RELATIONSHIP OF SURFACE ENERGY OF LITHOGRAPHIC PLATES AND INKS TO PRINTABILITY

R. W. Bassemir and F. Shubert

Abstract: Studies have been made of the surface energy of image and non-image areas of lithographic plates both new and after use on a press The surface energy of the inks and their polar and dispersion components have also been determined in an attempt to relate these values to the printing behavior of the ink/plate combination. Data on surface properties of worn plates and their relationship to scumming is also presented.

Introduction

Printability problems are frequently encountered by printing ink chemists when called on to assist a customer in maintaining trouble-free and
efficient printing operations. Studies of the efficient printing operations. surface topography and chemistry of printing plates, and changes in these due to interaction with inks during press runs, were undertaken. It was felt that a basic understanding of the nature of these surfaces and of their free energy would be helpful in resolving current problems, and in avoiding future difficulties.Cases investigated:

- A. The changes in a new photopolymer lithographic plate upon inking and running a laboratory test press with several different inks of known performance characteristics.
- B. The causes of a severe scumming problem on a photopolymer lithographic plate used in commercial heatset web offset magazine printing.
- C. The non-image area changes of a newspaper lithographic plate subject to non-reversible streak scumming when run on a high speed newspaper press using $anink/train$ dampening system.

D. The cause of a "halo" type of scumming in a wipe-on newspaper plate which occurred almost immediately after starting to run a new plate.

Discussion

The Surface Energetics of Lithography:

Previous results published throughout the literature utilize the geometric mean approximation as postulated by Fowkes⁽¹⁾, Girafalco and $\text{Good}(2)$.

$$
\delta_{SL} = \delta_S + \delta_L - 2 [(\delta_S^d \chi_d^d)]^{\frac{1}{2}} + (\delta_S^P \chi_l^P)^{\frac{1}{2}}] \qquad (1)
$$

 $Nu⁽³⁾$ claims that this equation overemphasizes the dispersion components of a system and has postulated a harmonic mean equation:

$$
\gamma_{52} = \gamma_{5} + \gamma_{2} - 4 \left[\frac{\gamma_{5} d \gamma d}{\gamma_{5} d \gamma d} + \frac{\gamma_{5} P \gamma}{\gamma_{5} P + \gamma_{2} P} \right] \qquad (2)
$$

This equation takes into consideration to a greater degree the non-dispersion components of a system inclusive of all its parts, e.g., dipole-dipole, dipole induced dipole, and other interactions.

We have based this study on Wu's equation in comparing printing inks ,dampening solution and plates as to their role in lithography because of the polar nature of many of these systems.

Contact angle measurements were made in a Rame' Hart environmental chamber at ambient temperatures which were 21°C₊ 1°C, under 100% humidity conditions utilizing-Rosos G7A"V" fountain solution at 2.5 vol%. The plate used in this study was a Kodak LN plate developed under normal conditions. A Davidson Multilith Press was used for tests.

Dampening solutions were characterized by measuring surface tensions with a DuNuoy interfacial ring tensiometer, and also by measuring contact angles on freshly prepared pure linear polyethylene pellets, pressed as needed.

Wu's equation was combined with the relation for Work of Adhesion (Wa) to give:

$$
h'_\theta = \sum_{\lambda} \left(1 + C_{\theta \theta} \theta \right) = 4 \left[\frac{\gamma_{\theta} q \gamma_{\theta}}{\gamma_{\theta} q + \gamma_{\theta} q} + \frac{\gamma_{\theta} q \gamma_{\theta}}{\gamma_{\theta} q + \gamma_{\theta} q} \right] (3)
$$

Since linear polyethylene consists solely of dispersion forces, the polar fraction cancels and therefore $\chi^2 = 0$. Rearranging, we have:

$$
\gamma_{2}^{ol} = \frac{\gamma_{s} \gamma_{c} (1 + C_{od} \sigma)}{4 \gamma_{s} - \gamma_{c} (1 + C_{od} \sigma)}
$$
 (4)

The inks were characterized by dilutions in Bromonaphthalene (which has a zero polar component of surface energy) and measuring the surface tensions via the DuNuoy Ring Interfacial Tensiometer. Then, by measuring contact angles of these solutions on linear polyethylene, the ink dispersion components for each dilution were calculated using equation (5), which as can be seen is similar to the harmonic mean used by Wu.

 d ℓ $4\frac{8}{21}\,\delta_{22}$ $\gamma_{11} = \gamma_{12} = \frac{m_{11} - m_{12}}{m_{11} - m_{12}}$ (5)

This equation was derived from equation (3) by cancelling the polar components.

Where: Liquid $1 = B$ romonaphthalene

Liquid 2 Printing ink diluted in Bromonaphthalene

The polar components for each dilution were obtained by difference from the total surface tension.

The limiting value of the ink polar component was then determined by two different methods and compared.

1. Plotting χ^2 calculated from equation (5), versus wt% ink and extrapolating the best curve to 100% ink. (Figure $\#1$)

2. Using the Lipatov and Feinerman equation (4) for concentration dependence of surface energy at an interface and modifying it to utilize polar components by using the additivity principle.

$$
\gamma_{2}^{\prime}=\frac{1}{6}\left(\frac{\Delta\gamma_{2}^{\prime}}{\Delta c}\right)+\gamma_{2}^{\prime}(2i\pi i\tau)\quad(6)
$$

where $C = ink$ concentration and $b = slope$ of the plot (Figure $#2$). The intercept of both provided results within reasonable agreement of one another.

A computer program was used to obtain all of the above results in order to facilitate the calculations.

Figure #1, Extrapolation of Polar Component of Surface Energy vs. Ink Concentration.

Figure #2, Lipatov and Feinerman Plot (ref. #4)

Case A:

Now, let us look at a small part of the lithographic process in detail.

Keep in mind that printing inks for lithography are rarely Newtonian liquids and are subject to high stresses, that cause viscosity changes in most inks.

First let us consider a conventional dampening system at the start of a run.

- l. Assume that only the dampening form roller has passed over a new plate. Conditions that exist at this moment are:
	- a. Dampening solution interacts with non-image and image areas under the influence of essentially 100% humidity. The surface free energy (dynes/em) of the photopolymer

plate tested is found to be:

Image	Non-Image
$\gamma_s = 46.7$	$\gamma_s = 72.6$
$\gamma_s^{\alpha} = 33.4$	$\gamma_s^{\alpha} = 21.8$
$\gamma_s^{\beta} = 13.3$	$\gamma_s^{\beta} = 50.8$

Calculating the work of adhesion and spreading coefficients for the dampening solution on the plate:

For image area:
$$
W_{A_i} = V_L (1 + \cos \theta) = 75.8
$$
 ergs
\n
$$
S_{2s} = W_A - W_C = -15.75
$$
\nFor non-image area: $W_{A_m} = V_S + V_L - Y_{LS} = 104.7$ ergs
\n
$$
S_S = W_A - W_C = +131
$$

Once the non-image is wet with dampening solution, it will be equivalent to the surface free energy of the dampening solution. Therefore,

Wa (non-image) =
$$
\gamma_s + \gamma_L - \gamma_{ss} = 45.8 + 45.8 - 0 = 91.6
$$

(Spreading Coefficient)
$$
\underline{\underline{\smash{\int_{-\infty}^{\infty}}\sum_{\mathbf{z}}-\sum_{\mathbf{z}}=\underline{\underline{\smash{\bigcirc}}}}}
$$

In this case, we have optimum wetting and spreading for the dampening solution on the nonimage area.

2. The next step in the process is when the ink form rollers contact the plate in the image and non-image areas, which were previously contacted with dampening solution.

a. Non-Image Area:

The wetting and transfer of ink by the ink form roll involves the interaction between ink and dampening solution on the non-image area.

The two inks used in Case A were: Ink (A-1) $\gamma_{\text{Ink}} = 32.5 \text{ ergs/cm}^2$
 $\gamma_{\text{Ink}} = 25.2 \text{ ergs/cm}^2$
 $\gamma_{\text{Ink}} = 7.3 \text{ ergs/cm}^2$ Ink (C-4) M_1 Ink = 31.9 ergs/cm² χ^2 Ink = 26.1 ergs/cm² $\sqrt[p]{r_{\text{Ink}}}$ = 5.8 ergs/cm²

According to Kaelble⁽⁵⁾, the Wa of the ink to the non-image area wetted by dampening solution involves three contributions:

 $Waink=Waink/DS + Waink/non-image-WaDS/non-image(7)$

Since the surface of the non-image area is wetted with DS, the Waink/non-image must be equivalent to Waink/DS.

In printing, we are forcefully applying thin continuous films, therefore, equilibrium contact angle is not a factor.

Thus the Waink/ η S can be calculated from equation (3) .

Calculating for the two inks: Wa = 72.31 ergs/cm² for ink A-1 $Wa = 69.8 \text{ erg/s/cm}^2 \text{ for ink } C-4$ Thus, from equation (7): Wa ink = $72.31 + 72.31 - 104.7 = 39.92 \text{ergs/cm}^2$ for Ink A-1 Wa ink = $69.8+69.8$ - 104.7 = 34.9 ${\rm ergs/cm}^2$ for Ink C-4

Or Spreading Coefficients:

 $S_A-1 = -25$ $S_C-4 = -29.9$

These are both highly negative thus indicating that ink has negligible tendency to spread in a dampened non-image area.

b. Image Area:

The wetting and transfer of ink during the first pass by the ink form roll involves the interaction between the ink and dampening solution on the image area. The surface presented to the ink form roll might possibly fall into two extreme cases:

> l. A thin continuous film of DS over image area (ink sees only DS). In this case: $Waink/DS = Waink/image$

Wa=Waink/DS + Wa_{ink/image}-Wa_{DS/image} For Ink

 $Wa=Wa_{DS}/i_{mag}$ + $Wa_{DS}/i_{nk}-Wa_{ink}/i_{mag}$ For Dampening Solution

For A-1: $Wa_{1nk} = 72.31 + 72.31 - 91.6$ dynes/cm= 53.03 ergs/cm²

For C-4: $Wa_{1nk} = 69.8 + 69.8 - 91.6$ dynes/cm = 48.0 ergs/ $cm²$

2. The thin film of dampening solution that was applied breaks up immediately into droplets on the photopolymer image and the ink sees mostly the actual image area, and emulsifies the dampening solution as it transfers ink to the image area during this initial pass. Thus, a thin film of ink interacts with the image area.

The measured contact angle of dampening solution on the image area at 100% humidity was 49°.

Therefore: (from previous calculations)

 $Wa_{DS}/image = V_{DS}$ ($+Cos\theta$) = 75.85 ergs/ em

\n
$$
\text{Waink/DS} = 72.31 \, \text{ergs/cm}^2 \, \text{for A-1}
$$
\n

\n\n $\text{Waink/BS} = 69.8 \, \text{ergs/cm}^2 \, \text{for C-4}$ \n

\n\n $\text{From equation (3):}$ \n

\n\n $\text{WaA-1/image} = 76.3 \, \text{ergs/cm}^2 \, \text{and WaC-4/image} = 74.75 \, \text{ergs/cm}^2$ \n

or:

Wa = $76.3+76.3-75.85=72.76$ ergs/cm² - A-1 $Wa = 69.8+74.75-75.85=68.70$ ergs/cm² - C-4 $S = +7.76$ for Ink $A-1$ $S = +4.9$ for Iuk C-4

These spreading coefficients are both positive, indicating favorable surface energetics for wetting the images.

3. For an actual model, contact angles of ink and DS on the plate image area were measured under influence of saturated DS atmosphere. These values were used to calculate work of adhesion and spreading coefficients as above:

> $Wa = 72.31 + 56.65 - 75.85 = 53.11$ ergs/cm² for A-1 Wa=72.31+55.61-75.85=52.07 ergs/cm² for $C-4$

and spreading coefficients are:

The spreading coefficient of the dampening solution on the uninked image area of the plate was also determined in a similar manner and calculated to be -6.0 ergs/cm². This would indicate

that surface energetics alone would favor the spreading of the dampening solution rather than the ink on the uninked image area.

Obviously, other factors must be involved otherwise lithography as we know it could not exist. Of course, these equilibrium results are only valid for an ink that has not been subjected to the mechanical forces existing on a press which are great enough to overcome the negative spreading coefficients of the ink on the image area.

On succeeding passes of the ink form rollers, a different situation exists, because the image area has been forced to become coated with ink by means of the multiple form rollers contacting the plate under pressure. Once this has occurred, calculations made of the spreading coefficients of the inks and dampening solution on $\overline{\text{the linked}}$ image are the following:

> $S = 6.43 \text{ ergs/cm}^2 \text{ for ink } A-1$ $S = 3.95 \text{ ergs/cm}^2 \text{ for ink } C-4$

for dampening solution $S_{\text{da}} = -24 \text{ ergs/cm}^2$

Here, we can see clearly the favorable surface energetics since the ink should now spread readily on the ink covered image areas and the dampening solution should be rejected due to a strongly negative spreading coefficient.

From the above discussion, it is apparent that the most critical step in the lithographic process is the initial inking of the image area with a properly formulated ink. This step overcomes the potentially unfavorable surface energetics of the image areas. of a new plate by changing their surface energy.

In relation to printability, the inks chosen had been previously press tested and their parameters critically evaluated in the laboratory by Bassemir⁽⁶⁾, and it was determined that ink A-l produced smoother solids than ink C-4. The values for spreading coefficients confirm that this should, indeed, be the case.

Case B

This situation concerned a severe scumming problem which occurred on a long running photopolymer lithographic plate being used on a typical high speed magazine press doing commercial heatset coated paper printing.

The problem observed occurred after about 75- 100,000 impressions. At this point in the run, scumming started to appear in parts of the nonimage area of the form but particularly in those areas which were in line with large solids.

Attempts to desensitize the plate by cleaning and etching were futile. At this point, a second ink was substituted having a differing emulsification behavior. This ink apparently ran fairly well although water balance was difficult and they were able to finish the run of 150,000 using the new ink.

Samples of the inks and the used plate were submitted for examination in an attempt to understand the nature of the problem.

The plate was subjected to S.E.M. examination where it was quickly determined that a severe wear problem had occurred in the non-image areas and particularly those places in line with large solid images. These are shown in Figures #3-6. The emulsification behavior of the two inks was then determined using the laboratory test pro-
posed by Surland⁽⁷⁾. These are shown in Figure posed by Surland⁽⁷⁾. An examination of the curve for Ink#1 indicates a type of lithographic behavior wherein the ink picks up water extremely rapidly and comes to its equilibrium water content of 31% in
less than two minutes. The curve for Ink $\#2$ less than two minutes. shows a much more normal type of behavior and reaches an equilibrium of 36% between 4 and 5 minutes.

An examination of the surface energy of both a worn and unworn non-image area from this plate was also made, utilizing the techniques previous-

Figure #3, Case B, 480X, Good non-image area of plate

Figure #4, Case B, 480X, Worn non-image area of plate

Figure #5, Case B, 3200X, Good non-image area of plate

Figure #6, Case B, 3200X, Worn non-image area of plate

ly described. The results were as follows for an 80% water/20% isopropanol saturated atmosphere.

Surface Energy-Dynes/em

These results clearly show a sharp drop in the polar component as well as an increase in the dispersion component of the worn areas which might be expected since much of the anodized sur-
face has been removed. The results also indicate The results also indicate why it was difficult to desensitize this area even though it was washed and re-etched. It has simply lost much of its hydrophilic surface character.

An examination of the above data points to the probability that this was an ink related problem, due primarily to the poor lithographic performance of Ink #1. This ink was difficult to run cleanly, even from the beginning, since it was destined to have a tight water balance. The tendency of this ink to emulsify water very quickly means that the non-image areas following large solids would, indeed, tend to be starved of dampening solution as compared to adjacent areas. This lack of lubrication is likely one of the major causes of the wear which was so obvious in the S.E.M. photo.

Ink #2 was able to run,mainly because of its superior litho characteristics as shown in the emulsion rate curve. The tight water balance it exhibited with the used plate is, of course, due to the large decrease in the surface energy (polar component) found in the worn areas but the good performance of the ink was sufficient to overcome this disadvantage to a sufficient extent.

Starting subsequent runs with an ink of good lithographic performance such as Ink #2, eliminated the problem for the customer.

Case C

A severe case of scumming concentrated in longitudinal streaks occurred on a high speed newspaper press utilizing a new type of ink train dampening system. The plate being used was electrochemically grained and anodized and because of this the non-image areas had a large number of relatively deep pitted areas due to the particular type of graining process used.

The symptom was irreversible scumming in direct proportion to the number of press stops or shutdowns encountered during a run. If no shutdowns occurred, the entire run could often be finished with no problem.

An examination of the non-image areas of plates which did exhibit the scumming problem showed inclusions of ink in the deep pitted areas of the plate which remained even after repeated attempts to scrub out these plates. Figure #8 shows a photograph of a new non-image and Figure #9 shows a photograph of the nonimage area on one of the scummed plates after washing.

S.E.M. 's of the scummed areas are shown in Figures #10 & 11, and illustrate the presence of ink in the bottom of the pitted areas.

Since the ink inclusions are fairly widely spaced, it was decided to make some surface energy measurements and see if the magnitude of change was significant enough to have been the sole cause of this scumming problem, and also to determine if the "clean" areas between the streaks of scumming were affected in their surface energetics.

Contact angle measurements were made, utilizing a saturated atmosphere of alkaline fountain solution, as used on the press. The results are listed below:

Figure #8, Case C, 17X, New non-image area of plate showing deep pits

Figure #9, Case C, 17X, Non-image area of scummed plate after washing with solvent,

shard and dale inclusions

Figure #10, Case C, 430X, Scummed non-image area showing ink inclusions

Figure #11, Case C, 1440X, Scummed non-image area

Surface Energy-Dynes/em @21°C

Atmosphere (Saturated alkaline dampening solution) Virgin Non-Image $62.5(19.8\text{M}_d, 42.8\text{M}_p)$ "Clean"Non-Image $52(19.5\text{K}_d, 32.5\text{K}_p)$ Scummed Non-Image $42.4(20.3\text{J}_d,21.9\text{J}_p)$

These data show clearly the decrease in total surface energy but more importantly the sharp decrease in the polar component which occurs not only in the scummed non-image areas but also in the "clean" non-image areas as compared to the values for a virgin plate. In this case, the used plate had been on the press for only about 20,000 impressions but had encountered a number of shutdowns for web breaks.

A possible explanation for this occurrence is the fact that the direct ink train dampener used on this press rolls ink directly on the plate after a shutdown, before very much dampening solution can be carried up to the plate from the point where the dampening solution is applied. During the shutdown, the alkaline dampening solution on the plate has had time to dry, so that there is little protection for the non-image areas because no gum arabic;is used and because of the deeply pitted surface, ink is forced down into these recesses in a virtually irreversible process.

It is apparent that each time the press shuts down, more and more of these pitted areas will become contaminated with ink, and the scumming increases in intensity until it becomes intolerable. One can also see that the "clean" areas are also decreasing in the polar component of surface energy sufficiently so that they, too, will eventually scum. The localization of the intense scumming in streaks is likely due to the uneven distribution of dampening solution across the form roller as the water balance is reestablished after a shutdown.

Case D

In this case, a wipe-on type photopolymer plate with an anodized non-image area was being used for newspaper printing. The problem encountered was scumming around the edges of image areas in the form of a halo which occurred almost immediately after starting to run a new plate, Figure #12. The plates were processed in an automatic platemaking machine starting with virgin anodized aluminum sheets. Microscopic examination with the S.E.M. did not show any clearcut reason for this scumming,than some slight discoloration of portions of the non-image area
adiacent to each image. (Figure #13). X-ray adiacent to each image. (Figure $\#13$). measurements of these areas indicated the presence of excessive amounts of sulphur which was also present in the photopolymer chemistry used. Measurements on the clean area of the plate showed much less sulphur. Since this element has sometimes been associated with scumming problems, it was decided to confirm this observation by use of surface energy measurements.

In this case, an undeveloped anodized plate was measured in an 100% R.H. atmosphere. In addition, a newly developed plate was also measured in the non-image area adjacent to an image in order to determine whether any changes had
occurred during the developing process. The occurred during the developing process. results obtained are shown below:

Atmosphere:lOO% R.H.

New Plate Non-Image Area 67.7(21.2), 46.5 λ_n Virgin Anodized Aluminum 68.1(17.1)_d, 51.0)_n)

In this case, not only did the polar component decrease, but the dispersion component increased. The combination of these changes is a significant effect even though the total surface energy showed very little change. The effect of this should be expected to decrease the hydrophilicity of the developed non-image in the area measured. The development process, in this case, did not totally remove all traces of the photopolymer from the areas surrounding the exposed images,

Ailbury Park Press mar's annual St. Patrick's Veneziano, Asbury Park. 'ownship, third runnerup.

ıll limit

ncil also is to look into the gate placed in the chain-link ting the Peninsula House parkthat of the borough.

an obn S. Forsman expresse. Figure #12, Case D, 2.5X, Print on left and litho plate on right, showing "halo" scumming.

Figure #13, Case D, 2000X, Non-image area adjacent to image, showing discoloration of some of the anodized layers. thus causing a scumming condition to occur almost immediately.

Conclusions

- 1. The use of Scanning Electron Microscopy and surface energy measurements is an extremely powerful combination in explaining the nature and causes of printing ink and plate problems.
- 2. The separation of surface energy into dispersion and non-dispersion values is essential to an understanding of ink/plate interactions.
- 3. The most critical step in a successful lithographic operation is the initial inking of the virgin image areas with a good lithographic ink.
- 4. The negative spreading coefficient for ink on the uninked image areas in case "A" shows that this process can be successfully used in spite of unfavorable surface energetics, providing that the proper mechanical forces and surface topography are present.
- 5. In case "B", the obvious wear in the non-image areas seen with the S.E.M. also correlated with a large decrease in the polar component of surface energy which made desensitization of the worn non-image areas marginal.
- 6. The emulsification behavior of the original ink in case "B" is shown to be the probable cause of the wear problem encountered.
- 7. In case "C", the scummed non-image areas were obviously caused by the presence of ink in
the deeply pitted grain of this plate. The the deeply pitted grain of this plate. surface energy polar components clearly showed that the alleged "clean" areas of this used plate were at least partly contaminated as compared to a virgin plate and destined to cause eventual scumming problems.
- 8. In case "D", the non-image area immediately adjacent to large image areas showed a significant decrease in the polar component and an

increase in the dispersion component of surface energy as compared to a virgin anodized aluminum plate. This was true even though the plate had never been on a press, thus, indicating contamination of the non-image area with photopolymer which had not been completely washed out.

References

- 1. Fowkes, F.W., J. Phys. Chem. 66, 382 (1962).
- 2. Girafalco, L.A., Good, R.J., J. Phys.Chem.61, 904 (1957).
- 3. Wu, Souching; J.Po1ymer Sci., Part C, No. 34, ppl9-30, (1971).
- 4. Lipatov, Yu S.; Feinerman, A.E., ;J. Adhesion $\overline{3}$, pp3-12 (1971).
- 5. Kaeble, D.H.; J.Appl. Poly.Sci. 18, 1869 (1974)
- 6. Bassemir, R.W.; Phy. Chem. of Lithographic Inks, American Ink Maker Feb. 1981.
- 7. Surland, A., TAGA Proceedings, 1980, p222.

Symbols used:

Subscripts:

- $L = Liquid Surface$
- $i = Image Area$
- ni = Non-Image Area
 DS = Dampening solu
- $=$ Dampening solution

Superscripts:

p = non-dispersion (polar) component