SURFACE ENERGY MEASUREMENTS OF LITHO INKS AND DAMPENING SOLUTIONS AS PREDICTORS OF PRESS PERFORMANCE.

Robert W. Bassemir and Fred G.Shubert
Sun Chemical Corp.

ABSTRACT: In continuation of some work previously reported (TAGA-82), studies have been made of the surface energy of a litho plate and inks in combination with dampening solutions containing isopropanol or an alcohol substitute. Spreading coefficients and work of adhesion for inks and dampening solutions in relation to the image area have been found to be more important than interfacial tension in predicting performance on press.

The spreading coefficients,emulsification behavior of a number of lithographic inks with different dampening solutions containing isopropanol or alcohol substitutes were determined in order to correlate these parameters to known press behavior patterns. It was found that the spreading coefficient of the ink on the dampening solution did relate to ink flotation problems on press.

The physical properties, dynamic and static surface tensions, and viscosities of several alcohol substitutes were determined and the important role of dynamic surface tension and viscosity of these materials in good press performance is discussed.

Introduction

Surface energy measurements of lithographic inks,plates and dampening solutions have provided us with a working model of the Lithographic process.(Bassemir & Shubert (1)) This original study compared the 3 phase interaction of the above materials and the results were reflected in the spreading coefficients for ink and dampening solution on the image and non-image areas of the plate.

In this paper, the effects of alcohol and an alcohol substitute on spreading coefficients are described. The Work of Adhesion has also proven to be an important parameter in attempting to understand these interactions.

Materials used:

1) Kodak LN plate exposed and developed in the same manner as in the original study.
2) Roso G7AV-spec.combo dampening solution
3) A-1 and C-4 inks from the original study.
4) 12 heatset web offset inks
5) 5 commercial alcohol substitutes

Instruments used:

1) Model A101 Rame' Hart goniometer with environmental chamber for contact angle measurements. These were reproducible to at least ±1 degree.

2) DuNouy ring tensiometer for static surface tension measurements.

3) Chemdyne Research Corp.'s Sensadyne 5000 max. bubble pressure tensiometer.

a) Static readings were taken at 0.033 bubbles/sec.

b) Dynamic readings at 2.5 bubbles/sec. or 400 millisec.

4) Emulsification test apparatus-Sun Chemical

Procedure:

1) Contact angle measurements were made in the environmental chamber with a saturated atmosphere dependent upon the dampening solution used. Inks and dampening solutions were measured on both the image and non-image areas.

2) Surface tension readings were taken on both DuNouy and Chemdyne instruments using a minimum sample of 50 ml. and "static" readings correlated well.(Bubble speeds of 30 secs.)

Table I

Surface energies (ergs/sq.cm.):

Dampening soln.	Total	Dispersion Comp.	Polar Comp.
Rosos/Water(1)	45.8	25.7	20.1
Rosos/BC/Water(2)	37.4	22.1	15.3
Rosos/IPA/Water(3)	33.0	19.1	13.9

(1) will be referred to as DS#1
(2) " " " " " DS#2
(3) " " " " " DS#3

IPA = Isopropyl alcohol 20% v/v
BC = Butyl cellosolve 3% v/v
Rosos conc. = 3 ozs./gal.

Inks	Total	Dispersion Comp.	Polar Comp.
A-1	32.5	25.2	7.3
C-4	31.9	26.1	5.8

Surface energies of the inks and dampening solutions were determined as previously described in our original paper(1).

Surface energies of the image and non-image areas of the plates were calculated using Wu's Harmonic mean equation based on the contact angles of Water and Methylene Iodide measured under the appropriate atmospheric conditions(2)

Discussion: As one can readily see, the non-image area shows relatively little change in the polar and non-polar components regardless of the atmosphere (Table II),and the total value is similar to that of water.

Table II - Kodak LN plate - Non-image area

Surface energies -(ergs/sq.cm.)

Chamber Atmosphere	Total	Dispersion Comp.	Polar Comp.
DS#1 atmos.	72.6	21.8	50.8
DS#2 atmos	72.1	21.0	51.1
DS#3 atmos.	71.7	22.2	49.5

The image area on the other hand shows dramatic differences, especially in the polar component of the surface energy. This increase in polarity is a result of the adsorbed organic species from the dampening solutions, causing an increase in their spreading coefficients on the image area. There is also little change in the work of adhesion for these dampening solutions, indicating an increase in their respective interfacial tensions.(Table III)

Table III - Kodak LN plate - Image area

Surface energies -(ergs/sq.cm.)

Chamber Atmosphere	Total	Dispersion Comp.	Polar Comp.
DS#1 atmos.	46.7	33.4	13.3
DS#2 atmos.	53.9	28.4	25.5
DS#3 atmos.	66.2	30.2	35.9

Although the dampening solutions wet the image area with greater efficiency as the surface tensions decrease, the work of adhesion shows that there are no real differences in displacing any one of them from the image area with ink. (Table IV)

Table IV

Surface energy of dampening solutions and their spreading coefficients on the Kodak LN Image area in different atmospheres - (ergs/sq.cm.)

Atmosphere	DS#	Surface Tension	Spr.Coeff.	Wa
DS#1	1	45.8	-1.5	90.1
DS#2	2	37.4	13.2	88.0
DS#3	3	33.0	20.9	86.9

Let us now compare the effects of these dampening solutions when interacted with an ink on the image area. For comparative purposes we looked at the initial inking process and then the final inked image to see the changes in both the spreading coefficients and the works of adhesion for the C-4 ink.

Definitions:

1) Work of adhesion = Wa
   The work required to seperate two materials in intimate contact with each other.
2) Work of cohesion = Wc
   The work required to create an interface within a homogeneous material or twice the surface tension.

The equations used were:

1)Wa(ink)= Wa(ink/ds)+Wa(ink/plate)-Wa(ds/plate)

2)Wa(ds)=Wa(ds/ink)+Wa(ds/plate)-Wa(ink/plate)

3) Sc(ink)= Wa(ink) - Wc(ink)

Table V

Image on Initial inking (ergs/sq.cm.)

Dampening soln.	Sc(ink)	Wa(ink)	Wa(ds)
#1	-14.2	53	91
#2	-13.8	50	79.4
#3	-6.6	57.2	63.8

In the initial inking stage, all inks have a negative spreading coefficient regardless of the dampening solution used, and in all cases the Wa(ds) > Wa(ink). The Wa(ds) decreases as the surface tension of the dampening solutions decrease.(Table V)

Table VI
Image on final inking -(ergs/sq.cm.)

Dampening soln.	Sc(ink)	Wa(ink)	Wa(ds)
#1	4.9	68.7	70.9
#2	0	63.8	65.6
#3	0	63.8	57.2

In the final stage, the Sc of the C-4 ink becomes positive with DS#1 and Wa(ds) > Wa(ink);these values are almost equivalent indicating competition for the image area. With DS#2 & #3 the spreading coefficient is now zero for both. Although this is the ideal wetting condition, a distinction can't be made as to which DS will function better. We must look to another parameter, that is the work of adhesion.(Table VI)

DS#3 with IPA not only allows for excellent wetting, but provides a work of adhesion on the image area which is less for the DS than for the ink. This is a desirable condition to insure the proper inking of the image area, and may explain why Isopropanol is such an efficient fountain additive. To date, isopropanol is the only additive found thus far to fufill this condition.

DS#2 with butyl cellosolve also allows for good wetting, but here the work of adhesion of the dampening solution for the image area is slightly greater than the work of adhesion of the ink.The competition for the image area has again increased, which would indicate that the butyl cellosolve is not as efficient as isopropanol.

Table VII

Spreading coefficients,Work of adhesion and interfacial tensions of the C-4 ink on the various dampening solutions.(ergs/sq.cm.)

Dampening solution	Sc	Wa	Interfacial tension
#1	6.0	69.8	7.9
#2	0.9	64.7	4.6
#3	-3.3	60.5	4.4

In addition, Table VII shows very graphically that IPA also provides a negative spreading coefficient and a Wa(ink/ds) that is less than the Wc of C-4 itself.(Wc of C-4 ink = 63.8 ergs/sq.cm.) This should allow for a much cleaner running plate; less tinting and scumming.

Table VIII

Contact angles of water and methylene iodide on the Kodak LN image and non-image areas under different atmospheres:(Degrees)

	Non-image		Image	
Atmosphere	H_2O	CH_2I_2	H_2O	CH_2I_2
DS#1	4	52	70	32
DS#2	8	54	52	39
DS#3	10	51	31	31

Table IX

Surface energies of materials used in this study:(ergs/sq.cm.)

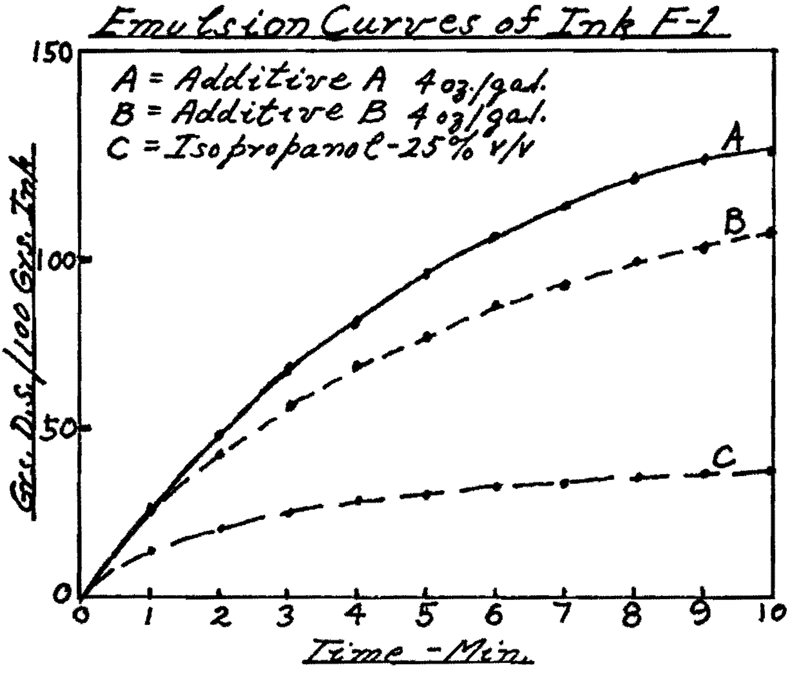
		Surface Energy	
Material	Total	Dispersion	Polar
Isopropanol	21.1	12.5	8.6
Butoxyethanol	26.9	21.4	5.5
2-ethyl 1,3, hexanediol	30.1	25.1	5.0
Dipropylene Glycol	33.0	23.4	9.6
Water	72.8	22.1	50.7
Rosos G-7AV Spec.combo	30.3	25.6	4.7

Press Performance of Alcohol Substitutes:

Using ink F-1, a commercial printer had experienced lithographic problems when switching from isopropanol as a dampening solution additive to two other additives sold as alcohol substitutes. The problems encountered were tight water balance and flotation on the surface of the water fountain, which at times also caused contamination of the dampening rollers with ink.

Emulsification rate curves were run using the procedure of Surland (4) and are shown in Fig. 1. In this case, the failure of the ink to reach an equilibrium in water uptake with additives A and B is the likely reason for the poorer litho performance. The isopropanol curve shows a more normal equilibrium water takeup and would be expected to perform better on press from a lithographic standpoint.

Figure 1



Spreading Coefficient Correlation:

The spreading coefficients of ink on dampening solution were calculated from measurements made using the techniques described previously (1) The values obtained for the ink used in Fig. (1) are in Table X.

Table X

Additive	Spreading Coefficient
A	+4.5
B	+3.5
C(Isopropanol)	-0.7

In this case the ink had positive spreading coefficients on both dampening solutions which contained alcohol substitutes and a slightly negative one on the solution containing Isopropanol. This would seem to correlate with the press problems showing ink flotation in the dampening system with A and B and none with C, since a negative coefficient generally indicates a tendency to resist spreading.

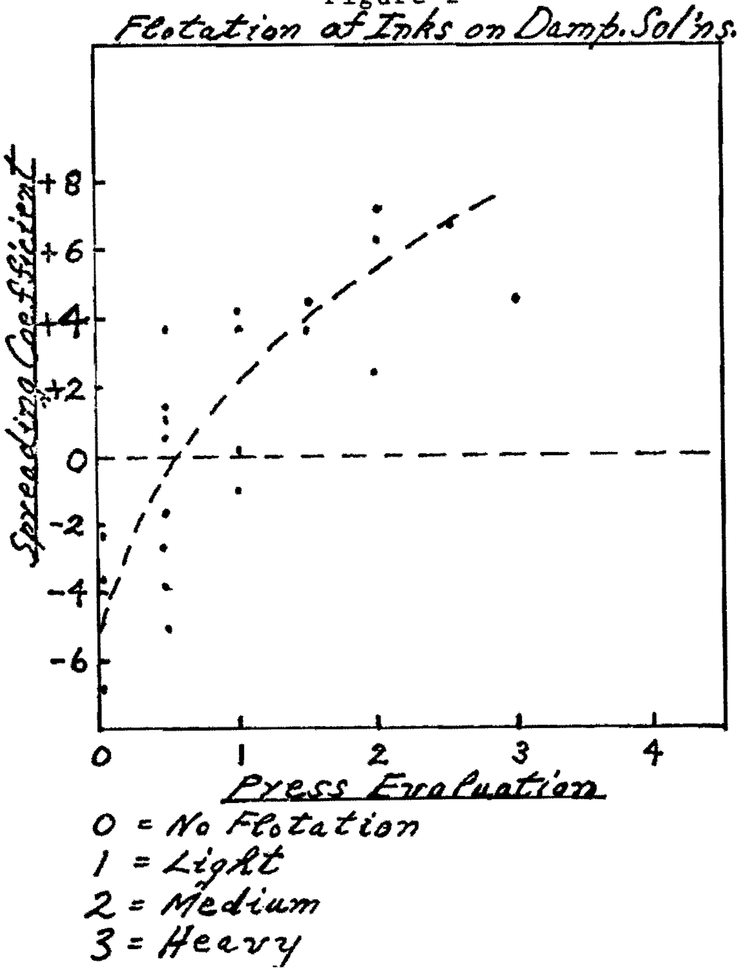
Further spreading coefficient tests were made with over 20 additional ink/dampening solution combinations. A subjective evaluation of ink flotation in the press dampening system was also made during press runs of these inks. The spreading coefficients were plotted vs. the subjective evaluation of ink flotation and are given in Figure 2.

Here the correlation still seems to exist, although there is considerable scatter in the data. No doubt some of this is due to the subjective visual determination of the degree of ink flotation in the dampening system. In general it seems that the higher positive spreading coefficient values correlate with poorer press performance in regard to ink flotation,and negative spreading coefficients with little or no ink flotation.

Study of Dampening Solution Additives:

During the past several years, we have had occasion to analyze an increasing number of dampening solutions and additives for use with ink train dampeners. This has been done in order to better understand the chemical nature of these materials and their consequent effect on our ink formulations. In particular the number of additives to be used as substitutes for alcohol has proliferated

Figure 2



(5). The results revealed a wide variety of solvents and blends of solvents being used in substitutes for isopropanol. However, there were several solvents which seemed to occur with greater frequency in the samples we examined and it was decided to examine the physical properties and surface chemistry of these in more detail.

One of the effects that should be of concern on a production press is the dynamic nature of the dampening process. The higher speeds being encountered necessitate the examination of possible dynamic effects on surface energetics of the system. Both Fadner (6) and Lyne (7) have indicated the importance of dynamic surface tension measurements of dampening solutions, and the fact that some wetting agents and surfactants with bulky molecular structure show little or no effect on dynamic surface tension.

As an example of this,we encountered one poorly performing proprietary fountain solution which proved to contain fairly large amounts of surfactant. Measurement of this solution on the Sensadyne at 30 sec. and 0.4 sec..bubble rate gave surface tensions of 40 and 70 dynes/cm. respectively.The latter reading is nearly as high as plain water. Aside from Isopropanol, four other solvents were chosen for investigation since they did occur in a number of commercially available alcohol substitutes. They are listed in Table XI along with some of their relevant physical properties.

Obviously these compounds are very much lower in volatility than isopropanol which was certainly one reason for their selection, along with their low surface tension. The solubility parameters are all high, with the notable exception of Butyl Cellosolve, which is one of the most popular of these additives. The lowered value may well be due to intramolecular hydrogen bonding, which can take place with this molecule.

Table XI

Additive	BP- C	VP-mm	Rel.Vol.	Surf. Tens.	Sol.Par.
IPOH	82	33	2.3	21.1	11.5
Butyl Cellosolve	171	0.6	0.07	26.9	9.9
2Ethyl 1,3 HexaneDiol	243	< 0.1	< 0.01	30.1	11.2
DiprGlycol	233	< 0.1	< 0.001	33.0	11.6
1,6 Hexane Diol	250	< 0.1	< 0.001	n/a	11.7

Note: S.T.is the DuNouy surface tension @25 C

Table XII lists viscosity and surface tension data taken at different rates of surface formation. The good agreement between the DuNouy static values and the low speed (30/sec/bubble) Sensadyne values is evident and increases our confidence in the bubble pressure technique as a useful method for both "static" and dynamic measurements of surface energy.

The viscosity data are notable for the relatively high viscosities of the isopropanol and its solutions which may be a factor in its generally superior performance on press.

TABLE XII

Solution	Viscosity	Surface Tension-dyne/cm		
	cps@25 C	DuNouy	Sensadyne	
			30sec.	0.4sec.
1.100% Water	0.95	72.8	72.8	72.8
2.100% IPOH	2.00	21.1	21.1	21.1
3.15%IPOH/H2O	1.35	36.2	36.4	38.2
4.3%ButCello. in H2O	0.95	41.6	41.5	41.6
5.3%2Ethyl 1,3 HexanDiol	1.06	33.0	32.8	32.8
6.4%1,6Hexane Diol	1.35	39.0	40.9	47.5

It is worth noting that the viscosity of 20% IPOH, another commonly used concentration in dampening solutions is 1.8 cps @ 25 C. This is nearly as high as pure IPOH and much greater than the substitutes at their recommended concentrations in water. The 1,6 hexanediol is somewhat higher in viscosity but has a definite problem in not effectively lowering dynamic surface tension. This indicates a slower rate of diffusion to the surface than the other substitutes and would be expected to perform poorly on higher speed presses. The better dynamic surface tension behavior of Solution #4 and #5 may be due to faster diffusion of the more compact intramolecularly hydrogen bonded molecules as compared to Solution #6.

Conclusions:

1. Isopropanol as a dampening solution additive will provide a much cleaner running

plate due to the decreased Wa on the image area and the negative spreading coefficient of the ink on the dampening solution.

2. These results indicates that the interfacial tension is not the key parameter in determining the performance of a lithographic ink .

3. Although Butyl Cellosolve is a widely used alcohol substitute, it does not show a favorable Wa in combination with the ink Wa on the image area of the plate.

4. The non-image area of the plate always has a surface energy comparable to the value for water, regardless of which additive is used in the dampening solution.

5. The spreading coefficient of ink on dampening solution appears to be a useful predictor of ink flotation on litho presses.

6. The bubble pressure technique gives an indication of dynamic surface effects and when extended to faster bubble rates should be even more useful.

7. The viscosity of dampening solutions for ink train dampeners may be another important parameter in determining press performance.

8. The behavior of alcohol substitutes in effectively lowering dynamic surface tension of dampening solution is a critical parameter in their performance on press.

Literature References

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