A Study Of UV-curable Offset Ink Emulsified With An Alternative Isopropyl Alcohol-free Fountain Solution

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In the present research, fountain solution without isopropyl alcohol (IPA) for Ultraviolet offset curing ink (UV ink) was prepared by using Ethylene Glycol Mono-butyl Ether (EGME) as a substitute for IPA. The effect of EGME concentration on the water pick-up characteristics, tack value, rheological behaviors, and curing time of UV offset inks was investigated. Water pick-up characteristics, tack value and rheological behaviors were measured by Duke Ink water emulsification tester, Tack-o-scope and cone-plate rheometer, respectively. The curing time of the UV ink was evaluated by the rub test of printed sheet samples proofed on the polymer film at the standard solid ink density and the same ink thickness. The results revealed that an increase in EGME concentration increased the water pick-up characteristics of the UV ink. There was no significant influence of EGME on the tack value of UV inks. However, the tack value of UV ink was significantly affected by fountain concentration in UV inks and UV ink color. The addition of EGME reduced the dynamic viscosity and thixotropic property of UV inks but did not change the flow behavior of UV ink as shear thinning. This study indicates that UV ink emulsified with a higher EGME concentration fountain solution needs a longer curing time. The cyan UV ink has the longest curing time. Finally, the fountain solution of 10% EGME exhibited good performance in water pick-up characteristics, tack value, rheological behaviors, and curing time of UV inks.

Keywords: UV offset ink, EGME, Water pick-up, Rheological behavior, Curing time

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1. Introduction

Nowadays, UV curable ink has become more and more popular in printing technology, especially in offset printing technology, due to its nearly instantaneous curing process and elimination of traditional solvents. Previously, UV curable offset inks included monomers, oligomers, crosslinking agents, gelling agents, photo-initiators, and organic solvents in their formulation [1, 2]. Therein, organic solvents play a role as diluents for pigments. However, the presence of organic solvents in ink formulations could cause environmental hazards due to their volatility. As a result, acrylate monomers and acrylate-based oligomers combined with free radical photo-initiators in the curing process to eliminate or replace organic solvents is more considered in present [1, 3]. Acrylate-based UV inks offer the advantages of curing at room temperature, producing high quality printed product, and being suitable for printing on various substrates. However, their disadvantages include high process costs and ozone formation, as well as the fast-moving of the printing sheet [4]. To address these concerns, Stone et al. used inexpensive vinyl monomers such as alkyl vinyl ether and cationic catalyst photo-initiators to substitute acrylate monomers and free radical photo-initiators in ink formulae for, thereby reducing manufacturing costs [5]. Additionally, some studies focused on improving ultraviolet curing units to control UV emitting devices individually. These devices are deactivated at unneeded curing zones to limit ozone formation [6]. Recently, bio-based resins, which are renewable resources and eco-friendly, have been studied as UV curing offset printing binder by scientists all over the world. The acrylate functional derivative of soybean has been used as monomer/oligomer in UV curable cold-set ink compositions [7]. Meanwhile, the derivative synthesized acrylate and epoxidased soybean oil have been researched to improve the hardness, chemical resistance, pigment wetting, and curing rate of UV ink film [8]. Moreover, the use of bio-based polyester itaconates as binder resins have been studied for free-acrylate UV curing offset printing ink [9]. These studies have helped make UV curing offset printing ink costs more suitable for product classes and create a friendly working environment.

In offset printing, the printing plate is divided into image and non-image areas based on their physic-chemical properties. The image areas are hydrophobic and receive ink, while the non-image areas are hydrophilic and receive fountain solution [10]. Fountain solutions are aqueous mixtures of chemical compounds, such as buffer systems, emulsifiers, conductive agents, and water [11], which keep the non-image areas free of ink and emulsify with the ink. Fountain solutions combine with isopropyl alcohol (IPA) to improve wettability on the non-image areas of the printing plate and keep water/ink balance in the printing process. However, IPA has recently been limited in offset printing technology due to environmental and health risks [12].

Furthermore, IPA may also negatively affect the quality of UV offset printing ink by causing image distortion [13]. Therefore, many studies have focused on developing IPA-free fountain solutions. These substitutes include surfactants such as ethoxylated linear alcohol [14] and specific polymers synthesized from ethylene monomers with multifunctional thiol groups or water-soluble organic solvents [14]. Some studies have also explored the use of ceramic filter systems to prevent rapid contamination of the fountain solution during long print runs [15]. Despite these efforts, substitute formulations still have drawbacks such as high costs and poor ink-fountain solution emulsions.

The quality of offset printing depends mainly on the properties of the printing inks, which includes their rheology behaviors, tack, and ability to emulsify with the fountain solution [12]. The rheology behaviors of the ink must be suitable for the printing process, including thinning shear in the rheology model, viscosity between 50 - 100 Pa.s, and tack unit between 20 - 30 [16–18]. However, if the ink is not well emulsified with the fountain solution, these factors become unstable. In the case of UV curable offset printing inks, there is a limit to amount of fountain solution that can be used [2]. This limitation means that even with excessive amounts of ink emulsified fountain solution, these inks cannot sustain the required printing density.

Moreover, UV inks with this limitation tend to cause many lithographic press problems, inferior ink transfer [3, 19]. This results in low printing density, toning, pilling, scum, and excessive dot gain [20]. Over many years, many researchers have studied to improve the rheological properties of UV curing offset printing ink [21]. Chatterjee et al. used formaldehyde-free Guamine resin to minimize oligomers in lithographic curable ink composition. The combination of alkyd resins or maleic modified rosin ester resins with acrylate-based monomers or oligomers in UV curable offset ink formulas has also been studied to widen the limited fountain solution [3]. Avci et al. used a blend of polyamide in combination with a carboxylic acid and a low volatility liquid alcohol as rheological additives for heat-set, sheet-fed, and UV curable offset ink [22]. These studies aimed to maintain the printability of UV curing inks in offset press without continual modification during press runs.

The studies on the emulsification of fountain solution in offset printing ink have been published for many years. These studies focused on interpreting droplet interactions in emulsions of lithographic ink and fountain solution with IPA by quantifying emulsion structures apparent in the CLSM visualizations [23]; and developing algorithm to estimate emulsion stability for conventional offset inks and IPA fountain solutions [24]. The research indicates that the rheological behaviors of UV offset ink decrease with increasing emulsification ratio [19]. Additionally, Bogdan et al. applied the randomness of the ink-water balance in the offset printing process to explain the transfer of ink/water emulsion from the printing plate to the blanket and predict the outcome of ink emulsion in the printing plate [25]. However, emulsions of IPA-free fountain solutions in UV curing offset ink have been limited. In our previous study, a fountain solution with ethylene glycol mono-butyl ether (EGME) as the IPA substitute was investigated and shown good wettability on the offset printing plates and be an efficient IPA substitution [26]. Moreover, EGME is derived from the family of glycol ethers which are useful solvents for various industrial products [27]. Therefore, this study uses a fountain solution with EGME to evaluate the influence of IPA-free fountain solution on UV curing offset printing inks. This study aims to evaluate the functional performance of UV curing offset printing inks emulsified fountain solution of EGME.

2. Materials and methods

2.1. Reagents and Material

Chemicals and materials used for the preparation of the fountain solution in offset printing included Tween 20 (99%. Sigma Aldrich), Magnesium nitrate hexahydrate $(MgNO_3.6H_2O)$ (99%. Merck), Disodium phosphate (Na_2HPO_4) (99%. Merck), Citric Acid (99%. Merck) and Ethylene glycol mono-butyl ether (EGME) (99%. Sigma Aldrich). All chemicals were mixed in distilled water until homogenous. This study utilized trademarked brand 3CP(BV curing sheet-fed offset inks, which are available in four process colors: Cyan, Magenta, Yellow, and Black, and were manufactured by SICPA company (Security Printing and Integrated Applications company - Australia). According to the manufacturer' report, these inks are suitable for printing on plastic card and have a viscosity of 100 Pa.s (at a shear rate of 1 s^{-1}). The printing substrate material was Polyethylene Terephthalate Glycol (PETG) sheet film MOP-NF® manufactured by (MKarte Material Technology (Tianjin) Limited. China). The chemical composition and structure of EGME was shown in Figure 1.

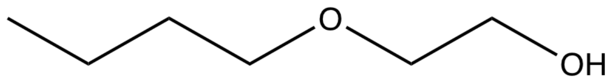

Fig. 1. The chemical composition and structure of Ethylene glycol monobutyl ether.

2.2. Preparation of fountain solution

McIlvaine's Buffer System, which is made by mixing 1.4 g of disodium phosphate and 1.94 g of citric acid in 200 g of distilled water, was used as the pH controller, and the buffer solution was fixed at pH level of 4.80. The fountain solution was prepared by physically mixing the constituents until homogeneous. A non-ionic surfactant, Tween 20, was used, and magnesium nitrate hexahydrate was added as a conductivity agent. Ethylene glycol monobutyl ether (EGME) was used as the IPA substitute. The surface tension of the fountain solution was measured using the DST 30 Digital tensiometer (SEO-Korea) based on the Du Noüy ring method. The conductivity and viscosity of the obtained fountain solutions were measured respectively by a Meterlab CDM210 conductivity meter and a glass capillary viscometer from Cannon Instrument Company (USA). The fountain solution formulas and their physicochemical properties are shown in Table 1.

2.3. Preparation of UV curing offset printing ink - free IPA fountain solution emulsions

The success of the lithographic process relies on the formation of a stable ink-in-water emulsion during printing, and the choice of fountain solution is crucial as the ink and fountain solution need to quickly react to form this emulsion. The characteristics of the ink-in-water emulsion are defined by not only the amount of water picked up by the ink but also the time at which the ink absorbs the water. Duke Ink Water Emulsification Tester Model D-10 (Duke Enterprises, The USA) was used for the emulsion preparation. The approach has been described in detail in the study of G.B. Burdall et al. [28] and only a brief account is given here. During the test, 100 g of fountain solution is added to 100 g of offset printing ink and stirred for one minute at a speed of 90 rpm. The excess fountain solution is then decanted, measured and added back to the ink, which is then stirred for another minute. This process is repeated for ten minutes. As the amount of fountain solution absorbed by ink in each one-minute test is known, the cumulative total of fountain solution absorbed over the duration of the test can be calculated. The results are presented in Table 2.

For statistical analysis, the software SPSS version 20.0 was used to evaluate the statistical tests of analysis of variance were done. Results are shown in Table 3.

2.4. Tack measurements

The ink tack testing was conducted according to the IGT operating manual and ASTM D4361 standard for an IGT Tack-o-scope. The test conditions were set to a fixed temperature of 30 ± 2 °C and a roller speed of 100 meters/minute. A quantity of 1.32 mL ink was applied using the IGT ink pipette on the IGT Tack-o-scope distribution roller, which was covered with rubber and in contact with the center metal roller. The ink was evenly distributed on the distribution roller for 30 seconds before the top measuring roller was brought into contact with the center roller. Figure 2 shows the effects of the obtained fountain solution on the tack of UV curable offset printing ink.

2.5. Rheological measurements

The emulsions were prepared by mixing 22.5 g of ink with 2.5 g of distilled water to obtain ten weight percent (% wt.) emulsions of the fountain solution in ink. The blade stirrer with two blades was rotated at a speed of (380 ± 40) min^{-1}. Rheological measurements were conducted using a control-rate rheometer Rotovisco RV20 from HAAKE GmbH (Germany) with cone and plate geometry, using a PK 100 sensor system and M5-Osc measuring system. The cone had a radius of 10 mm in cone radius, the plate had

Table 1. The fountain solution formulas.

The ratio of components (%)	The fountain solution samples			
	FS_1	FS_2	FS_3	FS_4
Buffer system	7.5	7.5	7.5	7.5
Tween 20	0.1	0.1	0.1	0.1
$MgNO_3.6H_2O$	0.2	0.2	0.2	0.2
EGME	5.0	10.0	15.0	20.0
Distilled water	87.4	82.4	77.4	72.4
Physico-chemical properties				
Conductivity (μScm^{-1})	525.3	545.5	551.2	560.5
pH	4.8	4.8	4.8	4.8
Surface tension (mN^{-1})	40.2	28.5	27.3	27.2
Viscosity $(10^{-2}\ g\ m^{-1}\ s^{-1})$	1.02	1.05	1.08	1.14

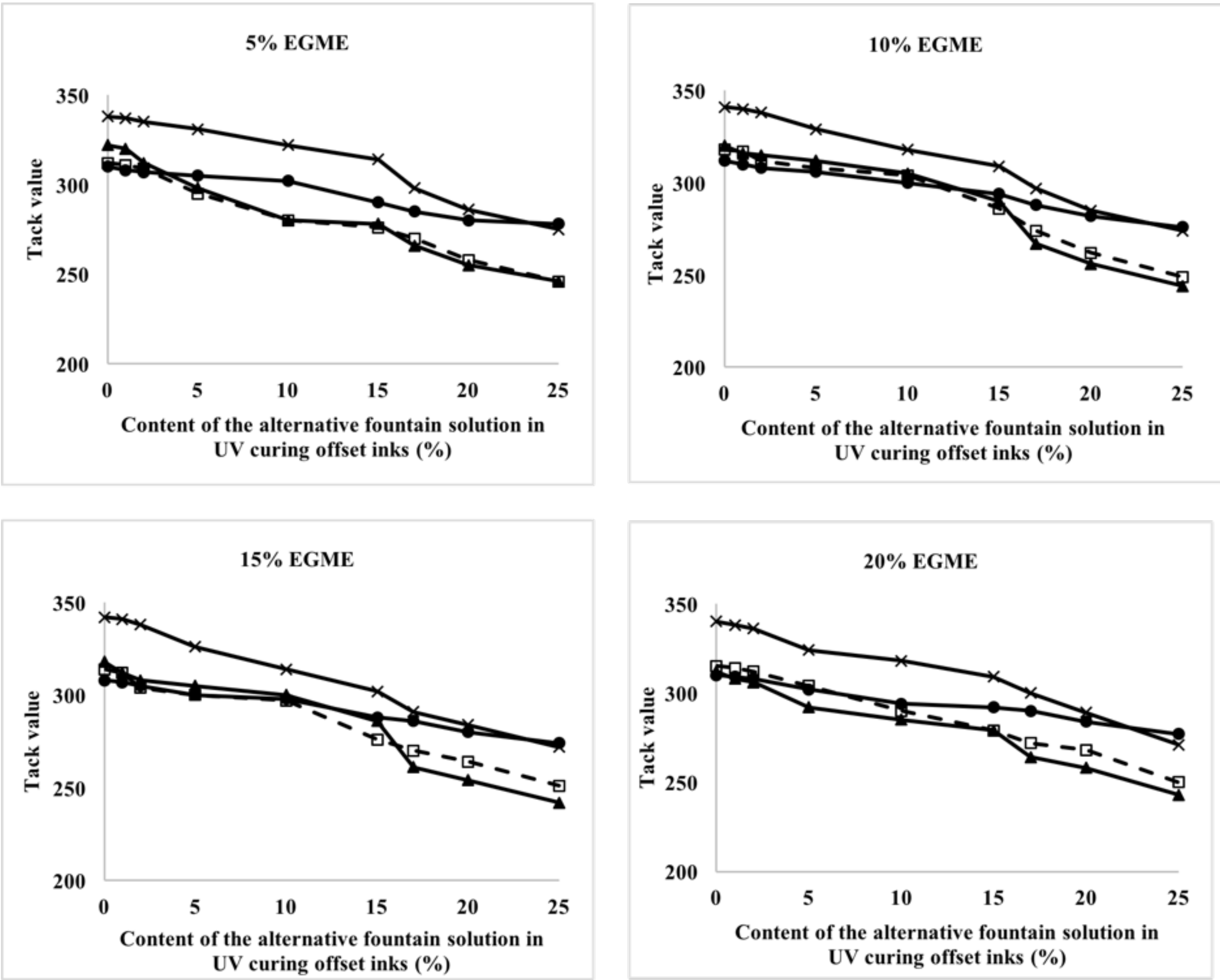

Fig. 2. Tack values of the color process UV inks (Cyan color (filled circle). Magenta color (filled triangle). Yellow color (square). and Black color (X-shaped cross)) emulsified with the fountain solutions of the EGME concentrations.

a radius of 15 mm, and the cone angle was 0.5 degree. All rheological measurements were performed at (25 ± 0.2) °C with a sample volume of ink of approximately 130 mm^3. Rheological measurements of 10 % wt. emulsions were performed for each ink sample. Viscosity values of the ink samples were determined using Rotovisco RV20 rheometer as below:

$$\text{Share rate D} : D = M * \%D \left(s^{-1}\right) \quad (1)$$

$$\text{Shear stress } \tau : \tau = A * \%\tau (Pa) \quad (2)$$

Table 2. Duke water pick-upup.

	Cyan UV curing offset ink			
	FS_1	FS_2	FS_3	FS_4
E_{max}(%)	20.86	25.94	30.16	37
t(min)	5	5	9	9
	Magenta UV curing offset ink			
	FS_1	FS_2	FS_3	FS_4
E_{max}(%)	23.5	28.74	28.96	29.56
t(min)	10	7	8	10
	Yellow UV curing offset ink			
	FS_1	FS_2	FS_3	FS_4
E_{max}(%)	27.6	31.66	34.84	36.86
t(min)	10	7	9	10
	Black UV curing offset ink			
	FS_1	FS_2	FS_3	FS_4
E_{max}(%)	33.56	35.38	27.94	28.38
t(min)	9	7	9	10

Table 3. Results of the statistical test of analysis of variance (ANOVA) of three factors as UV inks, EGME concentration and mass percent of the fountain solution in inks effect on the tack value of the UV inks. Significance is 0.05 (p = 0.05).

Source	df	F	p
UV inks	3	10.184	0.000
The mass percent of fountain solution in inks	7	37.248	0.000
EGME concentration	3	0.214	0.886
UV inks * Fountain solution	21	8.566	0.000
EGME concentration * Fountain solution	21	0.1	1.0
UV inks * EGME concentration	9	0.092	1.0

$$\text{Viscosity } \eta : \eta = \tau * D^{-1} \text{ (Pa.s)} \quad (3)$$

in which: M is shear rate factor, $M = 60$ for the $PK100$ sensor system %D is pre-set shear rate value set and displayed at the RV20 A is shear stress factor, A = 234 for the PK100 sensor system %τ is indicated shear stress value of the display.

The results of the viscosity were evaluated and shown in Table 4.

2.6. Curing process and dry testing

The emulsified inks were printed on Polyethylene Terephthalate Glycol (PETG) sheet film using RK paste ink proofer to generate printed proof samples. The fixed settings were a printing speed of 5 meters/minute, and substrate dimensions of 5 x 20 cm. A quantity of 1.0 ml ink was applied with the IGT ink pipette on the laser engraved ceramic roller and the start button was pressed to begin the automatic inking and printing process. The ink was distributed between the ceramic and blanket rollers at a controlled speed. The doctor blade removed excess ink from the engraved roller, leaving a known film thickness on the blanket roller. The printed samples were measured for color density using X-rite densitometer DT41, following North American (Status-T) measurement standards. The thickness of ink film was observed using Tabletop Microscopes TM4000 plus (Hitachi), operating at an accelerating voltage of 5 kV (Figure 5). Medium pressure mercury UV lamp (3000 W) arranged at a distance from the cured sample so that the light intensities used in all experiments were constant at 260 mW.cm^{-2}. The method of dry ink testing was evaluated via a scratch test on the printed substrate after every 5 seconds. The drying time of the printed samples is shown in Table 5.

3. Result discussions

3.1. Influence of EGME on the emulsion and tack of UV offset ink

Table 2 shows the results for the amount of water pick-up (Emax, %) and the time (t, min) required to obtain a saturated emulsion. It can be observed from the Table 2 that there are significant differences in the maximum water pick-up Emax amount, which ranges from 20 % to 38 %. This means that 20 to 38 grams of fountain solution are emulsified in 100 grams of UV inks. The time required to achieve saturated emulsion ranges from 5 to 10 minutes. The higher the concentration of EGME, the greater the amount of water pick-up. The fountain solution with 5 % EGME tends to achieve a saturated emulsion quickly with a low maximum water pick-up. In contrast, the fountain solutions with 15 % and 20 % EGME have large Emax and do not achieve a saturated emulsion. UV offset inks that pick up a higher amount of fountain solution can tend to scum. Finally, it can be seen that the fountain solution with 10 % EGME has a maximum water pick-up amount between 25 % and 36 % and takes between 5 and 7 minutes to achieve a saturated emulsion.

The results of tack measurements in figure 2 indicate that the concentration of EGME in the fountain solution has a significant effect on the tack value of UV offset inks. When the fountain solution contains 5 % wt. EGME, the tack value of cyan UV ink is less than 290. The tack values of magenta and yellow UV inks reduce to 270 when fountain solution concentration in these inks is increased to 5 % wt. or more. At 15 - 20 % wt. EGME in the fountain solution, the tack values of magenta and yellow inks are approximately 270 at when the fountain solution is added the inks to 15 % wt. Only cyan and black inks have tack values above 290. With a fountain solution of 10 % wt. EGME, the tack value of black UV ink is 320, and tack values of three UV inks, cyan, magenta, and yellow, are approximately 290 when the fountain solution concentration in the inks is

Table 4. Results of UV curing sheet-fed inks viscosity measurements.

UV inks	Without Fountain solution	FS1	FS2	FS3	FS4
D = 56 (s^{-1})					
Cyan	48.1	30.1	29.3	28.4	26.7
Magenta	59.8	46.8	45.5	30.5	21.3
Yellow	53.5	39.7	31.3	29.3	28.0
Black	65.2	49.3	44.7	27.2	25.9
D=126 (s^{-1})					
Cyan	29.7	23.4	22.7	22.2	24.4
Magenta	32.3	27.3	26.9	18.9	12.4
Yellow	30.8	26.7	23.4	22.1	19.3
Black	39.6	34.9	28.4	17.1	16.3

UV inks	Without Fountain solution	FS1	FS2	FS3	FS4
D = 56 (s^{-1})					
Cyan	48.1	30.1	29.3	28.4	26.7
Magenta	59.8	46.8	45.5	30.5	21.3
Yellow	53.5	39.7	31.3	29.3	28.0
Black	65.2	49.3	44.7	27.2	25.9
D=126 (s^{-1})					
Cyan	29.7	23.4	22.7	22.2	24.4
Magenta	32.3	27.3	26.9	18.9	12.4
Yellow	30.8	26.7	23.4	22.1	19.3
Black	39.6	34.9	28.4	17.1	16.3

Table 5. Curing time of the UV inks at different fountain solution (s).

	FS_1	FS_2	FS_3	FS_4
UV - Cyan	30	25	35	40
UV - Magenta	25	20	25	30
UV - Yellow	25	15	25	30
UV - Black	25	20	30	35

increased to 15 % wt. These values meet the requirements for printing UV offset ink on plastic substrates.

It can be observed that fountain solutions containing 10 % wt. EGME are suitable for maintaining tack of UV curing offset inks. At this EGME concentration, the percentage of emulsion in UV inks can reach 15 %, and the tacks of UV inks are above 290, meeting the requirements for offset printing. This result can be explained by EGME is an organic solvent with both polar and non-polar ends, and its HLB index is 10. Therefore, EGME plays the role of emulsifier or surfactant when used in the fountain solution. When emulsifying the fountain solution in UV inks, EGME decreases the surface tension of the interface between the fountain solution and ink, enabling emulsification occur through mixing and agitation. The droplets of the fountain solution were dispersed in UV inks.

At a concentration, of 5 % EGME, the EGME concentration is not sufficient to disperse the fountain solution in UV inks, resulting in low water pick-up of UV curing offset inks. Therefore, the ink-water balance occurs only at the low concentrations of the fountain solution in the inks (approximately 5 % wt.). At higher concentration of the fountain solution in UV inks, the emulsion becomes unstable, and the droplets of the fountain solution tend to aggregate and coalesce. Conversely, at 15 - 20 % wt. of EGME, the EGME compound plays the role of the emulsifier and interacts with the vehicles (such as oligomers) in UV offset inks. This interaction allows the UV ink to dissolve in the fountain solution, which explains the decrease in tack value of UV inks when the content of the fountain solution in the inks increases.

In summary, fountain solutions containing 10 % EGME are suitable for achieving ink-water balance and stable dispersion of the fountain solution in UV offset inks, resulting in tack values that meet the requirement for offset printing on plastic substrates.

The statistical analysis of variance was conducted to investigate the simultaneous influences of UV inks, EGME concentration, and mass percent of the fountain solution on the tack value. Table 3 presents the results of the analysis. The F value for the interaction of EGME concentration and UV inks was calculated to be lower than F (0.05,9,128) = 1.9 at a confident level of 95 %. This result implies that the interaction between EGME concentration and UV inks has an insignificant effect on the tack value of UV curing offset ink. Similarly, the calculated F value for the interaction of EGME concentration and the fountain solution content was also lower than F (0.05,21,128) = 1.9, indicating that this interaction has an insignificant effect on the tack value of UV offset inks. However, the calculated F value for UV ink was higher than F (0.05,3,128) = 2.6, and the calculated F value for fountain solution content was higher than F (0.05,7,128) = 2.1., suggesting that both factors have a significant effect on the tack value of UV curing offset ink.

3.2. Influence of EGME on the rheology of the UV curing offset inks

The rheological behavior of UV curing offset inks was measured at shear rates ranging from 3.5 - 269.5 s-1, and power function curve fitting was applied. As seen from Figure 3, the shear

This process is non-linear, and the emulsified UV ink samples exhibit shear-thinning flow behavior. The shear stress of UV inks decreases significantly with the addition of fountain solution. Moreover, it can be seen that the increase in EGME concentration in the fountain solution reduces the flow behavior of the UV inks and these reductions between UV ink samples are different. Specifically, in the case of cyan and yellow UV inks, the EGME concentration does not affect the flow behavior of emulsified ink samples. However, the flow behavior of the magenta and black UV ink emulsified with the fountain solution is noticeably reduced at EGME concentrations higher than 10% wt.

According to the viscosity values of UV inks, the cyan UV ink has the lowest viscosity compared to the viscosity values of three other color UV inks. The viscosity of black UV ink is the highest. The increase of EGME concentration reduces the viscosity of all UV process inks. The emulsified UV inks show very low viscosity from a 15 % EGME concentration of the fountain solution. The viscosity values of all UV offset inks are smaller than 30 Pa.s (D = 56 s^{-1}) and 25 Pa.s (at D = 126 s^{-1}). The emulsified UV inks show acceptable viscosity values with a 10 % EGME concentration of the fountain solution (Table 4).

Unlike conventional offset printing inks, UV offset inks are formulated based on oligomers, monomers, and modified thermo-setting resin. The pigment content is about 15 - 20 mass and other oligomers, monomers such as acrylate monomers, oligomers, vinyl monomers, and photo-initiators [2]. Printing requirements for offset inks are high viscosity, good flow and transfer properties, good tack values for sharp image, insolubility in water but stable emulsion formation with water. To obtain these desired properties, the oligomers and monomers in UV offset ink must provide excellent pigment wetting characteristics, and complete photo-initiator solubility. The appearance of fountain solution in UV ink leads to worse UV ink emulsion stability compared to the pure UV inks. This unstable emulsion may explain the decrease of viscosity of inks emulsified with the fountain solutions.

On the other hand, if the EGME concentration in the fountain solution is too high (over 10 % wt. in our experiments), the UV inks may dissolve in the fountain solution at a high shear rate, causing the emulsion of the fountain solution in UV ink is unstable. Therefore, the critical structure break down-point is changed to a much lower shear rate value. The effect of emulsification on the rheological behavior of the offset ink has also been reported by Kindernay et al. [16] and Luo et al. [19].

Thixotropy is a phenomenon of time-dependent rheology in which viscosity decrease under constant shear rate. Thixotropic ink exhibits properties in which ink viscosity declines under external force, but recover gradually once the external force is removed. This phenomenon is caused by interactions between ink components, such as oligomers, monomers, and pigment particles in UV inks. In this study, thixotropic measurements of flow curves are carried out at a range of gradually increasing shear rates from 3.5 s-1 to 77 s^{-1}, followed by a gradual decrease from 77 s^{-1} to 3.5 s^{-1}. The hysteresis loop area measures the ability of the ink structure to recover when the shear rate decreases during down curve measurement. A large hysteresis loop area is an indication of loss of structure recovery. The maximum shear rate of thixotropy measurement is 77 s^{-1} due to the wall-slip phenomenon of ink, which usually occurs with emulsion systems, suspended systems in general, and printing ink in particular. This phenomenon is explained that the measured viscosity value of ink will lower than the actual viscosity value of ink at an overly high shear rate.

Figure 4 shows that the higher the EGME concentration, the smaller the hysteresis loop area and the smaller thixotropy. The UV ink emulsified with the fountain solution containing 5 % EGME concentration has the largest hysteresis loop areas, followed by the UV inks emulsified with the fountain solution of 10 % EGME concentration. The values for 15 % and 20 % EGME concentration show the same hysteresis loop area and are the lowest. Since EGME helps increase the emulsification of the fountain solution in UV inks, the UV inks have a lower viscosity and need a less time for structure recovery after being damaged. Therefore, ink samples emulsified with fountain solution of higher EGME concentration have smaller hysteresis loop areas.

Moreover, Figure 4 shows that the UV inks emulsified with the fountain solution containing 5 % EGME concentration exhibit hysteresis loop areas at a high shear rate and high shear stress (3000 - 4000 Pa), indicating that the inks require considerable initial shear stress to reduce their viscosity, making them difficult to transfer in an offset inking

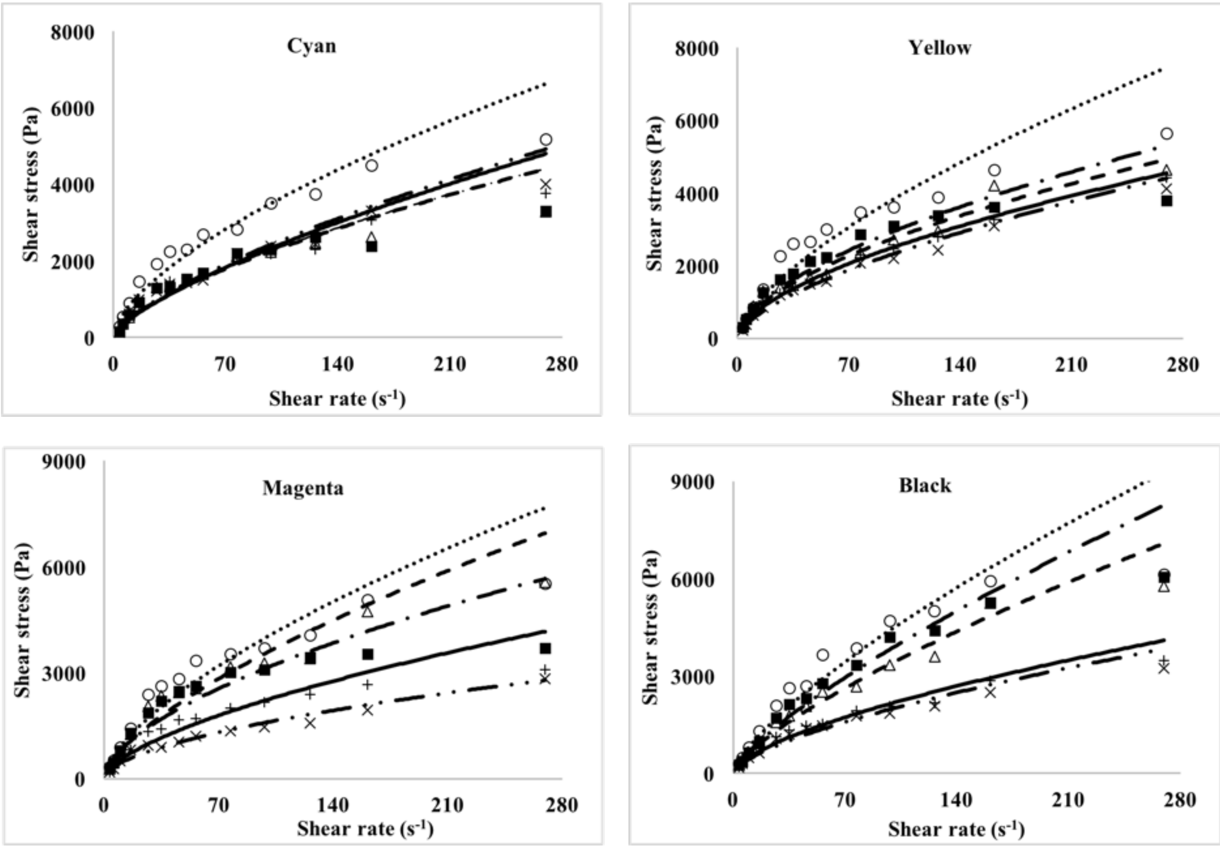

Fig. 3. Shear rate and shear stress for the process UV curing offset inks emulsified with the fountain solution with the different EGME concentrations, in which non-filled circle as UV offset inks without emulsification with the fountain solution, filled square as UV inks emulsified with fountain solution of 5 % EGME, non-filled triangle as UV inks emulsified with fountain solution.

system. Conversely, the UV inks emulsified with the fountain solution of 15 % and 20 % EGME concentration have hysteresis loop areas at a low shear rate and low share stress (approximately 1500 Pa), indicating that the thixotropy of the inks is too weak and dot spread may occur in the offset printing process. Finally, the UV inks emulsified with the fountain solution of 10 % EGME concentration show the hysteresis loop area at a shear rate of 40 - 60 s^{-1} and a shear stress of 2000 Pa, making them easy to move in the offset inking system.

3.3. Influence of EGME on curing time of UV offset ink

The solid ink densities of the printed samples are approximately 1.5 for Cyan and Magenta, 1.2 for Yellow, and 1.7 for Black UV ink, and the thickness of ink films ranges from 41.3 μm to 45.2 μm, indicating that the ink film thickness is similar for all printed proof samples (Figure 5). The curing time was determined using the scratch test after every 5 seconds, where samples without any scratch lines on the surface were considered completely dry. The procedure was repeated for other samples of each color. The result showed that different EGME concentrations for the same ink resulted in different drying times (Table 5).

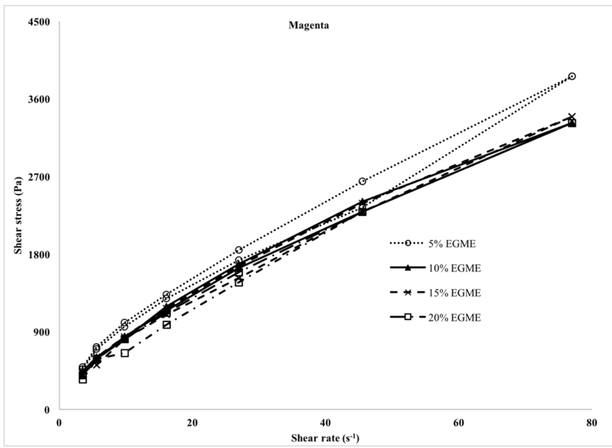

Fig. 4. Thixotropic curves of the Magenta UV curing offset inks emulsified with the fountain solution.

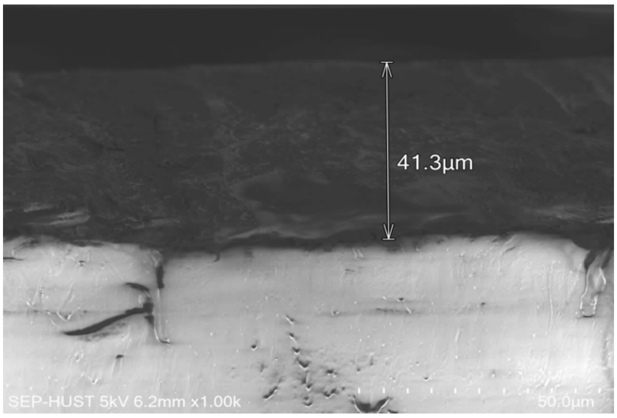

Fig. 5. The yellow ink film thickness printed proof on the PETG plastic film was measured by SEM image capture method.

The curing speed was found to be faster for all process ink colors with a fountain solution of 10 % EGME (FS2). As the EGME concentration increased, the curing speed slowed down, with the slowest curing speed observed for a fountain solution of 20 % EGME concentration (FS4). This suggests that higher water pick-up (high EGME concentration) for all process colors reduced the curing speed. Cyan ink was found to be the most challenging ink to dry, and the time needed to dry this ink was considerably longer than the other color. This difference can be attributed to the cyan pigment acting as a neutral density filter for the UV radiation. There is a possibility that the cyan pigment in ink has lower UV transmittance than the other color pigments, thus inhibiting the drying process. The attenuation of UV irradiation due to pigment absorption has been observed by Otsubo et al. [29].

4. Conclusions

In this study, the free IPA fountain solutions were prepared by using EGME as an IPA substitute. The effects of EGME on the water pick-up, the tack, the rheological behavior, and the curing time of UV offset inks was studied. Increasing the concentration of EGME results higher water pick-up rates for the UV inks, but also reduces the tack value and viscosity of the inks, and prolongs the drying time. The obtained fountain solution with a concentration of 10 % EGME showed good emulsification with the UV inks, making them suitable to offset printing.

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References

[1] S. Miezeiwski, P. Sirotto, M. Laksin, and J. Dominique-turgis. "Lithographic energy curable inks". U.S. pat. Lithographic energy curable inks. 2007.

[2] G. A. Tabbernor. *Rheology of printing inks*. Ed. by R. H. Leach, R. J. Pierce, E. P. Hickman, M. J. Mackenzie, and H. G. Smith. Dordrecht: Springer Netherlands, 1993, 766–803. DOI: 10.1007/978-1-4020-6187-5_14.

[3] S. Chatterjee, J. M. Laquidara, A. A. Kveglis, and B. J. Patel. "Formaldehyde free guanamine resin for lithographic energy curable inks". 5985984. 1999.

[4] J. Preston, S. Rousu, R. Wygant, D. Parsons, and P. Heard. "Interactions between UV curing offset inks and coated paper". In: *PIRA, Ink on Paper Conference, Dublin, Ireland*. 2004.

[5] E. Stone, G. Kotora, M. Laksin, S. Chatterjee, and B. J. Patel. "Low VOC cationic curable lithographic printing inks". U.S. Patent 6489375.

[6] J. E. Aylor, D. Cunningham, H. W. Demoore, and H. C. Secor. "UV curing assembly having sheet transfer unit with heat sink vacuum plate". U.S. Patent 6489375.

[7] R. P. Balmer, M. P. Hazell, and T. R. Mawby. "Energy-curable news ink containing soy oil". 20060079607. 2006.

[8] M. Bajpai, V. Shukla, D. Singh, M. Singh, and R. Shukla, (2004) *"A study of the film properties of pigmented UV-curable epoxidised soybean oil"* **Pigment & resin technology**: DOI: 10.1108/03699420410537278.

[9] T. Robert, S. Eschig, T. Biemans, and F. Scheifler, (2019) *"Bio-based polyester itaconates as binder resins for UV-curing offset printing inks"* **Journal of Coatings Technology and Research *16***: 689–697. DOI: 10.1007/s11998-018-0146-4.

[10] H. Kipphan. *Handbook of print media: technologies and production methods*. Springer Science & Business Media, 2001.

[11] T. Miyazaki and Y. Konishi. "Foutain solution composition for lithographic printing plate and lithographic printing method". 20120192740. 2012.

[12] S. Rossitza, (2015) *"Offset printing without isopropyl alcohol in damping solution"* **Energy Procedia *74***: 690–698. DOI: 10.1016/j.egypro.2015.07.804.

[13] K. Savchenko and O. Velychko, (2013) *"Printing Inks' Characteristics"* **Journal of Materials Science and Engineering. B** 3(7B): 464.

[14] R. Krishnan, J. Jones, J. Newton, and D. C. Henderson. "Foutain solutions for offset lithographic printing inks". 20120192735. 2012.

[15] G. Takanashi and H. Oohashi. *Fountain solution composition for lithographic printing*. 2013. DOI: 10.1210/jc.2004-1149..

[16] J. Kindernay, J. Panák, and M. Mikula, (2001) *"Rheoviscometry of offset inks and their emulsions with water"* **Chemical paper-slovak academy of science** ***55***(1): 15–22.

[17] C. Weisbecker, R. Durand, and G. Pace, (2008) *"Lithographic offset ink rheology related to sensory descriptions of appearance and handling"* **Chemometrics and Intelligent Laboratory Systems** ***93***(1): 20–26. DOI: 10.1016/j.chemolab.2008.03.004.

[18] D. Kapović, M. Rožić, M. Vukoje, and B. Lozo, (2019) *"Ink tack stability readings of the offset thermochromic inks"* **Pigment & Resin Technology** ***48***(4): 309–316.

[19] K. Y. Luo, X. F. Wei, and B. Q. Huang. "The Influence of Emulsification on the Rheological Properties of UV Curable Offset Ink". In: *Advanced Materials Research*. ***380***. Trans Tech Publ. 2012, 95–98.

[20] X. X. Ma, X. F. Wei, B. Q. Huang, and W. Zhang. "The Effect of Emulsification Ratio on Ink-Transfer Performance and Printing Quality of UV Offset Ink". In: *Advanced Materials Research*. ***380***. Trans Tech Publ. 2012, 77–80.

[21] S. Rousu, J. Gustafsson, J. Preston, and P. Heard, (2006) *"Interactions between UV curing, hybrid-UV and sheetfed offset inks and coated paper–commercial print trials"* **TAGA Journal 2**: 174–189.

[22] S. Avci and D. Merchant. "Compositions useful to provide improved rheology and mist control to ink formulations and ink formulations containing such compositions". 20060213393. 2006.

[23] D. N. Hohne, H.-Y. Chen, J. Lahann, and M. J. Solomon, (2008) *"Near-surface structure of lithographic ink–fountain solution emulsions on model substrates"* **Colloids and Surfaces A: Physicochemical and Engineering Aspects** ***326***(3): 138–146.

[24] L. Varepo, A. Y. Brazhnikov, I. Nagornova, and O. Novoselskaya. "Methods of measurement the quality metrics in a printing system". In: *Journal of Physics: Conference Series*. ***998***. 1. IOP Publishing. 2018, 012040.

[25] B. Kushlyk, (2013) *"Adjustment of Ink and Water Supply in Offset Printing"* **Journal of Materials Science and Engineering. B** *3*(8B): 545.

[26] A. T. Phung, Q. H. Nguyen, H. Q. Duong, and H. H. Cao. "Study of wetting on the non-imae area of offset printing plates by an alternative iso-propyl alcohol-free fountain solution". In: ***10***. 2. 2020, 50–57.

[27] M. Barzegar Jalali, A. Jouyban, H. Shekari, and S. N. Mirheydari, (2020) *"Density and Speed of Sound of Diethylene Glycol Monoethyl Ether+ Propylene Glycol at T=(288.15–318.15) K"* **Iranian Journal of Chemistry and Chemical Engineering** ***39***(3): 231–239. DOI: 10.30492/IJCCE.2020.34833.

[28] G. B. Burdall, D. Owen, and R. Paradine. "Lithographic inks". In: *The Printing Ink Manual*. Ed. by R. H. Leach, R. J. Pierce, E. P. Hickman, M. J. Mackenzie, and H. G. Smith. Dordrecht: Springer Netherlands, 1993, 342–452. DOI: 10.1007/978-1-4020-6187-5_6.

[29] Y. Otsubo, T. Amari, and K. Watanabe, (1986) *"Rheological measurements of cure rate of UV inks"* **Journal of applied polymer science** ***31***(7): 2099–2108. DOI: 10.1002/app.1986.070310713.