

Dynamic Spreading of Fountain Solution onto Lithographic Anodized Aluminum Oxide

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Abstract

The dynamic wettability of the non-image area of the plate is of prime importance within the context of the search for isopropanol substitutes in the Fountain Solution. The device constructed in the laboratory and described at TAGA 95 (Paris) is able to follow the spreading behavior of liquids onto solid surfaces within time scales going from 5 milliseconds to several minutes. Results related to the kinetics of fast spreading of droplets of various aqueous solutions onto anodized aluminum oxide are reported. One set of experiments dealt with the acid-base interactions between aqueous solutions of varying pH and the substrate and showed its amphiphilic character (albeit more basic) indicated by a higher tendency to spread at non-neutral pHs. The other set of runs dealt with the different roles of aliphatic alcohols added to water at different concentrations. The specific structure and vapor pressure of the additive were qualitatively and quantitatively related to the changes occurring in the spreading behavior, and interpreted in terms of a Marangoni effect. Indeed, the onset of the Marangoni flow manifested itself within a few tenths of a second, when the added alcohol had a vapor pressure higher than that of water. Finally, the role of different non-ionic surfactants was also studied. Ease of spreading onto the non-image areas of the plate was drastically decreased because of surfactant specific adsorption onto the plate. Some interpretation of the Water Window problem encountered with surfactant-based Fountain Solutions are given

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Introduction

Several studies have dealt with the characterization of the surface energy and wetting features related to the non-image area of offset plates in the past (Kaelble & al. 1975; Kato & al., 1982; Bassemir & al., 1982; Strom & al., 1984). In particular, Strom (1993) reviewed the different kinetic aspects of plate wetting during printing and Goodman & al. (1995, 1996) carried out an investigation on the slow kinetic aspects of competitive wetting both at the image/ink/water interface and the non-image/ink/water one in a configuration of non-zero contact angle. However, fast spreading on the non-image area (zero-contact angle behavior) is not well documented in the literature, and a better understanding is needed to explain the tremendous difference in plate scumming behavior of alcohol-based Fountain Solutions compared with surfactant-based counterparts. In a more general vein, dynamic spreading of pure liquids or liquid mixtures onto solids is important in a large number of industrial processes like textile cleaning, detergency, spray painting and floatation and there are therefore some pertinent studies related to the complex phenomena involved in dynamic spreading (Hardy, 1919; Bangham & al., 1938; Bascom & al., 1964; Fox & al., 1952; Marmur & al., 1980, 1981; Lelah & al., 1981 and Pesach & al., 1987). There is a consensus among these authors concerning the fact that the phenomenon of droplet spreading onto solids is always preceded by the advancing of a so-called "primary film", ahead of the bulk of the droplet. Depending on the specific characteristics of this primary film, the overall spreading behavior can vary greatly from enhancement, to stopping and even to recession. Most of the solid surfaces studied in the literature were steel, clean glass or freshly cleaved mica. The purpose of this paper is to provide a new contribution to the domain of the spreading behavior of different aqueous solutions onto anodized aluminum oxide, and, as a consequence, to offer new interpretations of the complex dynamic wetting phenomena which occur on the non-image area of the printing plate during offset printing.

Experimental

The lithographic anodized aluminum oxide surfaces were provided by Polychrome (Columbus, USA) and referenced as MO8 surfaces. The samples were taken from the production line before the deposition of both interlayer and coating. A decontamination/recontamination process was applied to each sample as described below.

Surface tensions were measured by the maximum bubble pressure method on a Sensadyne 6000 at 1 bubble/s, which constituted a semi-static measurement.

Spreading kinetics were recorded on the experimental set-up built in the laboratory and described elsewhere (Aurenty & al., 1995, 1996, 1997). A high speed video camera collected images at frequencies up to 200 Hz and the image analysis software calculated either the contact angle or the spreading area for each image.

The aqueous solutions were prepared shortly before testing with double distilled water. The pH values were adjusted with HCl and NaOH. Alcohols and acetone were commercial samples with a minimum purity of 99%. Surfynol surfactants were supplied by Air Products, and Pluronic one, by BASF.

Results and discussion

I. Solid surface characterization

Metal oxide surfaces are considered as *High Energy Surface* (Israelachvili, 1991) in that they are able to interact strongly with most materials with which they can establish molecular contact. On the one hand, this feature is of prime interest when considering adhesion of organic compounds onto metals or metal oxides (coating and painting industry, image area of the offset plate, ...) and surface wettability. On the other hand, these types of surfaces are strongly affected by organic contamination from atmospheric dust, grease and volatile compounds.

I.1. Contamination and sample preparation

The carbon contamination layer on stainless steel (C. Vittoz, 1997) and on lithographic anodized aluminum oxide (P. Aurenty, 1996) was characterized by XPS and its influence on surface wettability by water was studied in detail. The loss of reproducible wetting of this type of *High Energy Surfaces* was attributed to the different level of contamination of the samples, depending on their specific history. A decontamination procedure was set-up by Vittoz and applied to our offset plate samples, using an Argon Plasma (140 Watt; Argon pressure: 1 Torr) during 10 minutes. A 24 hours controlled recontamination procedure was then applied to each sample by leaving them in the controlled atmosphere chamber (21 deg. C, 35 % HR). The reproducibility obtained for wetting kinetics was therefore $\pm 1.5^\circ$ for the contact angle measurements and $\pm 10\%$ for the wetting areas at 21 ± 0.5 C and 35 ± 5 % HR.

1.2. Acid/Base character

The acid/base properties of our anodized aluminum oxide surface were characterized by the spreading kinetics of aqueous HCl or NaOH solutions with different pHs, namely 3, 4.5, 6.9, 9.3 and 12. Their surface tension, measured at 1 bubble/s (Sensadyne 6000), gave a mean value of 73.4 ± 0.15 mN/m at 21.5°C, confirming that a low concentration of ionic species in water has no influence on its surface tension. The contact angle evolution with time was recorded for the 5 solutions (Fig. 1) using the dynamic goniometer constructed in our laboratory.

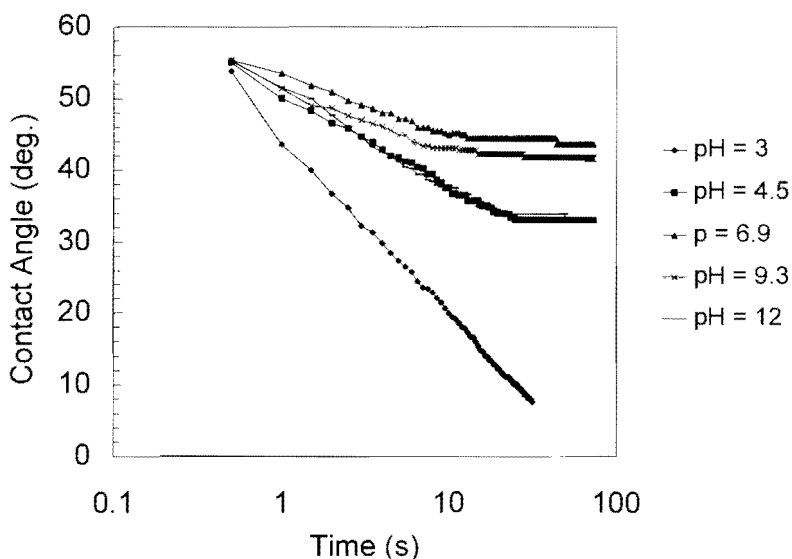


Fig. 1: Effect of pH on the wetting kinetics of aqueous solutions onto an anodized aluminum oxide surface (MO8)

Wetting was slow and the pH effect of prime interest. Although the initial contact angle value was in the range of 56 degrees, independent of the pH, its time evolution was strongly pH dependent. The most acidic solution (pH=3) spread totally down to zero contact angle within 50 seconds, whereas the others reached specific contact angle plateaux value after 10 to 20 seconds. The highest plateau value was obtained with the neutral solution, indicating an amphiphilic surface, albeit with a more pronounced basic character, which is not surprising for aluminum oxide. The long time scale kinetics observed could not be attributed to surface acid/base neutralization which should be many orders of magnitude faster. The high porosity and roughness ($R_{a} = 0.56 \pm 0.02$ μm and R_{z}

= $4.66 \pm 0.18 \mu\text{m}$) of the MO8 anodized offset plate, and its surface chemical heterogeneities due to contamination, could certainly act as mechanical and physico-chemical barriers to droplet spreading, and consequently slow down the surface neutralization kinetics.

II. Spreading kinetics of Water/Alcohol solutions

As emphasized previously (Karttunen 1986; Aurenty, 1996), the main advantage of using isopropanol (IPA) in Fountain Solutions is its dynamic efficiency on surface tension. Since IPA consists of small molecules, its diffusivity in water is high and the time needed by its molecules to reach and orient at interfaces will be very small. Furthermore, compared with a typical surfactant concentration of 0.1 %, the usual IPA concentration in Fountain Solutions is very high (about 10%), which implies that it gives rise not only to a surface effect, but also to a volume one, on the water surface tension.

Additives	Pv at 20 °C (Torr)	Concentration (% or mol/l)	Surface tension (mN/m)
Acetone	160.5	15.4 % (wt/wt)	45.1
Methanol	87.9	20.6 % (wt/wt)	46.0
Ethanol	41.1	13.1 % (wt/wt)	45.1
Isopropanol	31	6 % (wt/wt)	44.9
1-Butanol	5.6	1.9 % (wt/wt)	45.6
1-Octanol	0.1	$2 \cdot 10^{-3}$ mol/l	46.2
Water	23	-	73

Table 1: Composition and surface tension of the Fountain Solution models at 20 deg. C. As a reference, water has a vapor pressure of 23 Torr and a surface tension of 73 mN/m at 20 °C.

In the present study we focussed on hitherto unexplored aspects. IPA is a volatile organic compound with a vapor pressure of 31 Torr at 20 deg. C. It is well known in the printing industry that running an Offset press with a surfactant-containing Fountain Solution is more difficult than printing with one based on isopropanol, in terms of Water Window and Scumming. One of the

parameters which is drastically different between isopropanol and a conventional surfactant molecule is the near-zero vapor pressure of the latter. It was therefore decided to investigate the effect of this parameter on spreading efficiency onto the MO8 anodized aluminum oxide surface. For that purpose, five aliphatic primary alcohols with different volatility were used as additives to doubly-distilled water. The alcohol concentration was chosen so that the surface tension of these Fountain-Solution models would have a constant value of 45.5 ± 0.25 mN/m at 20°C (Table 1). In order to confirm the trends observed with this homologous series, a solution containing a high vapor pressure additive, namely acetone, was also prepared. Solution surface tension were recorded with the Sensadyne 6000 tensiometer at 1 bubble/s. The vapor pressures at 20 deg. C were calculated according to Schlessinger's equation and using the data of the Handbook of Chemistry and Physics. Because the surface tension was kept constant for all solutions and the density variations among samples were small, droplets of an almost constant volume, namely 6.9 ± 0.2 μ l, were laid on the plate surface by self-detachment from the tip of the syringe needle. Zero contact angles were obtained after a few tenths of milliseconds and the evolution of the wetting areas versus contact time recorded until spreading ended (Fig. 2). Before maximum spreading was reached, linear relationships between the logarithm of the area and the logarithm of the time were obtained for every solution suggesting the occurrence of the same kind of diffusion process as that encountered by Lelah (1981) and Pesach (1987) on mica and glass surfaces, respectively. A very specific feature was observed with solutions containing additives with vapor pressures higher than that of water, namely isopropanol, ethanol, methanol and acetone. These solutions exhibited a very efficient spreading behavior, reaching a maximum spreading area 5 to 10 times greater than those obtained with the other solutions, and with very high values of the rate of spreading as indicated by the slope of the linear portion of the curve.

Discussion

Although each solution had the same surface tension (Table 1), an improved spreading behavior was observed with solutions based on additives with a vapor pressure higher than that of water, namely acetone, ethanol, methanol and isopropanol. This phenomenon can be explained considering the build-up of a Marangoni flow. In fact, several authors (Hardy 1919; Bangham & al. 1938 and Bascom & al. 1964) showed that droplet spreading is always associated with the formation of a very thin primary film with a thickness lower than 10 nm

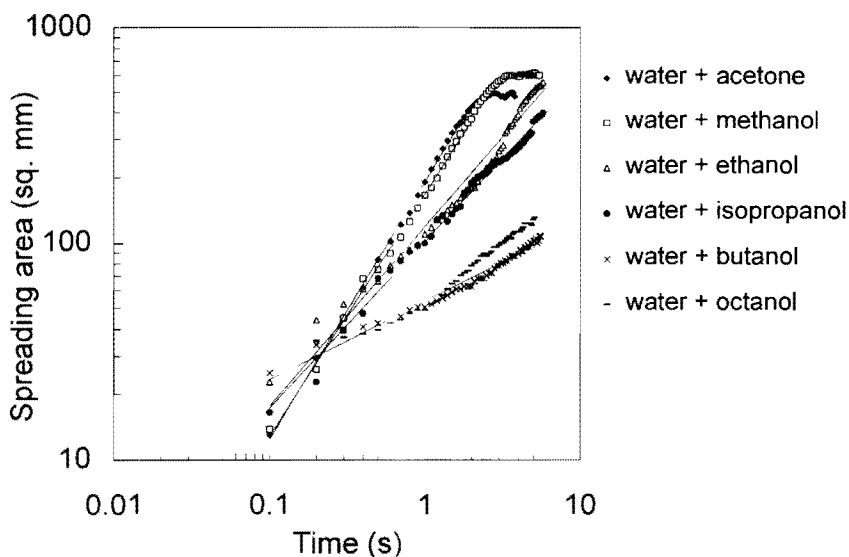


Fig. 2: Spreading kinetics of Fountain Solution models (Table 1) as a function of the additive's vapor pressure.

(Bascom & al., 1964). This primary film was showed to move forward, ahead of the bulk of the droplet (Fig. 3). Considering a mixture of two liquids L_1 and L_2 with different vapor pressures, $P_{v1} > P_{v2}$ (L_1 more volatile than L_2), and different surface tension, $\gamma_1 < \gamma_2$, the large difference in the *surface-to-volume* ratio between primary film and droplet, an unequal evaporative depletion of L_1 molecules will occur, favoring the film. This gives rise to a concentration gradient in L_1 molecules at the junction of the two domains, the primary film containing less L_1 than the droplet. The surface tension of a mixture of L_1 and L_2 depends of the concentration of L_1 molecules in L_2 . The above concentration gradient induces therefore a surface tension gradient, which generates a Marangoni flow of L_1 molecules towards the primary film and since $\gamma_1 < \gamma_2$. In the present context, viz. $P_{v1} > P_{v2}$ and $\gamma_1 < \gamma_2$, the Marangoni flow is a driving force which favors spreading.

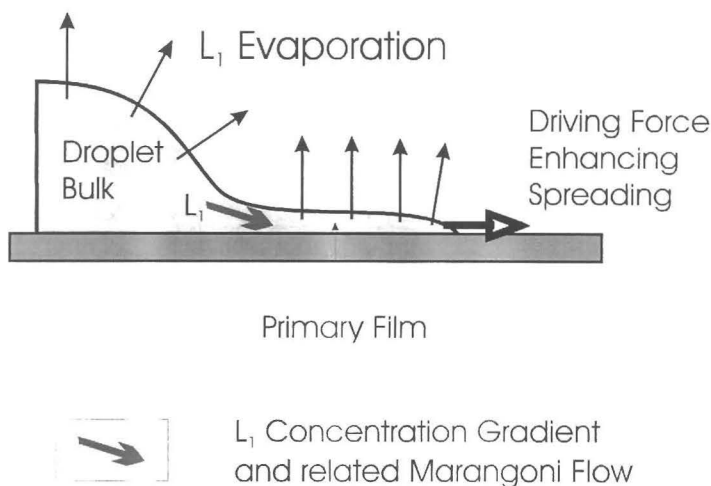


Fig. 3: Droplet spreading and primary film.

This feature was indeed observed (Fig. 2): the additives which were more volatile than water, i.e. acetone, methanol, ethanol and isopropanol (Table 1), all had a much lower surface tension than that of water. Therefore, the Marangoni flow manifested itself in the direction of the film and thus created a driving force which accelerated spreading. When using additives less volatile than water, like 1-butanol or 1-octanol, this effect disappeared, leading to maximum area of spreading 5 to 10 times smaller.

III. Spreading kinetics of surfactants solutions

The effect of the addition of non-ionic surfactants on spreading was particularly relevant because of their use in today's Fountain Solution formulations. Four common non-ionic surfactants were chosen: three ethoxylated decyne diols, the Surfynol 440, 465 and 485 with respectively 3.5, 10 and 30 ethoxy units and a POE-POP-POE block copolymer, the Pluronic 6100, with 30 propoxy units and 4 ethoxy units. Surfynol surfactants are well known for their superior dynamic activity at the air/water interface. The surfactant concentrations were chosen so that the surface tension was around 45 mN/m (Table 2). Spreading areas were recorded versus time and are presented on figure 4.

Additives	Concentration (mol/l)	Surface tension (mN/m)
Pluronic 6100	$1.5 \cdot 10^{-3}$	46
Surfymol 440	10^{-3}	44.90
Surfymol 465	$1.2 \cdot 10^{-3}$	45.1
Surfymol 485	$5 \cdot 10^{-3}$	45.5

Table 2: Composition and surface tension of the surfactant-based Fountain Solution models at 20 deg. C.

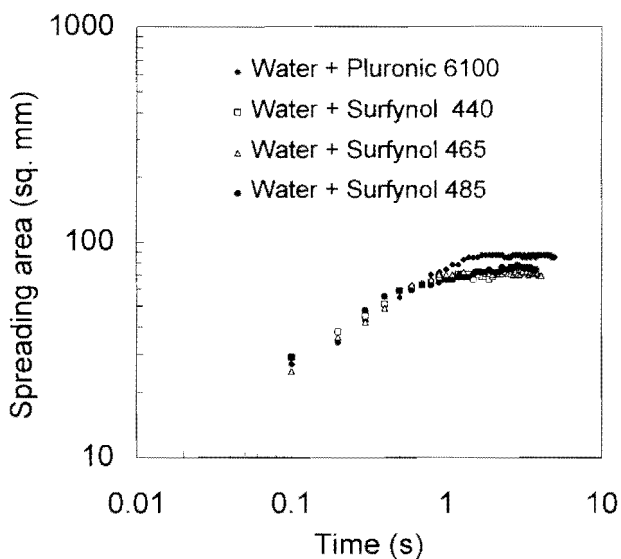


Fig. 4: Spreading kinetics of surfactant-based Fountain Solution models (Table 2).

The general behavior observed confirmed former results obtained on glass and mica flat surfaces (Lelah & al., 1981; Marmur & al., 1981), i.e. a linear relationship between $\log(A)$ and $\log(t)$ during spreading, followed by a plateau indicating that spreading stopped. In some particular cases, the plateau was followed by a slight decrease of the spreading area suggesting a retraction effect. This phenomenon was best observed *de visu*, because of the loss of contrast between “receding” and wetted areas.

The surfactant concentrations used in this study fell near the typical Critical Micelar Concentration (CMC) values, which indicates an almost saturation of the solutions and even in some cases, the presence of micelles. We could therefore envisage that the polar adsorption sites on the solid surface are immediately saturated. In fact, it seems reasonable to consider the existence of some strong interactions between ethoxylate/hydroxyl moieties and the acid/base sites on the aluminum oxide surface. Therefore, within the very thin primary film where water evaporation occurs on a short time scale (a simple calculation based on mass transfer) indicates the total evaporation of a 10-100 nm water film within 0.2-2 seconds), the solid surface becomes more and more hydrophobic with time because of the presence of the outwardly oriented alkyl tails (Fig. 5). The formation of a hydrophobic “ring” just ahead of the droplet front has therefore a tendency to stop spreading and in some cases even to cause a recession of the moving front.

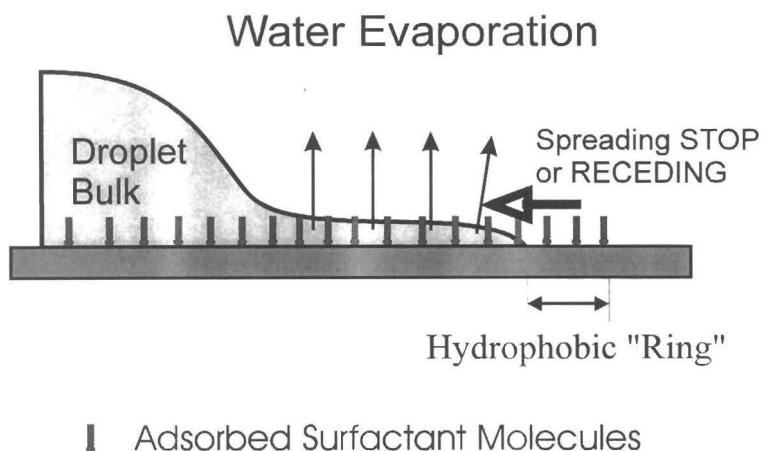


Fig. 5: Interpretation of the stoppage of spreading with surfactant-based solutions

IV. Practical implications for the printing process: Scumming and Water Window

The phenomenology described above represents a “wetting” process of an originally dry solid substrate. Looking now at the printing process, this “wetting” step seems to occur only at press start-up, and most of the printing problems, like *Scumming* and *reducing of the water window*, arise from a “dewetting” process of the non-image area, i.e. the apparition of “dry” pin holes or “water film break-up” onto the non-image areas, which become preferential sites for ink scumming. In fact, it was showed by Strom (1993) and confirmed by Aurenty (1996) that as long as the non-image areas are covered with an excess of fountain solution, no scumming can occur since the work of adhesion between ink and non-image area in its presence is equal to zero. The water film then acts as a “Weak Fluid Boundary Layer” in which the film split takes place at the exit of the nip. Therefore scumming occurs only when dewetting takes place i.e. when “dry” pin holes start to appear, because of insufficient water feed on the press. There are two possible opposite reactions to this water film break-up: (i) a process that will increase dewetting, through increasing pin hole areas provokes catastrophic plate scumming, or (ii) the presence of a driving force that will “close” the dry holes by a spontaneous “rewetting” process, which reduces the water feed level associated with plate scumming.

Following the conclusion of this study, an interpretation for both features can now be given. In the press room, printing with isopropanol-based Fountain Solutions was always related to the largest “water window”, i.e. the broadest scale of water feed level available without disturbing Ink/Water balance (Dolezalek, 1993). It is therefore believed that isopropanol-based Fountain Solutions allow to print with a lower water feed level and a thinner water film. In that context, the addition of a volatile additive into water induced a driving force which was shown to improve the spreading efficiency by the resulting Marangoni effect. It becomes therefore reasonable to explain the enlarging of the “water window” by a rewetting of the dry pin holes through this effect (Fig.6), which enables to print with less water and with a thinner water film.

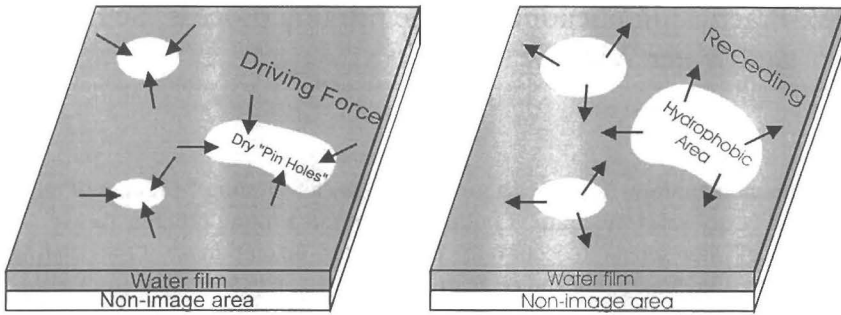


Fig. 6: Interpretation of the role of IPA and surfactants during water film break-up on the non-image areas.

Conversely, the surfactant-based Fountain Solutions (the so-called Substitutes) are generally associated with a narrow “ water window ” on the press and therefore a higher water feed level, which results in a thicker water film on the non-image areas. In that context their dewetting will depend on an increasing hydrophobicity of the “ dry ” areas and since surfactants are not volatile, water evaporation will leave them with their hydrophobic tails sticking out of the plate surface. In that case, “ rewetting ” will never be a spontaneous process and consequently dewetting will continue. A similar situation was observed in our study where spreading stopped rapidly when using surfactant-based solutions. The build-up of a “ hydrophobic ring ” around the droplet stopped the liquid from moving forward and even caused it to recede. It is therefore understandable why printers often observe that running a press with “ alcohol substitutes ” requires a higher water feed level and a thicker water film in order to prevent dewetting of the plate.

A very simple experiment (Fig. 7) was carried out in order to assess the validity of this conclusion. Two solutions with identical dynamic surface tension (32 mN/m) were prepared respectively with isopropanol and Surfynol 465. Two identical drops of each solution were deposited consecutively on the plate at two cm distance interval. In the case of the isopropanol-based solution, both droplet spread isotropically and merged without any difficulty. On the contrary, the Surfynol-based droplets spread anisotropically and never merged indicating that some sort of hydrophobic barrier had built up between them, while spreading

continued on each droplets opposite side. This experiment confirmed in our view the interpretations proposed above.

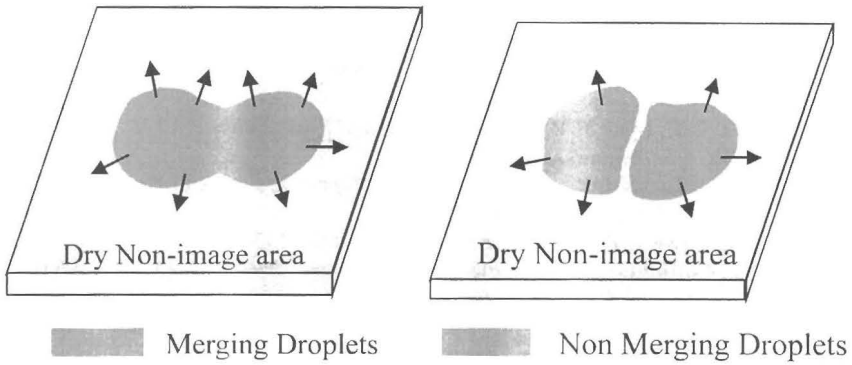


Fig. 7 Merging (isopropanol solution) and non-merging droplets (surfactant solution) on the non-image area.

Conclusion

The results obtained in this study enabled us to propose a new interpretation of the action of isopropanol and isopropanol substitutes (surfactants) during printing. The volatility of isopropanol, and the consequent Marangoni flow were shown to be the key parameters affecting the remarkable spreading improvement in the case of alcohol-based Fountain Solutions. The scumming behavior and reduction of the “ water window ”, often observed in the press room when using alcohol substitutes, becomes more understandable after the evidence gathered in our investigation.

Because of obvious environmental reasons, volatile additives like isopropanol will be banned from Fountain Solution formulations. Therefore, in order to complete this study, it would be of prime interest to diversify the surfactant structures concentrations focussing on the specific interactions which occur during surfactant adsorption onto anodized aluminum oxide and looking at some possible synergetic effect when using surfactant combinations.

Acknowledgments

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