Wetting of model fountain solutions in offset printing: The influence of additive concentration and surface roughness on wetting kinetics

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Abstract

The aim of the study was to investigate the role of model fountain solution formulations on wetting kinetics at both short and long time scales (at static conditions).The main individual components for adjusting wetting behavior of a fountain solution have been explored with respect to the sheet fed offset printing process. The influence of IPA concentration on fountain solution wetting was determined and compared with IPA-free surfactant based fountain solutions. The surface roughness effect on wetting behaviors of the fountain solutions were assessed with particular emphasis on the lateral spreading. The impact of surface chemistry of the substrates on the wetting behavior was distinguished by using a correction factor for the surface roughness.

As the IPA or the surfactant concentration in the fountain solution is increased, the surface tension is decreased followed by a faster wetting process, which is not only dependent on the formulation but also significantly on the surface roughness and the surface texture. Apparently, the wetting behavior is more dependent on the physical- than chemical features as the additive concentration is increased.

Introduction

The fountain solution in offset printing is an important part in the production of high quality prints. The mechanism of the fountain solution wetting is not extensively reported and better understanding of the phenomenology is needed, particularly when considering the evolution of the fountain solutions in modern offset printing machines. A typical fountain solution consists of different functional chemicals such as plate preservative agents, wetting agents, isopropyl alcohol (IPA), buffer substances, and anti-microbe additives mixed in water [1]. The fountain solution performs several essential functions such as the wetting of the non-image area of the printing plate but also as an emulsifier for the offset ink [1].

IPA is used in the fountain solution mainly to lower the surface tension and thus to increase the wetting rate [2], but also to increase the viscosity to achieve uniform transport, accelerate and stabilize the ink/water equilibrium and to improve the drying of the ink [3]. In recent years the use of IPA has been reduced, and in many cases eliminated, by using alcohol substitutes. A lot of research has been focused on non-ionic surfactants as replacements to IPA. The reason is due to the Volatile Organic Compound (VOC) emissions attributed to the evaporation of isopropyl alcohol and the level of environmental regulation this lead to [4]. Non-ionic surfactants are mainly used due to their biodegradable nature and because they create less foam than their counterparts [5]. The non-ionic surfactants used in fountain solutions are mostly glycol or glycol-ether based [6].

Aurenty et al. has interpreted the mechanism of the spreading of surfactant solutions and related the wetting kinetics to the Marangoni effect [7]. A lot of research concerning the influence of substrate heterogeneities on wetting phenomena has been published over the years. The most frequently used correction for the surface roughness is the Wenzel procedure [8]. This involves the determination of an r-ratio of the actual (rough) surface over the projected (smooth) Young surface. The Young equation is valid only for planar surfaces, but may be used for samples after introduction of a correction for the surface roughness [9]. A broad series of measurements on how surface texturing affects the contact angle as a function of chemical wettability of the solid has been published by Shibuichi et al [10]. The influence of surface roughness on the surface energy components [11], and on ink adhesion energy [12], has previously been reported. Topographical features of papers have also been related to the optical appearance of paper in terms of slope parameters of gloss and surface roughness [13]. Taniguchi and Belfort reported a contact angle correction using a captive air bubble technique and describing the surface roughness with a zigzag model with Atomic Force Microscopy (AFM) [14]. Alam et al. concluded that the surface spreading is a linear function of the droplet Reynolds number and the lateral spreading on irregular surfaces was found to be inversely proportional to the surface roughness [15]. By using a liquid-bridge technique, one is able to characterize point to point variation of surface energy and porosity [16]. Cassie defined an average contact angle for physically smooth but chemically heterogeneous surfaces [17]. Takeshita et al. manipulated individually and simultaneously the surface roughness and the surface chemical properties of polymer surfaces [18].

This study concerns model fountain solutions for SFO (Sheet Fed Offset) printing. The wetting has been studied on a coated paper substrate with Contact Angle measurements (CA). The wetting behavior has been studied both at short and long time scales. The fountain solution wetting is usually modeled for an ideally smooth surface with an average (homogeneous) chemical property. This feature must be considered and corrected when evaluating the wetting kinetics. In addition, the equilibrium concentrations in a mono- dual- or multi-component fountain solution during wetting needs to be established since it might change not only the wetting properties but also the kinetics (surfactant depletion). Hence, the preferential adsorption is of primary concern. Dynamic measurements of contact angles of dual-component fountain solutions may show wettability changes due to the transfer of surfactant to the interface of fountain

solution/substrate/air. The topographical characterization of the paper substrate was carried out with Atomic Force Microscopy (AFM) coupled to the Scanning Probe Image Processor (SPIP) software.

Experimental

Materials

The fountain solution wetting was investigated on a coated matte calandered paper with a coat weight of 7+7 g/m^2. A blade coater with a speed of 1200m/min was used and the calandering was performed with an Optiload calander to a target gloss level of 30% (TAPPI 75°). In Table 1, the main components used in the coating dispersion is presented.

Table 1. Coating dispersion for the paper sample

Coating colour recipes*	Pre coat	Top coat
Ground calcium carbonate	80	70
Talcum		15
Platy Kaolin		15
Brazilian Kaolin	20	
SB latex	10	11
Solids by weight, %	60	62

* Amounts given as pph - parts per hundred parts pigment by weight

At first, IPA based fountain solutions were prepared at three concentration levels, 5%, 10% and 15 vol-% in ion exchanged distilled water. The measured surface tensions for these references are presented in Table 2. Secondly, a certain amount of the non-ionic surfactant was added to reach the target surface tensions. It should be noted that the amount of surfactant needed to achieve the same surface tensions as the IPA references is decades smaller.

In Figure 1, the molecular structure of the surfactant is presented. It should be noted that the surfactant is low VOC (VOC%= 1.45). The surfactant HBL is 8, the cloud point 17.2 °C [5% in water] and the solubility limit in water is 0,032 wt% (Air Products and Chemicals Ltd). As observed, the molecule contains a carbon-carbon triple bond and two adjacent hydroxyl groups in the center of the hydrocarbon chain. This type of structure gives the molecule high electron density and thus hydrophilicity. Highly branched alkyl groups are attached to both sides of the hydrophilic part of the molecule, giving the whole molecule the hydrophobic-hydrophilic-hydrophobic properties [19]. The wetting ability of the surfactant based fountain solution is determined by the orientation of the molecule at the solid/liquid interface. Increasing the surfactant concentration leads to a re-orientation of the adsorbed molecules from a horizontal to a vertical direction [20].

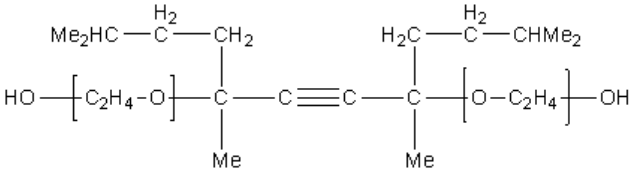

Figure 1. *Polyethylene glycol 2, 5, 8, 11-tetramethyl-6-dodecyne-5, 8-diolether*

Methods

Surface tension measurements

The surface tensions of the fountain solutions were measured with a bubble tensiometer. The temperature, varying between 23-24°C, was recorded during the measurement. A SensaDyne PC9000 bubble tensiometer (SensaDyne Instrument Division, Mesa, Arizona, USA) was used. The surface tensions were measured at a bubble rate of 1 bubble/s for water which constituted a semi-static measurement. The surface tension was monitored during 5 minutes altogether 4 times to get statistics.

Contact angle measurements

A well-known method to determine wetting phenomena is by measuring contact angles of liquids resting on solid surfaces [21] (sessile drop). An optical impact free contact angle meter with a high-speed camera (KSV Instruments Ltd, Helsinki, Finland) was used. The contact angles were calculated with the Laplace curve fit model [22]. The volume of the droplets was one micro liter, corresponding to a sphere diameter of ~1,5mm at t=0,1s. This obviously changes with time. The results are given as a mean of five measurements. The standard deviation of the contact angle values was less than 2°. The droplet spreading occurs at the three phase contact line. The transport equation is described with the flux equation:

$$J = \frac{dV/dt}{A_\phi} = \frac{D_V}{\eta} \times \frac{2\gamma_{LV}}{r} \times \cos\Theta = \frac{dA/dt}{l_\phi} \quad (1)$$

, where the former part refers to the bulk penetration and the latter part describes the surface spreading. $l_Ø$ is the length of the droplet perimeter (2πr). As the studied paper surface is hydrophilic, the droplet simultaneously follows the surface texture (spreading) and spreads inside the substrate (penetration). These processes generate a decrease in contact angle. The penetration can be investigated by monitoring the decrease in droplet volume as the initial volume is known. However, the penetration part was excluded from this study. It should be noted that the surface tensions and the contact angle measurements were performed separately. Thus the changes in surface tension during the droplet spreading could not be monitored. The wetting is a hydrodynamic process. As for dual component systems, the spreading is dependent on the fastest component.

Atomic Force Microscopy

The AFM measurements were carried out with a Nanoscope IIIa microscope, (Veeco Instruments Inc., Santa Barbara, USA). All images were measured with tapping mode. Topographical images (10μm×10μm) of the sample were captured and an average of ten measurements is reported which is enough to get statistics. The scanning probe image processor (SPIP, Image Metrology, Denmark) software was used for the image analysis. A line wise and a global correction were used to eliminate artefacts in the image. The surface structure of the paper sample is described using a roughness parameter, S_{dr} [23], which gives the effective surface area with respect to the projected area as percent increment [23]. S_{dr} = 0 %, refers to an ideally flat surface, where the surface area and the area of the xy-plane are the same (Young ideally flat surface). It is obvious that the roughness parameter value is

dependent on the scanned area, since the parameters are defined relative to a mean plane through the surface roughness, making the numerical values dependent on the surface frame chosen. A 10µm×10µm image size was considered to be suitable for the present study to describe the surface roughness of the paper. According to the Wenzel's roughness equation (Eq. 2), the relation between the measured contact angle Θ_m and the Young contact angle Θ_Y, may be written as:

$$\cos\Theta_m = r\cos\Theta_Y \tag{2}$$

where r is the ratio between the real and the projected surface area of the sample. The S_{dr} roughness parameter can be used to calculate r from the expression:

$$r = 1 + \frac{S_{dr}}{100} \tag{3}$$

The paper surface in this study was shown to be hydrophilic (water contact angles less than 90°) which is a precondition when using the Wenzel equation. For an r-value close to 1, the correction for surface roughness can be neglected [8]. This model also allows the determination of surface roughness, and the effect of roughness length scales, on wettability.

Results

The measured and the corrected contact angles for the different fountain solutions on the paper substrate at t=1s are presented in Table 2. The calculated r-value for the paper sample according to equations 2 and 3 is 1,539 corresponding to an S_{dr} value of 53,9%. It can be concluded that the difference between the uncorrected and the corrected contact angles for the fountain solution mixtures, ΔΘ, is increased with increasing IPA or surfactant concentration.

Table 2. Surface tensions, static measured and corrected contact angles for the model fountain solutions.

Fountain solution	IPA [vol-%]	Surf. tens. γ [mN/m]	Θ @ 1s [Meas.]	Θ @ 1s [Corr.]
FS 1	5	49,2	48	64
FS 2	10	40,9	35	58
FS 3	15	35,3	24	54
Fountain solution	Surfactant [vol-%]	Surf. tens. γ [mN/m]	Θ @ 1s [Meas.]	Θ @ 1s [Corr.]
FS 4	0,015	49,2	29	55
FS 5	0,024	40,9	21	53
FS 6	0,04	35,3	14	51

In figures 2-4, the wetting kinetics for the model fountain solutions is presented for both measured and surface roughness corrected advancing contact angles. In figure 2, the wetting at γ=49,2mN/m is investigated. The surfactant based fountain solution expresses slightly faster wetting at short time scales but a significant difference is seen at longer time scales. The IPA based fountain solution reaches saturation faster and declines differently compared to the surfactant based fountain solution.

When comparing the surface roughness corrected values, the difference in wetting behavior between the IPA based and the surfactant based fountain solution is observable. The corrected values provide the influence of surface chemistry on wetting. The wetting on a physically homogeneous but chemically heterogeneous surface is dominated by the liquid properties as well as the chemical properties of the substrate. It can also be seen that the surface chemical contribution to wetting is slightly stronger at higher surface tensions, thus being more influenced by the additive adsorption. The adsorption behavior is also time dependent together with the wetting front. The results indicate that it is really important to take the surface roughness into account when evaluating wetting phenomena for rough heterogeneous substrates.

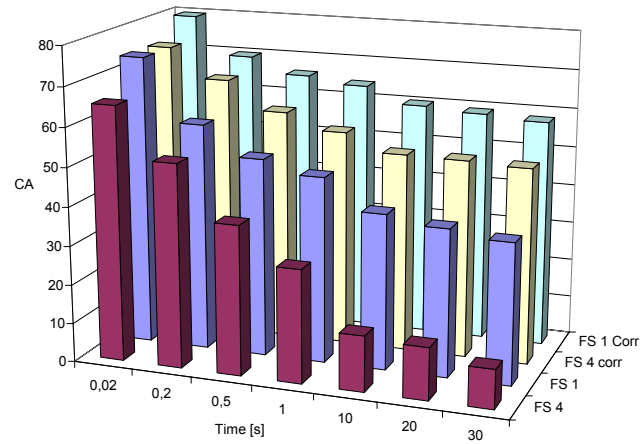

Figure 2. Fountain solution wetting at γ=49,2mN/m

Figure 3 presents the fountain solution wetting at γ=40,9mN/m. This corresponds to an IPA amount of 10%. At this surface tension level the surfactant based fountain solution again shows the fastest decrease in contact angle. The wetting rate is increased compared to the higher surface tensions presented in Figure 2.

The corrected contact angles are slightly lower for the surfactant based fountain solution. This concludes that an increase in IPA or surfactant concentration reduces the influence of surface chemistry but increases the influence of surface roughness on wetting.

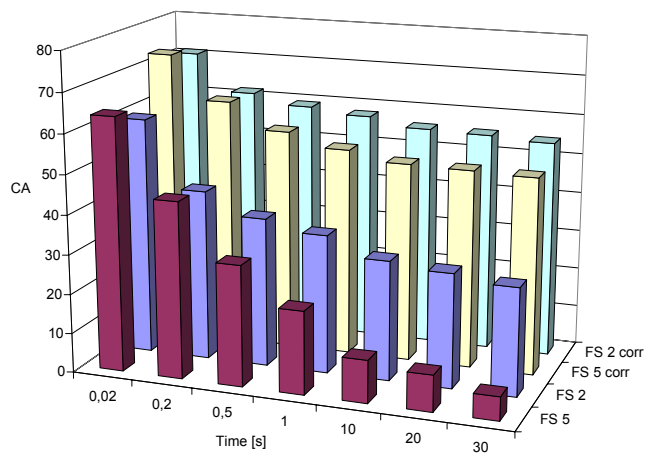

Figure 3. Fountain solution wetting at γ=40,9mN/m

Figure 4 presents the fountain solution wetting at (γ=35,3mN/m). As already seen at the higher surface tensions γ=40,9 and γ=49,2mN/m, the longer time scale wetting is much faster for the surfactant based fountain solutions. At short time scales, no significant differences are observed.

According to Figure 4, there is negligible difference between the fountain solutions when the contact angles are corrected, particularly at longer contact times. The uncorrected contact angles show that the adsorption increases with time and decreasing surface tension. However, the corrected values confirm that the adsorption is almost constant with time at lower surface tensions.

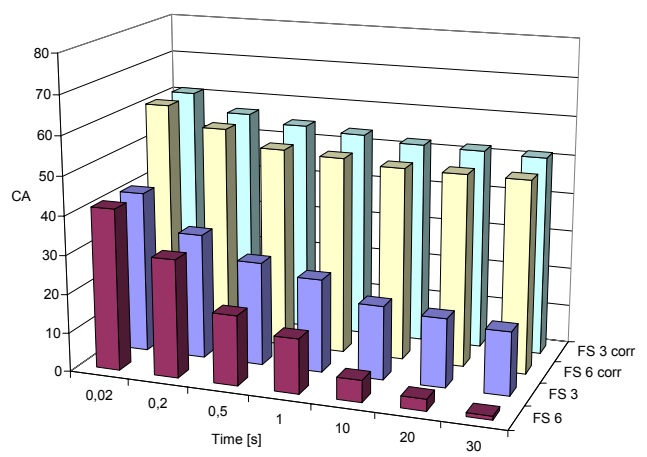

Figure 4. Fountain solution wetting at γ=35,3mN/m

It is observed in Figure 5 that the surfactant based fountain solutions have the fastest spreading across the paper surface compared to the IPA based. The surfactant based fountain solutions FS 4 and FS 5 have similar spreading behavior after 10s, while the initial spreading of the FS 5 fount is much faster. The interactions with the substrate are stronger as the surfactant concentration is increased. An ending line indicates that the contact angle has reached a value of zero, i.e., for FS 6 at t=15s. This means that the IPA based fountain solutions still spread after 30s, while the surfactant based fountain solutions reach complete spreading much earlier. Other observations are slight discontinuities in the surfactant based fountain solution spreading due to surfactant depletion which obviously changes the wetting. The droplet is thus not in stable equilibrium and a new equilibrium condition is found by balancing the three interfacial forces (solid-liquid-air) according to the change in surface tension and droplet volume. The Marangoni effect causes a surface-tension gradient in the liquid allowing the fountain solution to more easily spread on top of the rough surface.

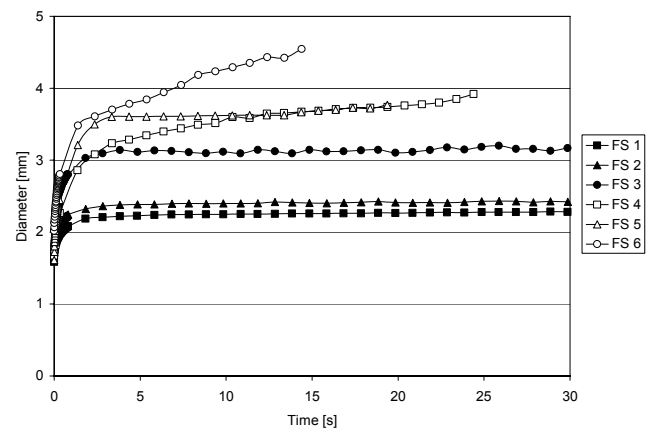

***Figure 5.** Lateral spreading of the model fountain solutions.*

Discussion

Figures 2-4 show that the influence of surface heterogeneities on wetting plays a significant role for understanding the wetting mechanisms. From the corrected and uncorrected contact angles, the spreading behavior and interaction with the substrate can be predicted. When analyzing the both systems at same surface tension values, it reveals that differences in the interaction with the surface exist.

The correction for surface roughness affects the wetting of the surfactant based fountain solutions stronger, as their wetting is faster compared to the IPA based. The low dynamic surface tension of the surfactants, enable rapid adsorption to the solid-liquid interface, altering the surface hydrophilicity. Introducing the surface roughness correction, it can be concluded that the difference in wetting behaviors between the systems are almost negligible, especially with decreasing surface tension. A saturation of the surface is reached faster with IPA than with the surfactant based fountain solution. By comparing the surface roughness corrected- to the uncorrected contact angles, saturation is reached simultaneously. The uncorrected contact angles also provide information that the adsorption is changed with time, thus being dependent on the surface roughness.

Figures 2-4 indicate that as the additive concentration is increased, the role of surface roughness and surface chemistry on wetting changes. A higher IPA or surfactant concentration leads to a wetting dominated by surface heterogeneities. Additionally the surface features become more important regarding the wetting, with the time elapsed. Figure 5 indicates that differences in

wetting are observed in the phenomena occurring on the paper surface.

Conclusions

IPA based fountain solutions have been compared to surfactant based fountain solutions in order to investigate the role of fountain solution components on the wetting of paper. Already at short time scales the wetting is rapidly increased due to a lowering of the surface tension. When using surfactants as IPA replacements, much smaller concentrations are needed to achieve functionality. When choosing a fountain solution for a specific substrate, the focus has to be put on the lateral spreading behavior. A too fast spreading can result in too great an emulsification of the printing ink and the fountain solution. Consequently, this will lead to an inexact separation of the ink and the fount followed by poor print quality.

By correcting the wetting behaviors of a fountain solution on heterogeneous substrates according to the surface roughness, one is able to distinguish the influence of physical and chemical features on the wetting phenomena. The structure corrected surface provides information of the interactions between the fountain solution and the substrate (adsorption to the interface; amount/unit area)

By obtaining information and understanding the wetting phenomena on an ideally flat, structure corrected surface, new possibilities are opened for the development and optimization of the fountain solution formulations. Additionally the coating layer and its interactions with the fountain solution are better understood. This opens new possibilities for predicting the quality of the final print. By combining the information from the topographical and the surface chemical contribution to wetting, valuable information for better control of the on-press behaviors is attained.

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