

THE ROLE OF WETTING IN PRINTING

F.J. Micale, S. Iwasa, J. Lavelle,
S. Sunday, and J.M. Fetsko
National Printing Ink Research Institute
Sinclair Lab., Bldg. #7
Lehigh University
Bethlehem, PA 18015

INTRODUCTION

Wetting is an important factor in printing for controlling printability no matter what printing process is involved in the ink transfer. The problem has been to identify both the mechanism whereby wetting influences ink transfer, and the measurable physical parameters which relate to ink transfer and printability. The purpose of this paper is: to present selective equations, not all of which are universally accepted, which relate physically measurable parameters to wetting; to propose limitations and physical interpretations of the theory; to present data related to lithographic and flexographic printing; and to correlate the wetting results to at least preliminary laboratory ink transfer experiments.

The theoretical approach and the experimental results presented in this paper are intended to identify and evaluate meaningful methods for the characterization of the surface tension and wetting properties of solid surfaces and inks, and to provide the knowledge to determine how and in what direction to control the surface or interfacial properties of the inks. The long range objectives of the theoretical approach and of the line of research presented in this paper are to provide the tools for the ink formulator in the form of test methods designed to elucidate the total characterization of the surface tension of interfaces, and to provide the knowledge which relates surface tension to wetting and wetting to printability.

An additional problem addressed in this paper is the formulation of water based flexographic printing inks for nonpermeable substrates such as filmbase materials. Water based inks on nonpermeable surfaces present unique problems which are not generally common for solvent inks. Water is a highly polar solvent with a high surface tension compared to organic solvents. Although water based inks can be formulated to yield equilibrium surface tension values similar to solvent inks, ink transfer in the nip occurs in fractional seconds where the instantaneous surface tension of the water based ink is high and presents wetting problems. Experimental approaches designed to understand the nature of this problem will be proposed.

THEORY OF WETTING

The definition of wetting involves concepts which relate to how a liquid interacts with a solid surface. The experimentalists over the years have attempted to evaluate the magnitude of this interaction by contact angle measurements of the liquid drop on the solid surface, i.e. low contact angle results from high degree of interaction and high contact angle is indicative of low degree of interaction. The theoretician attempts to quantify this interaction by means of mathematical expressions which are, at least in part, based on their perceptions of the physical laws of nature. Since not all perceptions are the same, different equations have appeared in the scientific literature to define the solid/liquid interfacial tension, which is the result of a liquid interacting with a solid, as a function of the surface tension properties of the solid and liquid phases. It is not the purpose of this paper to review the different theories, but rather to present one theory and attempt to evaluate the utility of that theory. A comprehensive literature survey (1) has been published by one of us, Fetsko, which reviews the different theories of wetting and includes references for the equations presented below.

1. Solid/Liquid Interfacial Tension

The geometric mean theory (2) defines the interfacial tension, γ_{sl} , between a solid and a liquid, or between two immiscible liquids, according to the following equation:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2 (\gamma_s^d \gamma_l^d)^{1/2} - 2 (\gamma_s^p \gamma_l^p)^{1/2} \quad (1)$$

where

γ_s = the surface tension of the solid,

γ_l = the surface tension of the liquid,

γ_s^d = the dispersion component of surface tension of the solid,

γ_l^d = the dispersion component of surface tension of the liquid,

γ_s^p = the polar component of surface tension of the solid,

γ_l^p = the polar component of surface tension of the liquid.

The dispersion components of surface tension are non-specific in the sense that the dispersion component of surface tension of one material will always undergo total interaction with the dispersion component of surface tension of another material. If, for example, a solid and a liquid were to possess only dispersion components of surface tension and they were of equal magnitude, then Equation 1 would predict that the resulting interfacial

tension would be equal to zero. If the surface tensions were not equal, then the resulting interfacial tension would be greater than zero.

The polar components of surface tension, however, are by definition specific in nature. The types of interactions which may result from polar components include acid-base, hydrogen bonding, and polar interactions. Since polar interactions are specific in nature, an interaction may or may not occur between the polar components of the solid and the liquid. For example, a strongly acidic polar component would be expected to undergo total interaction with a strongly basic polar component, and zero interaction with a strongly acidic polar component. All levels of intermediate degrees of interaction, of course, are possible. Equation 1 predicts that the solid/liquid interfacial tension will be reduced to the extent that the polar components of surface tension undergo interaction.

Experimental evaluation of the dispersion and polar components of surface tension depend upon direct measurement of the surface tension of the liquid, i.e. the total surface tension, and the contact angle of the liquid, θ , on the solid surface. The calculations assume that the total surface tension is equal to the sum of the components of surface tension and assume the validity of the Young Dupre Equation:

$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta \quad (2)$$

The procedure for evaluation of the surface tension components of an unknown liquid is to measure directly the surface tension of the liquid and the contact angle of that liquid on a solid surface of known surface tension which contains no polar component of surface tension. The solid surface used for the calculations in this paper is a commercial grade of polyethylene which has a surface tension of 36 dynes/cm, and contains no polar component of surface tension. The procedure for evaluation of the surface tension components of a solid surface is to measure the contact angles of one liquid which is known to contain no polar component and another liquid of known dispersion and polar component of surface tension. The two liquids used for the results reported in this paper are 1-bromonaphthalene, which has a surface tension of 44.6 dynes/cm and contains no polar component, and water which has dispersion and polar components of surface tension of 21.8 and 51.0 dynes/cm, respectively.

This method is used to calculate the magnitude of the dispersion and polar components of surface tension of the liquids and solids reported in this paper, but does not imply any knowledge concerning the nature of the polar component of surface tension. Since polar components are by definition specific in nature, a liquid in contact with a solid may or may not undergo polar component type interactions depending upon the nature of the

polar components of the two phases. The last term in Equation 1 predicts the decrease in the solid/liquid interfacial tension when the polar components of the two phases are undergoing total interaction.

2. Application of the Theory

The driving force for evaluating the dispersion and polar components of surface tension of solids and liquids is to predict the solid/liquid interfacial tension which is so important in wetting theory. The above theory permits two different methods for calculating this interfacial tension depending upon what information is available. A comparison of the results of these two methods is important for obtaining knowledge concerning the nature of the polar interactions.

Method A - Experimental

The Method A calculation of the solid/liquid interfacial tension, γ_{sl} is based upon Equation 2 which is solved for γ_{sl} . The surface tension of the liquid and the contact angle of that liquid with the solid surface of interest must be measured. The total surface tension must be determined from evaluation of the dispersion and polar components of surface tension, as presented above.

Method B - Theoretical

The Method B evaluation of the solid/liquid interfacial tension involves the use of Equation 1. Implicit in the use of Equation 1 is the assumption that the polar components of surface tension of the liquid and the solid totally interact since the last term in Equation 1 results in a decrease in the solid/liquid interfacial tension due to this interaction. If, however, the respective polar components undergo zero interaction, e.g. a strong acid interaction with a strong acid, then there should be no decrease in the solid/liquid interfacial tension due to polar component interaction and the last term in Equation 1 should be equal to zero. Method B of the solid/liquid interfacial tension results are presented in this paper in the format of a range where the minimum value assumes total interaction of the polar components and the maximum value assumes zero interaction of the polar components.

Comparison of Methods A and B

There is a fundamental difference between the interfacial tensions calculated from Method A and Method B. Method B calculates the interfacial tension from experiments with test liquids and test solids for evaluation of the dispersion and polar components of solids and liquids, respectively. The results are entirely theoretical in the sense that the liquid is

not brought into contact with the solid for the calculations of interfacial tension. Method A, however, is based on the contact angle measurement of the liquid with the solid, and the calculations obtained from this method are considered to be the experimental result of the liquid interacting with the solid.

The interpretation of results based on the two methods is as follows. If the Method A value is at the low end of the Method B range, than the conclusion is drawn that the polar components of each phase are undergoing total interaction. If the Method A value is at the high end of the Method B range, than the conclusion is drawn that the polar components of each phase are undergoing zero interaction. Experiments are in progress to prepare and evaluate test surfaces and test liquids, where the nature of polar components of each are known. This approach could, in principle, be used to obtain knowledge concerning the nature of polar components of unknown liquids and solids by comparing results obtained from Method A and Method B calculations. If, for example, The Method A calculations for the solid/liquid interfacial tension of an unknown liquid on an acidic surface is at the high end of the Method B calculated range, than it can be concluded that the polar components of each phase are undergoing minimum interaction and the liquid must be acidic in nature.

3. Spreading Coefficient

The spreading coefficient of a liquid on a solid surface, $S_{l/s}$, is defined by the equation:

$$S_{l/s} = \gamma_s - \gamma_{sl} - \gamma_l \quad (3)$$

where a positive value indicates spontaneous spreading and a negative value nonspreading. The magnitude of the spreading coefficient in the positive direction is a measure for the tendency of a liquid to spread. Equation 3 can be combined with Equation 2 to give:

$$S_{l/s} = \gamma_l (\cos \theta - 1) \quad (4)$$

The use of Equation 4 would be the equivalent of calculating the spreading coefficient according to Method A. Equation 3 can also be combined with Equation 1 to give:

$$S_{l/s} = -2 \gamma_l + 2 (\gamma_s^d \gamma_l^d)^{1/2} + 2 (\gamma_s^p \gamma_l^p)^{1/2} \quad (5)$$

The use of Equation 5 would therefore be the equivalent of calculating the spreading coefficient according to Method B.

The spreading coefficient has the significance of predicting the ink-substrate interaction where a high spreading coefficient can

lead to ink penetration and feathering, and a low spreading coefficient can lead to poor ink transfer and nonuniform coverage in the solid areas. The spreading coefficient in lithographic printing can also be used as a measure of the tendency for the ink to dewet the fountain solution on the image and nonimage areas of a lithographic plate. An appropriate method for evaluation of this competitive spreading is the spreading index, ΔS which is defined as follows:

$$\Delta S = S_i - S_{fs}, \quad (6)$$

where S_i is the spreading coefficient of the ink and S_{fs} is the spreading coefficient of the fountain solution.

Positive values of the spreading index would be a measure of the tendency of the ink to displace the fountain solution and preferentially wet the lithographic plate. Likewise, negative values of the spreading index would indicate a preferential wetting by the fountain solution. Positive values of the spreading index, therefore, are expected on the image area and negative values on the nonimage area of the lithographic plate.

EXPERIMENTAL RESULTS

1. Lithographic Printing

A commercial blue heatset ink and commercial fountain solution were used for the litho results reported in this paper. The duNuoy tensiometer was used to measure the surface tension of the ink, fountain solution, and test fluids. The Rame-Hart goniometer was used to measure the contact angles of liquids on test surfaces.

Surface Tension of Paste Inks

Historically there have been experimental problems associated with measuring the surface tension and contact angle of litho inks because of their high viscosity. The ink must first be diluted so that reliable and reproducible measurements can be made. The problem is that the ink must be diluted in a manner which allows valid extrapolation to 100% ink because the physical properties of what is being measured is expected to be a function of the concentration of ink in the diluent. A number of litho inks were measured in different organic solvents, including one ink whose surface tension could be measured directly, and it was found that the highest degree of reliability occurred when the surface tension of the ink was measured at different concentrations in at least two solvents which exhibit higher and lower surface tensions than the pure ink. Typical results are presented in Figure 1 for two litho heatset inks diluted in Magie Oils and 1-bromonaphthalene. The extrapolated values of the

surface tensions are 33.5 and 31.5 dynes/cm. These results suggest, based on the limited number of inks measured, that reliable surface tension and contact angle measurements can be obtained with minimum ink dilution in a nonpolar solvent such as 1-bromonaphthalene.

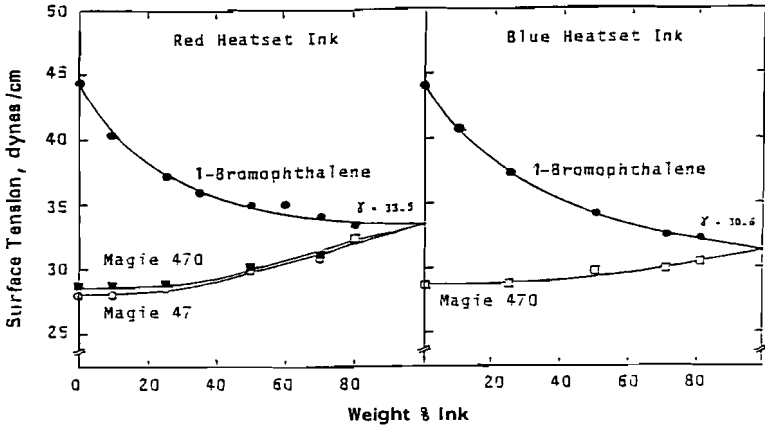


Figure 1. DuNuoy Surface Tension of Red and Blue Heatset Inks Diluted with 1-Bromonaphthalene, Magie 47 Oil or Magie 470 Oil.

Surface Tension of Fountain Solutions

The dispersion and polar components of surface tension of a commercial fountain solution at 3 oz/gal, FS, the fountain solution with 20% isopropanol, FS + IPA, a blue heatset litho ink, and two litho plates, Kodak LNL, were evaluated by means of the geometric mean theory presented above. The test fluids were distilled water and 1-bromonaphthalene, and the test surface was polyethylene. The evaluation of fresh and used litho plate relates to laboratory lithographic ink transfer experiments carried out on the modified Prufbau Printability Tester(3). The fresh plate performed normally and the used plate had reached the point where the prints showed pronounced signs of scumming in the nonimage area of the plate.

The results, Table I, show that the fountain solutions with and without isopropanol exhibits similar surface tension properties, which are about 35% polar and 65% dispersion. The surface tension properties of water with 20% isopropanol is very similar to the surface tension properties of the fountain solutions. The surface tension of the blue ink is lower than the surface tension

of the fountain solutions primarily due to a lower value of the dispersion component of surface tension. The results for the fresh litho plate show that the total surface tension of the nonimage area is 50% higher than the image area primarily due to a higher value for the polar component of surface tension. The results for the used litho plate show that the surface tension properties of the image area are similar to the image area of the fresh litho plate, which is consistent with laboratory ink transfer experiments. The printing problem has been identified in the nonimage area where the used plate, compared to the fresh plate, has a lower surface tension due to a decrease in both the dispersion and polar components of surface tension.

The results in Table I were used to calculate the interfacial tension between the liquids and the image and nonimage areas of the litho plates according to Method A, which is based on contact angle measurements of the liquids on the designated solid surfaces and utilizes Equation 2, and according to Method B, which utilizes the geometric mean theory according to Equation 1. The results obtained from the Method A calculations are considered experimental in the sense that they are the result of contact angle measurements of the liquid on the solid, which is always a function of the degree of interaction of that liquid with the solid surface. The results obtained from the Method B calculations are considered totally theoretical because they are predicative in the sense that they are based on measurements which do not involve bringing the liquid into contact with the solid surface. The Method B calculations also require interpretation with respect to the polar components of surface tension of the solid and the liquid. Since polar interactions are specific in nature, the molecules at the surface of a liquid may or may not interact with the molecules at a solid surface. If the polar components of the liquid and the solid undergo 100% interaction, than the interfacial tension is reduced by the values calculated in the last term of Equation 1. If the respective polar components undergo zero interaction, than the last term in Equation 1 is equal to zero.

Interfacial Tension Results

The solid/liquid interfacial tension, which are based on Method A and Method B calculations, are presented in Table II. The results show that, with the exception of pure water, the Method A calculations essentially fall in the upper range of the Method B calculations for both the image and nonimage areas of the fresh plate. This observation suggests that the polar components of the ink and fountain solutions are not undergoing interaction.

The results for the used plate show that the Method A calculations fall at more intermediate levels of the Method B calculations, which suggests that plate deterioration results in limited polar interactions of the ink and fountain solutions with

the plate. The most pronounced differences of the used plate compared with the fresh plate is in the nonimage area where the used plate results in a pronounced decrease in interfacial tension for the ink and the fountain solutions.

Table I
Surface Tension Components of Test Fluids,
Fountain Solutions, Ink, and Litho Plates

Surface	Surface Tension dynes/cm		
	γ^d	γ^p	γ
Water	21.8	51.0	72.8
1-Bromonaphthalene	44.6	0	44.6
Polyethylene	35.0	6	35.6
FS	25.4	13.1	38.5
FS + IPA	23.2	12.7	35.9
Water + IPA	23.2	12.4	35.6
Blue Heatset Ink	18.9	11.7	30.6
<u>Fresh Litho Plate</u>			
Image	39.1	12.1	51.2
Non-Image	42.5	33.4	75.9
<u>Used Litho Plate</u>			
Image	35.9	12.8	48.7
Non-Image	34.3	21.3	55.6

Table II
Solid/Liquid Interfacial Tensions, dynes/cm
of Blue Ink and Fountain Solutions

Liquid	Blue Ink	FS	FS + IPA	Water	Water + IPA
<u>Substrate</u>					
Fresh Plate					
Image					
Method A	24	23	22	16	22
Method B	4-27	1-27	2-27	16-66	2-27
Non-Image					
Method A	52	45	46	7	42
Method B	12-52	9-51	10-51	7-90	10-51
Used Plate					
Image					
Method A	21	17	20	14	23
Method B	3-27	1-27	1-27	14-65	1-27
Non-Image					
Method A	28	23	25	7	24
Method B	3-25	1-34	2-34	7-73	2-34

Spreading Coefficient Results

The physical implications of the interfacial tension results are best expressed in terms of the spreading coefficient which is a function of interfacial tension and which was calculated according to Equation 4. The interpretation is that the higher the positive values, or the lower the negative values, indicate a greater tendency to spreading. The results, Table III, show that all the values are zero or less than zero, and hence spontaneous spreading is not expected. The results also show that a 10% emulsification of fountain solution in the blue ink does not have an appreciable effect on the spreading characteristics of the ink. The spreading coefficients are primarily important in the relative sense of the tendency of the ink to displace the fountain solution on the litho plate. The spreading index, ΔS , Equation 6, which is the spreading coefficient of the ink minus the spreading coefficient of the fountain solution, was defined to show directly this relationship. Positive values of the

spreading index indicate a preferential wetting of the ink, and negative values a preferential wetting of the fountain solution.

Table III
 Spreading Coefficients*, dynes/cm,
 of Ink, Fountain Solution, and
 Ink Emulsions on Lithographic Plates

Sample	Fresh Plate		Used Plate	
	Si	Sn	Si	Sn
FS	- 7.8	- 5.9	- 7.0	-13.7
FS + IPA	- 7.2	- 3.6	- 7.6	- 5.5
Water	-37.5	- 2.2	-38.6	-25.0
Water + IPA	- 6.4	0	-10.1	- 5.1
Blue Ink	- 3.3	- 4.4	- 2.9	- 3.6
<u>10% Blue Ink Emulsions</u>				
FS	- 3.1	- 4.2	- 2.5	- 2.9
FS + IPA	- 2.9	- 3.3	- 2.6	- 3.3
Water	- 2.6	- 3.4	- 3.7	- 6.0
Water + IPA	- 2.6	- 3.8	- 2.9	- 3.6

*Si - spreading coefficient on the image area.

Sn - spreading coefficient on the non-image area.

The spreading index results, Table IV, show that the ink is predicated to displace the fountain solution on the image areas of both the fresh and used plates. The ink is not predicated to preferentially wet the nonimage areas of the fresh plate except for the fountain solution without isopropanol. The used plate, however, exhibits positive spreading index values in the nonimage areas for all fountain solutions, which indicates that printing would occur on the nonimage areas. These results are qualitatively consistent with ink transfer experiments on the Prufbau Printability Tester which was modified for lithographic printing.

Table IV

Blue Ink Emulsions and Fountain Solution
Spreading Indices*, ΔS , dynes/cm

Fountain Solution	Fresh Plate		Used Plate	
	ΔSi	ΔSn	ΔSi	ΔSn
FS	4.5	1.5	4.1	0.6
FS + IPA	3.9	-0.8	4.7	1.9
Water	34.2	-2.2	35.7	21.4
Water + IPA	3.1	-4.4	7.1	1.5

* ΔSi - spreading index on the image area.

ΔSn - spreading index on the non-image area.

An important aspect of ink/water interaction is the interfacial tension between the ink and the fountain solution. Lower interfacial tensions are always expected to lead to more efficient emulsification of the fountain solution in the ink. Table V presents the results which were measured experimentally with a 75% ink in 1-bromonaphthalene, and which were calculated according to Method 2 and the results presented in Table I. The experimental results, with the exception of water, fall in the midrange of the Method 2 calculations for all the fountain solutions, which suggests that the polar components of the ink and fountain solution are undergoing limited interaction.

2. Flexographic Printing

Three model water based flexographic inks were developed, with the assistance of the NPIRI Liquid ink Committee, where Ink A and Ink B both contained 2% isopropanol and Ink C contained 8% isopropanol. The resin for Ink A and Ink C was Joncryn 74F and the resin for Ink B was Joncryn 620. All three inks contained the same concentration of a predispersion of a blue pigment. The flexographic plate was a commercial photosensitive polymer. The printed substrates were polyethylene films which were corona treated, PE I, and untreated, PE II. The experimental and theoretical characterization of the surface tension of the three inks, the flexo plate, and the polyethylene films was evaluated according to the techniques discussed above.

Table V
Liquid/Liquid Interfacial Tension, dynes/cm
of Fountain Solution with Blue Ink

Fountain Solution	Interfacial Tension, dynes/cm	
	Experimental*	Method B
Water	15	14-63
Water + IPA	11	0-24
FS	10	1-25
FS + IPA	11	0-25

*Measured with duNuoy Tensiometer using 75% ink diluted by 1-bromonaphthalene.

The dispersion and polar components of surface tension and the total surface tension results for the liquids and solids of interest are presented in Table VI. Ink B, which has a different resin than Ink A, has a lower surface tension primarily due to a decrease in the dispersion component of surface tension. Ink C, which has a higher concentration of isopropanol than Ink A, has a lower surface tension primarily due to a decrease in the polar component of surface tension. The surface tension of the flexo plate, 51 dynes/cm, was somewhat higher than reported by the manufacturer, which could be due to an unrepresentative plate or the swelling problem associated with measuring an organic test fluid, i.e. 1-bromonaphthalene, on a polymer substrate. This plate, however, was used in the ink transfer experiments. The corona treated polyethylene film, PE I, exhibited a higher surface tension than the untreated film, PE II, due to a pronounced increase in the polar component of surface tension. This result is consistent with proposed mechanisms such as increased oxidation and/or ionization of the surface.

The results in Table VI and contact angle measurements were used to calculate the solid/liquid interfacial tensions presented in Table VII. Ink A has a somewhat lower Method A interfacial tension with the flexo plate and falls within the Method B range which indicates limited interaction of the polar components of the ink with the plate. Ink B and Ink C have somewhat higher interfacial tension values according to Method A, which is

attributed to a lack of polar component interaction. All the inks with PE I exhibit Method A interfacial tensions which fall at the upper end of the Method B calculation due to a lack of polar component interaction. The results for the inks on PE II show lower Method A interfacial tensions than PE I with Ink A and Ink B indicating limited polar component interactions with the substrate. The interfacial tension results for water on the PE films according to the Method A calculations show a much lower interfacial tension with PE I compared with PE II, which reflects the increased polarity of the corona treated film and the fact that the polar components of surface tension are undergoing interaction. This result is in contrast with the inks where the polar components of the inks are not interacting with the PE I film.

Spreading coefficients for water and the inks on the flexo plate and the PE films were calculated according to Equation 3 by utilizing the results presented in Tables VI and VII. The results, Table VIII, show that none of the fluids will spread spontaneously, as would be indicated by a positive spreading coefficient, but that the inks will have a greater tendency for spreading on the flexo plates than the PE films. There is very little difference, furthermore, in the spreading coefficients for all the inks on the corona treated PE I and untreated PE II. The spreading coefficient and interfacial tension results for the inks on PE I and PE II do not predict greater ink receptivity on PE I even though ink transfer experiments show that PE I is more ink receptive than PE II. Also, ink transfer experiments show that PE I is more ink receptive for Ink C than the other two inks, even though the spreading coefficient and interfacial tension results show very little differences. The interpretation is that other factors are involved such as dynamic surface tension and wetting predictions based on dynamic surface tension results.

3. Dynamic Surface Tension

There is no question that dynamic surface tension plays an important role in ink transfer and printability for all printing processes. An ink is exposed to a surface and undergoes splitting in the nip in fractional seconds. All the results presented above were based on equilibrium surface tension and contact angle measurements, which would be expected to be valid for the analysis of solid surface, but are open to interpretation for the liquids such as the inks and fountain solutions. Another important consideration is the concept that the surface tension for any solution at zero time, i.e. at the instant of generation of a new surface, will be equal to the surface tension of the pure solvent. This conclusion is based upon the fact that the concentration of surface active molecules at the interface at time zero will be equal to the concentration of the molecules in solution, which is generally very low. The dynamic surface

Table VI
Surface Tension Components, dynes/cm, of Flexo Inks,
Test Fluids, Flexo Plates and Polyethylene Films*

Surface	Surface Tension, dynes/cm		
	γ^d	γ^p	γ
Water	22	51	73
Ink A	24	13	37
Ink B	20	12	32
Ink C	25	9	34
Flexo Plate	46	5	51
PE I	33	10	43
PE II	35	1	36

*PE I - Corona treated polyethylene.
PE II- Untreated polyethylene.

Table VII
Solid/Liquid Interfacial Tension, dynes/cm

Fluid	H ₂ O	Ink A	Ink B	Ink C
<u>Substrate</u>				
Flexo Plate				
Method A	30	16	23	20
Method B	28-60	6-22	7-22	4-17
PE I				
Method A	16	22	21	20
Method B	17-63	1-25	2-24	1-20
PE II				
Method A	39	11	10	10
Method B	40-54	9-16	8-15	3-11

Table VIII
Spread Coefficients, dynes/cm

Fluid	H ₂ O	Ink A	Ink B	Ink C
<u>Substrate</u>				
Flexo Plate				
Method A	-52	-2	-4	-3
Method B	-52 - -112	8 - - 8	12 - -3	13 - 0
PE I				
Method A	-46	-16	-10	-11
Method B	-46 - -109	5 - -19	9 - -13	8 - -11
PE II				
Method A	-76	-12	-6	-8
Method B	-76 - -130	-10 - -17	-4 - -11	-1 - -9

tension for solvent inks, therefore, is expected to be less important than for water based inks because the surface tension of pure water is much higher than pure organic solvents, whereas the equilibrium values for both are of the order of magnitude.

Several experimental methods are currently being evaluated for measuring dynamic surface tension, including the maximum bubble pressure method and measuring the surface tension of a pure fluid as a function of time with an automatic balance after exposure to a solution. The experimental results presented in this paper were obtained from the drop-weight method and are preliminary in the sense that the research is in progress for evaluation and interpretation of results. The results which have been obtained, however, do relate to the interpretation of the wetting results presented above with respect to isopropanol in fountain solution and water based inks.

Experimental Technique

The experimental technique involved a variable speed pump to generate drops from teflon tips at a rate up to 24 drops/sec, where the drop rate was found to be a function of drop size. The drop rate was determined by a strobe and the drop volume calculated from a knowledge of the drop rate and the fluid flow rate. The drop weight method of measuring surfaced tension is based upon the fact that the size of the drop is proportional to the magnitude of the surface tension. The experimental problem

is that there are artifacts which control drop size as a function of drop rate, and which are not a function of surface tension. Water and ethanol, which are not expected to exhibit dynamic surface tension in the time frame of these experiments, were among some of the pure solvents used as controls to correct for experimental artifacts.

The drop volume as a function of drop rate was measured for water ethanol as controls, and for different concentrations of ethanol and isopropanol in water. The results, Figure 2, show that the drop volume initially increases and then decreases over a wide range for all samples. Since the pure solvents are not expected to exhibit dynamic surface tension, the initial increase in the drop volume for water and ethanol is theorized to be due to excess fluid being pumped into the drop before the drop has sufficient time to detach under it's own weight. The decrease in the drop volume at higher drop rates is assumed to be due to momentum factors which result in premature detachment of the drop. There is evidence that the correction factors, which were used for evaluation of dynamic surface tension, are a function of drop size and fluid density.

The drop volume results in Figure 2 for the alcohol solutions, where dynamic surface tension is expected, were treated to a point by point correction based on the results for pure water and ethanol. The surface tension results as function of drop age for the ethanol and isopropanol solutions are presented in Figure 3. The major decrease in surface tension occurs in the time frame of less than 0.1 seconds. The rate of initial surface tension decrease is related to the equilibrium surface tension as evidenced by the fact that the 2% solutions of isopropanol and ethanol result in a faster decrease for the isopropanol solution which has a lower equilibrium surface tension. The 5% isopropanol solution yields the fastest initial rate of surface tension decrease due primarily to the higher concentration of molecules in solution. Equilibrium is apparently achieved for all the alcohol solutions within one second.

The most important parameters for controlling dynamic surface tension are the concentration, the surface activity, and the diffusion coefficient of the surface active molecules. Surfactant molecules tend to have a high degree of surface activity, which is by design, and a low diffusion coefficient, which is the result of their high molecular weight compared to alcohols. Surfactants also tend to be used at relatively low concentrations because of economics and adverse effects which occur in printing. The result is that commercial surfactants generally require several seconds or more to arrive at equilibrium with respect to adsorption at newly generated interface. Lower alcohols have the advantage of a low diffusion coefficient and they can be used at high concentrations.

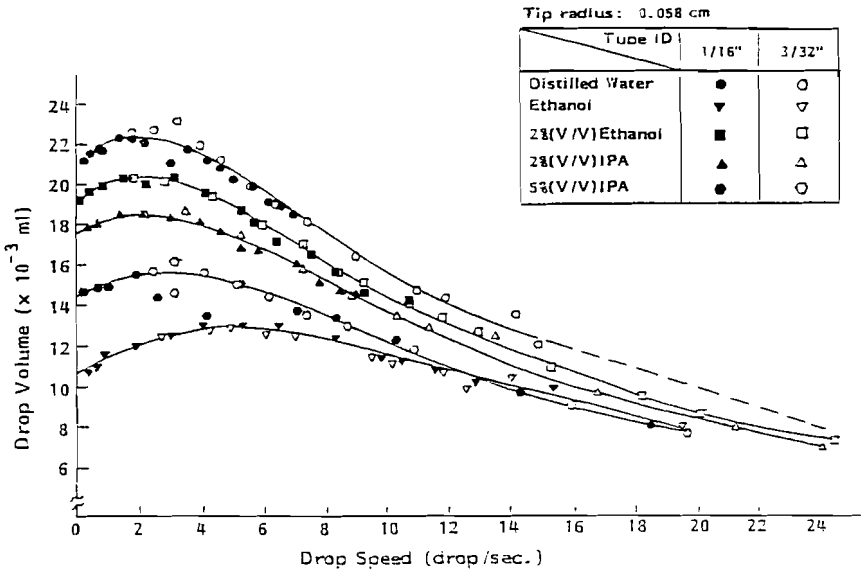
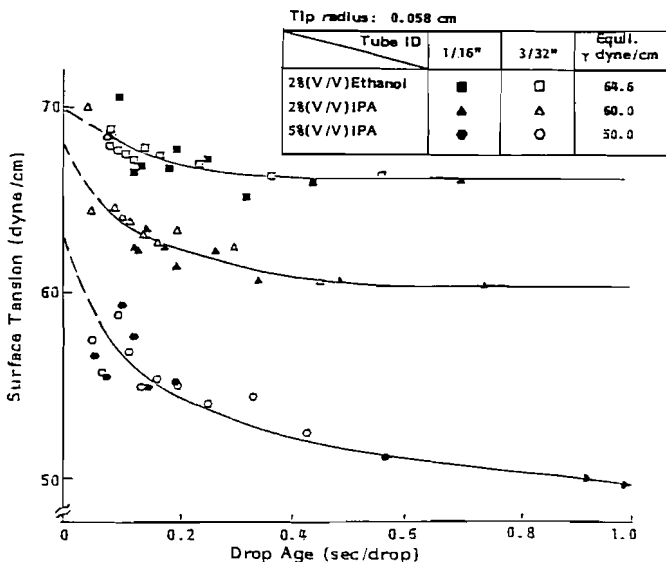


Figure 2. Drop Volume as a Function of Drop Speed, Flow Rate.

The concept of dynamic surface tension is important for the interpretation of the experimental results used to calculate the dispersion and polar components of surface tension of liquids. The calculated results, which are used for predicative analysis of the wetting characteristics of liquids on solid surfaces, are based on contact angle measurements of the unknown liquid on a known nonpolar surface. The problem is that dynamic contact angles of the time frame required cannot be measured. If the dynamic surface tension information for an ink is available, then the ink could be diluted with pure solvent to match the surface tension at some specified time. For example, the results in Figure 3 show that the surface tension of the 5% isopropanol solution at 0.05 sec is 60 dynes/cm, which is the equilibrium surface tension for a 2% isopropanol solution. The dispersion and polar components of surface tension of the 5% isopropanol solution could, therefore, be evaluated by contact angle measurements with the 2% isopropanol solution.



The drop weight method is not necessarily being proposed as a viable method for the routine measurement of surface tension. It is being investigated as a method to obtain results which can be compared with results obtained with commercially available instrumentation. There is no question that the measurement of surface tension of inks in the time frame of 0.1 sec or faster is not a trivial matter. There is also no question that reliable dynamic surface tension measurements are critical for an understanding of the role of wetting in all aspects of printing.

CONCLUSIONS

1. Theory of Wetting

The theory of wetting as it currently exists definitely represents an approximation to physical reality. This is not an unusual statement because all theories are approximations. The problem that the experimentalist must address is what theory should be applied, if more than one exists, and how close an approximation is the theory and what are the limitations with respect to interpretation of calculated results. The current trend in the scientific literature is the proliferation of different theories and criticisms of those theories. The attitude adopted in this paper is to present one theoretical approach and attempt to evaluate the validity and limitations of that approach. Certainly not all the required results are included in this paper to arrive at this grand goal, but rather

this paper should be viewed as the initiation of an experimental approach to test the theory and to relate wetting phenomenon to the printing process.

The novel approach adopted in this paper is the use of existing wetting theory to calculate the solid/liquid interfacial tension according to Method A and Method B, and then to compare results in order to obtain information concerning the degree of interaction of the polar components of surface tension of the liquid and the solid. The problem is that polar interactions are by definition specific in nature, and the method of analysis is designed to evaluate the magnitude of the dispersion and polar components of surface tension but does not yield information concerning the nature of the polar components. Experiments are currently in progress to coat solid surfaces with different and known polar components of surface tension. This approach is designed to lead to a test method for the ink formulator where the contact angle of the test inks are measured on the different surfaces, the results of Method A and Method B calculations compared, and an analysis made concerning the magnitude and nature of the polar components of surface tension. This information will permit the ink formulator to prepare an ink with predictable wetting properties on a characterized surface.

2. Lithographic Printing

The spreading index, which is defined as the spreading coefficient of the ink minus the spreading coefficient of the fountain solution, represents a convenient method for evaluating the degree of preferential wetting of the ink or the fountain solution on a litho plate. The measurements required are the surface tension of the ink and the fountain solution, and the contact angle of the ink and the fountain solution on the image and nonimage areas of the plate. Since these measurements are difficult for the viscous litho inks, it is recommended that reliable results can be obtained by measuring the surface tension and contact angle with a minimum 75% concentration of ink in 1-bromonaphthalene.

The fact that fountain solutions formulated with and without 20% isopropanol exhibit similar surface characterization and wetting properties, and yield different ink transfer results, suggest that the dynamic surface tension of the fountain solution plays an important role in the wetting properties related to ink transfer.

3. Flexographic Printing

The printing of waterbased inks on filmbase substrates is controlled to a large extent by the wetting behavior of the ink on the substrate. Corona treatment of polyethylene film results in an increase in surface tension, primarily due to an increase

in the polar component of surface tension, and a film which was determined from ink transfer experiments to be more ink receptive than an untreated film. The importance of the dynamic surface tension properties of the ink is deduced from the fact that the equilibrium wetting properties, and especially the spreading coefficients, of the ink are very similar on the corona treated and untreated polyethylene film.

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