick-up. The rheological properties (flow behaviour, thixotrophy, and viscosity relaxation) were measured with rotational rheometer RV1 HAAKE, the tack and misting with Tackmaster-92.

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Introduction

The quality of offset printing process depends on many chemical and physical specifics of the materials and components involved in the process. The most important are printing inks (e.g., rheological properties, surface tension, temperature behaviour), damping solution (e.g., water hardness, additives, pH value, surface tension), printing plate (e.g., surface tension of printing and nonprinting areas, roughness), inking rollers and their blankets (e.g., surface tension and roughness, viscoelastic properties, ink acceptance and ink transfer behaviour), printing press (e.g., design of the printing, inking and damping unit, temperature control), etc [1].

UV offset printing inks dry by chain reaction (free radical or cationic polymerization). This type of ink contains a photoinitiator which, when activated with correct wavelength of radiation (mostly UV radiation), undergoes a rapid polymerization reaction. Binders consist of monomers and oligomers and do not contain volatile organic compounds (VOCs). UV inks have a number of advantages compared to conventional offset printing inks. Between the most important ones belong rapid curing time (fractions of second), high print gloss, abrasion resistant surface, very good chemical resistance and also less problems of sample blocking.

Hybrid inks are based on conventional offset printing inks, but contain part of UV curable components as well and are able to run on conventional press machine equipped with UV radiation source. Oxidative drying of conventional offset inks containing drying oils is caused by molecular linkage with oxygen from the air. Oxidative drying can be accelerated by catalysts such as cobalt or manganese salts of oil soluble acids. Cobalt driers are “surface driers”. The drying process is started on the ink surface and slowly proceeds to the substrate. Manganese driers are “through-driers”. One of the major advantages of hybrid ink technology is the fact that smaller commercial printers can add inline UV varnishing to their operations at relatively low cost [2]. The hybrid inks should be printable with blankets that are also suitable for conventional inks (NBR rubber) compared to UV inks that need special blankets (based on EPDM).

Experimental

Materials and Methods

In this study, two hybrid (cyan and magenta) and two UV (cyan and magenta) sheetfed offset printing inks were tested (Table I). Emulsions of tested inks were prepared using fountain solution containing 90 % water (water hardness of 8.4 °dH), 5 % fountain solution additive V50 (POOLA) and 5 % isopropyl alco-

Table I Sheetfed offset printing inks tested in this work

Name of product	Drying	Producer	Ink denotation
Cyan UV Hybrid Plus/Litho UO350080	Hybrid	XSYS Print Solution	HC
Magenta UV Hybrid Plus/Litho UOH30080	Hybrid	XSYS Print Solution	HM
Cyan Suncure Starluxe	UV	Sun Chemical	UVC
Magenta Suncure Starluxe	UV	Sun Chemical	UVM

hol. Conductivity of prepared fountain solution was 1517 mS cm^{-1} (measured by conductometer LF315 from WTW at 25 °C) and pH 5.02.

Duke Ink Water Emulsification Tester Model D-10 (HDuke Enterprises, USA) was used for preparation of emulsions. The emulsion properties were defined by the amount of fountain solution pick-up and time needed for achievement of saturated emulsion. During the test, 50 g offset printing ink and 50 g fountain solution was stirred (90 rpm) and after every 90 turns of stirring tools amount of fountain solution pick-up was measured.

The flow behaviour and the viscosities of unemulsified inks and emulsions were measured on rotational rheometer RotoVisco 1 (HAAKE, Germany). All tests were done with a one cone-plate measuring system (titanium cone with 10 mm radius and 1° angle). Thermostat DC 30 (HAAKE, Germany) was used for temperature control during the tests. Flow characteristics were measured at shear rates from 3 to 3,000 s^{-1} and temperature of 32 °C.

The Tackmaster-92 (Kershaw Instrumentation, USA) was used to measure the tack and misting characteristics of unemulsified inks and their emulsions. The temperature of tackmaster rollers was set at 32 °C for all the measurements. The ink was applied to the tackmaster with a small pipette that holds 1.2 cm^3 and left at low speed (300 rpm) for 180 seconds to equilibrate. During the tack measurement (10 minutes), the speed was 1 200 rpm. Misting test was performed by placing a white paper behind the tackmaster rollers which collects the mist for 10 minutes at 1 200 rpm. The measured parameter was the dot area estimated by Image Analysis method. The applied ink volume was triplicated (3.6 cm^3) in comparison with tack measuring.

Results and Discussion

Emulsions

In Table II there are summarized the results of the amount of fountain solution pick-up (E_{max}) and time (t) needed to achieve saturated emulsion (1 minute = 90 turns of stirring tools). From Table II, it is apparent that both hybrid inks have the same behaviour and UV inks are different. Ink UVC picks-up the same amount of fountain solution as hybrid inks (40 %), but needs a little bit more time to reach stable emulsion. Opposite these three inks, UV magenta ink pick-up much more fountain solution (60 %) and needs longer time to reach stable emulsion. Offset inks that pick-up higher amount of fountain solution can have tendency to scumming during the print.

Table II Duke fountain solution pick-up

	HC	HM	UVC	UVM
E_{max}, %	40	40	40	60
t, min	5	5	6	9

Flow Curves

To determine the flow behaviour of unemulsified inks and their emulsions with fountain solution, rotational tests were run at shear rates 3-3,000 s^{-1}, and curve fitting with rheological model function was applied. Characteristics of tested inks were evaluated by means of Casson model function (Eq. (1)) and Ostwald–de-Waele model (Eq. (2)) [3]

$$\tau^{0.5} = \tau_{0C}^{0.5} + \eta_{\infty C}^{0.5}\,\gamma^{0.5} \qquad (1)$$

where τ is shear stress (Pa), τ_{0C} Casson yield point (Pa), $\tau_{\infty C}$ Casson viscosity (Pas) and γ shear rate (s^{-1}).

$$\tau = K\,\gamma^{n} \qquad (2)$$

where K is flow consistency index (Pa s^n) and n flow behaviour index.

The measured inks and their emulsions differ in shear rate, where flow curve breaks away from the true curve. This critical shear rate (CSR) indicates that ink was partly sucked out from the gap between cone and plate (response of viscoelastic samples when they are subjected to shear) [4]. Another explanation can be breaking of emulsion due to high shear rate. The evaluated critical shear rates of tested inks are summarized in Table III. It is obvious that all emulsions have CSR much lower then unemulsified inks.

Table III Critical share rates of unemulsified inks (unemul.) and their emulsions

Type of ink	HC		HM		UVC		UVM	
	unemul.	emulsion	unemul.	emulsion	unemul.	emulsion	unemul.	emulsion
CSR, s^{-1}	1,710	630	1,290	850	2,260	730	>3,000	240

Table IV summarizes the parameters of both models for unemulsified and emulsified inks with determination coefficients (R_C^2 for Casson model and R_0^2 for Ostwald-de-Waele model). The flow curves were evaluated from beginning to the value of critical share rate.

Table IV Characteristics of unemulsified and emulsified inks evaluated from flow curves by Casson and Ostvald-de-Waele models

Type of ink	Parameters	Unemulsified inks	Emulsions
HC	τ_{0C}, Pa	210.4	82.7
	$\eta_{\infty C}$, Pa s	12.5	3.2
	R_C^2	0.999	0.997
	$\tau_{0C} / \eta_{\infty C}$, s^{-1}	16.8	25.8
	K, Pa s^n	69	27.2
	n	0.78	0.72
	R_0^2	0.999	0.996
HM	τ_{0C}, Pa	135	160.7
	$\eta_{\infty C}$, Pa s	12.7	2
	R_C^2	0.999	0.995
	$\tau_{0C} / \eta_{\infty C}$, s^{-1}	10.7	79
	K, Pa s^n	52.6	60.7
	n	0.81	0.55
	R_0^2	0.999	0.988

Table IV – Continued

Type of ink	Parameters	Unemulsified inks	Emulsions
	τ_{0C}, Pa	45.8	42.6
	$\eta_{\infty C}$, Pa s	11.4	3
	R_C^2	0.999	0.994
UVC	$\tau_{0C}/\eta_{\infty C}$, s^{-1}	4	14.4
	K, Pa s^n	41	14.5
	n	0.82	0.78
	R_0^2	0.997	0.998
	τ_{0C}, Pa	125.6	175.9
	$\eta_{\infty C}$, Pa s	8.4	3.8
	R_C^2	0.999	0.996
UVM	$\tau_{0C}/\eta_{\infty C}$, s^{-1}	15	46.7
	K, Pa s^n	97.9	124.5
	n	0.66	0.46
	R_0^2	0.997	0.995

The difference between unemulsified inks and emulsions at 32 °C was primarily in parametr $\eta_{\infty C}$. In all cases, the estimated values of $\eta_{\infty C}$ were lower for emulsions than the unemulsified inks. Casson yield point of emulsions was lower for cyan inks and higher for magenta inks compared to unemulsified inks. Casson yield point prevents uncontrolled flow from ink duct, but too high value can cause a big amount of ink remaining in the duct. Casson yield point, thixotropy and capillarity of ink influence dot sharpness and penetration to the substrate. The higher the Casson yield point, the lower the amount of spread of the ink onto the print medium. Parameter $\tau_{0C}/\eta_{\infty C}$ describes the tendency of inks to mist. Inks with higher $\tau_{0C}/\eta_{\infty C}$ have lower tendency to mist than inks with lower $\tau_{0C}/\eta_{\infty C}$. From Table IV it is apparent that unemulsified inks have lower $\tau_{0C}/\eta_{\infty C}$ than emulsions (emulsions will have lower tendency to mist than unemulsified inks). Results of mist values (dot area of mist droplets) of unemulsified and emulsified inks are summarized below (see Table VII). Flow behaviour index n is in all cases lower than 1 which means that all inks and their emulsions have shear thinning behaviour. In comparison of unemulsified and emulsified inks, emulsions have lower flow behaviour index than unemulsified inks (their viscosity will change more strongly with increasing shear rate).

Thixotropy

Thixotropic behaviour means the reduction in structural strength during the shear load phase and complete structural regeneration during the subsequent rest phase. Thixotropy is a decrease in the apparent viscosity under shearing, followed by a gradual recovery when the shear is removed. The effect is time dependent. If the viscosity reduces and immediately returns after shearing, the material is not thixotropic but just shears thinning. Substances change from a high viscosity gel to a much lower viscosity sol under exerted high shear during a test period. For real thixotropic substances the transformation from a gel to a sol and conversely is reversible [2].

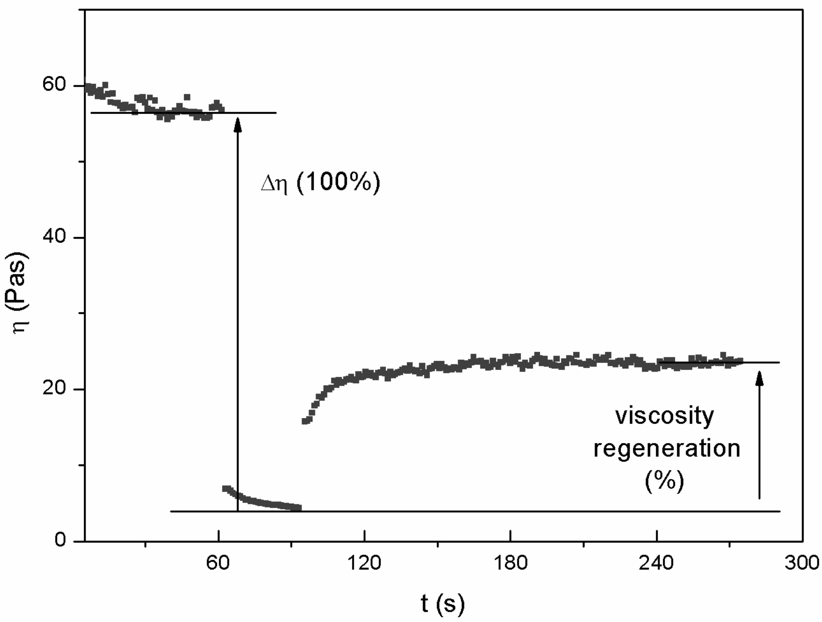

Fig.1 Evaluation of viscosity regeneration (emulsion of UVM)

In this work, thixotrophy of unemulsified and emulsified inks was evaluated by the method of viscosity regeneration. The test was divided into three intervals, the first interval with $\gamma = 5\ s^{-1}$ for 1 minute, the next interval with $\gamma = 250\ s^{-1}$ for 30 seconds and the last interval with $\gamma = 5\ s^{-1}$ for 3 minutes. From the first and second interval, the value of parameter $\Delta\eta$ (100 %) was determined (difference between viscosities, see Fig. 1). From the third interval (after 3 minutes), the percentage of regeneration was calculated. The temperature during the measurement of viscosity regeneration was 32 °C. Figure 1 shows a typical progress and evaluation of viscosity regeneration during the test (emulsion of UVM).

The rate of recovery is an essential factor for levelling the ink on the substrate. The results of viscosity regeneration of unemulsified and emulsified inks are summarized in Table V. Unemulsified inks show faster regeneration of viscosity than emulsions. Faster regeneration facilitates the ability to achieve the required layer thickness, as the ink film strength is reached in shorter time. A slower rate of structural regeneration offer a good levelling behaviour, but too slow rate can cause an increase in dot gain. Both hybrid inks have faster regeneration of viscosity than UV inks.

Table V Viscosity regeneration of unemulsified (unemul.) and emulsified inks

Type of ink	HC		HM		UVC		UVM	
	unemul.	emulsion	unemul.	emulsion	unemul.	emulsion	unemul.	emulsion
Vis. reg., %	66.3	54.4	53.1	39.0	91.7	34.2	-	35.6

Tack and Misting

Tack is the force required to split ink film between two rollers. Tack is an important property in the inking system as well as in the ink/paper interaction and in the ink trapping for multi-colour printing. In order to trap properly, first printed ink should have a higher tack than the following one [2].

Figure 2 shows a typical progress and evaluation of tack (similar for both types of ink). The tack of the ink was characterised with two parameters (the tack reached after one minute (T1) and the final tack (T2) at the end of the test (after 10 minutes)). In Table VI are summarized results of tack for unemulsified and emulsified inks at 32 °C. High tack is generally desirable, but if the tack is too high it could cause picking (fibres are pulled out of the paper). Usually the tack of offset printing inks is between 12 and 20 g m^{-1}. From this point of view, tackiness of studied inks is at lower limit and picking caused by emulsions will be low. The UVM ink shows the lowest tack.

Misting, the tendency of ink to fly away from the rollers, was also evaluated on Tackmaster-92. Misting can result in colour contamination and servicing problem for the operator. Papers with misted ink were captured by digital microscope z-Pix 200 (Carson) and the obtained images (see Figure 3) were analysed by Image Analysis method (software AnaTis2). The evaluated parameter was dot area of mist droplets. In Table VII, the results of misting of unemulsified and emulsified inks at 32 °C are summarized.

Emulsified inks misted much less than unemulsified inks and the mist droplets were smaller compared to those of unemulsified inks. The lower misting of emulsions is in agreement with the results of rheology measurements (parameter $\tau_{0C}/\eta_{\infty C}$, see below). In comparison of hybrid and UV curable inks, the lower misting is exhibited by hybrid inks.

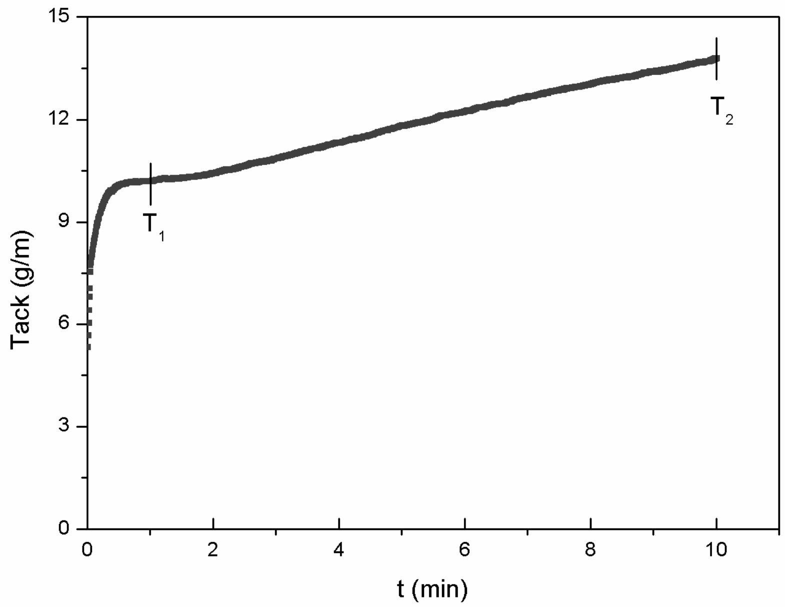

Fig. 2 Evaluation of tack (emulsion of HM)

Table VI Tack of unemulsified (unemul.) and emulsified inks

Type of ink	HC		HM		UVC		UVM	
	unemul.	emulsion	unemul.	emulsion	unemul.	emulsion	unemul.	emulsion
T1, g m^{-1}	13.4	14.5	12.7	10.5	10.7	14.5	7.3	8.8
T2, g m^{-1}	16.1	17.6	14.2	13.8	13.5	17.5	10.1	13.5

Table VII Comparison of unemulsified and emulsified inks misting dot area of mist droplets]

Type of ink	HC		HM		UVC		UVM	
	unemul.	emulsion	unemul.	emulsion	unemul.	emulsion	unemul.	emulsion
Dot area, %	36.1	14.8	34.3	19.1	39.4	22.5	42.7	25.8

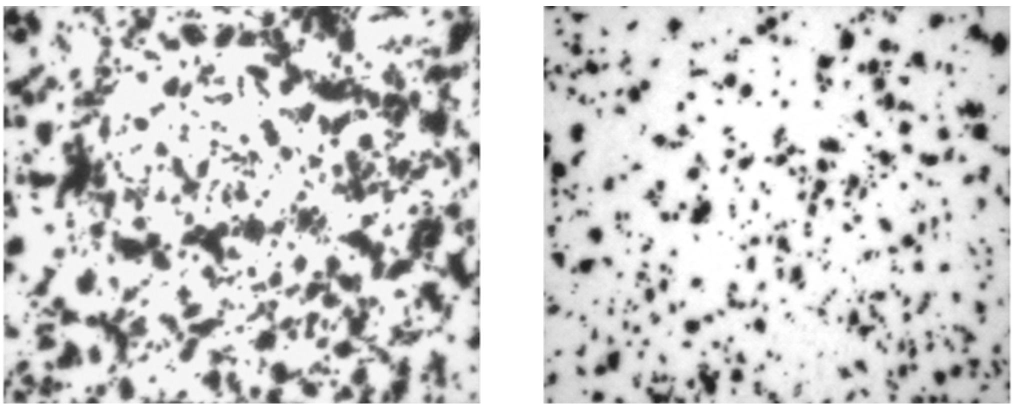

Fig. 3 Misting of unemulsified (left) and emulsified (right) UVC ink

Conclusion

The rheological properties, tack and misting of two UV curable and two hybrid (drying by free radical polymerization induced by UV radiation and by oxypolymerization) offset printing inks (unemulsified and emulsified) were investigated. The estimated characteristics were mostly similar except UV curable magenta ink. This ink has almost all parameters worse than other inks and the print with this ink will be less stable. UV magenta ink picks-up more fountain solution (60 % compared to 40 % for both hybrid and UVC inks), and the time required to reach stable emulsion is longer (9 minutes compared to 5 minutes for hybrid inks). Inks that pick-up more fountain solution can have tendency to scumming during the print. UV magenta ink has also approximately three times lower critical share rate (240 s^{-1}), low tack and the highest misting.

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