#### INK/PLATE INTERACTIONS IN WATERLESS LITHOGRAPHY

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Abstract: With the elimination of fountain solution used in conventional lithography, the ink/plate interactions become important in the operation of waterless lithography.

An important parameter akin to the ink/water balance in conventional lithography is Critical Toning Index (CTI). It is the temperature at which the non-image area starts to accept ink or "tone".

Rheological and surface chemical studies on several inks and plates have enabled us to identify some of the relevant physico-chemical properties of the plates and inks which have an influence on CTI. An empirical equation was then derived which indicates the directions for these properties to obtain higher CTI.

Ink/Plate Interaction in Waterless Lithography

#### I. <u>Introduction:</u>

It is well known that ink-water balance is generally difficult to control in lithography except by highly skilled pressmen and properly matched ink/fountain solution systems. To overcome this and other problems associated with the use of dampening fluids such as start up waste, increased drying time and temperature, etc. the concept of waterless lithography was first proposed by Curtin [1] in 1970.

The plate was diazo sensitized and coated with silicone. After exposure the image areas were dissolved by an organic solvent, leaving the bare metal. The non-image area was then the silicone layer.

Some of the problems associated with the waterless lithography were as follows:

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Even though the non image area was low in surface energy, inks available at that time still caused toning. In order to overcome this problem inks were made tackier. But this led to linting and picking problems with most stocks. Also the plate themselves were very tender because of left over sensitizer which was very difficult to completely remove.

One of the variations tried to overcome this problem was to incorporate photosensitivity into the silicone polymer itself rather than having a separate photosensitive coating. However, these groups decrease the ink repellency of the silicone.

Another approach was to deposit ink receptive materials by xerographic methods. However, adhesion of these materials to low energy silicones was difficult and during the course of press operation tends to be removed by tacky inks.

These problems proved insurmountable at that time and ultimately led 3M to discontinue driography in 1977

In 1979, Toray commercialized a waterless plate. Some of the earlier problems noted above were overcome by photoinduced adhesion between a specific silicone rubber layer and a specific photo sensitizer.

In 1985 Toppan Printing in Japan started to use this technology on a regular basis. In 1990 GPI developed inks in the United States for these plates using domestic raw materials and printers started to practice waterless lithography.

Earlier studies by researchers in Xerox [7-9], dealt with aspects of surface energetics and kinetics of ink transfer.

It is the aim of this paper to analyze the ink/plate interactions from an acid/base aspect of surface energetics. A brief introduction to this now well established surface chemical procedure is followed by results from laboratory press trials. Finally an empirical relationship is proposed to estimate the critical toning index from surface chemical and rheological properties of inks.

# II. Acid/Base Aspects of Surface Energetics:

It is now well known from the pioneering work of Fowkes [13, 14] that the interfacial interactions can be classified into two components. One that is nonpolar and the other that is due to acid/base interactions. Hence for a solid surface.

$$\gamma_s = \gamma_s^d + \gamma_s^{ab}$$

The acid/base properties of a sample such as the waterless plate can therefore be calculated by measuring the contact angle of the three liquids whose dispersion and acid-base properties have been well characterized.

The equations for performing such a calculation are shown in Appendix I.

III. <u>Results of Physico Chemical Measurements on</u> <u>Inks and Plates:</u>

The three liquids used in our study as surface probes were: water, methylene iodide and glycerol. In TABLE I, the surface properties of the image and non image areas as calculated by the equations derived in Appendix I, are shown.

## TABLE I

Surface Characteristics of the Used Toray Plate

Surface	<b>γ</b> Total	γ disp	γ Acid	γ Base
Image Area	37.5	35.9	0.025	24.87
Non-Image Area	11.4	9.8	0.13	4.84

Similarly for characterizing the surface properties of inks, contact angles on three solid surfaces were measured. The three surfaces chosen were: Polypropylene, Nylon and Teflon.

TABLE II

Surface	γ Total	γ disp	γ Acid	γ Base
Polypropylene	36.0	36.0	0	0
Nylon	43.8	36.5	2.0	6.7
Teflon	22.5	20.5	1.67	0.6

Again following a procedure similar to that shown in Appendix I, equations were derived to calculate the surface energy and its dispersion and acid/base properties of the inks. The results are shown in Table III for a number of different inks.

TOTAL	ACID	BASE	VISC	TACK	сп	R.H
DYNES/CM			POISE	G-M	OBSERVED	
36.60	42.25	0.02	227.00	11.20	36.00	60.00
34.60	25.75	0.12	303.00	11.40	41.00	62.00
36.60	33.66	0.00	351.00	12.10	43.00	60.00
33.40	21.93	0.10	325.00	11.90	42.00	62.00
37.40	40.74	0.00	281.00	12.00	41.00	62.00
32.00	33.00	0.19	293.00	12.30	40.00	60.00
33.80	19.44	0.23	291.00	12.00	36.00	60.00
34.20	62.91	0.08	394.00	11.80	37.00	60.00
33.60	16.62	0.22	184.00	11.50	27.00	60.00
37.20	29.38	0.10	208.00	12.00	32.00	60.00
38.80	24.62	0.13	292.00	12.40	39.00	52.00
38.80	5.16	0.03	360.00	12.10	38.00	52.00
37.00	11.87	0.50	306.00	11.60	45.00	52.00
37.40	11.04	0.67	331.00	12.20	40.00	58.00
35.20	1.91	0.72	345.00	12.00	38.00	58.00
39.80	17.94	0.05	344.00	12.30	48.00	60.00
38.20	14.24	0.24	391.00	12.00	50.00	60.00
37.90	9.01	0.68	236.00	11.50	37.00	50.00
37.60	0.25	1.18	392.00	11.90	40.00	50.00

TABLE III

Since it is expected that the rheological properties such as viscosity and tack will also have an influence on CTI, these were measured and included in Table III.

Finally all the inks were printed using a lab press with Toray plates. Details of the C.T.I. test machine are given in Appendix II. The critical toning index was measured and listed in Table III.

Using non-linear regression, an empirical relationship between Critical Toning Index (CTI) and the surface and rheological properties of the ink shown in Table III can be obtained.

Here we present the results of the non-linear regression:

 $CTI = -30.4 \gamma_{total} + 0.438 \gamma_{total}^{2} + 0.801 \gamma_{acid} - 0.0117 \gamma_{acid}^{2} + 5.66 \gamma_{base} + 0.272 visc. - 0.000311 visc.^{2} + 228 tack - 9.97 tack^{2} - 798$ 

A graph showing the observed and predicted C.T.I. is shown in Figure 1. Considering the changes in the Relative Humidity of the pressroom, variations in surface chemistry and morphology of plates due to we r and batch differences, the correlation is reasonably good.



# IV. <u>Discussions:</u>

With respect to waterless plates, the image area seem to have a high ratio of base to acid component of surface energy (c.a.1000) as compared to the non-image area (c.a.35). Hence it is gratifying to note that regression model predicts that a high acid component of surface energy is desirable to obtain higher CTI. This is because the ink will then have higher affinity to the image rather than the non-image area. Of course the temperature dependence of these surface properties should also be investigated to truly quantify this relationship.

Regarding the relationship of CTI with respect to Viscosity and Tack the result is somewhat obvious. However, runnability problems which may be encountered, such as poor stability of inks due to solvent evaporation, poor transfer due to changes in rheological properties of ink, picking of paper etc. are not taken into consideration in this analysis, but must be when formulating a workable ink. .

## V. <u>Conclusion:</u>

1). In addition to rheological properties of waterless inks their surface chemical properties also influence CTI.

2). With respect to surface chemical properties, the acid/base components of surface energy seem to be more relevant than the total surface energy.

3). A method to estimate these surface chemical properties has been developed following now well known surface chemical equations.

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## APPENDIX I

# <u>Surface Energy of a Solid from Contact Angle</u> <u>Measurements of 3 Fluids</u>

The Surface energy  $(\gamma_s)$  and its components dispersion  $(\gamma_s^d)$ , acid  $(\gamma_s^a)$  and base  $(\gamma_s^b)$  can be calculated, by measuring contact angles  $\theta_1$ ,  $\theta_2$  and  $\theta_3$  of three fluids water  $(l_1)$ , methylene iodide  $(l_2)$  and glycerol  $(l_3)$  whose surface energy components have been characterized and are shown below:

Fluid	Total Surface Energy	Dispersion Component	Acid	Base
Water	72.8	50.8	25.4	25.4
Methylene Iodide	50.8	50.8	0	0
Glycerol	64.0	34.0	3.92	57.4

From Young's equation and using the geometric mean approximation one can write:

$$\gamma_{11} \frac{(1 + \cos \theta_1)}{2} = K_1 = (\gamma_s^d \gamma_{11}^d)^{\frac{1}{2}} + (\gamma_s^a \gamma_{11}^b)^{\frac{1}{2}} + (\gamma_s^b \gamma_{11}^a)^{\frac{1}{2}}$$

$$\gamma_{12} \frac{(1 + \cos \theta_2)}{2} = K_2 = (\gamma_s^d \gamma_{12}^d)^{\frac{1}{2}}$$

and

$$\gamma_{13} \frac{(1 + \cos\theta_3)}{2} = K_3 = (\gamma_s^d \gamma_{13}^d)^{\frac{1}{2}} + (\gamma_s^a \gamma_{13}^b)^{\frac{1}{2}} + (\gamma_s^b \gamma_{13}^a)^{\frac{1}{2}}$$

From Eq(2): 
$$\gamma_s^d = K_2^2 / \gamma_{12}^d$$

From Eq(3): 
$$\gamma_s^{a\frac{1}{2}} = \frac{K_3 - (\gamma_s^d \gamma_{13}^d)^{\frac{1}{2}} - (\gamma_s^b \gamma_{13}^a)^{\frac{1}{2}}}{\gamma_{13}^{b\frac{1}{2}}}$$

Substituting Eq(5) in Eq(1) one obtains

$$\gamma_{s}^{b} = \frac{\frac{1}{2}}{\frac{1}{(\gamma_{11}^{a} - K_{5}K_{3} + K_{5}K_{6}, \frac{1}{(\gamma_{11}^{a} - K_{5}\gamma_{13}^{a})}}$$

1

Where, 
$$K_5 = \gamma_{11}^{b \frac{1}{2}} / \gamma_{13}^{b \frac{1}{2}}$$

$$K_8 \equiv (\gamma_s^d \gamma_{13}^d)^{\frac{1}{2}}$$
$$K_4 \equiv (\gamma_s^d \gamma_{11}^d)^{\frac{1}{2}}$$

From Eq[4], [5] and [6], one can calculate the total surface energy as,

$$\gamma_{s} = \gamma_{s}^{d} + 2\sqrt{\gamma_{s}^{a}} \gamma_{s}^{b}$$

#### APPENDIX II

## C.T.I. (Critical Toning Index) Test Machine

#### 1. <u>Introduction:</u>

In waterless offset printing, since there is no cooling effect by dampening water, inks on the press break down by heat to cause toning in the non-image area of the plate.

The temperature of the plate cylinder at which background toning starts to show is called Critical Toning Temperature (C.T.T.), which is a measurement of toning resistance (anti-toning property) of waterless inks.

The C.T.T. measurement, however, is much dependent on the printing conditions such as press type, ink roller assembly, ink roller setting, printing speed, thickness of ink film on rollers etc.

So, it is important to employ the C.T.T. values which were measured at the standard printing condition when comparing the toning resistance of inks.

Toray developed a test machine to standardize the C.T.I. (Critical Toning Index).

2. <u>Construction and Mechanism:</u>

The C.T.I. test machine is a Davidson 700 press which is modified as follows for C.T.I. measurement.

1). Heating Elements

Plane electric heaters are glued ont he plate cylinder which is curved for extra cut-down.

A waterless plate with an image is mounted on the heater to warm it from underneath.

The plane electric heater is connected to brushes so that they can be activated while running the press. A rheostat is employed to adjust the rate of heating of the plate.

2). Driving Motor

The original driving motor of the Davidson press is replaced with an induction motor with a ring-cone speed controller in order to run the press at extremely low speeds (1800 sheets/hr).

- 3). How to measure C.T.I.
  - Control the room temperature at approximately 25°C./
  - Set the ring-cone of the driving motor at the minimum position of the higher gear (1800s/hr).
  - 3). Use a waterless plate of 0.3mmx450mmx400mm size with the specified image.
- 4). Ink the plate and check that the background of the plate is clean. (If the plate tones at the start, the reasons would be that oily residue on the plate or on the rollers causes toning or that the C.T.I. of the particular ink sample is lower than the temperature of the plate).
- 5). Check the plate temperature by the infra-red thermometer. Fix the thermometer probe on the press at 4-5cm distance from the plate surface to check the temperature while printing

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