Optimizing Lithographic Performance-
A Physical-Chemical Approach

R.W.Bassemir* and R.Krishnan*

ABSTRACT:

In order to obtain the best startup performance on a lithographic press, it is postulated that the thermodynamic driving force should have a positive value. An equation to calculate this driving force is derived, which takes into account the surface energies of the litho plate, ink and fountain solution and their polar and dispersion components.

In order to correlate with press performance, particularly at higher speeds, a time scale for the dynamic measurement of surface energy is suggested and the magnitude of some of the times involved in printing is calculated.

From rheological measurements on fountain solution/ink emulsions, it is concluded that thermodynamic stability of such emulsions is desirable for optimum press performance.

INTRODUCTION:

Several phenomenological descriptions of the lithographic process have been given in the literature [1-5]. Surface energy considerations were taken into account first by Padday [6]. He used concepts of work of adhesion and work of cohesion between the image area, non-image area, ink, fountain solution, blanket and paper. A mechanism based on the concept of fracture theory in conjunction with surface energetics was proposed by Kaeble,Dynes and Pav[7].Schlapfer [8]

* Sun Chemical Corp.,Carlstadt,N.J.

used the concept of critical surface tension to explain the mechanism of the lithographic process. Fadner [9] concluded that the viscous and dynamic mechanical forces rather than surface energetics apparently controlled lithography.

The quantitative evaluation of the spreading coefficients of ink and fountain solution on the image and non-image areas of the plate were carried out by Kato, Fowkes and Vanderhoff [10] and by Bassemir and Shubert [11] using separated interfacial forces. In both of the above studies, commercial ink and fountain solution combinations were used, and there were some unfavorable thermodynamic driving forces found. Therefore, the conclusions reached were that mechanical energy factors were necessary to explain the functioning of the existing commercial systems,especially during startup.

Bassemir and Krishnan [12] derived some conditions for optimum lithography. A thermodynamic driving force for good lithographic performance includes ink and fountain solution energetics. In addition, the surface energies of the different areas of the litho plate were combined in a plate constant. Also identified were some ink/fountain solution parameters that should be controlled for best lithographic performance. The equation for thermodynamic driving force was based on the assumption of constant interaction parameters in the Girifalco and Good equation [16]. Because of the assumption in this equation no provision could be made for resolving the polar and dispersion components of surface energy.

It is the intent of this paper to extend these theories and to derive a more generalized equation for lithographic driving force. This should aid in specifying the relationships between the surface energetics of ink, fountain solutions and litho plate to obtain the best press performance. In addition, the effect of the dynamic nature of the press operation on the surface energetics are dealt with quantitatively. Finally, rheological effects on the

thermodynamics and shear stability of emulsions are considered.

Thermodynamic Driving Force for Lithography:

This derivation is based on the assumption that the spreading coefficient of ink on the image area of the litho plate should be greater than that of the fountain solution. In addition, the spreading coefficient of the fountain solution on the non-image area of the plate should be greater than that of the ink. The difference between these speading coefficients yields a driving force per unit length of surface.

Spreading Coeff.$_{(ink/image)}$ >

$$> \text{Spreading Coeff.}_{(FS/image)}$$

or using the definition of Spreading Coefficient with Y=Surface Energy and I=Interfacial Tension

$$Y_{(image)} - Y_{(ink)} - I_{(ink/image)} >$$

$$> Y_{(image)} - Y_{(FS)} - I_{(FS/image)} \qquad (1)$$

Similarly:

Spreading Coeff.$_{(FS/NI)}$ >

$$> \text{Spreading Coeff.}_{(ink/NI)}$$

or as above:

$$Y_{(NI)} - Y_{(FS)} - I_{(FS/NI)} >$$

$$> Y_{(NI)} - Y_{(ink)} - I_{(ink/NI)} \qquad (2)$$

Where NI = Non Image and FS = Fountain Solution

Adding relations 1 and 2 one obtains:

$$I_{(ink/NI)} - I_{(ink/image)} >$$

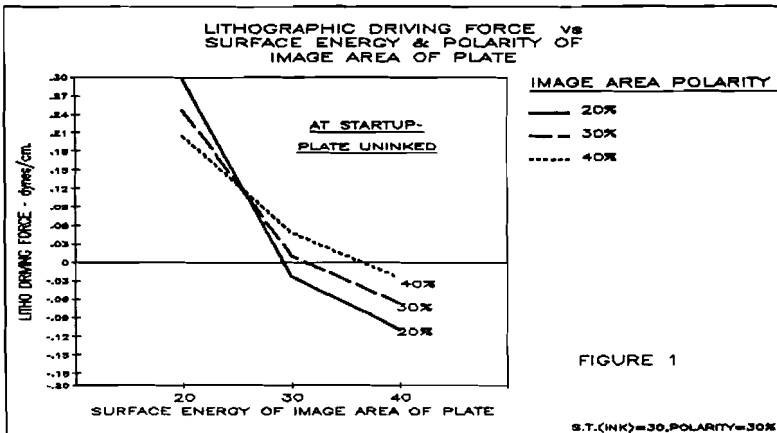$$> I_{(FS/NI)} - I_{(FS/image)} \qquad (3)$$

The difference between the two sides of relation (3) constitutes a thermodynamic driving force for good lithography in a start-up situation. This is due to the importance of the term involving the interfacial free energy of the ink and image area of the plate.In (3),if the interfacial tensions are resolved into polar (p) and dispersion (d) components, one obtains:

$$\text{Driving force} = K_p^d[(\gamma^d_{ink})^{0.5} - (\gamma^d_{FS})^{0.5}]$$

$$+ K_p^p [(\gamma^p_{ink})^{0.5} - (\gamma^p_{FS})^{0.5}] \qquad (4)$$

$$\text{Where, } K_p^d = [(\gamma^d_{NI})^{0.5} - (\gamma^d_{image})^{0.5}] \qquad (5)$$

$$\text{and } K_p^p = [(\gamma^p_{NI})^{0.5} - (\gamma^p_{image})^{0.5}] \qquad (6)$$

K_p^d and K_p^p are the resolved plate constants,which may be used to characterize the efficiency of a litho plate during start-up, either on initial inking of the plate or after prolonged shut downs,during which the plate has been cleaned. While under start-up conditions, the driving force equation (4) should ideally be positive. A plot of driving force versus surface energy of the plate image area is given in Fig.(1) and versus the fountain solution surface energy in Fig.2a

LITHOGRAPHIC DRIVING FORCE vs
SURFACE ENERGY & POLARITY OF
IMAGE AREA OF PLATE

IMAGE AREA POLARITY
——— 20%
— — 30%
······· 40%

AT STARTUP-
PLATE UNINKED

LITHO DRIVING FORCE - dynes/cm.

40%
30%
20%

FIGURE 1

20   30   40
SURFACE ENERGY OF IMAGE AREA OF PLATE

S.T.(INK)=30,POLARITY=30%

However,when the press operator has achieved an equilibrium ink-water balance, we must consider the changes that may have occured in the value of the surface energy of the ink covered image area

on the plate as well as those in the non-image area, which is then saturated with fountain solution. For example, in [17], it is shown that the image area of a photopolymer plate can change its polar component of surface energy dramatically,depending on the composition of the fountain solution with which it is used. For example a Kodak LN plate nearly doubled its polarity in the image area when it was exposed to a fountain solution containing alcohol versus one made with plain water. Therefore, the sensitivity of the image area to fountain solution components may strongly influence the lithographic driving force at startup.Similarly, when at water balance equilibrium, the plate image area will approach the value of the emulsified ink and this value can differ from that of the uninked image area. Also the non-image area will approach the value of surface energy for the fountain solution.

Experiments in this laboratory have shown minimal change in the surface energy of ink/fountain solution emulsions as compared to virgin ink,if they run well on press.Thus as a first approximation,substituting the value of the surface energy of the ink for that of the image area of the plate, and the surface energy of the fountain solution for that of the non-image area, equation (4) becomes:

$$\text{Equil.Driving Force} = 2(Y^d_{ink}\ Y^d_{fs})^{0.5} +$$

$$2(Y^p_{ink}\ Y^p_{fs})^{0.5} - Y_{fs} - Y_{ink} \qquad (7)$$

$$= -\text{Interfacial Tension}$$

The equilibrium driving force equation is seen to be equivalent to the negative of the interfacial tension between the ink and fountain solution. Under equilibrium running conditions, this driving force equation (7) should ideally approach a maximum(a very small negative value). Thus this indicates that a low interfacial tension is desirable to obtain the maximum equilibrium driving force.(see Fig.2b)
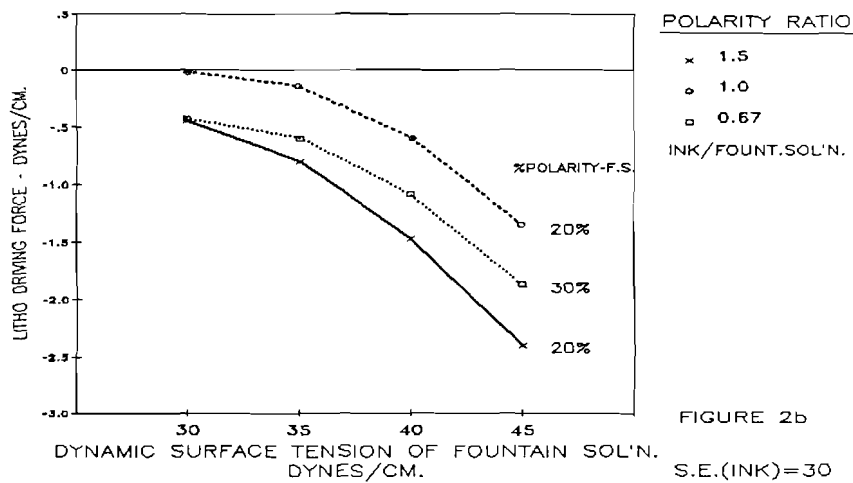
Dampening Systems:

It should be recognized at the outset that

STARTING DRIVING FORCE
vs DYNAMIC SURFACE TENSION and
POLARITY of FOUNTAIN SOL'NS.

FIGURE 2a
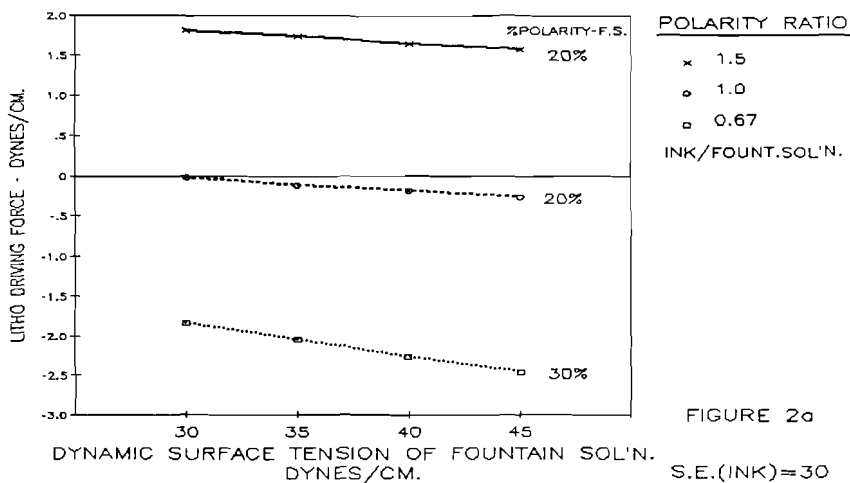
EQUILIBRIUM DRIVING FORCE
vs DYNAMIC SURFACE TENSION and
POLARITY of FOUNTAIN SOL'NS.

FIGURE 2b

565

many commercial ink/fountain solution combinations that are performing commercially in a more or less satisfactory fashion may not be truly optimum in a thermodynamic sense. One might readily ask why they then seem to perform as well as they do? It is clear that the mechanical energy input of the press system, including the high energetics in the various nips must play an important part in overcoming the unfavorable thermodynamics of these marginal systems. In addition, some commercial dampening systems are particularly forgiving of mediocre dampening solutions and others are particularly demanding that the dampening solution be optimized for surface energetics. This may explain the prevalent use of isopropanol in fountain solutions used with certain dampening systems since the alcohol has an exceptional effect in optimizing the physical properties of the fountain solution. Thus, it may be inferred that fountain solutions can be tailored for a given dampening system or conversely that a truely optimum fountain solution may work well with any dampening system, however demanding the design.

Effect of Press Speed on Surface and Interfacial Tensions

The surface and interfacial free energies which are used to calculate the driving force (equation 4) are usually altered by surface active constituents. These could be due to resin systems and additives used in inks ,as pointed out by Carlick [13] or to surfactants which are used in the fountain solution [14].

The ink and fountain solution surfaces and the ink/fountain solution interface are constantly being renewed by the mechanical action on the press. The time for surface renewal can be calculated from the speed and geometry of the press. Thus, for a press operating at 2000 ft/min. with a plate circumference of about 25 inches, the surface renewal time is much less than 60 milliseconds, depending on the number and spacing of the form rollers contacting the plate.

As the surfaces are renewed, the surface active species will diffuse from the bulk of the

fluid to the interface. This diffusion time (t)
may be estimated [see Appendix A] as:

$$t = x^2/D \qquad\qquad (8)$$

where, x = the thickness of the fountain
solution on the plate surface.
$\qquad\qquad\qquad\qquad$ D $\quad$ = $\quad$ the $\quad\quad$ diffusion
coefficient of the surface active materials
present.

For a film thickness of 1 micron, and a
surfactant with a diffusion coefficient of 10^{-11}
m^2/sec., the diffusion time equals 100
milliseconds. This diffusion coefficient
magnitude is typical of many nonionic
surfactants.

Since the diffusion time is greater than the
time available for surface renewal, the surface
would behave as one with a reduced amount of
surfactant under these dynamic press conditions.
Fig.(3) shows a plot of Log diffusion time vs
diffusion coefficient for several fountain
solution film thicknesses.

Thus the surface free energy of the ink and
the fountain solution should really be measured
under dynamic conditions creating a surface age
similar to the press surface renewal times if we
are to correlate well with press performance.

The results of a number of experiments
conducted on a 25 inch sheetfed press equipped
with Dahlgren dampening and using a series of
fountain solutions with varying dynamic surface
tension and one ink are shown in Figure 4. It
is apparent that as the dynamic surface tension
of the fountain solution decreases, the range of
water balance obtained between scumming and
washout increases. The total feed rate of the
fountain solution is also decreased as the
fountain solution dynamic surface tension
decreases.

For the experiments described in Figure 4,
the speed of the press was 5500 iph with a plate
circumference of 24 inches. Thus, the surface
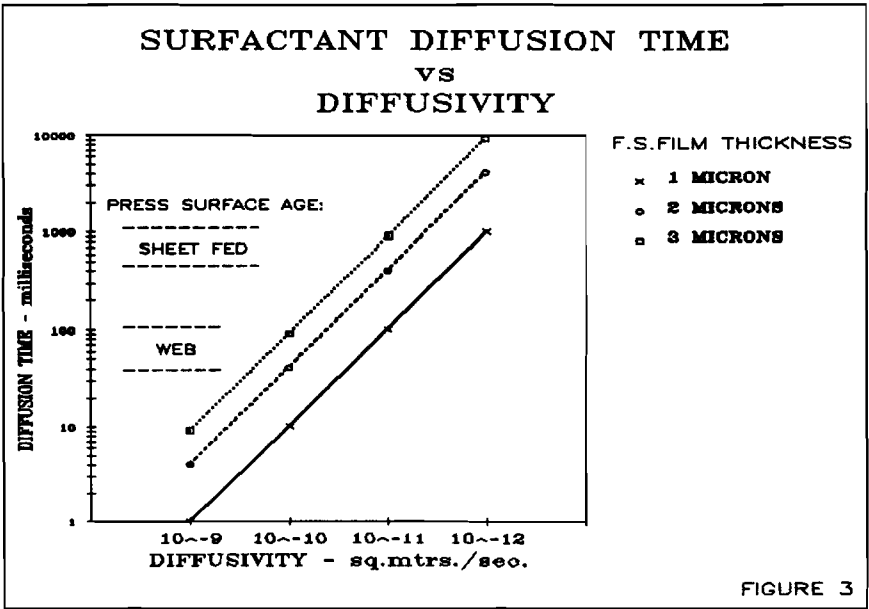renewal speed was in the order of 1000

SURFACTANT DIFFUSION TIME
vs
DIFFUSIVITY

F.S.FILM THICKNESS

x 1 MICRON
o 2 MICRONS
□ 3 MICRONS

PRESS SURFACE AGE:

SHEET FED

WEB

DIFFUSION TIME - milliseconds

DIFFUSIVITY - sq.mtrs./sec.

10^-9   10^-10   10^-11   10^-12

FIGURE 3

PRESS WATER BALANCE vs
DYNAMIC SURFACE TENSION
of FOUNTAIN SOLUTIONS

WATER BALANCE(RHEOSTAT SETTING)

| BREAK
| CATCH UP

FS1   FS2   FS3   FS4   FS5   FS6   FS7   FS8
43.6 40.9 40.3 38.8 37.5 35.2 33.2 31.9
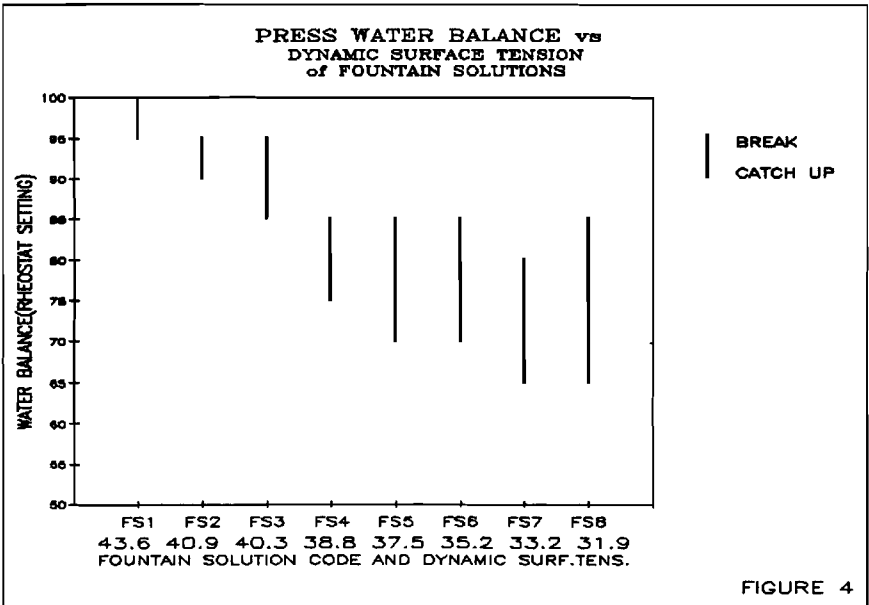FOUNTAIN SOLUTION CODE AND DYNAMIC SURF.TENS.

FIGURE 4

568

milliseconds. The dynamic surface tension readings in this case were therefore taken at a similar speed using 1 bubble/second on a Sensadyne Tensiometer.

Rheology of Ink, Fountain Solution and F.S./Ink Emulsion

The viscosity of the fountain solution will influence the transference of it to the plate and can affect the thickness of the film of fountain solution on the plate, which in turn alters the diffusion time and hence the dynamic surface tension.

Increasing elasticity of the ink reduces the dynamic interfacial tension between ink and fountain solution, and is therefore desirable for increased emulsion stability [12, 15]. Because of this, it may be important to evaluate ink vehicles with regard to their effect on the normal stresses. Many gelled vehicles can exhibit large normal stresses and therefore, improve not only the rheology of the ink, but also its inherent lithographic efficiency.

Perhaps the most important properties are those pertaining to the rheology of the emulsion of fountain solution in ink as the volume fraction of the internal phase is increased. Experiments on a composite heatset vehicle with emulsified fountain solution indicate that a microemulsified vehicle has a lower viscosity than a macroemulsified vehicle at the same volume fraction of fountain solution.In addition,the fracture shear rate of the microemulsion was 5000 sec^{-1} greater than the fracture shear of the macroemulsion.Significantly,the vehicle forming the microemulsion performed better on press,having a wider water balance and a lower water feed than the one that formed the macroemulsion. The data obtained are shown below.

Sample	App.Viscosity @3000sec^{-1} Poises@25C.	Clarity	Fracture Shear Rate
Neat Ink Vehicle	37.4	Clear	5200
10% F.S.MacroEmulsion	37.	Cloudy	3000
10% F.S.MicroEmulsion	22.6	Sl.Haze	8000

Thus for optimum transfer and printability of an F.S./ink emulsion, it would seem that the fountain solution should form a microemulsion in the ink, thus implying a thermodynamically stable emulsion.

Stability of Emulsion

A study of the lithographic literature invariably raises the question of whether stable fountain solution/ink emulsions are desirable on a press. In order to properly answer this question, it is necessary to examine some of the various types of emulsion stability and relate these to conditions that we might encounter in a press room.

Types of Emulsion Stability

1. Shear or Mechanical Work Stability

2. Thermal Stability

3. Compositional Stability

4. Time or Age Stability

If we examine these types of stability, we should be able to relate them to conditions that occur on the press.

Shear or Mechanical Work Stability

High energy input occurs in the press nips and the emulsion is subjected to a partial vacuum when passing through these nips, thus creating the possibility of coagulation of the internal phase at each nip on the press where the emulsion exists. Emulsions may, therefore, be created or destroyed under these severe conditions of agitation and unstable emulsions can break out large quantities of fountain solution on the rollers which may lead to roller stripping, particularly if the rollers have any residual hydrophilic glazing deposits.

Thermal Stability

The large amount of mechanical energy that is input to high speed presses is partly converted to heat which is never completely dissipated by the cooling effect of the tempering water in the press ink rollers or the evaporative cooling of the fountain solution. This residual heat can affect the stability of the ink/fountain solution emulsion adversely by encouraging the coagulation of the aqueous phase, thus breaking the emulsion. It has been shown in our laboratory experiments that increasing temperatures only 15 - 25 deg.C. can reduce the stability of many fountain solution/ink emulsions.

Compositional Stability

By this we are inferring that as the volume fraction of the internal phase is increased, a point will be reached where the emulsion will break and invert. On the press, there are areas on the surface of the printing plate where an excess of fountain solution is present and these occur at the interface between the image and non-image areas. Thus, it is possible that a small amount of inversion may occur which can cause flotation on or tinting of the fountain solution. Obviously, if the ink/fountain solution combination produces a more stable emulsion, the likelihood of this occurring would be minimized.

Time Stability

It is known that many emulsions can coagulate upon aging, but normally the time spans involved are exceedingly long by comparison with the time spans encountered on a printing press. Thus these should not be relevant to the stability of those emulsions formed on press. This type of stability can be important however, when considering pre-emulsified inks particularly those made in the laboratory to evaluate emulsion rheology and other physical parameters.

CONCLUSIONS:

1. For optimum startup performance on a lithographic press, the thermodynamic driving force defined in equation (4) should ideally be

positive. For optimum running performance, the interfacial tension between the ink and fountain solution should be low. Thus at equal polarity, this implies a fountain solution surface energy at least close to or even lower than that of the ink. This is particularly important on presses with dampening systems that do not mechanically encourage the formation of good emulsions and also those which operate at slower speeds.

2. Ink/fountain solution systems with unfavorable thermodynamic driving forces can still be printed reasonably well on certain energetically favorable dampening systems and presses. However, truly optimum performance even on presses of this type, should be obtained when the driving forces are favorable,as described in conclusion 1 above.

3.Good stability of ink/fountain solution emulsions is generally desirable for optimum lithographic performance and in particular, the shear and thermal stabilities, which are those most influenced by press mechanical conditions.

4. It appears that ink/fountain solution combinations having low interfacial tensions tend to perform better in a lithographic sense, because of the tendency to form microemulsions which this condition encourages.

5. There is evidence that lower dynamic surface tension of the fountain solution helps to decrease water feed and widen the water balance range.

6. A resolution of the dispersion and polar components of the surface energy provides some important additional parameters to correlate inks, fountain solution and plates with press startup performance.

References

1. MacPhee, J., TAGA Proc, 237 (1979).

2. Bock,R.F."10th International Conference

of Printing Research Institutes",Banks, W.H. Ed; Pergamon Press (1971).

3.   Wilkinson,   M.C.;   Aronson,   M.P., Vanderhoff,   J.W.; Zettlemoyer, A.C., Adhesion Sci. Technol. 9b, 725 (1975).

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

5. Bassemir, R.W., American Ink Maker, 33ff Feb. (1981).

6.   Padday, J.F., Printing Technol. 13(1) 23-31 (1969).

7.   Kaeble, D.H.; Dynes P, J. and Pav, D., Adhesion Sci. Technol. 9b, 735-761 (1975).

8.   Schlapfer, K.   13th IARIGAI Conference, Banks, W.H. Ed. pp 85-100 (1977).

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

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

11. Bassemir, R. W. and Shubert, F., TAGA Proc. (1982).

12.   Bassemir, R.W. and Krishnan, R., GATF International Lithographic Dampening Conference, Aug.1986, Itasca, IL.

13. Carlick, D. J., American Ink Maker, Dec. (1984).

14.   Smith,   D.E.,   1977 Annual Research Department Report, GATF, Pittsburgh, PA 135-144 (1979).

15.   Vanoene, H., J. Colloid Interface Sco. 40, 448 (1972).

16.   Girafalco and Good, J. Phys. Chem. 61, 904 (1957).

17.   Bassemir R.W.,and Shubert F.,TAGA Proc.p 555 (1984).