# Modeling Studies of Ink, Plate, and Fountain Interactions by Contact Angle Measurements (2)

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**Abstract:** Representative plate image and non-image areas are characterized by ink spreading forces calculated from contact angles of ink-surrounded fountain droplets. The results indicate that the optimum ink-fountain combination varies from plate to plate. The interplay of kinetic and thermodynamic aspects is also discussed with respect to the effects of surfactants in fountain solutions.

# Introduction

Lithographic printing is a complicated process that involves various interactions at interfaces between ink, fountain and plate (MacPhee, 1979). Such interactions are generally characterized in terms of interfacial energies. In a simplified model (Bassemir, 1982), the relevant interfacial energies are combined into a parameter called spreading index, which is defined as the difference between spreading coefficients of ink and fountain. It has been shown that spreading index defined as such can be also expressed as sum of ink spreading forces at liquid-air and liquidplate interfaces (Huang, 1995). Ink spreading force is simply the difference between the interfacial energy of ink and the interfacial energy of fountain at a given interface. The ink spreading force at liquid-plate interface is particularly important because it differentiates plate image and non-image area and provides a direct measure of a plate performance for a given combination of ink and fountain. Ink spreading force should be positive in plate image area and negative in plate non-image area. The magnitude of ink spreading force provides a measure of latitude in printing. A wrong sign of spreading force may be indicative of a printing failure such as toning and blinding.

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One method of measuring ink spreading force on a plate surface (f1) is to measure contact angle of an ink-surrounded fountain droplet on a plate surface ( $q_{isfd}$ ). In this method, f1 is calculated according to the following equation:

(1)

 $f l = \gamma_{fp} - \gamma_{ip} = -\gamma_{fi} \cos \theta_{ISFD}$ 

where  $\gamma_{fi}$  is interfacial energy at the ink-fountain interface. According to the above equation, in order for f1 to be positive in plate image area and negative in the plate non-image area,  $\theta_{isfd}$  should be larger than 90° in

plate image area and less than  $90^{\circ}$  in plate non-image area. For a better printing latitude, a larger  $\theta_{isfd}$  is preferred in plate image area and a smaller  $\theta_{isfd}$  is preferred in plate non-image area.

In this paper, we will evaluate ink spreading forces on several common plate image and non-image areas as a function of time under various ink-fountain combinations.

# Experimental

The image areas of several conventional negative plates from various commercial sources were studied using two model inks and two model fountain solutions. After exposure and development as per instructions of these commercial plates, the image areas were rinsed

thoroughly with DI water and dried in 60 <sup>o</sup>C oven for 10 minutes before contact angle measurements. Plate samples include diazo plates, photopolymer plate, and hybrid plates. These three types of plates represent a majority of negative plates used in off-set printing.

The non-image areas were also studied using the same model inks and model fountain solutions. Samples for contact angle measurements were prepared by developing unexposed commercial plates followed by rinsing and drying (60 °C oven for 10 minutes).

Two model inks were a mineral oil (Magie 470, Magie Bros.), and a Soy oil (technical grade, Cargill, Inc.). The former is often used as solvent in heat-set inks, and the latter used in news inks. Two fountain solutions were DI water and a composition prepared according to the following formulation. The latter will be referred to simply as fountain solution in the following discussion.

Component	wt %
Acidic fountain concentrate(Polychrome PR 637)	1.87
Alcohol substitute(Polychrome PR 628)	2.24
Isopropyl alcohol (Polychrome PR 273)	10.00
Water	85.89

Table 1. Formulation of a model fountain solution.

Contact angles were measured on a video contact angle (VCA 2000) system manufactured by Advanced Surface Technology, Inc. A typical experimental set-up for measuring ink-surrounded fountain droplets is illustrated in the following figure.



#### Figure 1. A schematic diagram for measuring contact angles of inksurrounded fountain droplet (ISFD).

The previously determined oil-water interfacial tensions were used in converting contact angles to ink spreading forces. These interfacial tensions are listed in the following table.

Table 2. Interfacial tensions at the interfaces of model inks and model fountain solutions.

	water (dyne/cm)	Fountain (dyne/cm)
Soy oil	16	13
Magie oil	19	14

# **Results and Discussion**

### Plate Image Area

### **Negative Diazo Plates**

Negative diazo plates represent a class of printing plates whose image coating is primarily made of photosensitive diazo resins and polymeric binders. Two diazo plates from two different commercial sources were measured in this study. Figure 2 shows a plot of ink spreading forces calculated from the contact angles of ink-surrounded fountain droplet ( $\theta_{isfd}$ ) on the image area of one negative diazo plate (A) as a function of contact time. As seen, ink oils have smaller spreading force against fountain droplets than against water droplets. The difference between fountain and water may be interpreted by the effect of surfactants in fountain, which reduces the interfacial tension at the fountain-plate interface and therefore more effectively counteracts the spreading forces of ink oils. According to the data shown in Figure 2, Magie oil has stronger spreading forces than soy oil, especially in the case of water as the aqueous phase. Figure 3 shows the results of the same experiment done on the image area of another negative diazo plate (B). Comparing Figures 2 and 3, we see that both plates have similar

dependence on ink and fountain compositions, although the absolute spreading forces are smaller on plate A than on Plate B, indicating that plate B image area is less likely to have blinding problems than plate A when water level is set high on a printing press.



Figure 2. Ink Spreading forces on the image area of a negative diazo plate (A).



Figure 3. Ink Spreading forces on the image area of a negative diazo plate (B).

#### **Hybrid** Plates

Hybrid plates refer to those plates whose images are generated by a combination of negative diazo photochemistry and photopolymerization of unsaturated monomers or oligomers. Figure 4 illustrates the behaviors of a typical hybrid plate in the image area. In contrast to diazo plates shown in Figures 2 and 3, this hybrid plate favors fountain solution over water for a large ink spreading force. This phenomenon is not understood yet. One possibility is that fountain solution dissolves some hydrophilic species on the plate surface and makes the plate image area less hydrophilic. As to the effect of oil type, the hybrid plate image area exhibits stronger affinity with Magie oil than with soy oil. In this respect, the hybrid plates are similar to diazo plates.



Figure 4. Ink Spreading forces on the image area of a negative hybrid plate (C).

#### **Photopolymer Plates**

Photopolymer plates are often used in high speed projection applications. The plate coatings before processing usually consist of an oxygen barrier coating over a photosensitive layer. Light exposure polymerizes unsaturated monomers or oligomers in the photosensitive layer via a free radical mechanism, and subsequent development removes the oxygen barrier coating and the unexposed photosensitive layer in the non-image area. Figure 5 plots the ink spreading forces versus contact time on a typical photopolymer plate. The data within the recording time show that this photopolymer plate strongly favors the combination of soy and water, although the persisting slope indicates that this favorable state is not stable. Magie-water combination exhibits a curve far below the soywater line and the ink spreading force decreases even faster than watersoy combination. As expected, presence of surfactants in fountain solution results in smaller spreading forces of soy and Magie oils on this plate.



Figure 5. Ink Spreading forces on the image area of a photopolymer plate (D).

#### Plate Non-image Area

Non-image areas of offset printing plates are usually prepared by roughening an aluminum sheet followed by surface anodization and treatment of anodic oxide layer with hydrophilic materials. Aluminum surface can be roughened either mechanically as in a process called pumice graining (PG), or electrochemically (EG). Commonly used hydrophilic materials for treating anodic aluminum oxide are silicate and polyvinyl phosphonic acids (PVPA). In this section, we present results on representative non-image areas.

#### Silicated Aluminum Oxide Surface

After roughening and anodization, the aluminum oxide surface on top of aluminum base can be made hydrophilic by dipping into an alkaline silicate solution. Figure 6 shows a plot of ink spreading forces versus contact time on such a silicated aluminum oxide layer on top of an electrochemically grain aluminum base. In contrast to the image areas of diazo plates, surfactants in fountain solution tend to increase ink spreading forces. In this case, the interfacial energy between aqueous phase and plate substrate is small even without surfactants, and therefore, will not be affected very much by the presence of surfactants. On the other hand, the interfacial tension between plate non-image area and inks is high and therefore, provide a thermodynamic driving force for surfactant adsorption at this interface. Such adsorption can be achieved via diffusion of surfactant molecule along plate surfaces. Probably in the non-image area, the plate-Magie oil interfacial tension is higher than the plate-soy oil interfacial tension because soy oil is more polar than Magie oil. If this is true, then the thermodynamic driving force for surfactant to diffuse to the plate-Magie oil interface is bigger than to

the plate-soy oil interface. This ma Magie oil seen Figure 6.



Figure 6. Ink Spreading forces on EG Silicate substrate (E).

Combining the results in Figures 2, 3, and 6, we see that for a plate with negative diazo coating on an EG-silicate substrate, presence of surfactant has an undesirable effect on plate surface chemistry in both image and non-image areas. Of cause, surfactant and other components in fountain solutions are needed for other reasons such as viscosity requirement and the capability of emulsifying aqueous phase into inks. For example, without emulsification capability, it is kinetically difficult for an aqueous drop to penetrate an ink film and reach the plate surface. The kinetic and thermodynamic aspects of such a process is schematically illustrated in Figure 7, where vertical axis represents energy level, (A) represents an initial state, (B) is a transition state, and (C) the final state. Apparently, a water droplet in a transition state (B) has higher energy than a fountain droplet. Therefore, although more stable than the fountain droplet in the final state, the water droplet has to overcome a higher energy barrier to reach the final state.



Figure 7. A schematic diagram for kinetic and thermodynamic aspects of surfactants in fountain solution.

Figure 8 shows the results obtained on silicated aluminum oxide layer on top of pumice-grained base (PG). The relative values of the four different water-oil combinations are similar to those shown in Figure 6, although the differences among these combinations are much smaller.





### PVPA Primed Aluminum Oxide Surface.

Polyvinyl phosphonic acid (PVPA) can greatly enhance hydrophilicity of aluminum oxide layer if the substrate is kept in contact with an aqueous phase. Under dry conditions, such a substrate can temporally lose hydrophilicity, which can be readily restored with acid, or base, or a surfactant, or even a polar oil. Such behaviors can be seen in Figure 9, which shows results obtained on a PVPA primed aluminum oxide layer on an EG base. The curves in this figure are similar to those shown in Figures 6 and 8 for silicated substrates except for the combination of Magie oil and pure water. Apparently, Magie oil is not capable of triggering conversion of hydrophobic state of PVPA primed substrate into a hydrophilic state. Depending upon how PVPA is applied during manufacturing, the difficulty of hydrophobic-to-hydrophilic conversion in the absence of an external trigger may vary. Figure 10 shows the results on a PVPA primed substrate obtained from another commercial source. It can be seen that on this plate, the ink spreading force for the combination of Magie oil and water slowly but continuously to drop even below other combinations.



Ink Spreading forces on EG-PVPA substrate (G).

Figure 9.



Figure 10.

# Summary

Representative plate image and non-image areas were characterized by measuring contact angles of ink-surrounded fountain droplets under various model ink and fountain combinations. The results have indicated that the most favorable ink-fountain combination for one plate may not be the best for another plate. In other words, each plate has its own optimum conditions for operation on press. The interplay of kinetic and thermodynamic aspects was also discussed especially with respect to the effect of surfactants in fountain solutions. A recognition of such an interplay may alleviate frustrations, which may occur when one attempts to use surface chemistry on plate to explain every phenomenon on press.

# Literature Cited

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