

Wettability of Model Fountain Solutions and Their Influence on Offset Paper Properties

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Abstract

A surface chemical and physical characterization of offset paper was determined before and after application of isopropyl alcohol -based and isopropyl alcohol -free surfactant based fountain solutions, respectively. The paper surface features were characterized with Atomic Force Microscopy and the surface energies were determined from contact angle measurements. Changes in the surface chemical properties induced by the fountain solutions were investigated with Time-of-Flight Secondary Ion Mass Spectroscopy.

Wetting of the coated papers with different model fountain solutions revealed a slight increase in Root Mean Square roughness with the surfactant based fountain solution. This change in sub- microroughness is not only ascribed to substrate swelling or migration of coating constituents but rather to the presence of surfactants on the surface. A change in the surface energy and particularly the polar contribution could be observed after application of the surfactant based fountain solution. Time-of-Flight Secondary Ion Mass Spectroscopy analysis showed further that the isopropyl alcohol based fountain solution does not change the elemental composition of the surface, while the surfactant based fountain solution clearly changed the chemical composition of the surface which thus is associated with the characteristic composition used.

Keywords: Atomic Force Microscopy, Contact Angle, Fountain Solution, Surfactant, ToF-SIMS

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Introduction

The interactions between ink, paper and fountain solution in offset printing are important to understand in order to be able to predict the quality of the printed product. The transfer of the fountain solution to the paper causes various challenges during the process such as dimensional changes (e.g. misregister) and surface picking and a reduction in surface strength. There may also be interference in the transfer of ink to paper. Parameters affecting the amount of fountain solution transferred to the paper are the nature of the fountain solution, how much fountain solution is emulsified in the ink, the porosity and the chemistry of the surface of the paper and the printing layout. The fountain solution passes via the rubber blanket to the paper partly to the non-image areas and partly emulsified in the ink. To our knowledge, the impact of fountain solution composition on the paper surface properties after printing is not well reported in the literature. Isopropyl alcohol (IPA) is a solvent evaporating liquid and will both evaporate and penetrate with the liquid phase into the substrate, whereas surfactants will not evaporate and thus remains on the surface or penetrates into the bulk. It can be assumed that the different fountain solution formulations results in different paper properties.

Key functions to be controlled by the fountain solution are, e.g., keeping the ink off the non-image area with a film of fountain solution, maintaining the hydrophilic nature of the non-image areas, promoting fast spreading over the plate (Leks-Stepien and Khadzhyanova, 2005), lubricating the plate and the blanket and controlling emulsification of ink and water (Kipphan, 2001). The dampening system supplies a very thin film of fountain solution (approx. 2 μ m) over the printing plate. Too much water causes disturbances in ink transfer (water marking) (Lindqvist, 1981) and if the plate is allowed to run dry, ink will begin to wet the whole plate, i.e., scumming occurs (Fujihunt, 2003). The composition of the fountain solution has to have interplay with the ink composition. Thus many ink suppliers offer an ink and a fountain solution in one package, in order to guarantee trouble-free printing. The interactions are important to recognize thoroughly in order to achieve optimal press performance.

Fountain solution additives are used to promote rapid wetting across the printing plate, rubber blanket and the paper surface. The fountain solution usually contains plate preservative agents, wetting agents, IPA, buffer substances and anti microbial additives (Kipphan, 2001). Biocides help control bacteria growth. IPA is used to reduce the surface tension of the fountain solution but also to increase its viscosity (Ain and Stevens, 2002). An increase in the IPA amount will promote the wetting both at short and long time scales, the wetting being more structure dependent with time (Tåg et al., 2008).

During the last decade, a lot of research has been made on acetylenic glycol-based surfactants and their use as IPA replacements (Medina, 1997). Non-ionic surfactants are increasing in popularity due to Volatile Organic Compound (VOC) legislations. Surfactants aid in the cleaning of the ink from the non-image area of the plate, reducing scumming and toning (Lee, 1998). Surfactants with high Hydrophilic Lipophilic Balance (HLB) numbers are usually ethoxylated, which stabilise foam (Lee, 1998). When decreasing the IPA amount, the fountain dosing has to be increased and the plate surface has to be rougher which will lead to a coarser print. Today, printing houses in North America are completely run alcohol-free, while in Europe, IPA is still used in high concentrations.

The scope of the present study was to establish the effect of fountain solution composition on paper properties after printing. The topographical features on the surface was determined with Atomic Force Microscopy (AFM) which can be used to give information on the surface roughness, defined in terms of Root Mean Square (RMS) roughness and (Wenzel) r -values. The influence of surface roughness and texture on wetting behaviors has been reported in several publications (Wenzel, 1936; Shibuichi et al., 1996; Bico et al., 1999; Taniguchi and Belfort, 2002; Alam et al., 2007; Tåg et al., 2007) and also related to the interaction between fountain solution additives and the substrate (Tåg et al., 2008). The changes in surface chemical properties of the paper were analyzed with Secondary Ion Mass Spectroscopy (ToF-SIMS) and surface energy measurements. ToF-SIMS enables semi-quantitative determination of the chemical composition and the distribution of molecular species on surfaces (Briggs, 1992) and has been used to e.g., determine nature and location of contaminants and their impact on offset print mottle (Zimmermann, 1995) and the effect of surface properties (binder concentration) on print quality. Moreover, Dalton et al. (2002) reported on the distribution of ink components over the paper surface using the XPS and SIMS techniques. The surface energy components were derived from measured contact angles using the van Oss, Chaudhury, Good method (vOCCG) (van Oss et al., 1988) before and after fountain solution application. This method has shown to produce exaggerated basicity and almost zero acidity for most solid surfaces (Berg, 1993; Morra, 1996). Despite the generally agreed weakness of probe liquid determination of relative surface energies, it is the most used and accepted method.

Experimental

Materials and methods

The surfactant used in the model fountain solution was a non-ionic surfactant delivered from Air products and Chemicals, Inc. The Dynol 607 surfactant is a 100% pure surfactant based on the Gemini technology. The VOC content is

1.45%, and the surfactant Hydrophilic-Lipophilic Balance (HLB) is 8. The cloud point occurred at 17.2 °C in water determined at a concentration of 5 wt%. The solubility limit in water is 0.032 wt%. IPA (C₃H₈O) is a colorless liquid, fully miscible in water, has a flashpoint of 12 °C, and a density 0.785 g/cm³. The vapor pressure at 20°C kPa is 4.1. The model fountain solutions were prepared to IPA and surfactant concentrations typical to the offset printing process. These were 15% for the IPA based and 1% for the surfactant based fountain solution, corresponding to surface tensions of 35.3mN/m and 26.5mN/m, respectively.

The hydrophobic-hydrophilic-hydrophobic structure gives the surfactant its distinct properties. 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 (Krishnan and Sprycha, 1999). The hydrophilic group distinct itself by the ability to interact with Lewis acids and bases. Ethylene Oxide/Propylene Oxide (EO/PO) surfactants are a group which both may interact with polar solvents but due to the branching in PO, the structural difference shows a difference in water interaction leading to a surface active behavior. For that case, the PO behaves like the hydrophobe.

The substrate used in the study (hereafter called reference) was a double-coated matte calandered paper with a coat weight of 7+7g/m². The coating was made with a blade coater at a speed of 1200m/min after which the reels were calandered (Optiload twinline, Optisoft 2, Metso) to a target gloss level of 30% (ISO 8254-1). In Table 1, the mineral and latex components are shown. In addition, rheology modifiers and additives were added to adjust coater runnability.

Table 1. The coating dispersion for the paper sample.

Coating colour recipes*	Pre-coating	Top-coating
Ground Calcium Carbonate	80	70
Talcum		15
Platy Kaolin		15
Kaolin (Brazil)	20	
SB Latex	10	11
Solids by weight, %	60	62

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

The paper sample was applied with the model fountain solutions with a lab blade coater (DT Paper science Oy Ab). The amount of water transferred to the paper was estimated to be a bit higher than a real offset process (Lim, 1996).

However, this is not a concern since even small concentrations enhance the studied properties.

Surface tension measurements

The dynamic surface tensions were measured with a bubble tensiometer, SensaDyne PC9000 bubble tensiometer (SensaDyne Instrument Division, Mesa, Arizona, USA). The temperature was recorded during the measurement (23-24°C) and the bubble frequency was 1 bubble/second for water. The method is based on measuring ΔP between two capillaries with different diameters. Dry air flows through the capillaries that are immersed to the same depth in the liquid and the maximum pressure in the bubbles is observed. The surface tension $\gamma \propto \Delta P$.

Atomic Force Microscopy (AFM)

The AFM measurements were carried out with a Nanoscope IIIa, (Veeco Instruments Inc., Santa Barbara, USA). All images were measured with tapping mode using standard Si_3N_4 cantilevers. Topographical images ($10\mu\text{m} \times 10\mu\text{m}$) of the sample were captured and an average of ten measurements is reported which is enough to get statistics (Peltonen et al., 2004). 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 artifacts in the image. The surface roughness was defined in terms of Root Mean Square (RMS) roughness and (Wenzel) r-values (Peltonen et al., 2004). RMS is the square of the deviations of height data from the central plane. The S_{dr} parameter gives the effective surface area with respect to the projected area as percent increment. $S_{dr} = 0\%$, 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. According to the Wenzel roughness equation (Eq. 1), the relation between the measured contact angle and the Young contact angle, may be written as:

$$\cos \Theta_m = r \cos \Theta_Y \quad (1)$$

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:

$$r = 1 + \frac{S_{dr}}{100} \quad (2)$$

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 (Wenzel, 1936). This model also allows the determination of surface roughness, and the effect of roughness length scales, on wettability.

Contact angle measurements

A well-known method to determine wetting phenomena is by measuring contact angles of liquids resting on solid surfaces (sessile drop) (Young, 1805). 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 (Laplace, 1805). 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°. 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.

By measuring contact angles of probe liquids with known acid-base values, the acid and base components of the solid can be determined. Three reference liquids with different properties, water, ethylene glycol (EG) and diiodomethane (DIM) were used in the calculations of the surface energy components. The surface energy components were calculated from measured contact angles using the van Oss, Chaudhury, Good method (vOCG). The “equilibrium” contact angle was determined before any liquid penetration had occurred, by following the decrease in droplet volume.

Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

ToF SIMS elemental characterization gives information about molecular species present on the outermost surface (Briggs, 1992). The analysis depth related to the ToF-SIMS technique is from 1–5 nm of the surface (Briggs, 1998; Isotone, 1995). The instrument used was PHI Trift II spectrometer. High-mass-resolution spectra in both positive and negative ion modes over the mass range of 2–2000 Da were acquired using Ga primary source on a raster size of 100 µm x 100 µm with an applied voltage of 15 kV and a primary ion current of 600 pA. The acquisition time was 5 min. The samples were scanned from three spots. The intensity of the TOF-SIMS spectra cannot be taken as a quantitative result (only estimation) since the secondary ion yield is influenced by the chemical states of the sample surface, i.e., some ions are more easily ionized than others.

Results and discussion

Paper surface properties before and after fountain solution application

Topographical characterization

The change in paper surface properties before and after fountain solution application was investigated with AFM. As seen in figure 1, the fountain solution with IPA does not change the surface in terms of the RMS roughness parameter. However, as the surfactant based fountain solution is applied on the surface, an increase in RMS is clearly seen together with less variation in the surface roughness, i.e., the surfactant is located on the surface. The change in roughness is thus not only due to substrate swelling or migration of coating constituents. In some cases, the surfactant is not visible in an atomic force microscope image as a separate phase, but the surface compositional analysis reveals the presence of surfactant on the surface. Additionally the degree of surfactant coverage will be dependent on the surfactant concentration in the solution (Aulin et al., 2008).

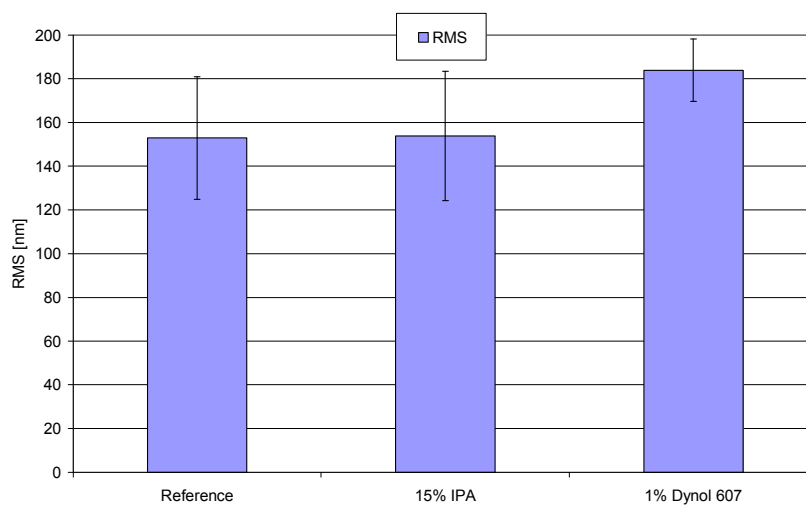


Figure 1. RMS roughness [nm] measured before and after fountain solution application.

Figure 2, presents high amplitude AFM images of the reference sample before and after fountain solution application with the surfactant based fountain solution. The phase images show slightly more contrast differences for the sample containing post added surfactants. The morphology of the plate pigments and the ground calcium carbonate can be identified from both the topography

and the phase images. The surfactants are randomly located on the surface as aggregates and not as micelles based on AFM topography and phase images. The calculated r -value for the reference paper sample according to equations 1 and 2 was 1.539 corresponding to an S_{dr} value of 53.9%.

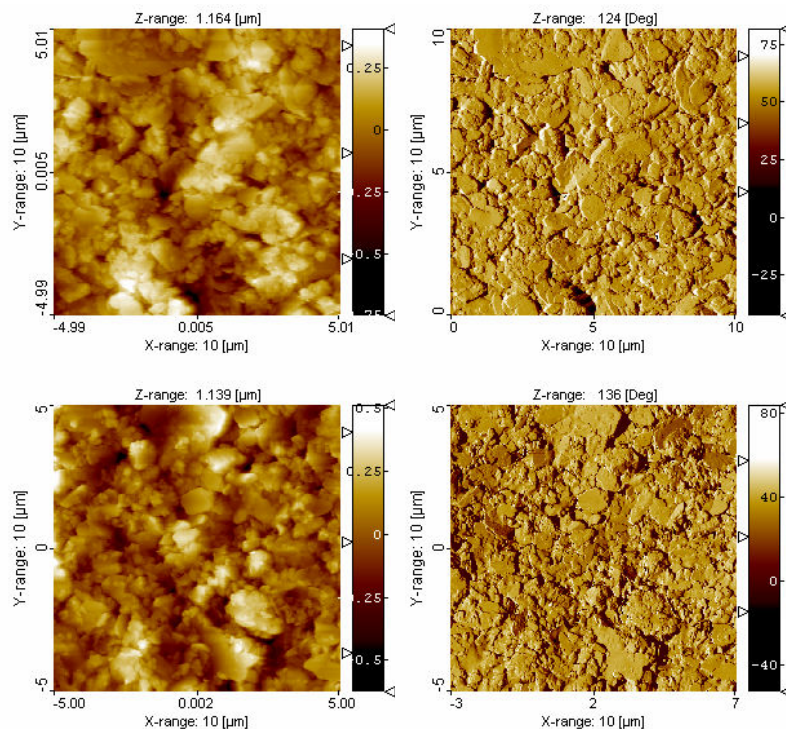


Figure 2. Top-view (left) and phase (right) image of the reference paper sample (above) applied with the 1% surfactant based fountain solution (below).

Surface chemical characterization

In figure 3, measured and surface roughness corrected contact angles with water on the paper sample before and after fountain solution application are presented. The IPA based fountain solution does not influence the wetting behavior of water compared to the reference sample. The same tendency was observed with ethylene glycol (not reported here) which indicates that the surface is insensitive to polar liquids. In the case of the paper sample applied with the surfactant based fountain solution, a rapid decrease in dynamic contact angles with water is observed over the first stage of spreading until an almost constant value is reached. The surface wettability (increased hydrophilicity) is thus significantly increased (Shepherd, 1999). From the spreading kinetics, two different wetting

zones can be distinguished. During regime I ($t < 0,3s$), the wetting of water is dominated by the post-surface properties. In regime II ($t > 0,3s$), the surfactant on the surface is apparently solubilised in the wetting liquid, and the wetting rate is decreased and finally reaches an equilibrium as the surface becomes saturated. The second regime is also related to an increase in average pore size of the paper fiber network (swelling), which also could be observed in the AFM measurements (Figure 1). Hence, according to the Lucas Washburn equation (Eq. 3),

$$v = \frac{r\gamma \cos \Theta}{4\eta l} \quad (3)$$

v =absorption rate; r =pore radius; γ =liquid surface tension;
 Θ =contact angle; η =liquid viscosity; l =wetting length

the absorption rate is increased if the radius (pore size) is increased or the contact angle Θ is reduced (increased hydrophilicity), or both. This of course requires that the liquid viscosity and the surface tension are constant.

The corrected contact angle values provide information about the chemical interaction between the fountain solution additive and the substrate (Tåg et al., 2008). As observed, the chemical interaction between water and the surface applied with the surfactant based fountain solution is much stronger compared to the surface applied with the IPA based fountain solution.

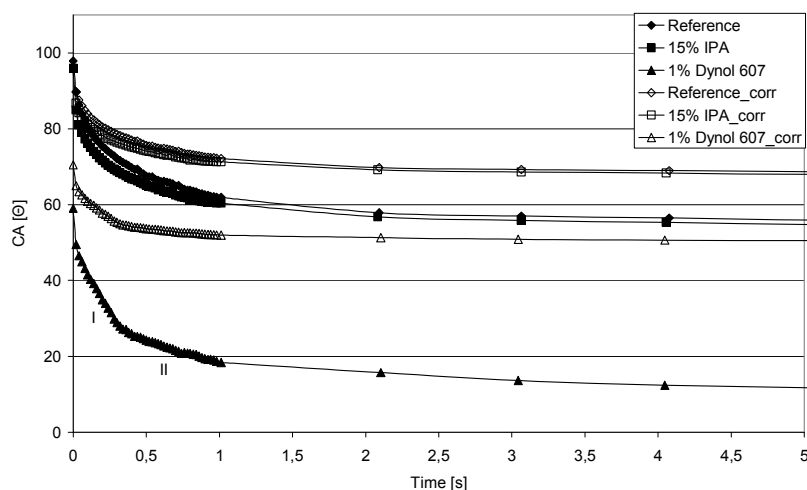


Figure 3. Measured and surface roughness corrected contact angles (CA) with water on the paper sample before and after fountain solution application. The closed symbols correspond to the uncorrected values and the open symbols to the corrected, respectively.

Contact angles with diiodomethane (DIM) on the paper sample before and after fountain solution application are presented in figure 4. When the paper is applied with an IPA based fountain solution, the wetting rate for the dispersive liquid increases. According to the topographical analysis with AFM, no structural changes were observed for the sample applied with the IPA based fountain solution. The surface chemical analysis with ToF-SIMS also revealed that the surface is not significantly changed. Thus, IPA will probably have a cleaning effect of hydrophilic groups on the surface (reduced polar component) (Table 2). This will induce the wetting of the dispersive liquid. When the paper is applied with the surfactant based fountain solution, the wetting rate of DIM is slightly decreased. This will have a clear influence on the problems related to too fast absorption of dispersive fluids. The wetting may also be controlled by the viscosity of the liquids and the roughness of the paper surface. However, the initial spreading at very short time scales is almost entirely determined by the surface chemical properties of the liquid and the substrate (Tåg et al., 2008). The wetting behavior of the dispersive liquid on an ideally smooth surface (corrected contact angles) is slightly lower for the surface applied with the IPA based fountain solution. Hence, the chemical interaction with dispersive liquids is stronger for the surface applied with the IPA based fountain solution.

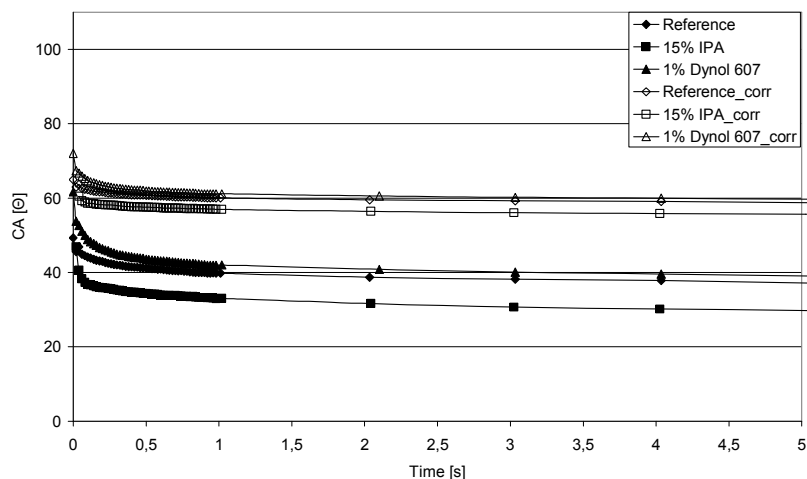


Figure 4. Measured and surface roughness corrected contact angles (CA) with diiodomethane (DIM) on the paper sample before and after fountain solution application. The closed symbols correspond to the uncorrected values and the open symbols to the corrected, respectively.

Surface energy determination

The surface energy components have been derived according to the van Oss Chaudhury Good (vOCG) model. As the paper is applied with the IPA based fountain solution the total and the dispersive surface energy slightly increased (Table 2). However, a clear rise in the polar surface energy and especially the base component was observed for the paper exposed to the surfactant based fountain solution. The exaggerated basicity is related to the unbalance between the acid-base components calculated with the vOCG model. A decrease in surface energy after fountain solution application with the surfactant based fountain solution was due to the reduction of the dispersive component. An increase in the polar surface energy will reduce the adhesion to dispersive liquids. This agrees with the wetting of DIM on the IPA exposed surface, since the polar component of that is smallest compared to the other two substrates (e.g., stronger adhesion to DIM).

Table 2. Change in surface energy components (σ_{SL} [mJ/m²]) before and after fountain solution application. The surface energy components are calculated from uncorrected contact angles.

Sample	σ^{tot}	σ^{LW}	σ^{AB}	σ^+	σ^-
Reference	41.50	39.00	2.49	0.10	14.97
15% IPA	44.32	42.31	2.01	0.06	15.81
1% Dynol 607	41.61	37.78	3.84	0.06	61.60

Elemental composition analyzed with the ToF-SIMS technique

In Figures 5-7, positive ion spectra (200-700 Daltons (Da) (mass/charge ratio, m/z)) of the studied paper samples are presented, both before and after fountain solution application. High molecular weight paper making chemicals, such as surfactants, binders and optical brighteners, can be seen between 200-700 Daltons of the spectra (Fardim and Holmbom, 2005). However, they are very challenging to identify without the reference spectra from each chemical. In the spectrum of the reference paper, the peaks 382.5, 410.5 and 466.5 can be observed. This series has also been presented in previous studies (Brinen and Kulik, 1994; Kulik and Brinen, 1998), but it is still unidentified.

No significant changes were detected in the spectra after IPA fountain solution application. However, the application of the 1 % Dynol 607 fountain solution decreased the intensity of the peaks at 410 and 466 Da, and brought some new peaks in the spectra (Fig.7). These characteristic fragments are assigned to the surfactant molecule, because the surface is not significantly changed as the paper is applied with the IPA based fountain solution. The new peaks can be divided into two series (215, 219, 233, 243, 303, 347 and 453, 497, 523, 541, 585, 629, 673), in which the peak distance is 44 Da indicating the occurrence of the COO⁺ fragment.

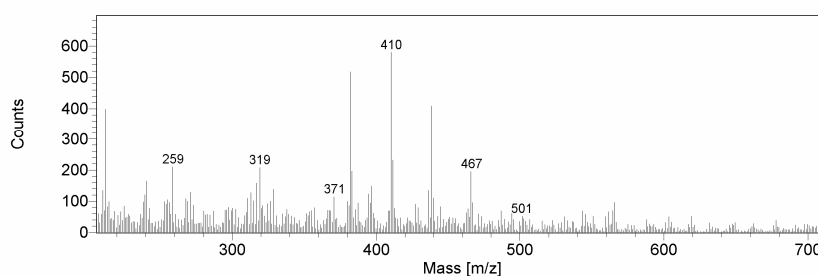


Figure 5. Positive ion spectra of the reference paper sample.

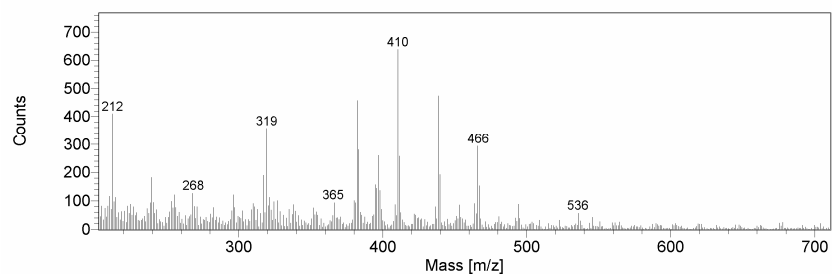


Figure 6. Positive ion spectra of the paper sample applied with a 15% IPA fountain solution

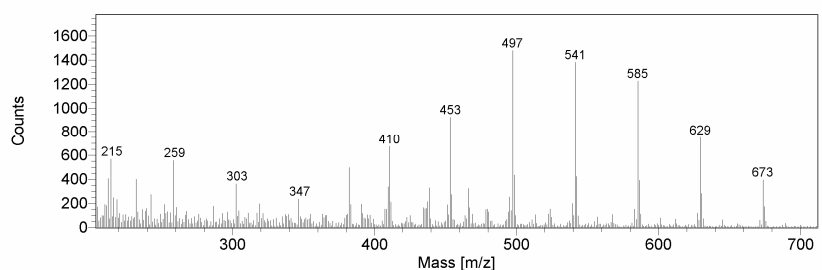


Figure 7. Positive ion spectra of the paper sample applied with the 1% Dynol 607 fountain solution.

A separate analysis was performed to the peak at 43 Da, in which peaks for hydrocarbon C_3H_7 (43.05 Da) and acetylate group C_2OH_3 (43.02 Da) are well separated as can be seen in Figure 8 (Juhanoja et al., 2006). The intensity of the acetylate peak increased after the addition of the surfactant based fountain solution compared to the reference sample. For the sample applied with the IPA based fountain solution, no significant changes were observed according to the peaks at 43, which correlate to previous assumptions from ToF-SIMS spectra. It seems that for the surfactant solution, the amount of the positive ion (C_2OH_3) of the acetylate group increases.

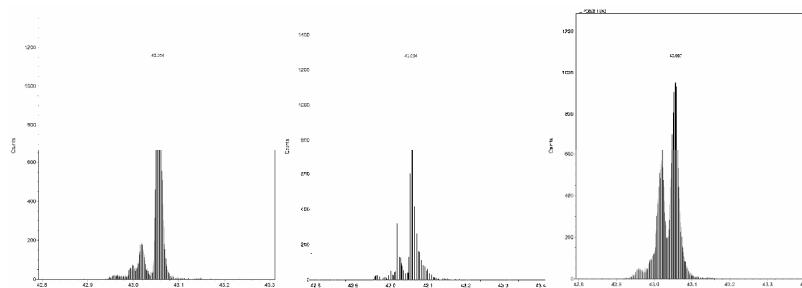


Figure 8. Peak at 43 Da for the reference sample (left), 15% IPA (middle) and 1% Dynol 607 (right).

In Table 3, the acetyl group C_2H_3O (43.02 Da), C_2H_7 (43.05 Da) and the CH_3 (15.02 Da) have been normalized to CH_3 . As observed, there is a clear increase in peak intensity at 43 Da when the surfactant based fountain solution is used.

Table 3. Normalized values for the peak at 43 Da.

Sample	C_2H_3O/CH_3 Average	C_2H_3O/CH_3 Std
Reference paper	0.41	0.04
15% IPA	0.65	0.06
1% Dynol 607	1.86	0.13
Sample	C_3H_7/CH_3 Average	C_3H_7/CH_3 Std
Reference paper	2.41	0.17
15% IPA	2.52	0.18
1% Dynol 607	3.18	0.16
Sample	C_2H_3O/C_3H_7 Average	C_2H_3O/C_3H_7 Std
Reference paper	0.17	0.02
15% IPA	0.26	0.02
1% Dynol 607	0.59	0.04

For the negative ion spectra (not reported here), no significant differences compared to the reference paper sample, was observed. Some components were absent in the negative spectra, which indicate that the components have been completely removed or chemically degraded during exposure. For the paper applied with the 15% IPA based fountain solution, no changes were observed over the whole band width. For the paper applied with the 1% surfactant based fountain solution, some peaks were missing compared to the reference sample.

In the 100-200 Da range, some peaks were chemically degraded, e.g., the intensities for 156, 172, 197 clearly drop. Between 200-400 Da, the peaks 363, 391 were completely removed.

The presence of surfactants on the non-inked areas may lead to a pick up of loosely bonded particles by the print blanket and the plate (highly dependent on the surfactant concentration). Under the influence of nip pressure, the piling may wander to the trailing edges of print areas. When there is enough piling, especially concerning long production runs, this is observed as a lower density on the trailing edge of print areas.

Concluding remarks

Different model fountain solutions were applied on a coated paper substrate in order to investigate the change in paper surface properties before and after fountain solution application. AFM measurements revealed an increase in surface roughness when using a fountain solution containing surfactants. The presence of surfactants, which could be confirmed from ToF-SIMS analysis, did not only change topography but also post-wetting properties, particularly for polar liquids. The wetting behavior could be divided into two regimes controlled by two different mechanisms. The initial wetting was dominated by the “new” surface and the second part dominated by a solubilisation process of the surface. In case of the paper applied with the IPA based fountain solution, substantially no change in the topography or in surface chemical composition could be detected. However, a slight increase in wetting rate for the dispersive liquid was observed on the sample applied with the IPA based fountain solution.

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