

# Characterization of surface energies of waterless plates

Véronique Lanet \*, Alessandro Gandini \*

**Keywords :** Image Analysis, Contact Angle, Surface Energy,  
Waterless Plates

## Abstract

Contact angle measurements of liquid drops were carried out on image and non-image areas of a positive Toray waterless printing plate using an image analysis setup. Seven liquids were used : water, methylene iodide, formamide,  $\alpha$ -bromonaphthalene, nonane, hexadecane and glycerol. From the values obtained, surface energies were calculated using different approaches (namely those developed by Fowkes, Owens-Wendt, Zisman, and Van Oss) and critically compared.

## Introduction

Surface energy aspects are primordial in the lithographic printing process. At each stage of this process, different interfaces are involved, especially at the level of the plate. In conventional lithography, the latter consists of a hydrophobic image area which accepts the ink and of a hydrophilic non-image area which is wetted by the fountain solution. The strong surface energy difference between the two areas represents the fundamental feature of the process.

\* Polymeric Materials, Laboratoire Génie des Procédés Papetiers, URA 1100 CNRS  
Ecole Française de Papeterie et des Industries Graphiques,  
INPG, BP 65, 38402 Saint Martin d'Hères, France  
e-mail : lanet@efpg.grenet.fr, gandini@efpg.grenet.fr

In waterless lithography, the elimination of the fountain solution implies a fundamental change in the surface properties of the non-image area of the plate, which is a low-energy silicone layer, the image area being kept in the form of a typical photopolymer as described by O'Rourke (1992).

This novel kind of plate was first introduced by Toray Industries at DRUPA in 1977.

Studies on its physico-chemical behavior have been carried out only during the past five years. To our knowledge, Krishnan and Klein (1991) and Ström (1993) are the only authors who have published surface energy values for both areas of this plate.

This paper presents first the different methods used in order to calculate the surface energy values from contact angle measurements and then a description of the image analysis setup. The last part concerns the results obtained i.e. contact angle and surface energy values and their comparison both as a function of the calculation procedure used and with the values found in the literature.

### **Different approaches to evaluate surface energy**

The surface energy ( $\gamma$ ) is the energy required to create a unit area of a new surface. The surface energy of a liquid ( $\gamma_L$ ) is obtained easily from direct measurements. On the contrary, it is much more difficult to have access to reliable values of the surface energy of a solid ( $\gamma_S$ ). The majority of the methods involve contact angle measurements but none gives an absolute value of the total surface energy. More recently, inverse gas chromatography has been used as an alternative experimental technique for this purpose.

The values of contact angle can be processed in different ways according to the following approaches.

#### **Zisman 's approach**

This theory is empirical and its authors (Fox and Zisman, 1950) introduced a parameter called critical surface tension ( $\gamma_C$ ) which is defined as the maximum surface tension a liquid must have to completely wet a polymer (contact angle  $\theta=0$ ).  $\gamma_C$  is obtained by measuring the contact angle of a series of liquids on the same solid surface and by plotting  $\cos \theta$  vs.  $\gamma_L$ . The point of intersection of the "straight line" thus obtained with the line  $\cos \theta = 1$  gives the critical surface tension. This value is not equal to  $\gamma_S$  but, in some cases, it comes close to it.

In this paper, this approach was applied using water, methylene iodide, formamide, nonane, hexadecane and glycerol for the non-

image areas. For the image areas, nonane and hexadecane were replaced by  $\alpha$ -bromonaphthalene because contact angles obtained with alkanes were too low to be measured reliably.

### Fowkes' approach

The theory developed by Fowkes (1964) is the most currently used and is based on the assumption that the surface tension is the sum of the different types of cohesive interactions operating within a material. Thus, in its simplest form :

$$\gamma = \gamma^d + \gamma^{nd} \quad (1)$$

with,

$\gamma^d$  : dispersive component (London forces) of the surface tension

$\gamma^{nd}$  : non-dispersive component (also called "polar contribution"  $\gamma^p$  by some authors) which comprises Debye, Keesom and hydrogen-bonding forces

The work of adhesion between a solid and a liquid can be written in the same way as :

$$W_{SL} = W_{SL}^d + W_{SL}^{nd} \quad (2)$$

For systems involving only dispersive interactions, i.e. using an entirely dispersive liquid, Fowkes defines a "geometric mean" for the dispersive forces contribution to solid/liquid attraction :

$$W_{SL}^d = 2\sqrt{\gamma_s^d \gamma_L^d} \quad (3)$$

From this equation and the Dupré-Young relationship, one obtains :

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_s^d \gamma_L^d} \quad (4)$$

which allows to determine  $\gamma_s^d$  but under no circumstances  $\gamma_s$ .

When non-dispersive interactions occur, Fowkes introduces a new parameter  $I_{SL}$  to account for these specific adhesion forces between the solid surface under investigation and different liquids.

In this paper, the entirely dispersive liquids used were hexadecane for non-image areas and  $\alpha$ -bromonaphthalene for image areas, water being the only polar liquid tested.

### Owens-Wendt's approach

Some authors like Owens and Wendt (1969) extended the hypothesis of the geometric mean to the non-dispersive forces, viz.

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_s^d \gamma_L^d} + 2\sqrt{\gamma_s^p \gamma_L^p} \quad (5)$$

From the contact angle values of two known liquids, a system with two equations and two unknowns must be solved to obtain  $\gamma^d$  and  $\gamma^p$ . In this paper, in order to increase the accuracy of the calculations, four liquids were employed, namely, water, methylene iodide, formamide and glycerol.

The plot of :

$$\frac{\gamma_L(1 + \cos \theta)}{2\sqrt{\gamma_L^d}} \text{ vs. } \sqrt{\gamma_L^p / \gamma_L^d} \quad (6)$$

gives a slope equal to  $\sqrt{\gamma_s^p}$  and an intercept equal to  $\sqrt{\gamma_s^d}$ .

### Ström's approach

When the liquid is water, Ström (1993) proposes to determine  $\gamma_s^d$  by Fowkes' method and to introduce an empirical factor  $K$  ( $0 \leq K \leq 1$ ) for the characterization of a solid surface.

$K$  is given by the following expression :

$$K = \frac{W_{S,water}^{nd}}{W_{water}^{nd}} \quad (7)$$

with,

$W_{S,water}^{nd}$  : non-dispersive part of the work of adhesion between the solid and water

$W_{water}^{nd} = 2\gamma_{water}^{nd}$  : non-dispersive part of the cohesive work of water

$K$  reflects the polar contribution to the adhesive interactions by linking the solid surface hydrophilicity to that of water and can be obtained from contact angle measurements.

### The acid/base approach

In this theory the non-dispersive forces were assimilated by Fowkes (1983) and by Van Oss (1987) to acid/base interactions, i.e. :

$$\gamma = \gamma^{LW} + \gamma^{ab} \quad (8)$$

with,

$\gamma^{LW}$  : "Lifshitz-Van der Waals" forces including all the Van der Waals contributions (London, Debye and Keesom)

$\gamma^{ab}$  : acid/base interactions in the most general sense, viz. all forces involving donor/acceptor interactions

Van Oss developed this theory by defining  $\gamma^{ab}$  as the geometric mean between the donor character  $\gamma^-$  and acceptor character  $\gamma^+$  of the surface :

$$\gamma = \gamma^{LW} + 2\sqrt{\gamma^- \gamma^+} \quad (9)$$

The acid/base term only has a meaning in this context for materials having both acid and basic character.

The work of adhesion is thus given by :

$$W_A = \gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_s^{LW} \gamma_L^{LW}} + 2\sqrt{\gamma_s^- \gamma_L^+} + 2\sqrt{\gamma_s^+ \gamma_L^-} \quad (10)$$

From contact angle values with known liquids, here water, hexadecane and glycerol, on non-image areas and water, methylene iodide, and glycerol, on image areas, a system with three equations and three unknowns was obtained. Its solution by a simple computer program gives  $\gamma^{LW}$ ,  $\gamma^+$  and  $\gamma^-$  of the solid surface.

### Values of the surface energy components for the test liquids

The tables 1 and 2 give the test liquids surface energy components used for our calculations.

	$\gamma$	$\gamma^d$	$\gamma^{nd}$
Water	72.8	21.8	51.0
Methylene iodide	50.8	48.5	2.3
Formamide	58.2	39.5	18.7
$\alpha$ -bromonaphthalene	44.6	44.6	0
Hexadecane	27.5	27.5	0
Nonane	22.7	22.7	0
Glycerol	63.4	37.0	26.4

Table 1 : Surface tension (mN/m) components for test liquids according to Fowkes (1964)

	$\gamma$	$\gamma^{LW}$	$\gamma^{ab}$	$\gamma^+$	$\gamma^-$
Water	72.8	21.8	51	25.5	25.5
Methylene iodide	50.8	50.8			
Hexadecane	27.5	27.5			
Glycerol	64.0	34.0	30.0	3.9	57.4

Table 2 : Surface tension (mN/m) components for test liquids according to Van Oss (1990)

## Experimental

Measurements were carried out : (i) on an exposed but non-developed non-image area of the waterless plate ; (ii) on an exposed and developed non-image area and (iii) on an image area which, by definition, was exposed and developed. The term "developed" means here that a manual developer product and a cleaning product were applied to the plate.

Contact angles were measured with a CCD camera and processed by an image analysis video card which calculated  $\theta$  using the following equation :

$$\tan \frac{\theta}{2} = \frac{2h}{D} \quad (11)$$

with,

h : height of the drop  
D : diameter of the drop

The volume of the drops ranged between 1 and 2  $\mu$ l in order to assimilate them to a spherical shape and to avoid problems arising from gravity.

The image acquisition begun just when the drop was placed onto the solid surface except for glycerol for which the measure started after about ten seconds because of the viscosity of the liquid.

## Results

The mean contact angle values obtained for the seven test liquids on the different parts of the plate are given in the table 3 :

	Non-image expos./non-devel.	Non-image exposed/devel.	Image
Water	115 ± 0.3	108.7 ± 1.3	69.4 ± 0.7
Methylene iodide	97.1 ± 1	98.8 ± 0.5	30 ± 2.3
Formamide	108.2 ± 0.6	105.9 ± 2.3	48.6 ± 3.3
α-bromonaphthalene			24 ± 1.4
Nonane	34.1 ± 1.4	33.1 ± 0.7	
Hexadecane	49.8 ± 1.3	53 ± 1.3	
Glycerol	103.9 ± 2.7	99.7 ± 1	68 ± 1.3

Table 3 : Mean contact angle values and their standard deviation determined on the different areas of the waterless plate

The surface tension values calculated by the different methods discussed above are summarized in table 4.

		Non-image expos./non-devel.	Non-image exposed/devel.	Image
Fowkes	$\gamma^d$	18.6	17.6	40.8
	Ws/water	42	49.5	98.4
	Is/water	1.73	10.3	38.8
Owens/Wendt	$\gamma$	9.2	9.7	43
	$\gamma^d$	8.1	6.6	36.5
	$\gamma^p$	1.1	3.1	6.5
Zisman	$\gamma_c$	13.1	10.9	42
Ström	$\gamma^d$	18.6	17.6	40.8
	K	0.02	0.1	0.38
Van Oss	$\gamma$	18.8	17.7	46.9
	$\gamma^{LW}$	18.6	17.6	44.2
	$\gamma^+$	0.04	0.0004	0.11
	$\gamma^-$	0.15	0.99	15.5

Table 4 : Surface tensions (mN/m) of the different areas of the waterless plate from different approaches

With Owens-Wendt's method, the lines obtained had variation coefficient going from 0.95 to 0.91 (see figure 1 for developed non-image area). With Zisman's method, variation coefficients ranged between 0.98 and 0.93 (see figures 2 and 3).

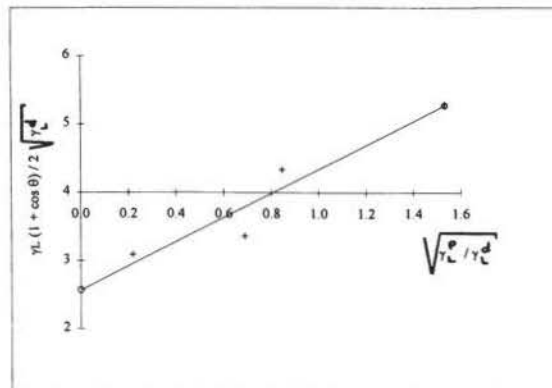


Figure 1 : Determination of the  $\gamma$  value for exposed and developed non-image area (Owens-Wendt's method)

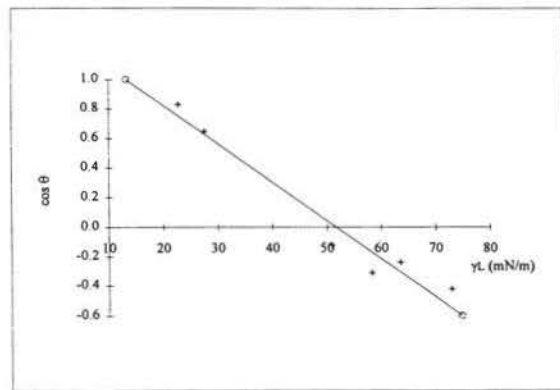


Figure 2 : Determination of  $\gamma_c$  for non-developed non-image area



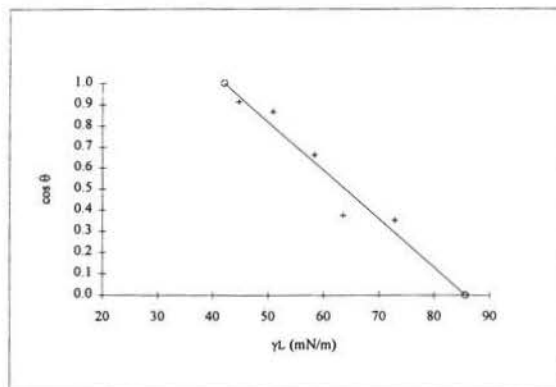


Figure 3 : Determination of  $\gamma_c$  for image area

## Discussion

Several tendencies appear from the above results.

### For non-image areas :

- the main feature is the difference between surface tension values obtained with Owens-Wendt's method on the one hand and Fowkes' or Van Oss' procedures on the other hand. Owens-Wendt's theory underestimates considerably the  $\gamma$  value ;

- the  $\gamma^d$  values calculated with Fowkes' method are close to those indexed in the literature by Brandrup (1989) for polydimethyl siloxane (the probable constituent of the silicone layer) ;

- the  $\gamma_c$  values obtained with Zisman's method are low, but in tune with Zisman's theory which implies that  $\gamma_c$  is lower than  $\gamma$ . Measurements carried out with a series of homologous liquids would perhaps lead to a more reliable value ;

- the K value calculated with Ström's treatment is very low i.e. the surface is poorly hydrophilic as all other methods also show : low  $I_{s/water}$ ,  $\gamma^p$ ,  $\gamma^+$  and  $\gamma$  values ;

- $\gamma_s^{LW}$  values calculated with Van Oss' method are close to Fowkes'  $\gamma_s^d$ . This means that Keesom and Debye effects are very modest for this silicone surface, in accordance with its weak hydrophilicity ;

- the plate development brings about an increase in the polar character of the surface. This can be seen by the increase in  $I_{s/water}$ , the

increase in the Owens/Wendt's  $\gamma^p$  value and the increase in the K value. The developer product contains some additives and has a pH close to 4, two facts which explain our observation.

**For image areas :**

- all the methods used give very similar surface tension values, viz. slightly higher than 40 mN/m, with a certain polar character, as showed by the  $I_{s/water}$ ,  $\gamma^p$  and K values ;
- we find again a Zisman  $\gamma_c$  value which is slightly lower than the considered total surface tensions obtained with other methods ;
- Van Oss' theory predicts a basic character which is higher than the acidic one. We have no clear-cut explanation for this without a knowledge of the precise chemical feature of the photopolymer ;
- $\gamma^{LW}$  is higher than Fowkes'  $\gamma^d$  which means that Keesom and Debye effects have a certain importance in this solid, as confirmed by its "polar" character.

**Comparison with literature values :**

We do not know if the non-image area in Ström's work was exposed or not (or indeed developed or not), but we can conclude that our results are very similar to his as shown in table 5.

		Non-image area	Image area
$\gamma^d$	Ström	18	41
	us	17.6 to 18.6	40.8
K	Ström	0.03	0.4
	us	0.02 to 0.1	0.38

Table 5 : Comparison with Ström's values (1993)

Krishnan's values (table 6) are lower than ours, but the basic character of the image area appears in both. The observed differences may be due to the fact that measurements in Krishnan's work were carried out on a "used plate".

		Non-image area	Image area
$\gamma$ total	Krishnan	11.4	37.5
	us	17.7 to 18.8	46.9
$\gamma^{LW}$	Krishnan	9.8	35.9
	us	17.6 to 18.6	44.2
$\gamma^+$	Krishnan	0.13	0.025
	us	0.0004 to 0.04	0.11
$\gamma^-$	Krishnan	4.84	24.87
	us	0.15 to 0.99	15.5

Table 6 : Comparison with values found by Krishan (1991) for a "used plate"

## Conclusion

The characterization of the non-image area of a waterless plate is much more delicate than that related to the image area.

We consider that the best methods to evaluate the surface tension of the non-image area are Fowkes' or Van Oss'.

For the image area, all the calculation procedures used gave similar results.

## Acknowledgements

We are grateful to SunChemical France for active support.

## Selected Bibliography

- Brandrup, J., and Immergut, E.H.  
1989. "Polymer Handbook" (Wiley-Interscience Publication), 3rd ed.
- Festko, J.M.  
1988. "Relationship of ink-water interactions to printability of lithographic printing inks" (A literature Survey - NPIRI).

- Fowkes, F.M.  
1964. "Attractive Forces at Interfaces", *Ind. Eng. Chem.*, vol. 56, no 12, pp. 40-52
- Fowkes, F.M.  
1983. "Acid-Base Interactions in Polymer Adhesion" In. "Physicochemical Aspects of Polymer Surfaces-2" (New-York and London : K.L. MITTAL), pp. 583-603
- Fowkes, J.M., Riddle Jr, F.L., Pastore, W.E. and Weber, A.A.  
1990. "Interfacial interactions between self associated polar liquids and squalane used to test equations for solid-liquid interfacial interactions", *Colloids and Surfaces* , vol. 43, pp., 367-387.
- Fox, H.M. and Zisman, W.A.  
1950. "The spreading of liquids on low-energy surfaces. I. Polytetrafluoroethylene" *J. Colloid Interface Sci.* vol. 5 pp. 514-531.
- Krishnan R. and Klein D.  
1991. "Ink/plate interactions in waterless lithography", *TAGA Proceedings*, pp. 478-489
- O'Rourke John  
1992. "The Waterless printing process : U.S. market. Considerations and Applications", *TAPPI Proceedings*, pp. 305-313
- Owens, D.K. and Wendt, R.C.  
1969. "Estimation of the surface free energy of polymers", *J. Appl. Polym. Sci.*, vol. 13, pp. 1741-1747.
- Ström, G.  
1993. "The importance of surface energetics and dynamic wetting in offset printing", *J. Pulp & Paper Sci.*, vol. 19, no 2, pp. J79-J85.
- Van Oss, C.J., Good, R.J. and Chaudhury, M.K.  
1986. "The role of Van der Waals Forces and Hydrogen Bonds in Hydrophobic Interactions Between Biopolymers and Low Energy Surfaces", *J. Colloids Interface Sci.*, vol. 111, no 2, pp. 378-390
- Van Oss, C.J., Good, R.J. and Busscher, H.J.  
1990. "Estimation of Polar Surface Tension Parameters of Glycerol and Formamide for use in Contact Angle Measurements on Polar Solids", *J., Dispersion Sci. Tech.*, vol. 11, pp. 75-81