Modeling Studies of Ink, Plate, and Fountain Interactions by Contact Angle Measurements(3)

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Abstract: The concept of the ink spreading force measured with an ink-fountain-plate three phase contact angle setup is applied to study positive litho plates. In model studies, it is found that the non-image area of positive plates strongly interacts with soy oil. Measuring the contact angles of soy oil surrounded water and fountain droplets thus can be a useful technique to differentiate positive plates and related developers. In contrast, interactions between positive plate non-image area and Magie oil are insignificant, so are the interactions between plate image area and either oil.

Introduction

Surface energetics is now a relatively old topic in the graphic arts literature (MacPhee, 1979; Bassemir, 1982). Nevertheless, new authors still strive to find new experimental evidences or theories to support the correlation between surface energetics and lithographic printing (Strom, 1993; Jallu, 1995). Whether a person believes or does not believe these evidences or theories really depends on his or her attitude. Among the non-believers, some are concerned about the lack of strong evidences that should correlate to their real experiences, whereas others are questioning the theoretical bases underlying the approach of measuring contact angles of standard liquid probes and converting these data into surface energies. These theories generally require strict control of sample conditions and therefore may not apply to experimental results from real world samples. We have chosen a path which we believe bypasses the use of unsubstantiated or non-applicable theories.

In the first presentation in this series (Huang, 1995), we described a method of measuring ink spreading forces with a contact angle measuring system. 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 the liquid-plate interface is of particular interest 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

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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.

In the second presentation in this series (Huang, 1996), we demonstrated the utility of experimentally measured ink spreading forces. The results based on a series of representative negative plates 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.

Unlike the negative litho plates, the variations among positive plates from different commercial sources are relatively small. Most of the commercial positive plate coatings consist of diazido-naphthaquinone sulfonate (often known as positive diazo) and phenolic resins plus some additives and colorants for visual image inspection before and after image development. The positive diazo functions as a dissolution inhibitor for alkaline soluble binders. Exposure to ultraviolet radiation destroys the dissolution inhibitor so that the coating in the exposed area becomes soluble in alkaline developers (see DeForest, 1975 for details). In the unexposed area, some surface energy changes are expected during image development. A small amount of phenolic resin near the surface is expected to dissolve before the inhibitor concentration builds up. Depending upon the coating and developer compositions, the extent and nature of such surface energy changes may vary from plate to plate. Such variations will be a focus in this presentation.

The other part of this presentation will be devoted to the ink-spreading forces in the non-image area. Typical positive developers consist of silicates and hydroxides of alkaline metals such as sodium and potassium. The hydroxides are stronger than the silicate in removing exposed coating in the non-image area. Once the coating is dissolved, hydroxides continue to attack the anodic aluminum oxides until silicates form an adequate passivation layer on the aluminum oxide. Etching by hydroxides and passivation by silicate are two concurrent processes, and the relative rates will greatly affect the characteristics of non-image area of positive litho plates. For a detailed review on interactions of aluminum and its anodic oxides with caustic solutions, the readers are referred to Wernick, 1987.

Experimental

In this experiment, ink spreading force f_1 is calculated according to the following equation:

$$f1 = \gamma_{fp} - \gamma_{ip} = -\gamma_{fi} \cos \theta_{ISFD} \qquad (1)$$

where γ_{fi} is interfacial energy at the ink-fountain interface, and (θ_{isfd}) is the contact angle of an ink-surrounded fountain droplet on a plate surface. A schematic diagram for measuring θ_{isfd} is shown in Figure 1.

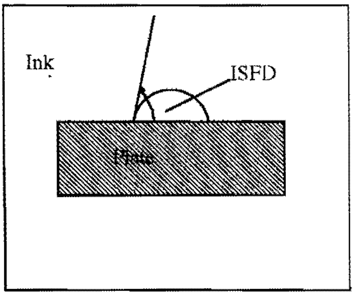

Figure 1. A schematic diagram for measuring contact angles of ink-surrounded fountain droplet (ISFD).

Note that ink spreading forces can also be measured from the contact angles of fountain surrounded ink droplets (θ_{fsid}). The details of this method and differences in ink spreading forces measured from these two experimental techniques are discussed in our first presentation in this series (Huang, 1995). In this study, only the ink surrounded fountain droplets are monitored.

Two model inks were used. One was mineral oil (Magie 470, Magie Bros.), and the other was 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.

Table 1. Formulation of a model fountain solution.

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

The interfacial energy values needed for converting contact angles to ink spreading forces are listed in Table 2.

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

Sample plates were exposed to UV light for 800 mj/cm2, and then soaked in developers for a given amount of time, followed by rinsing and drying at ambient temperatures.

Contact angles were measured on a video contact angle (VCA 2000) system manufactured by Advanced Surface Technology, Inc. The automated image analysis was conducted with a program developed in house, which provides batch calculation of images in a movie, and sends results directly to a spread sheet program for analysis.

Results and Discussion

Effect of soy oil-plate contact time on water droplet evolution

In our previous work on negative plates, involving contact angles of model fountain droplets on printing plates surrounded by model inks, primary attention was given to the evolution of the fountain droplets as a function of contact time between the fountain droplets and plate surfaces. The time of contact between the model inks and plates before introduction of the fountain droplets was ignored, and was generally in the range from 1.5 to 5 min. When we applied the same approach to the study of the non-image area on positive plates, inconsistent data were obtained. Such inconsistency may be related to the interaction between model inks and positive plate non-image area.

Figure 2 illustrates the effect of ink-plate contact time on the evolution of fountain droplets. In this example, soy oil was used as model ink and water as model fountain. The plate was a commercial plate (hereafter referred to as PA) exposed for 800 mJ/cm^2, soaked in a commercial developer (here after referred to as developer DA) for 1 min, thoroughly rinsed, and dried as described above. After the plate specimen was immersed in soy oil for 1.5 min, a water droplet was applied, and contact angle was monitored thereafter. Two more water droplets were applied at 5 and 10 min after the initial contact between the soy oil and the plate test coupon. For easy comparison with the data shown in other graphs, contact angles have been converted to ink-spreading forces in Figure 2 using equation (1). It is apparent from equation (1) that decreasing ink spreading force represents advancing of a fountain droplet. Therefore, data shown in Figure 2 indicate that the water droplet advances at a slower pace on the plate specimen immersed in soy oil for a longer period of time, although the final or equilibrium ink spreading forces appeared to be the same.

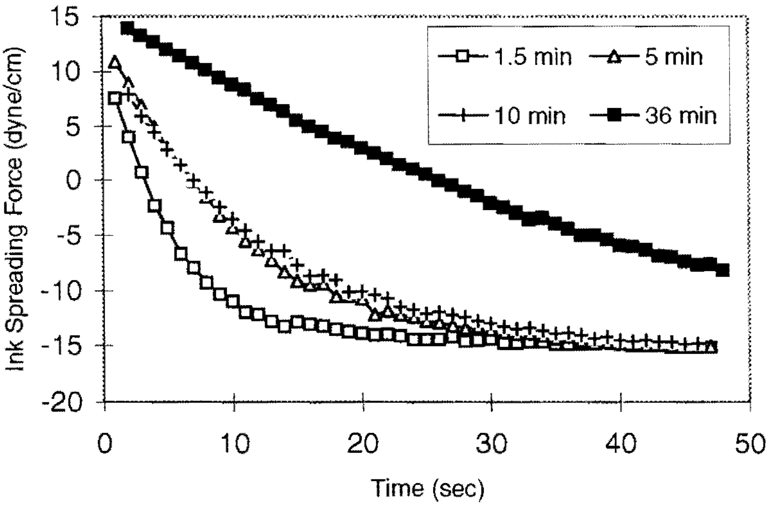

Figure 2. Ink spreading forces as a function of water-plate contact time on a positive plate non-image area (PA) after being immersed in soy oil for 1.5, 5, 10 and 35 min.

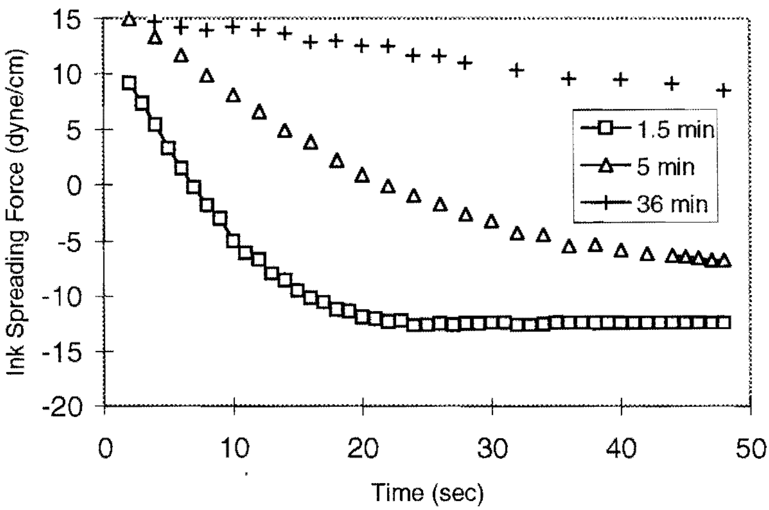

Figure 3. Ink spreading forces as a function of water-plate contact time on a positive plate non-image area (plate PB) after being immersed in soy oil for 1.5, 5 and 36 min.

The extent of the interation between soy oil and plate non-image area may vary from plate to plate. This is clearly shown in Figure 3, where the conditions were the same as those for Figure 2 except that another commercial plate (hereafter referred to as PB) was used. In comparison with plate PA, plate PB exhibits much stronger interaction with soy oil. After 36 min oil-plate contact, the water droplet advances very slow, and it is not even clear whether or not the droplet is going to reach the same equilibrium contact angle as those droplets applied earlier on the same plate specimen.

Effect of developer choices

The plate surface in the non-image area is greatly affected by the choice of developers. For example, plates PA and PB developed in another commercial developer (hereafter referred to as developer DB) exhibit high water contact angle (or large positive ink spreading force) after immersed in soy oil for as short as 1.5 min. The results are summarized in the following table:

Table 3. Contact angles (deg) of water droplets on soy oil surrounded positive plate non-image area developed with developer DB

Age of plate in soy oil	Age of Water droplet on plate PA		Age of Water droplet on plate PB	
	1 min	5 min	1 min	5 min
1.5 min	149	149	155	155
5 min	>170	>170	158	158
10 min	>170	>170	158	158

The high contact angles in the above table may indicate fast oil-plate interaction, an interaction faster than the speed that the water droplet can be applied and monitored.

It should be pointed out that all test coupons used in Table 3 were completely wettable by water before they contacted soy oil. When these plates were examined by measuring contact angle of water in air, little or differences among these plates and developers were detected.

Studies in Model developers

To understand the drastic difference between developers DA and DB, we prepared a series of model developers by mixing 2.57 % KOH solution with various amounts of potassium silicate solution (42.5°). The exact compositions of these developers are listed in the Table 4. All plate specimens exposed 800 mj/cm^2 were soaked in these developers for 1 min, followed by rinsing and drying. The contact angles (deg) of 1 min old water droplets on soy oil surrounded positive plate non-image areas developed with these model developers are tabulated in Tables 5 and 6 for plates PA and PB, respectively. The contact angle reading at 1 min after drop application is chosen because of the fact that, in most cases, contact angle readings are near their asymptotic values at this point, and that the interactions between soy oil and plates are clearly reflected in this reading.

Table 4. Composition of model developers.

Ingredients	D1	D2	D3
d.i. water	97.43	93.59	90.21
potassium hydroxide	2.57	2.47	2.38
42.5° potassium silicate	0.00	3.94	7.41

Table 5. Contact angles (deg) of 1 min old water droplets on soy oil surrounded positive plate non-image area (PA) developed with model developers

Age of plate in oil	D1	D2	D3
1.5 min	>170	124	138
5 min	>170	>170	>170
10 min	>170	>170	>170

Table 6. Contact angles (deg) of 1 min old water droplets on soy oil surrounded positive plate non-image area (PB) developed with model developers.

Age of plate in oil	D1	D2	D3
1.5 min	155	9	81
5 min	155	35	131
10 min	158	57	

As seen in Tables 5 and 6, water droplets in soy oil advance very slowly, if they do at all, on both plates PA and PB when a developer (D1) contains no silicates. The function of silicate is to form a protection layer on the aluminum oxide and render it hydrophilic. The fact that plate PB has a slightly lower contact angle may be attributed to the different interlayers between the positive coating and the aluminum substrate in plate PB. As roughly 4 % silicate is added as in developer D2, plate PB became hydrophilic when it was relatively fresh in soy oil (1.5 min). In contrast, the effect of 4 % silicate in developer on plate PA was quite small. In this case, the anodic oxide layer on plate PB was etched too fast before silicate could build a protection layer on the oxide.

When silicate level was increased further, the resulting developers become weaker. In developer D3 which contains 7.4 % silicate, both plates PA and PB had higher water-in-oil contact angles than the corresponding plates developed in developer D2.

Effect of soy oil-plate interaction on fountain droplet contact angle.

The interaction between soy oil and positive plate non-image area also affects the contact angle of soy oil surrounded fountain droplets. Figures 4 shows the results obtained on plate PA developed in developer DA. Comparing Figure 4 with Figure 2, we see that water and fountain droplets give similar response to soy oil-plate interaction except that fountain droplets advance at slower rate, especially after soy oil-plate has experienced a longer interaction. This may be related to relatively low interfacial energy of fountain droplets in soy oil (see Table 2). The ink-fountain interfacial energy may correspond to a low kinetic driving force to reach the equilibrium state of fountain droplets on oil surrounded plates. Recalling that strong interaction between soy oil and plate PB (see Figure 3), fountain droplets with such low kinetic driving force may be difficult to advance even if the plate is fairly fresh in oil. This is the case as can be seen from Figure 5, which shows ink spreading forces converted from the contact angles of soy oil surrounded fountain droplets on plate PB developed in developer DA.

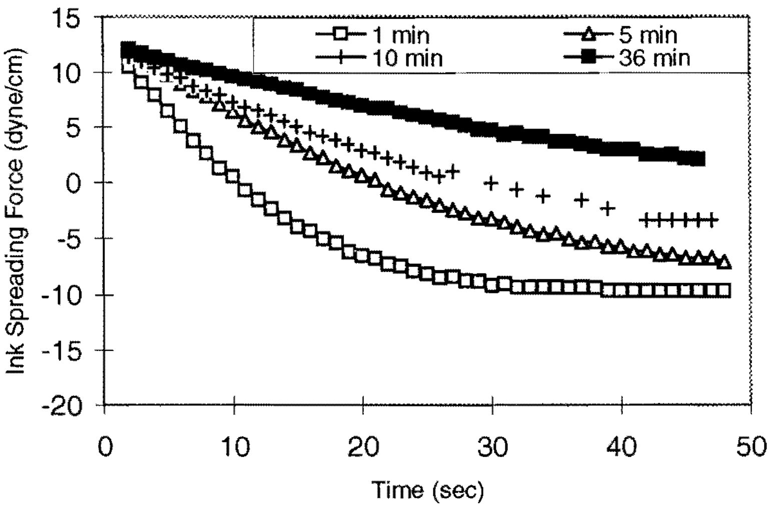

Figure 4. Ink spreading forces as a function of fountain-plate contact time on a positive plate non-image area (plate PA, developed in DA) after being immersed in soy oil for 1, 5, 10 and 36 min.

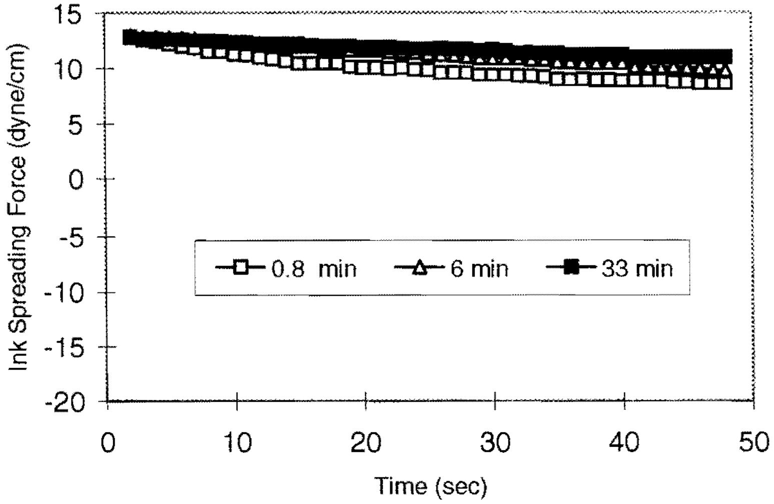

Figure 5. Ink spreading forces as a function of water-plate contact time on a positive plate non-image area (plate PB, developed in DA) after being immersed in soy oil for 0.8, 6 and 33 min.

As mentioned earlier, choice of developer affects the surface of plate non-image area and therefore affects the extent of interaction with soy oil. The results obtained on plates PA and PB developed in developer DB are similar to what we have found when water droplets are monitored. In other words, the contact angles of fountain droplets on plates surrounded in soy oil also indicate that developer DB made both plates PA and PB interact stronger with soy oil.

Interactions between Magie oil and positive plates.

Up to this point, one may start to wonder what will happen if the positive plates and Magie oil are brought in contact with each other. We have found out that, unlike soy oil, Magie oil shows little or no interaction with positive plate non-image areas. Both water and fountain droplets in Magie oil spread rapidly on plates PA and PB. The choice between developers DA and DB makes little or no impact.

Characteristics of positive plate image areas.

To complete this study, we measured the contact angles of oil surrounded water droplets on virgin plates and the plate image area after being soaked in developers for 1 min, rinsed and dried as described above. The data were taken 1 min after the water droplets were applied. It can be seen that the age of plate image areas in oil is not a major factor affecting contact angle readings. It can also be seen that both plates PA and PB, whether developed or not developed, have similar contact angles of water droplets in soy oil. In Magie oil, however, the developing step increased the ink-spreading forces (likewise the contact angle of Magie oil surrounded water droplets) on plate PA, but slightly decreased the ink spreading forces on plate PB. In other words, the image developing step made plate PA image area more favorable and plate PB less favorable for the acceptance of ink.

Table 7. Contact angle of oil surrounded water droplets on plate PA image area

	soy oil			Magie oil		
Age of plate in oil	ND	DA	DB	ND	DA	DB
1.5 min	163	167	165	148	162	158
5 min	166	167	167	147	162	158

ND = not developed

Table 8. Contact angle of oil surrounded water droplets on plate PB image area.

	soy oil			Magie oil		
Age of plate in oil	ND	DA	DB	ND	DA	DB
1.5 min	166	163	144	150	142	146
5 min	164	163	161	150	148	146

ND = not developed

Summary

The concept of ink spreading force measured with ink-fountain-plate three phase contact angle setup has been applied to study positive litho plates. It is found that the non-image area of positive plates strongly interacts with soy oil. Because of this interaction, the age of plate test coupons in soy oil is another variable which greatly affects the advancing of water or fountain droplets, and the final contact angle readings. When this new variable is controlled, measuring the contact angles of soy oil surrounded water and fountain droplets can be a useful technique to differentiate positive plates and related developers. In contrast, interactions between positive plate non-image area and Magie oil are insignificant, so are the interactions between plate image area and either oil.

Our work strongly suggests that, in certain circumstances, wetting the non-image area of an exposed and developed positive printing plate with soy oil (polar oil) creates a surface which has an energy barrier to wetting by water or fountain solutions. The longer the surface is in contact with the oil, the higher the apparent barrier to the wetting by the fountain. Further, this phenomenon is quantitatively dependent on the exact chemistry of the non-image area (presence and kind of interlayer for example), the chemistry of the developer used and the chemistry of the fountain.

As a practical matter, it known that one can have plates toning in the background during certain roll-up or restart situations. Nevertheless, the work of Strom (Strom, 1993) strongly suggests that, on fundamental grounds, a non-image area should have a such a strong affinity for fountain in preference to ink oil, that the ink would be displaced in milliseconds. We can only reconcile these results with the finding that non-image areas left in contact with polar oils for extended periods of time adopt surface states dramatically different from the supposed equilibrium state. One possible explanation is that under certain circumstances the porous nature of the anodic layer is revealed and the polar oils can penetrate into these pores. Extracting the oils from such pores thus becomes a very high energy barrier process. The effect of extended soaking to produce the effect supports this mechanism. Thus, our results are a good determinant for the relative tendency for a developed positive plate non-image area to pick up oil and lead to scumming.

For the graphic arts supplier, the soy oil-plate interaction may provide a useful tool to optimize plate structure and developer formulations. For printers, the results presented here may provide a clue to solving some mysterious printing problems on press. One implication of soy oil - plate interaction points to the importance of proper sequence of ink and water loading before starting print jobs. If soy oil based inks are applied first on to positive plates before adequate dampening water is applied, toning may occur. In real life, the problem may be less serious if the positive plates are properly gummed. Another implication of the present findings is plate non-image area contamination by soy based inks during storage. Such contamination may not be automatically cleaned by the fountain solution upon restarts.

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