# Effect of Paper Surface Properties on Coated Paper Wettability with Different Fountain Solutions

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Wetting of coated papers by isopropyl alcohol (IPA)-based fountain solutions or surfactant solutions was studied in this paper. Additionally, the effect of paper surface properties on wetting was analyzed. To that end, six fountain solutions were prepared. Three solutions had increasing amounts of IPA, and three were made from surfactant-based dampening agents. Eight commercial coated papers were selected and characterized in terms of roughness and surface free energy. Paper resistance to wetting by fountain solutions was evaluated by measuring the static and dynamic contact angles. Static contact angles between the paper surface and the IPA-based fountain solutions decreased as the alcohol concentration increased, whereas the wettability with surfactantbased fountain solutions was highly dependent on their surface tensions. Paper surface free energy strongly affects the static contact angle and only moderately affects the dynamic contact angle.

Keywords: Coated paper; Contact angle; Dampening agents; Surface free energy

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## INTRODUCTION

Multicolor offset printing is one of the most common printing methods. This is an indirect printing process in which the printing and non-printing areas lie on the same plane of the printing plate. As a result of a chemical treatment, the image and non-image areas of the printing plate show different surface properties. The image areas (oleophilic) receive the ink, whereas the non-image areas (hydrophilic) catch a water-based film, known as fountain solution. In the printing unit, the printing plate is dampened with the fountain solution first, and a continuous film is generated on the non-image areas; then the printing plate is inked, and the small ink droplets are only on the image-areas. Both ink and fountain solution are transferred from the plate to the rubber blanket and, subsequently, to the paper surface (Fig. 1).

Dampening agents are added to the fountain solution to reduce the surface tension of water to therefore improve the wetting of the printing plate, rubber blanket, and paper. Isopropyl alcohol (IPA) is the most common dampening agent used in offset printing. However, due to current environmental restrictions on volatile organic compounds, its use must be reduced. Thus, this printing auxiliary is being gradually replaced by dampening agents based on non-ionic surfactants.

One of the main differences between IPA and surfactants is that the latter are active at lower concentrations. Compared to a typical surfactant concentration of 0.1 wt%, the IPA concentration required to reach the same surface tension is about 10 wt% (Aurenty *et al.* 1999). On the other hand, the IPA-based fountain solutions evaporate

faster as a result of IPA's higher vapor pressure; surfactants have a nearly zero vapor pressure. Although paper wettability is one of the most critical factors in offset print quality, the mechanism of wetting, either by an IPA-based fountain solution or by a surfactant solution, is only partially understood.



Fig. 1. Schematic drawing of an offset printing unit

Paper wetting takes place when the fountain solution comes into contact with the sheet in the first printing unit, spreading over the surface and imbibing into the porous paper structure. Before the paper passes to the second printing unit, the fountain solution must have been sufficiently absorbed into the sheet or completely spread on the paper surface (Etzler *et al.* 1995; Tåg *et al.* 2009). Otherwise, some print defects are likely, such as mottling and ink repellence (wet trap). Mottling consists of an uneven printing result caused by insufficient and spotty water absorption by the paper, followed by uneven ink absorption. The wet trap occurs when ink is repelled because the water film has not completely penetrated the paper. These defects are even more important in coated papers, as the low porosity of the coating layer and its rather singular chemistry determine the wetting phenomena more markedly than in other paper grades.

Paper's resistance to wetting is assessed by measuring the contact angle between the liquid and the paper immediately after the liquid droplets hit the surface (static contact angle), as a function of time (dynamic contact angle). The static contact angle is considered to be a measure of the paper wettability, whereas the dynamic contact angle is commonly used to assess the absorption and spreading of a liquid on the paper surface: in other words, the dynamic wettability of a paper.

The static contact angle of a particular liquid depends mostly on the texture and the chemical properties of the surface of the solid. The influence of paper roughness on the static contact angle has been broadly discussed elsewhere, and several authors have reported decreasing contact angles with increasing paper roughness (Wenzel 1936; Swain and Lipowsky 1998; Chibowski 2003; Ferreira *et al.* 2008). Additionally, the surface free energy and its components (polar and dispersive) are often used to characterize the chemistry of the paper surface. The effect of these properties on paper wettability has been studied when using water. Thus, a paper with a high polar component has more affinity for water, *i.e.*, lower static contact angles (Oliveira *et al.* 2004; Moutinho *et al.* 2007). This property has been used to study the paper wettability with inkjet inks

(Moutinho *et al.* 2007; Santos and Velho 2010). However, to the best of our knowledge, there is only scarce data on the role of the surface free energy on coated paper wettability when using fountain solutions.

The dynamic wettability of a paper provides information about how a liquid spreads on its surface and penetrates the sheet in time. Again, roughness significantly reduces the spreading rate of the liquid on a paper surface, regardless of the type of liquid tested (Semal *et al.* 1999; Modaressi and Garnier 2002; Tåg *et al.* 2012). The effect of the paper surface free energy on dynamic wettability has been studied, but reports have been contradictory. Modaressi and Garnier (2002) found that the wetting rate was independent of surface chemistry and surface chemical heterogeneity, when using water and sizing papers as substrate. In contrast, Järn *et al.* (2010), using water and ethylene glycol on offset papers, established that the hydrodynamic and molecular-kinetic model should be corrected, and take into account the acid and base components of the surface energy.

The aim of this study was to assess the wetting phenomenon in coated papers using different fountain solutions. To that end, eight commercial coated papers, with different coating weight per side, were selected. Also, commercial dampening agents were used to prepare the fountain solutions, some based on IPA and some based on nonionic surfactants. Thus, the influence of the paper properties and the fountain solutions on the static and dynamic contact angles was studied.

## EXPERIMENTAL

### Materials

#### Fountain solutions

Six fountain solutions were prepared. Three of them were made using increasing amounts of IPA (4 wt%, 7 wt%, and 14 wt%), adding 2 wt% of pH buffer to each one. The remaining three fountain solutions were prepared with different dampening agents based on surfactants: Böttcher Fount S-3010+, Emerald Premium 3545, and Hidromask 3.6. The concentrations of these agents were in accordance with the manufacturer's recommendations. All the printing auxiliaries were commercial and commonly used in offset printing.

The fountain solutions were mixtures of laboratory water and isopropyl alcohol, or dampening agents based on non-ionic surfactants. The term "laboratory water" refers to a solution prepared using distilled water and specific concentrations of Ca<sup>2+</sup> (40 mg/L), Mg<sup>2+</sup> (8 mg/L), and HCO<sub>3</sub><sup>-</sup> (10 mg/L). The resulting hardness, pH, and conductivity were within the range of those recommended for offset printing (Olejniczak *et al.* 2004): a hardness of 8 to 10 °dH; pH value of 6.8 to 7.6; and conductivity of 290 to 350  $\mu$ S/cm. Table 1 lists all the fountain solutions investigated in this study, as well as some of their physicochemical properties.

The surface tension was measured using a ring tensiometer, School Tensiometer K6 (Krüss). The method consists of measuring the maximum force needed to pull a platinum ring lying flat on the liquid surface. Before testing, the tensiometer was calibrated with double distilled water (interfacial tension at 20 °C = 72.8 mN/m). After calibration, the surface tension was measured ten times in the laboratory water and each fountain solution. Temperature was also measured and used to correct the surface tension values, in combination with water-calibration correction factors.

Code	Fountain solutions	рН	Conductivity	Surface tension	
			(µS/cm)	(mN/m)	
W	Laboratory water	6.5	369	72.8	
14	W + 4 wt% IPA*	5.0	1078	47.3	
17	W + 7 wt% IPA*	4.7	959	45.7	
l14	W + 14 wt% IPA*	4.8	851	42.3	
F1	W + 5 wt% Böttcher Fount S-3010+	4.9	2470	46.2	
F2	W + 4 wt% Emerald Premium 3545	4.7	1930	27.0	
F3	W + 3 wt% Hidromask 3.6	4.6	1831	40.9	
* Plus 2 wt% of pH buffer. wt% = weight percentage					

Table 1. Properties of Laboratory W	Nater and Fountain Solutions
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The pH and the conductivity of the laboratory water and fountain solutions were also measured using a CRISON pH-meter (GLP 22+) and a CRISON conductometer (EC-Meter GLP 31), respectively, according to the manufacturer's specifications.

#### Coated papers

The commercial coated papers used in this study are described in Table 2. The selection criteria were the coating weight on each side of the papers and the finished grade: gloss and matte.

Code	Description	Coat weight (g/m <sup>2</sup> /side)	
FG	Film-coated paper; Gloss finished	< 5	
LG	Light-weight coated paper; Gloss finished	5 - 10	
MM	Medium weight coated paper; Matte finished	10 – 20	
HG1			
HG2	High weight coated paper; Gloss finished		
HG3		20 – 40	
HM4	High weight exceed paper: Matta finished		
HM5	nigh weight coaled paper, malle mished		

### Table 2. Description of the Coated Papers

These eight papers were characterized in terms of basis weight (ISO 536:1997) and surface pH (TAPPI 529-09). Additionally, a qualitative analysis of mineral filler and mineral coating of paper was carried out, according to TAPPI standard T421-97.

## **Confocal Laser Profilometry**

Paper roughness was studied with the use of laser profilometry parameters obtained with AltiMet Profilometer Altisurf 500, a white light sensor device which yields 2000 profiles from each 4 mm x 4 mm paper sample. The parameters assessed here were the root mean square roughness (Sq) and the developed interfacial area ratio (Sdr). The roughness is calculated as the arithmetic average of absolute values of the surface height deviations, measured from the best fitting plane; Sdr is defined as the percentage of additional surface area contributed by the paper topography, compared to the projected ideally flat area (Peltonen *et al.* 2004). The roughness values were averages of at least three measurements.

## **Contact Angle Measurements**

#### Static contact angle

Paper wettability was studied by means of contact angle measurements in air ( $\alpha$ ), both with laboratory water and fountain solutions. This was also the technique used to determine the paper surface free energy ( $\gamma$ ), as the contact angle measured with liquids of known surface tension is an indirect method to assess the surface free energy of a solid, and it is a fast simple technique based on easy-to-use equations. Several studies can be found in the open literature concerning the fundamentals of this method (Owens 1969; Tiberg *et al.* 2001; Chibowski 2003).

Measurements were performed with a DataPhysics Instrument OCA 15 plus, running on SCA 20/21 software and using the sessile drop method. The images of the initial resting drop are taken by a CCD camera immediately after the drop hits the paper surface. The corresponding contact angle is calculated after fitting the drop contour line numerically, using the Young-Laplace method.

All the static contact angles were measured under controlled atmosphere conditions (T =  $23 \pm 1$  °C and RH =  $50 \pm 2\%$ ). In this study, 15 drop tests were conducted with the laboratory water and each fountain solution, applying the smallest possible drop volume depending on the fountain solution (4 to 9 µL). The surface free energy was calculated by the OWRK (Owens, Wendt, Rabel, and Kaelble) method, which considers the interfacial tension as a function of the dispersive ( $\gamma_d$ ) and the polar ( $\gamma_p$ ) interactions (Owens 1969). In this study, n-hexane, ethylene glycol, 1, 2-propanediol, formamide, and distilled water were used as probe liquids, with a 20- to 25-drop test and 7 µL for each drop.

Several authors have reported the influence of surface topography on the contact angle, and have recommended using the Wenzel's roughness correction (Wenzel 1936; Ferreira *et al.* 2008; Tåg *et al.* 2009). This equation (1) establishes that the relationship between the measured contact angle ( $\alpha_m$ ) and the corrected angle in an ideal flat surface ( $\alpha_c$ ) may be written as follows,

$$\cos \alpha_m = r \cdot \cos \alpha_c \tag{1}$$

where r is the topographical correction factor obtained as,

$$r = 1 + \frac{Sdr}{100} \tag{2}$$

where Sdr is the developed interfacial area ratio provided by the profilometer. The Wenzel's correction was carried out for all the contact angles measured in this study.

#### Dynamic contact angle

Dynamic wettability, both with laboratory water and fountain solutions, was assessed by monitoring the change of the contact angle and the drop base diameter as a function of time. The same automated contact angle tester was used. For each combination of paper and liquid, four videos were recorded to characterize the evolution of the drop for 10 s, taking 25 frames per s. As described above, droplet volumes ranged from 4 to 9  $\mu$ L, depending on the fountain solution. Contact angles and drop base diameters were calculated using the ellipse fitting method per frame.

## **RESULTS AND DISCUSSION**

## **Paper Properties**

Grammage and surface properties

The arithmetic mean values of the grammage, surface pH, and topographical parameters of the papers are summarized in Table 3. All papers tested were similar in terms of surface pH, with their surfaces slightly alkaline. The Sq data were consistent with values reported by other authors for smooth coated papers (Ström *et al* 2003; Järnström *et al*. 2010). The roughest papers were LG, MM, and FG, which were the papers with the least amount of coating (Table 2). Even so, the texture of the papers tested was quite similar. The *Sdr* values were below 1.5%, resulting in low topographical correction factors (*r*). When *r* is close to 1, the correction for surface roughness can be neglected, since differences between the measured and the corrected contact angles will be minimum (Wenzel 1936). However, in this study, all the contact angles were corrected.

The qualitative analysis of mineral filler and mineral coating of the papers revealed that calcium carbonate was the major component in all the papers tested. This material is extensively used in paper coatings.

Coated papers	Grammage (g/m <sup>2</sup> )	Surface pH	<i>Sq</i> (μm)	Sdr (%)	r
FG	59.7	7.6	1.06	0.70	1.007
LG	65.0	8.2	1.97	1.30	1.013
MM	147.7	8.2	1.53	0.81	1.008
HG1	166.2	8.4	0.49	0.18	1.002
HG2	169.3	8.4	0.35	0.16	1.002
HG3	167.4	8.3	0.49	0.19	1.002
HM4	165.9	8.2	0.56	0.40	1.004
HM5	170.1	8.9	0.57	0.30	1.003

Table 3. Grammage, Surface pH, and Topographical Parameters of the Papers

## Surface free energy

The surface free energy and the polar/dispersive components of the eight papers are presented in Fig. 2. As can be seen, the papers assessed show surface free energy values ( $\gamma$ ) between 20 mN/m and 32 mN/m, which are in the same range as those reported by other authors for coated papers (Oliveira *et al.* 2004; Tåg *et al.* 2009).



Fig. 2. Surface free energy of the papers: polar and dispersive components

The papers showed similar values of dispersive component ( $\gamma_d$ ), ranging from 12.1 mN/m to 19.7 mN/m (coefficient of variation 16.5%), whereas variability in the polar component ( $\gamma_p$ ) was greater, from 3.7 mN/m to 15.3 mN/m (coefficient of variation 40.5%). Variability in this component is mostly provided by the matte papers, especially MM and HM4 ( $\gamma_p < 6$  mN/m). The polar component is related to the paper wettability with water. A higher  $\gamma_p / \gamma$  means more water affinity, so the paper surface will be more easily wetted by water, resulting in low static contact angles (Oliveira *et al.* 2004; Moutinho *et al.* 2007).

## Paper Wettability

Paper wettability was studied through the static contact angles ( $\alpha$ ) obtained with laboratory water (W), and with each fountain solution (Fig. 3). Static contact angles obtained with W differed across the types of papers. MM exhibited the greatest static contact angle measured with W, which is consistent with this paper having the smallest polar component ( $\gamma_p$ ) (Fig. 2). This finding confirms that the static contact angle between water and paper increased with decreasing  $\gamma_p$  (Oliveira *et al.* 2004; Tåg *et al.* 2009).





As can be seen in Fig. 3a, static contact angles with IPA-based fountain solutions (I4, I7, and I14) were always smaller than static contact angles with W. However, the dampening agents based on surfactants do not lead to a significant decrease in the static contact angle, except for F2 (Fig. 3b). To study in detail the differences in the wetting behavior of the papers, a new parameter was defined: "change of wettability" ( $\Delta W$ ). This parameter represents the change of the static contact angle obtained with the fountain solutions, using as reference the static contact angle with laboratory water. Therefore,  $\Delta W$  was calculated as follows:

$$\Delta W (\%) = \left(\alpha_{W} - \alpha_{f,s}\right) \cdot 100 / \alpha_{W}$$
(5)

where  $\alpha_w$  is the static contact angle with laboratory water and  $\alpha_{f,s}$  is the static contact angle with each fountain solution. Table 4 shows the  $\Delta W$  values; data below 10% have not been considered.

Coated papers	14	17	I14	F1	F2	F3
FG	16	27	33		66	17
LG	16	26	50	10	58	19
MM	28	37	51	15	62	25
HG1	12	19	59		67	16
HG2	22	31	53		57	11
HG3	10	36	46		61	
HM4		14	33		41	
HM5	25	30	34	10	62	13

Table 4. Change of Wettability for Each Fountain Solution

With regard to the IPA-based fountain solutions, Table 4 shows that  $\Delta W$  increased with the amount of IPA, especially with I14, because the contact angle was reduced by twice that in most of the papers ( $\Delta W$  is approx. 50%). However, this result cannot be seen in HM5, as paper wettability only improves slightly with increasing IPA concentration. It should be noted that there are marked differences between the papers for a specific IPA concentration. Thus, when the IPA concentration is 4 wt%, HM4 does not show a remarkable change in contact angle compared to water ( $\Delta W < 10\%$ ); and if 7 wt% of IPA is added, HG1 and HM4 show less change of wettability ( $\Delta W < 20\%$ ) than the other papers.

Regarding the surfactant-based fountain solutions, the contact angles obtained with F1 (Fig. 3b) were quite similar to the ones obtained with laboratory water for most papers, and then the corresponding  $\Delta W$  values were less than 10% (Table 4). In contrast to this, fountain solution F2 greatly improved paper wettability, as the  $\Delta W$  values were greater than 55% for most of papers. Also, fountain solution F3 caused moderate enhancements of change of wettability. As it was mentioned when discussing IPA, some differences between papers have been also found for these fountain solutions. All of them modified the static contact angle in LG, MM, and HM5.

To study differences by fountain solution and by paper grades, the previous results have been analyzed and discussed below, including in the analysis the surface tension of the fountain solutions and the surface free energy of the papers. Influence of the surface tension of the fountain solution

The change of wettability ( $\Delta W$ ) in HG1 as a function of the surface tension of the fountain solutions is shown in Fig. 4. Similar behaviors were observed in all the papers assessed.



**Fig. 4.** Relation between the surface tension of the fountain solutions and the change of wettability ( $\Delta W$ ) for HG1

It should be noted that IPA at 4 wt% markedly reduced the surface tension of water (72.8 mN/m), but greater IPA concentrations did not lead to a significant decrease in the surface tension, as this parameter remained in the range of 40 to 50 mN/m. These values are similar to those reported by Gigac *et al.* (2011) and Tåg *et al.* (2012). Although the surface tension of IPA-based fountain solutions did not fluctuate greatly, the corresponding  $\Delta W$  data did. Thus, the  $\Delta W$  value for I14 was three times as high as the one for I7. Because IPA has greater vapor pressure than water, the wetting is enhanced (lower  $\alpha$ ) (Aurenty *et al.* 1999).

The surface tensions of surfactant solutions ranged from 27.0 mN/m to 56.2 mN/m. Also noteworthy in Fig. 4 is that F1, whose surface tension exceeded 45 mN/m, slightly modified the paper wettability ( $\Delta W < 10\%$ ), as mentioned above. On the contrary, F3 (40.9 mN/m) slightly increased the change of wettability. F2, with a much smaller surface tension (27.0 mN/m) than the other surfactant solutions, stood out with a much bigger  $\Delta W$  value.

Comparing the results obtained for IPA and surfactant fountain solutions, the two showed different behavior. When using IPA as a dampening agent, the concentration of this alcohol in the fountain solution was a key factor in determining wettability. In contrast, when using surfactant agents, the wettability of these fountain solutions seems to have been mainly influenced by their surface tension.

A more environmentally-friendly printing process may be achieved by replacing IPA with dampening agents based on surfactants, which should significantly reduce the surface tension in fountain solutions. In addition to be sustainable, a smaller surface tension of the fountain solution means that the printing plate could be easily wetted, which improves the runnability of the printing process.

#### Influence of the surface free energy of the papers

Figure 5 shows the relationship between paper surface free energy and the static contact angles ( $\alpha$ ) obtained with the fountain solutions. As the graph shows,  $\alpha$  decreased when the paper surface free energy increases.



**Fig. 5.** Relation between the paper surface free energy and the static contact angles obtained with (a) the IPA and (b) the surfactant - based fountain solutions

The regression analysis of the surface free energy of the papers and the static contact angles revealed a significant correlation between both parameters at a 95% confidence level. IPA fountain solutions yielded *r* values lower than those of fountain solutions with dampening agents based on surfactants. Because F2 and F3 show that *r* was greater than -0.90 ( $\mathbb{R}^2 > 80\%$ ), more than 80% of the variability in the static contact angle was accounted for by the surface free energy.

These findings may provide an important understanding of the role of the coated papers in the printing press. The paper's behavior in the press will be determined by its surface free energy and the type of fountain solutions used, which could explain why commercial coated papers with similar properties lead to different levels of print quality. Therefore, if the composition of a paper coating is modified so as to increase the paper surface free energy (Musselman and Chander 2002; Chinga and Helle 2003; Oliveira *et al.* 2004), the paper printability would be improved, especially when using fountain solutions made from dampening agents based on non-ionic surfactants. In addition, as was demonstrated in a previous study, papers with high  $\gamma_p/\gamma$  could result in better print quality because they demand less ink to reach the target print density (Quintana *et al.* 2012).

#### **Dynamic Wettability of the Papers**

Evolution in time of the contact angle and drop base diameter

Dynamic wettability was studied by examining how the contact angle ( $\alpha$ ) and the drop base diameter ( $\emptyset_{DB}$ ) change with time, for laboratory water and for each fountain solution. In order to compare the papers, both  $\alpha$  and  $\emptyset_{DB}$  values were normalized in relation to the corresponding initial values at 0 seconds. As an example, Fig. 6 shows graphs of the evolution of normalized  $\alpha$  and  $\emptyset_{DB}$  obtained with W, I7, and F3 in paper HG3.

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**Fig. 6.** Evolution of (a) the contact angle and (b) the drop base diameter with W, I7, F3, and the paper HG3

Figure 6 shows a strong initial decrease in the contact angle and a significant increase in the drop base diameter, as soon as the drop came into contact with the paper surface. After 3 s, the rate of change of both  $\alpha$  and  $\emptyset_{DB}$  decreased because the surface became saturated. The fountain solutions I7 and F3 wet and spread faster than W on HG3 surface, which confirms, as expected, that the dynamic wettability was improved when adding dampening agents to water.

To quantify differences in the evolution of  $\alpha$  and  $\emptyset_{DB}$  between papers and between fountain solutions, wettability rates (*WE<sub>r</sub>*) and spreading rates (*SP<sub>r</sub>*) were calculated and defined as follows:

$$WE_{r}(\%) = (\alpha_{0} - \alpha_{r}) \cdot 100 / \alpha_{0}$$
(6)

$$SP_{r}(\%) = \left(\phi_{DB_{o}} - \phi_{DB_{o}}\right) \cdot 100 / \phi_{DB_{o}} \tag{7}$$

where  $\alpha_0$  and  $\emptyset_{DB^0}$  are the corresponding values of normalized contact angle and drop base diameter at time 0; and  $\alpha_t$  and  $\emptyset_{DB^t}$  are the respective values at a specific time, in seconds. Therefore,  $WE_r$  and  $SP_r$  represent the change of the contact angle and the drop base diameter at a specific time in relation to the initial values at 0 s.

In this study, the  $WE_r$  and  $SP_r$  rates were calculated at 1 s. Although in a printing machine the sheet goes from one printing nip to the next one in less than 1 s, the calculated rates in this study were erratic at very short times. However, at 1 s, both rates are less affected by errors and reveal more significant differences among the papers.

Figures 7 and 8 show the  $WE_r$  and  $SP_r$  values for each paper, obtained with the laboratory water and the fountain solutions. No data could be obtained with F2 because this fountain solution spread on the paper surface very quickly and drops rested on it for less than 0.25 s.



Fig. 7. Wettability rates (a) and spreading rates (b) at 1 s for IPA-based fountain solutions



Fig. 8. Wettability rates (a) and spreading rates (b) at 1 s for surfactant-based fountain solutions

As can been seen in these figures, some of the papers showed a slight decrease in both rates compared to laboratory water. These differences in  $WE_r$  and  $SP_r$  were inconsistent and should not be taken into account, as they may be related to the accuracy of the method. The graphs show that the  $WE_r$  and  $SP_r$  values differ depending on the fountain solutions and/or the papers; this finding will be broadly discussed below.

#### Influence of the fountain solutions

Figure 7 shows that adding IPA to water only increased the dynamic wettability in the papers FG, HG2, and HG3. For the rest of the papers,  $WE_r$  and  $SP_r$  obtained with W did not differ significantly from those obtained with I4, I7, and I14.

Figure 8 shows similar  $WE_r$  and  $SP_r$  values between F1 and W in most papers. This is consistent with the results previously explained for static contact angles (Table 4). In contrast, F3 shows higher  $WE_r$  and  $SP_r$  values than those of W in most papers. The same group of papers (FG, HG2, and HG3) as the one mentioned above when discussing IPA fountain solutions, shows more noticeable increases in their  $WE_r$  and  $SP_r$  rates compared to W. These results confirm that the surface tension of fountain solutions based on surfactants had a great effect on paper wetting, because the lower the surface tension is, the greater the dynamic wettability (F1 < F3 < F2).

Although the use of IPA and non-ionic surfactants in fountain solutions did not lead to a noticeable increase in dynamic wettability (except for F2), one should take notice that some of these fountain solutions noticeably reduced the static contact angle, when the capillarity forces still do not play a role, leading to a significant improvement of the paper wetting.

#### Influence of the paper properties

Regarding surfactant solutions, only F3 was considered in this section because this was the one that modified the wettability and spreading rates in relation to water and, although F2 exhibited a similar effect, no data could be obtained with that fountain solution, as mentioned above. Therefore, considering F3 and the IPA-based fountain solutions, Figs. 7 and 8 indicate that the papers FG, HG2, and HG3 had the highest increase of dynamic wettability. These papers had in common that they were smooth and glossy. Also, LG and HG1 show a slight increase of both wettability and spreading rates. In contrast, the matte-finished papers (MM, HM4, and HM5) did not reveal changes in WE<sub>r</sub> and SP<sub>r</sub> in relation to laboratory water.

In the light of these results, a trend between the paper roughness (Sq) and  $WE_r$  was found for the fountain solutions considered here, especially for I4 and F3 (Fig. 9). No correlation between Sq and  $SP_r$  could be established.



**Fig. 9.** Relation between the paper roughness (Sq) and the wettability rates ( $WE_r$ ) with fountain solutions (a) I4 and (b) F3

As Fig. 9 shows, the rougher a paper was, the lower were the  $WE_r$  values obtained with both fountain solutions, which means that the dynamic wettability decreased as the paper roughness increased. This finding has been reported by Wågberg (2000) and Modaressi and Garnier (2002) with water droplets, but not with fountain solutions.

The dynamic wettability should not be only accounted for by the paper microroughness and other paper properties must be considered. Therefore, the influence of the surface free energy ( $\gamma$ ) and its components ( $\gamma_d$  and  $\gamma_p$ ) on the WE<sub>r</sub> and SP<sub>r</sub> rates was studied. Except for fountain solution I4, paper surface free energy had a significant influence on WE<sub>r</sub> rates at a 90% confidence level (r > 0.65). No correlation between  $\gamma$ ,  $\gamma_d$ ,  $\gamma_p$ , and SPr could be established.



**Fig. 10.** Relation between the surface free energy of the papers and the wettability rates ( $WE_r$ ) with fountain solutions (a) I7 and (b) F3

In Fig. 10, the relation between the surface free energy and  $WE_r$  for I7 and F3 is plotted. It can be observed that the dynamic wettability increased proportionally with the paper surface free energy. These results were in line with the conclusions obtained for the static contact angles (Fig. 5). This means that manufacturing coated papers with greater surface free energy could give rise to papers more easily wetted in the press, reducing some printing problems associated with the inadequate absorption or spreading of the fountain solutions, such as mottle and ink repellence (Etzler *et al.* 1995, Tåg *et al.* 2009). However, the insufficient supply and/or the rapid dissipation of the fountain solution may result in the ink being transferred to the non-printing areas at the paper/blanket printing nip, leading to other printing defects such as negative pilling and mottle (Wygant *et al.* 1995). Therefore, it would certainly be interesting to study the effect of the coating composition of a paper on the surface free energy and, in turn, on the wetting phenomena. As can be seen in Figs. 7 and 8,  $WE_r$  values were slightly higher than  $SP_r$  values. This means that, when a droplet of fountain solution hits the paper, it spreads on the surface and also penetrates into the porous structure.

## CONCLUSIONS

- 1. The static contact angles between the paper and the IPA-based fountain solutions decrease as IPA concentration increases. In contrast, the static contact angles obtained with surfactant-based fountain solutions are highly dependent on the surface tension.
- 2. When studying paper wettability at short times, neither the IPA concentration nor the surface tension of the surfactant-based solutions noticeably change the way a drop spreads on the paper surface and is absorbed into the coating layer.
- 3. Differences in paper wettability stem from variations in surface properties. The paper surface free energy strongly affects the static contact angle and has a moderate effect on the dynamic contact angle. Both parameters decrease proportionally to the surface free energy, this result being especially significant for the fountain solutions based on surfactants. Also, the influence of paper roughness on paper wettability has been confirmed.

4. Adequate modification of paper surface free energy and paper roughness in papermaking can result in coated papers that are more easily wetted by fountain solutions. A proper combination of these three paper properties is expected to improve paper printability.

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