<u>PREDICTION OF LITHO PRESS PROBLEMS FROM/PHASE</u> <u>EQUILIBRIA OF INKS AND FOUNTAIN SOLUTIONS</u>

R.W. Bassemir* and R. Krishnan*

<u>ABSTRACT</u>: Experiments show that the steady state ratio of fountain solution to ink present at the litho plate surface gives rise to various types of phase equilibria. It is proposed that each of these can be identified with various press problems as well as the water balance range from scumming to washout. This ratio is also affected by the nature of the plate, the ink, the fountain solution and the paper, as well as the speed of the press and the coverage of the form. The effect of these variables is also examined with a simple mass flow-rate balance.

I. Introduction

It has long been recognized that an analysis of ink/dampening solution interaction on press is central to an understanding of the lithographic process. Several studies are published in the literature [1-6] on this topic. Basically these can be classified into two categories, those based on the thermodynamics or physical chemistry of the fluids and others based on test methods that simulate the ink/fountain solution contact on press.

In one class of studies authors have attempted to measure rheological and dynamic surface chemical properties of ink and fountain solution and apply thermodynamic theories of lithography. Low dynamic surface tension of fountain solution, high polarity and surface tension of inks and low interfacial tension between ink and fountain solution have been

*Sun Chemical Corporation

deemed desirable for optimal litho performance. This approach suffers from a lack of suitable techniques to measure <u>dynamic</u> interfacial property measurements, which must play an important role in this interaction.

In the other studies, experiments are carried out in which emulsions of fountain solution/ink in various mixers and roller devices are formed. The results of this emulsification are then used to calculate amount of water pickup and kinetics of emulsification and demulsification. These are then associated with ideal combinations and those leading to press problems. A variation of this procedure is to introduce temperature as a variable and hence study thermal stability of the emulsions so created. The major problem in this approach is the simulation of dynamic mechanical stresses of the order of those present in a high speed press.

In both of these methods, no provision is generally made to take into account the effect of paper, plate, speed, nature of the form and type of dampening system. Experience has shown that the same ink/fountain solution combination which performs well under one set of conditions of the above variables, may perform marginally when one or more of these other conditions are changed.

It is apparent that a total evaluation of ink/fountain solution while also accounting for a combination of all of these variables, would require the press itself as a piece of test equipment. Even in this case, one cannot account for variations in press performance with plates, paper, etc. using current theories.

One objective of this paper is to account for these variations with a simplified mass balance model for the fountain solution. The major premise of our theory is that under steady state operating conditions, changes in one or more of these variables essentially alter the ratio of fountain solution to ink that exists at the plate surface. This in turn produces changes in the phase equilibria of the two fluids which ultimately determine the press performance.

To determine the effect of these changes, experiments were conducted to observe the phases resulting from various ink/fountain solution chemistries for mixtures of a range of ratios of the two fluids. This included a series of tests at a constant volume of combined fluids. А second series of tests were also performed holding the ink volume constant. They show that both the type and number of phases change as the ratio of fountain solution to ink is increased. The results enable us to predict the effect of changes in printing variables on ink/water balance by assuming that their major effect is one of altering the ratio of ink to water. In addition, we propose to show that these phase equilibria may be identified with water balance range from scumming to washout, as well as with various press problems.

II. <u>Effect of Press Variables on Ink/Fountain</u> <u>Solution Ratio on the Plate</u>:

Apart from their physical and chemical properties, the most important parameter in the interaction between ink and fountain solutions is the relative ratio of one fluid to another. Tn a prior paper, it was shown that the amount of water needed to just keep the nonimage area of a plate from scumming, is inversely proportional to the efficiency of the fountain solution.[7] This fountain solution efficiency (FSE) was defined as the ratio of its dynamic surface tension divided by it's viscosity, and subtracted from the same values for water. Similarly, the rate of ink feed to obtain a desired density depends on both the ink feed settings and the transfer efficiency of the ink. But apart from the inherent nature of inks and fountain solutions, other external factors such as plates and paper can also affect their relative ratio. In order to estimate the influence of these factors, several relationships can be developed by considering the following schematic of the litho press and the balance of flow rates of ink and fountain solution:

The minimum thickness of the fountain solution film to be fed to the plate, $(X_{f.s.})$ in cm., for a given ink and a fountain solution of efficiency FSE in m/sec to just prevent catch-up of



X_{f.s.} = K_{ink/plate} / 100FSE

where, the value of ^Kink/plate (cm²/sec.) is a function of the ink chemistry and the plate graining and surface chemistry, and should be a constant for a given ink/plate combination.

(1)

The rate of fountain solution feed $\rm F_{f.s.}$ in $\rm cm^3/sec.$ then becomes:

 $F_{f.s.} = A \quad S \quad X_{f.s.}$ (2) where: $A = \text{total plate area in } \text{cm}^2 \text{ and}$ S - speed in impressions/sec.

This holds for all dampening systems having no lateral control on water feed and provides a measure of total fountain solution input to the plate. A mass balance of fountain solution can be accounted for by absorbtion by the paper, emulsification by the ink and evaporation. Note that the emulsified F.S. flowing to the ink train is returned as an internal phase in the ink.

Thus for a steady state operation, the rate of availability of fountain solution to ink on the plate is therefore: $R_{f.s./ink} = (F_{f.s.}) - (A_{paper})(1-C) - (W_{evap.})$ (3)

where A paper = the rate of dynamic water absorbence of the substrate, (1-C) is the fractional non-image coverage of the plate and W evap = rate of evaporation of water from the ink train, blanket and plate, all in cm³/sec.

However $R_{f.s./ink}$ does not imply that all of this available fountain solution is <u>emulsified</u> into the ink, indeed in most cases it is not and exists as both emulsified and surface water on the plate.

Similarly one can write the feed rate of ink (F_{ink}) to the plate as:

(4)

 $F_{ink} = A C S X_{ink}$

where C is the fractional coverage of the plate by image areas and X_{ink} is the thickness of the ink film in cm.immediately preceding the dampening form roller or point of introduction of fountain solution. This assumes a transfer of 50% of the ink film from the plate to the blanket and a value of about 1 um for X_{ink} .

At dynamic equilibrium the ratio of the amount of fountain solution to ink, can then be calculated by:

Steady State Ratio of f.s./ink (SSR)= $(R_{f.s./ink})/(F_{ink})$ (5)

Using equation 5, calculations of the ratio of fountain solution to ink present at the plate were made assuming various operating conditions. The results are shown in Figures 1-3. For all the figures the following constants were assumed. Plate area = 2600 cm^2 , $\text{K}_{i/p} = 5 \times 10^{-1} \text{ cm}^2/\text{sec.}$ which leads to a thickness of 1.6 microns, for a fountain solution with an F.S.E. parameter of 30. The value for $\text{K}_{i/p}$ was extrapolated from experiments conducted on a Miehle press with a Kodak LN plate and a commercial heatset ink. A value of $0.5 \text{ cm}^3/\text{sec.}$ for W_{evap} was calculated from mass transfer equations in the Chemical Engineering literature (see appendix). The effect of coverage on the steady state ratio of fountain solution to ink as calculated from Eq. [5] is shown in Fig. 1. The ratio is seen to vary from a high value of 8.5 [corresponding to low coverage (10%) and a poor fountain solution (FSE = 30)] to a low value of 0.9 [corresponding to very high coverage (90%) and an excellent fountain solution having a FSE of 50]. The significance of high ratios will be examined in the next section.



The rate of absorption of fountain solution into the paper was assumed to be constant at 13 $cm^3/sec./M^2$ for Figs. 1 & 3. This value was derived from data given by Salminen [13] for uncoated and light weight coated paper. Other values for papers were obtained from Bristow tester results done by Weyerhauser Paper Co. This value was calculated from the slope of dynamic water absorption vs. contact time using a Bristow tester on a commercial LWC stock.

The influence of papers with varying water absorption rate on the fountain solution/ink ratio is shown in Fig. 2. The speed of the press is assumed to be 1500 feet per minute, and a 30% coverage. It shows that the ratio can be reduced from 3.3 down to below .02 with a combination of highly absorbent stock $(23 \text{ cm}^3/\text{sec/m}^2)$ and an efficient fountain solution (f.s.e. = 50). However a press could never be operated at such a low ratio without showing catchup or scumming and the press operator would immediately increase the water feed to satisfy the demand of this very highly absorbent paper. This would increase the ratio calculated from equation (5). Very highly absorbent stocks can lead to other press problems such as paper or coating piling, especially if it should lead to loss of stock surface strength.



The effect of press speed is examined assuming that the transfer efficiency of ink and fountain solution remain constant. The rate of dynamic absorption of fountain solution into the stock may well vary with speed. Unfortunately, no expressions are known that account for these changes, as the speed of the press increases.

With the above reservations, the mass balance approach is used to estimate the effect of speed at a fixed medium coverage (50%) and a stock of fixed water absorption rate. Fig. 3 shows that the steady state ratio of fountain solution to ink increases moderately as the speed increases. The significance of an increased ratio will be established in the following discussion.



III. Ink/Fountain Solution Phase Equilibria

Because of the large number of components present in ink and fountain solution mixtures, their phase equilibria (the number of phases resulting and their composition) can be quite complex. Also due to the presence of pigments, these phases are not easily observable. Therefore, the phase equilibrium experiments were conducted on pigment free inks (a composite vehicle with solvents, resins and additives). Two ink compositions were chosen, one having a wide water balance range on press, irrespective of pigment type, and the other with a narrow window of water tolerance. Two fountain solutions having dynamic surface tensions of 50 dynes/cm (FSE=22) and 35 dynes/cm (FSE=37) were chosen for the tests.

A fixed amount of each composite varnish was mixed using a high speed stirrer with varying amounts of each fountain solution and allowed to come to equilibrium without stirring at a constant temperature of 25° C. The experiments were also repeated at a higher temperature (40° C).

The results are shown in Figs. 4-6.

At very low ratios of fountain solution to varnish, a single phase emulsion of the water in oil type is formed with all combinations of temperature, type of ink chemistry and fountain solution chemistry.

As the ratio is increased, two phases formed. A water in oil emulsion in equilibrium with excess water.

As the ratio is further increased, the amount of water in the varnish decreases and two phases again form, a water in oil emulsion in equilibrium, with an oil in water emulsion is formed. The onset of the inverted oil in water emulsion occurs at a lower ratio with the poorer varnish and at the higher temperature.

At still higher ratios two phases again form, oil in water in equilibrium with oil.



Good F.S./Ink @ 25^oC. Ratios=5,2,1,.5,.2 Fig. 4



Good F.S./Ink@40^OC.Ratios=5,2,1,.9,.75,.67,.5,.2 Fig. 5



Poor F.S./Ink @ 25⁰C.Ratios=5,2,1,.5,.2 Fig. 6

The progression of the phase equilibria for a good fountain solution, good varnish combination at 25° C is shown, in Fig. 4. The onset of two phase formation occurs at a ratio of 0.50. The formation of the inverted oil in water emulsion corresponds to a ratio of 4.88. Repeating the same experiment at higher temperatures, the onset of two phase formation occurs at a ratio of 0.75 and the formation of oil in water occurs at a lower ratio (2.03) than occurred at 25° , as seen in Fig. 5. This shows why the water balance range is narrowed as the temperature is raised, a commonly observed phenomenon in the pressroom.

The phase equilibria at $25^{\circ}C$ for a fountain solution having a lower fountain solution efficiency (FSE) and a varnish having a narrower press water balance is shown in Fig. 6. Again the onset of the oil in water emulsion as found to occur at lower ratios of fountain solution to ink (2.03 for the poor ink/F.S. vs. 4.88 for the good).

These results offer a basic explanation for the generally observed detrimental effect of high temperatures and low coverage (large ratios of fountain solutions to ink) on lithographic performance.

IV. Phase Equilibria and Press Performance

It is apparent from the above experiments that the type of phases formed when an ink is contacted with a fountain solution is critically dependent on their relative ratios. Also, as seen from the earlier theoretical considerations of this paper, the ratio will vary depending on press operating conditions. This is the main reason why the presently used water pickup tests on inks and fountain solutions often do not adequately predict their press performance under the widely varying conditions existing in the printing industry.

We propose a scheme of types of phase equilibria and identify them with press performance as shown in Fig.7.

Type I, phase equilibrium corresponds to



complete lack of emulsification between ink and fountain solution. This can happen when for example, the surface tension of fountain solution is high and the ink vehicle is completely non polar. This extreme usually leads to stripping and lack of transference.

Type II, the optimum is obtained when a water in oil emulsion in equilibrium with excess water (called surface water in the lithographic literature) is obtained. From the catch up point, the additional amount of water tolerated by the water in oil emulsion as surface water, without phase changes or drastic rheological changes (as compared to unemulsified ink) represents the water balance range from scumming to wash out. Rosenberg [12] has shown that the presence of surface water is essential to prevent catch up from occurring.

Also the emulsion formed in type II is a stable one with very small droplet size, since these type of emulsions give rise to less drastic changes in tack and other rheological properties that affect ink emulsion transfer.

Type III systems are formed at medium to high ratios when the inks have a tendency to "emulsify" as it is commonly called and pile on the rollers, plate image or blanket image. In reality it corresponds to formation of a single phase of water in oil emulsion, where the droplets tend to be coarse and polydisperse and excessive rheological changes take place. These elmulsions also tend to be unstable.

It is to be noted that at small volume fractions of water nearly all inks lead to single phase W/O systems; but the difference is that, at these ratios with good ink systems, the water droplet sizes are small and rheological changes are minimal and as the water feed is increased to eliminate catch up, they will give rise to type II systems. On the other hand, a poor ink/f.s. system emulsifies the water as relatively large polydisperse droplets and will never lead to a type II system having good rheology and a stable emulsion. Formation of a type II system is also essential for the operation of Dahlgren type dampening systems. The excess surface water provides the dampening from the first ink form roller and the stable water in oil emulsion leads to good printability.

The over emulsification of the type III system ink leads to narrow water balance and tinting, since with a given feed of fountain solution, rate of absorption by the ink exceeds the available fountain solution at the plate. If higher amounts of water are used to solve this problem, the ink "emulsifies" or fails to transfer due to excessive changes in rheology.

The type IV system is obtained with all inks when operating at very high ratios of water to ink. However, the ratio corresponding to the onset of type IV is much higher with good ink/fountain solution systems than with poor ones, so it is less likely to occur with good performing systems even when feeding excessive water. The result of this type of phase equilibria in continuous dampening systems is the problem of feedback of ink onto the metering rollers in a Duotrol system and into the fountain solution pans in a Dahlgren dampening system. This will eventually cause loss of color control and tinting. In a brush dampening system, the result of type IV behavior is lack of good color control.

Finally if the ink/fountain solution combination leads to a single phase of oil in water emulsion, either alone or in equilibrium with excess oil, wetting of the entire plate with water results. This will appear to be severe blinding of the image, and can be distinguished from chemical or mechanical image blinding, because it is reversible when the plate is cleaned, and a good ink or fountain solution substituted.

V. <u>Conclusions</u>

 In addition to the ink/f.s. composition, variations in the ratio of the amount of fountain solution to the amount of ink available are the key factor in determining press performance; because they can lead to different equilibrium phase formations.

2) It has been shown that for optimum water balance and lithographic performance, the type II system, where surface water coexists with a stable W/O emulsion, is the preferred one.

3) The water balance range on press can be associated with a range of f.s./ink ratios. This range starts with the ratio that results in the appearance of surface water (just above catchup). It ends with the ratio which results in the onset of inverted oil in water emulsion formation (wash marks).

4) A mass balance of fountain solution and ink feed rates aids in the estimation of the effects of varying press parameters.

5) Lower F.S.E. fountain solutions and stocks having very low water absorbance contribute to high F.S./ink ratios, thus narrowing the water balance range.

6) Higher temperatures, higher speeds and low coverages also lead to tighter water balance ranges.

7) A technique has been found to examine the phase equilibria of fountain solution/ink combinations in the laboratory, which leads to a basic understanding of the ink/water interactions occurring on a lithographic press.

We wish to acknowledge the invaluable help of Dr. Arthur Lowell of Sun Chemical Corporation in performing the phase equilibrium studies that led to many of the important conclusions stated in this paper.

254

REFERENCES

1) Zettlemoyer, A., Buckingham, J.S. and Schaeffer, W.D., J. Coll. Int. Sci. pp. 104 (1963).

2) Kato, Y., Fowkes, F.M. and Vanderhoff J.W., Ind. Eng. Chem. Prod. Res. Dev. Vol. 21, 3 (1982).

3) Padday, J.F. Printing Technology 13 1 (1969).

4) Bassemir, R. and Krishnan, R., GATF International Lithographic Dampening Conference, Itasca Ill Aug. 1986.

5) Bassemir, R. and Krishnan, R., TAGA Proceedings pp. 560-573 (1987)

6) Surland, A., TAGA Proceedings pp. 222-47 (1980)

7) Bassemir, R. and Krishnan, R., TAGA Proceedings pp. 339-353 (1988)

8) Kartunen, S. and Lindquist, V., 15th IARIGAI Conference, Norway (1979).

9) Fadner, T.A. and Doyle, F., ACS Surface and Colloid Symposium N.Y.C. August 1981.

10) Bock, R.F., 10th Int. Conf. of Printing Research Institutes, Banks, W.H. Ed. Pergamon Press (1971).

11) Juhola, H. Lehtonen, T. and Lipponen, M. Graphic Arts in Finland 14, pp. 11-15 (1985).

12) Rosenberg, A., GATF International Lithographic Dampening Conference, Itasca, Ill Aug. 1986.

13) Salminen, P.J., TAPPI Journal, Sept. 1988, pp. 195-200.

14) Perry's Chemical Engineering Handbook.

APPENDIX

Estimation of Evaporation Rate of Water:

The rate of water evaporated from the outside of cylinders into an airstream flowing parallel to the axis of the cylinders at a temperature of 25° C and standard atmosphere may be estimated by the following equation from [14].

 $W = 3.17 X \frac{10^{-8}}{10^{-8}} \frac{u^{0.8}}{L^{0.2}},$

where

 $W = water evaporated, g/cm^2/sec.$

Pw = water-vapor pressure at surface temperature, mm Hg (18)

Pa = partial pressure of water in air stream, mm Hg

u = velocity of air stream, cm/sec

L = length of cylinder, cm

For a surface area of 10,000 $\rm cm^2$ air velocity of 7.5m/sec. and length of 45cm the rate becomes 0.5 $\rm cm^3/sec$.