IMPACT OF INK/PAPER INTERACTIONS ON PRINTABILITY OF AQUEOUS PUBLICATION GRAVURE INKS

Part I. Dynamic Contact Angle and Paper Wetting

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ABSTRACT

Dynamic behavior of a printing ink within the first 1,500 milliseconds of contact with the paper surface was examined. Water based and solvent based inks, as well as their components, and a representative set of paper substrates were included in the study. Dynamic Surface Tension (DST), and chemical interactions between the ink and substrate, were found of unique importance with the water based system. Viscosity, surface tension and solvent penetration into the substrate, had about the same strong impact on the behavior of both solvent and water systems. The dynamic surface tension data alone were inadequate in explaining the ink/paper interactions, which appeared to be a complex function of all the factors mentioned above. It was also confirmed that DST values would become relevant to a high speed printing process only if obtained under dynamic conditions respective to about 30 - 60 bubbles per second, whereas the DST data quoted most often in the literature relate to the rates at 5 - 10 bubbles/sec.

INTRODUCTION AND BACKGROUND

Environmental and workplace safety considerations exert ever growing pressure on the Graphic

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Arts Industry to limit the use of organic solvents. As a result, the share of water based printing inks in packaging printing (including corrugated) has achieved a respectable level of about 50%, and in newspaper printing it is estimated at about 10% of the total. Toluene, the major solvent used in publication gravure printing, has recently come under environmental scrutiny again. To be prepared for a possible ban on toluene use, the industry is exploring the viability of water based technology. The challenge is enormous: to meet the high print quality and low cost of publication gravure printing which have been perfected over years of diligent research and pressroom practice.

Technical problems related to the application of water based inks to high speed, high quality publication gravure printing on a variety of paper substrates have been discussed in detail elsewhere (Smith, 1989; Rooney, 1989; Hruzewicz, 1990). In any printing process using liquid inks, including publication gravure, the ink wetting and spreading over the substrate are fundamental factors controlling the outcome of the process (Bassemir and Krishnan, 1990 and 1991). Wetting and spreading phenomena are well described, theoretically and experimentally, for systems at thermodynamic equilibrium. They are related, in terms of contact angle, to the interfacial tensions by the well known Young equation (Ross and Morrison, 1988):

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \Theta \qquad [1]$$

where:

γ_{sv} - tension at solid/vapor interface

γ_{sl} - tension at solid/liquid interface

γ_{lv} - tension at liquid/vapor interface

Θ - contact angle

The cells of a gravure cylinder are about 100 micrometers across in size. At such a small size of the ink meniscus, the curvature of the wetting line may have to be taken into account. Then, the Young equation, modified to include the, so called, line tension (Drelich and Miller, 1993 and 1994; Gaydos and Neumann, 1987; and Good and Koo, 1979) should be used rather than equation [1].

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\Theta + \frac{\gamma_{slv}}{r} \qquad [2]$$

where: γ_{slv} - line tension
r - radius of the line curvature.

The size of liquid drops used in this work was about 10,000 times larger than the gravure cell volume. The literature, however, does not provide an unambiguous way of determining the line tension value and we were not able to estimate the error involved.

The final equilibrium reached by a droplet of liquid brought into contact with a solid surface is considered a measure of wettability of the solid surface by the liquid or, alternatively, a capability of the liquid to wet the solid and is expressed in terms of the contact angle, Θ. For theoretical purposes, it is convenient to distinguish three different cases:

a. Complete spreading - the liquid forms a uniform film on the solid surface; contact angle equal 0°.

b. Partial wetting - the droplet changes its shape (flattens) and spreads to a limited extent on the solid surface; contact angle between 0° and 180°.

c. Complete non-wetting - the droplet does not change its shape; contact angle - 180°.

Most of the "partial wetting" type systems also exhibit some hysteresis. Then, advancing and receding contact angles are recorded. The most common reasons for the hysteresis are roughness and heterogeneity of the surface (Ross and Morrison, 1988; Myers, 1991).

Due to its macroscopic appearance and for mathematical convenience, the contact area of the three phases (gas, liquid and solid) is considered as a geometrical line. Microscopically, however, it makes a sizeable transition area within which there is a gradual change of the phase properties. It becomes especially important under dynamic conditions, when the movement of the line of wetting was noticed to be "halting and jerky" rather than smooth (Patrick and Brown, 1970; Oliver and Mason, 1977). Incidentally, it explains the dependence of the advancing and receding contact angles on the velocity of the liquid. Unfortunately, there is not much information available for systems under nonequilibrium (dynamic) conditions, both in terms of methodology and reliable experimental data.

In the course of work on improving printability of water based inks, it has become apparent that interactions occurring within the first few hundred milliseconds of ink contact with paper are of paramount importance. Accordingly, surface tension and wetting properties of the ink have to be studied under much more dynamic conditions than they traditionally have been, in order to obtain data relevant to high speed printing. The surface tension of water based inks is brought down to that characteristic of solvent inks by using surfactants. Under the dynamic conditions of the printing process, however, there is always a period of time required for the molecules of the surfactant to arrive at the newly-created surface, position themselves, and modify the interface properties (Bendure, 1971; Hua and Rosen, 1987). It has to happen within the time ranges needed for the ink in the gravure cell to travel from the doctor blade to the printing nip and then, on the paper, from the nip to the dryers. Otherwise, the addition of the surfactant will be irrelevant to the outcome of the process. A recently published paper (Vogel, 1992) reported surface lifetime of 200 milliseconds as relevant for a gravure press with a 20 inch diameter cylinder running at the web speed of 1,500 feet per minute. This would well relate to the rate of 5 bubbles per second on Sensadyne 6000, which can easily be achieved. However, a closer look at a publication gravure press reveals (Fig. 1), that a much faster bubble rate is needed. As a new ink surface is actually formed at the doctor blade, located about 6 - 10 inches before the printing nip, it takes about 20 - 30 milliseconds for the surface to travel this distance before it hits the paper in the quoted example, and this is all the time available for any equilibration. This time is respective to

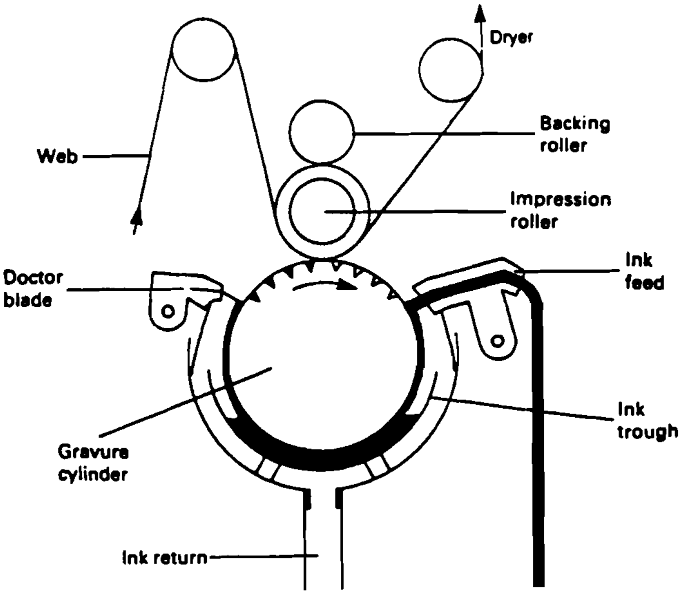


Figure 1
Gravure Printing Unit

the bubble rate of about 40 bubbles per second on the Sensadyne 6000, which is well beyond the capacity of the instrument. It appears that only photooptical techniques of measuring dynamic contact angle, like Fibro 1100 by FIBRO System ab, can bring the conditions closer to the time intervals of interest. Even though the data reported in the literature were not very consistent (Triantafillopoulos et al, 1992; Oliver, 1982; Oliver, 1984), we decided to apply this approach to study the behavior of water based ink when brought into contact with a paper substrate. This study is focused on the phenomena occurring within the first 1,500 milliseconds of such a contact, and identifying the parameters which govern ink/paper interactions important for printability.

This paper is the first of a series of four dealing with the impact of ink/paper interactions on printability of water based publication gravure inks. Part II will describe acid/base interactions at the paper/ink interface. Sorption of liquids by the paper during the ink setting and drying, and water based ink transfer from the gravure cell, will be dealt with in Part III and Part IV, accordingly.

EXPERIMENTAL

Materials

The commercial papers chosen for this study covered three grades commonly used in publication gravure printing: supercalandered, light weight coated and high quality, heavy coated substrate. Moreover, specially prepared light weight coated sheets, differing only in the pH of the wet coating (alkaline, neutral and acidic), were obtained, courtesy of International Paper Company. The following is a complete list of the substrates:

a. 35 lb. supercalandered A (SCA) from Myllykoski Paper (Finland).

b. 40 lb. light weight coated (LWC) from Champion International Corporation.

c. 60 lb. coated from Westvaco.

d. Three light weight coated papers from International Paper: alkaline, neutral and acidic (the wet coatings' pH values were pre-adjusted to 9.2, 7.1 and 5.0, respectively).

The samples of papers had been stored for ten days prior to the measurements in a conditioning room at a temperature of 20 degrees centigrade and relative humidity of 50% .

The following liquids were used in this study:

a. Water based gravure process blue ink.

b. Solvent based gravure process blue ink.

c. Distilled water.

d. Aqueous surfactant solutions.

e. Toluene, chromatographic grade.

Methods

A set-up of goniometer, by Rame-Hart, Inc., and Pro-Line VHS Panasonic video camera, was put together to measure the dynamic contact angles. A microsyringe and a hypodermic needle were used to produce droplets of a given liquid of constant size of 7 - 8 microliters and to deposit the droplet onto the surface studied. The image of the liquid droplet and paper surface was projected onto a frosted glass plate. The camera was started a moment before the droplet was deposited on the surface and the image was videotaped. Then, using the frame-by-frame analysis on the Panasonic AG-3600 VHS deck, the contact angles were measured every 33 milliseconds. Great care was taken to prevent the droplet from being in contact, simultaneously, with the paper and the needle - a situation which leads to a substantial distortion of the apparent contact angle. The paper samples were always oriented machine direction perpendicular to the viewing, to reduce interference of the directional properties of the paper surface (Oliver, 1982).

Sensadyne 6000 was used to measure dynamic surface tension at bubble rates of 2.5 to 7 bubbles/sec. The instrument was calibrated using distilled water (surface tension = 72.9 dynes/cm) and isopropyl alcohol (surface tension = 21.3 dynes/cm) at a temperature of 20 degrees centigrade.

Several methods for determining pH of the papers were evaluated: cold extraction and surface electrode methods, as described in TAPPI Test Methods T509 om-83 and T 529 om-82, respectively, as well as the chemical pH indicator method, TAPPI UM 471. The chemical indicators method, modified for the purpose of this work, was found to be the most informative, especially for determining kinetic aspects of pH equilibration between the surface and the bulk of a paper sheet. The detailed description of this modified method will be given elsewhere.

RESULTS AND DISCUSSION

Basic properties of the paper substrates used in this study are presented in Table I. Interestingly, differences in pH between the papers, including those specially prepared by International Paper, were quite small in spite of the substantial differences in pH of the wet coatings. Great care was taken to use paper samples representative of the sheets.

Table I. Properties of Paper Samples

				(4) Profilometer Data			(5)
	(1)	(2)	(3)	R(m)	R(z)	R(a)	pH
35# SCA	1.60	25.6	46	20.3	15.9	0.66	4.4
LWC 40# Champion	1.34	25.6	56	23.5	18.1	0.98	5.0
Coated 60# Westvaco	1.36	19.2	79	16.9	12.1	0.71	5.5
IP - LWC Alkaline	1.57	25.0	56	21.1	14.4	0.63	5.5
IP - LWC Neutral	1.57	32.3	51	17.9	13.9	0.69	5.1
IP - LWC Acidic	1.57	22.7	51	16.5	10.8	0.60	4.7

(1) Compressibility; Parker Print-Surf Roughness

(2) Penetration; IGT Dynamic Absorption Test

(3) Caliper; micrometers

(4) Profilometer roughness; micrometers

(5) Surface pH; pH indicators method

The relationships of the contact angle vs. the time of residence of the droplet on the substrate surface are presented in Figs. 2 through 7. As the most rapid changes in the contact angle values were happening within the first 500-600 milliseconds, Figs. 4 and 6 present the magnified graphs within this time range. Although the numerical values of the contact angles on different substrates vary, the run of the curves, as well as their relative positioning,

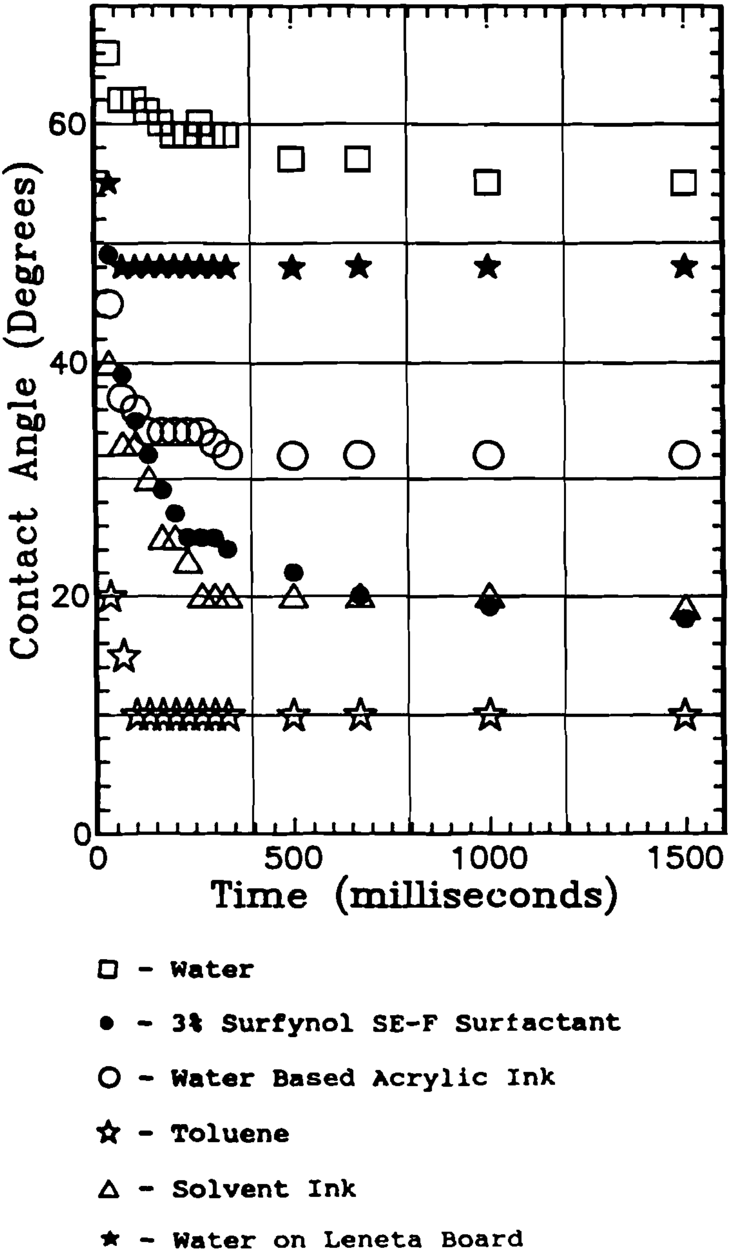
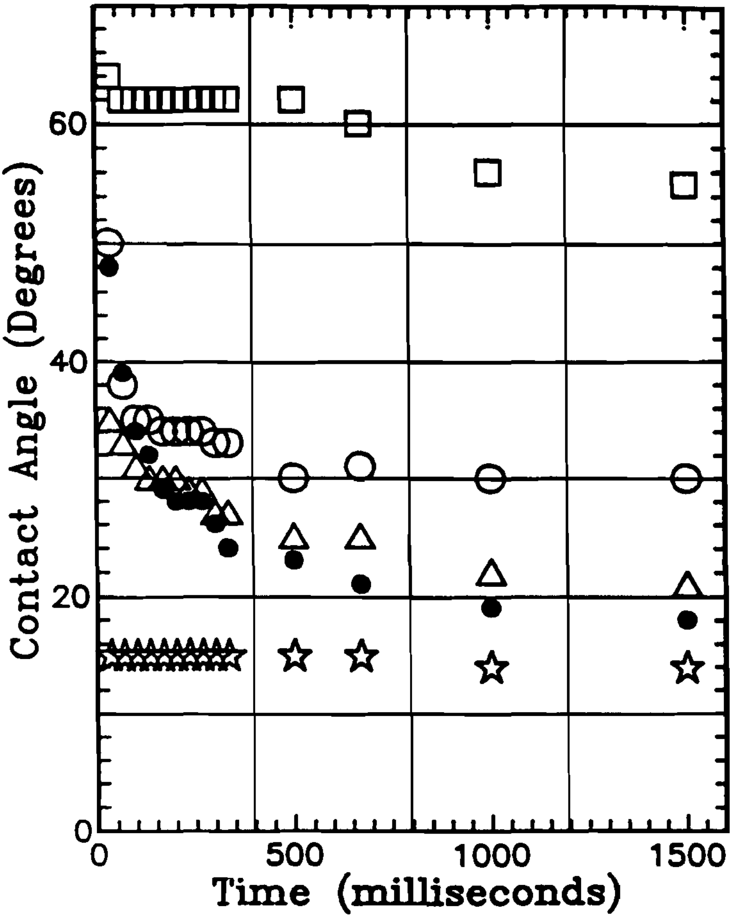


Fig. 2. Contact angle vs. time; 35 lb. SCA Myllykoski paper.



□ - Water

● - 3% Surfynol SE-F Surfactant

○ - Water Based Acrylic Ink

☆ - Toluene

△ - Solvent Ink

Fig. 3. Contact angle vs. time; 40 lb. LWC Champion paper.

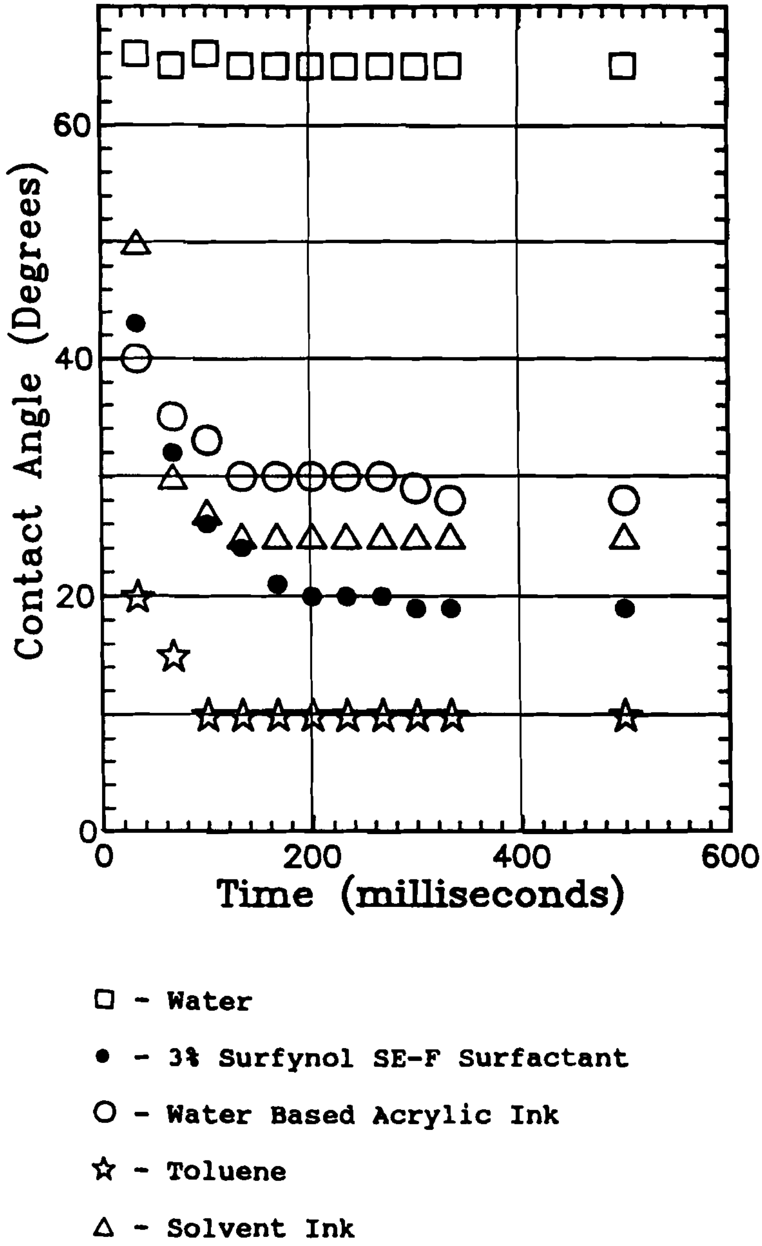


Fig. 4. Contact angle vs. time; 60 lb. coated Westvaco paper.

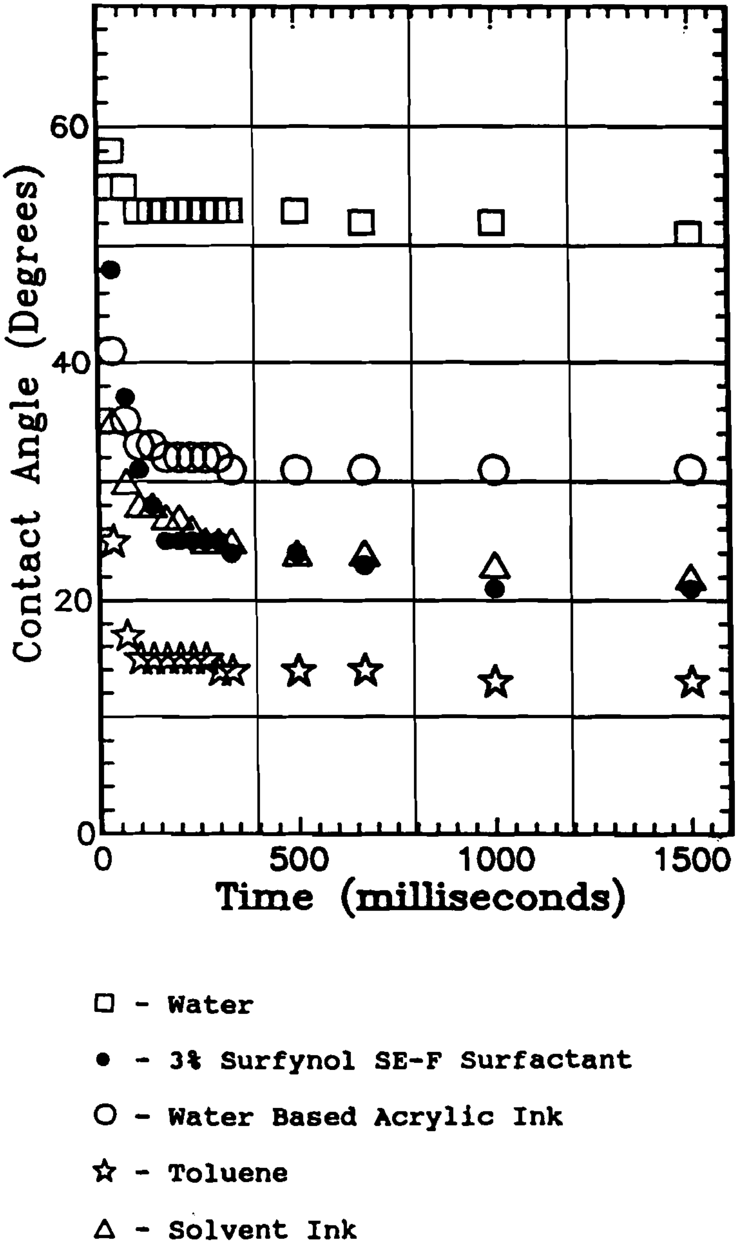


Fig. 5. Contact angle vs. time; LWC experimental alkaline paper (International Paper).

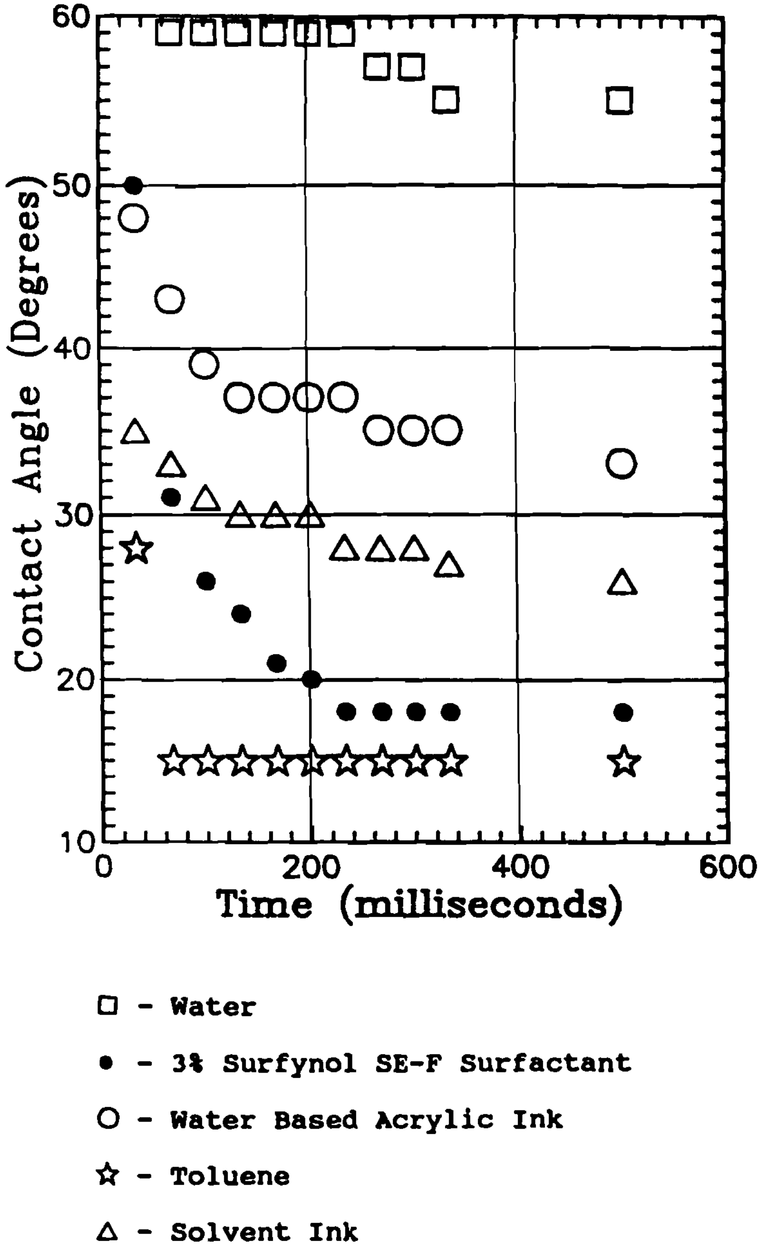


Fig. 6. Contact angle vs. time; LWC experimental neutral paper (International Paper).

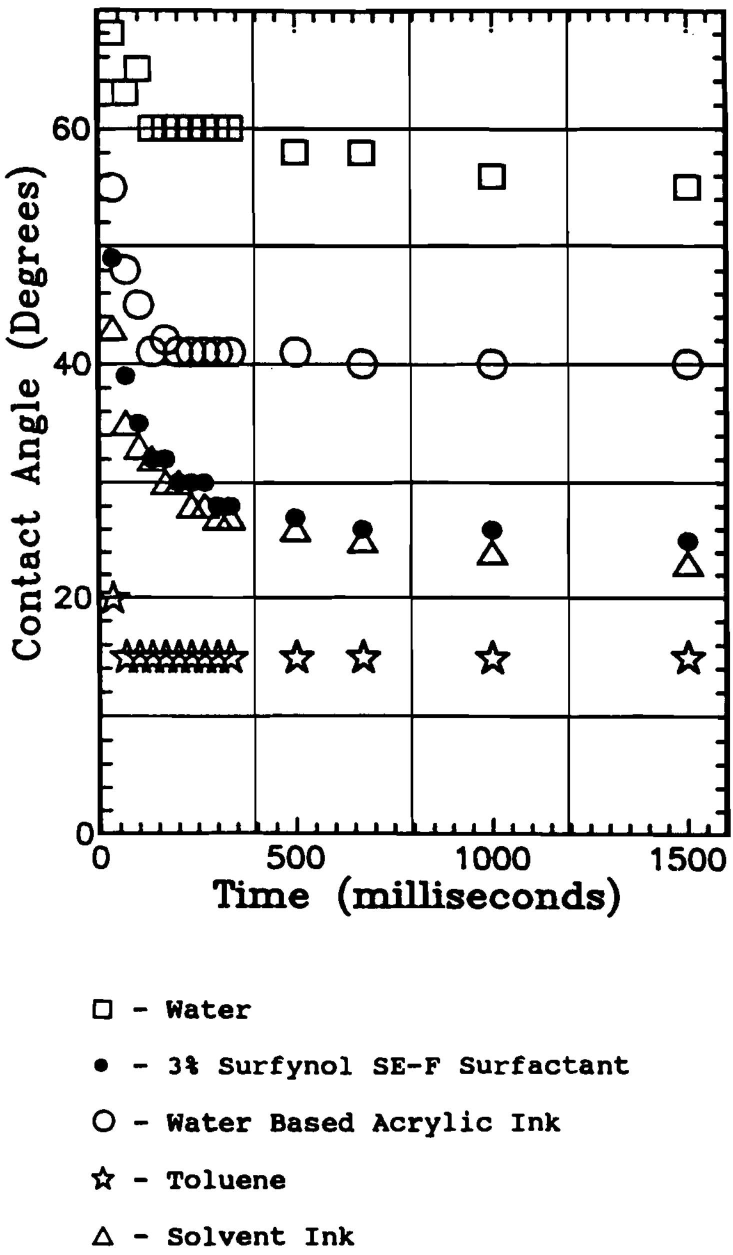


Fig. 7. Contact angle vs. time; LWC experimental acidic paper (International Paper).

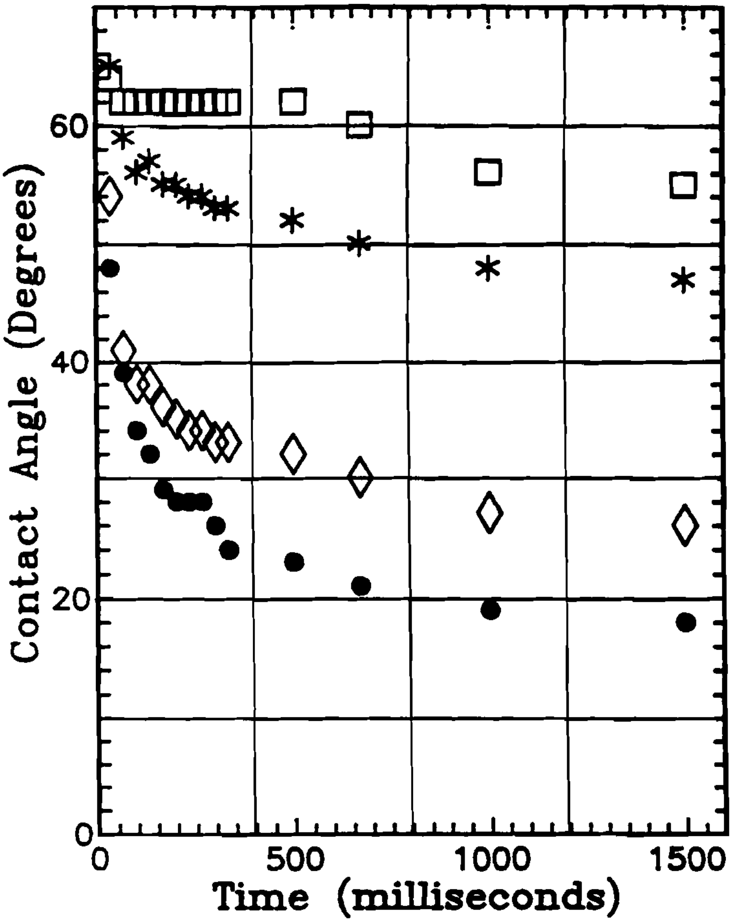
are quite similar for all the liquids except water. The clear dependence of the behavior of a pure water droplet on the type of paper indicates a strong impact of water absorption into the substrate. This is well illustrated by comparison of the water curves for the porous supercalandered paper and the impervious Leneta board presented in Fig. 2. In the case of the Leneta board, the contact angle arrived to the well defined "equilibrium" within 66 milliseconds and remained practically unchanged thereafter. On the supercalandered substrate, however, it took about three times as long to reach the "equilibrium", and the contact angle values kept drifting further after that. On the LWC substrate (Fig. 3) the water droplet apparently went through at least two "equilibria": first, it achieved the "wetting equilibrium" within about 66 milliseconds; then, after about 500 milliseconds, the contact angle value started drifting down again. Apparently, it took about 500 milliseconds for water to penetrate down across the paper coating and reach the highly hygroscopic cellulose fiber core. This created a strong capillary suction and caused further changes in the contact angle, related to the drainage into the sheet rather than the surface wetting. Microscopic observation of the paper cross-section confirmed such an explanation, which is also well in agreement with water sorption studies reported by others (Sandas and Salminen, 1987; Eklund and Salminen, 1986; Salminen, 1988). Interestingly, the time pure water needed to permeate across the paper coating showed some dependence on the coating acidity (Figs. 5 - 7). On the other hand, the water droplet behavior on 60 lb. heavy coated Westvaco substrate resembled very much that on the Leneta board. In general, even though wetting by water was found dependent on the substrate, the contact angle values were all within a narrow range of 53 to 65 degrees.

Similar wetting behavior was observed earlier by others (Lyne and Aspler, 1982; Lepoutre et al, 1985 and Aspler et al, 1987). They found, so called, "wetting delay time" dependent on the type of substrate (coated vs. uncoated) and on the surface tension of the liquid. The data presented here, however, do indicate that the wetting, itself, occurs very rapidly and the delay in further changes in contact angle values is caused by sorption.

In the case of surfactant solutions, the contact angle came close to the "equilibrium" on all the substrates within about 500 milliseconds (Figs. 2 - 7), while the shape of the curves, as well as the final contact angle values, depended strongly on the surfactant concentration (Fig. 8). There are no "kinks", indicative of a "sorption delay", on any of the curves except for that for pure water. The initial values of contact angle (the first recorded) obtained with the surfactant solutions (see Fig. 8) did not differ greatly from that for pure water. The differences were 16, 12 and zero degrees for the 3%, 0.1%, and 0.01% solutions, respectively, in spite of the fact that the droplet was kept at the needle tip long enough for the surfactant to migrate to the droplet surface and lower the surface tension. Apparently, such a "static equilibrium" on the surface of the droplet was drastically disturbed at the instant of contact with the substrate and the initial impact of the surfactant was much smaller than one could expect. This is in agreement with a well known fact that a surfactant concentration required for good printability of water based ink is always much higher than the surface tension data suggest.

Pure toluene achieved the equilibrium in 33 to 66 milliseconds at the level of 10° - 15°, almost independently of the kind of substrate, and there was no sign of any sorption delay. This is certainly one of the reasons why toluene ink systems render such high print quality.

The equilibrium contact angle for solvent ink fell within 20 to 24 degrees and was basically independent of the substrate. The rate of achieving the equilibrium was much slower than with pure toluene, and in some cases (Figs. 4 and 6) even somewhat slower than with the 3% surfactant solution. This seems to be related to the



□ - Water

∗ - 0.01% Surfynol SE-F Surfactant

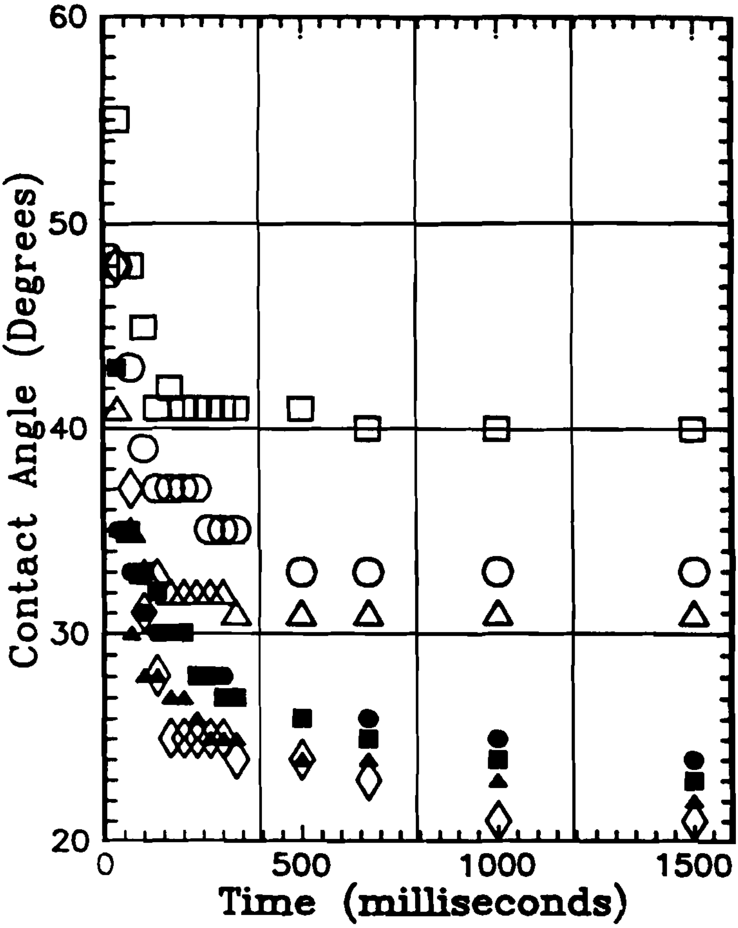
◊ - 0.1% Surfynol SE-F Surfactant

● - 3% Surfynol SE-F Surfactant

Fig. 8. Contact angle vs. time; solutions of Surfynol SE-F.

rapid increase in the ink viscosity at the ink/substrate interface due to the solvent drainage. The close overlapping of the solvent ink and the 3% surfactant solution curves seen in Figs. 2 through 7 is probably a matter of coincidence.

The "equilibrium" contact angle values for water based inks were significantly higher than those for solvent inks and were strongly substrate-dependent. The differences between the solvent and water inks were the smallest, 4 to 6 degrees, on heavy coated and alkaline papers, (Figs. 4 and 5, respectively); and the biggest, 12 to 18 degrees, for the supercalandered and acidic papers (Figs 2 and 7, respectively). The rates of arriving at the "equilibrium", on the other hand, seemed comparable to that with the solvent ink. Obviously, ink viscosity changes played a major role here. However, the strong dependence of the curve runs on the acidity of the substrate indicates to chemical interactions occurring between the alkaline ink (pH = 8.8) and the acidic paper. It is important to remember that surface pH of the "alkaline" paper ended up much lower than the pH of the wet paper coating (Table I), 5.5 vs. 9.2. Furthermore, as soon as the paper coating becomes saturated with water, the acidic base sheet starts participating in the acid/base reactions at the ink/paper interface. As a result, the alkaline printing ink gets rapidly neutralized on contact with the paper and the polymeric binder immediately precipitates at the interface. This, obviously, hinders the spreading of the ink, as well as the water penetration into the substrate. On the other hand, the precipitation of the polymer facilitates water release from the ink, which helps both water vaporization and absorption. These pH changes within the ink film occur very rapidly - within less than 66 milliseconds. Apparently, interactions of water based ink with the paper substrates are much more complex than those of solvent inks. An illustration of those differences is presented in Fig. 9. The surfactant solution (3%), as well as the solvent ink, achieved "equilibrium" very fast and wetted the substrate very well. Moreover, the solvent ink



WATER BASED ACRYLIC INK
△ - Experimental LWC alkaline paper
○ - Experimental LWC neutral paper
□ - Experimental LWC acidic paper

SOLVENT INK
▲ - Experimental LWC alkaline paper
● - Experimental LWC neutral paper
■ - Experimental LWC acidic paper

3% SURFYNOL SE-F SURFACTANT
◊ - Experimental LWC alkaline paper

Fig. 9. Contact angle vs. time; LWC experimental papers (alkaline, acidic, neutral).

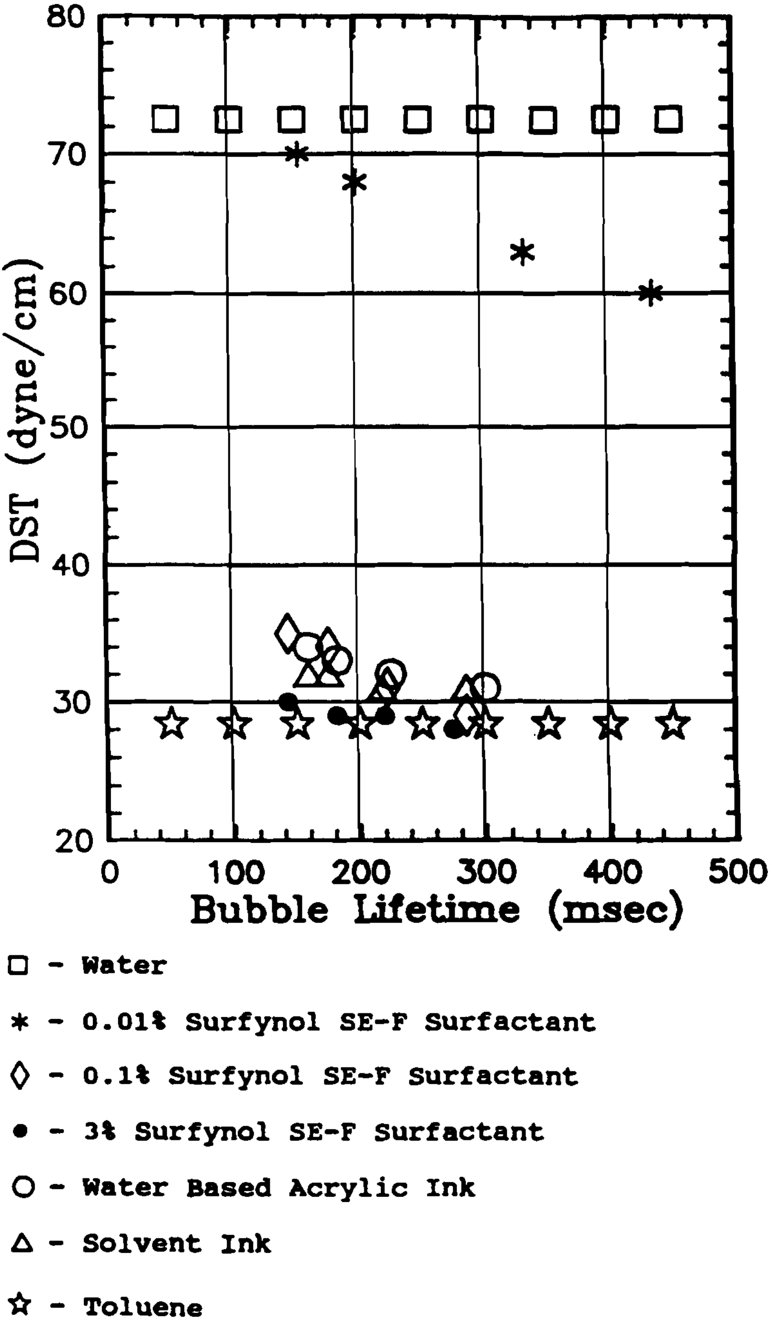


Fig. 10. Dynamic Surface Tension vs. Bubble Lifetime.

curves obtained on the three substrates of different coating pH practically coincided, indicating that the impact of the substrate was negligible. In the case of water based ink, however, changing the substrate from alkaline to acidic resulted in an "equilibrium" contact angle change by 10 degrees. The rate of achieving the "equilibrium" was also faster on the acidic substrate.

In this study, reproducible dynamic surface tension values could be obtained within the range of 2.5 through 7 bubbles per second on the Sensadyne 6000 (Fig. 10), which correspond to the contact angle values obtained within the time range of 140 to 400 milliseconds (Figs. 2 through 7). Comparison of these two sets of data reveals that even the solutions with almost negligible differences in DST's render very significant differences in contact angle values. It seems rather obvious that the DST data alone do not allow for any reliable conclusion on the wetting phenomenon.

Reportedly, the bubble rate range of Sensadyne 6000 could be extended up to 20 bubbles per second upon a fine-adjusting of the instrument and acquiring special software. It will be very interesting to see the DST values at this high bubble rate. Even though it is a far cry from the dynamic conditions of a high speed publication gravure printing press, at least better extrapolations can be expected.

CONCLUSIONS

1. Static or dynamic surface tension data alone are totally inadequate for an interpretation of printing ink/paper substrate interactions. Moreover, DST data truly relevant to the high speed publication gravure printing process would require bubble rates higher than 40 bubbles per second.

2. The most important wetting phenomenon occurs within the first 50 - 100 milliseconds of ink contact with the paper.

3. Wetting of a substrate by a printing ink is a complex function of local interfacial tension, surfactant migration to the interface, solvent penetration into the paper, and viscosity changes at the interface. It seems to be of paramount importance to learn about their respective contributions, as most of them can be controlled to a certain degree by a judicious adjustment of ink and /or paper composition.

4. Interactions of water based ink with the paper appear to be much more complex than those of solvent ink and involve some chemical reactions.

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