Further understanding on the surface chemistry of conventional lithography

Wei Shen*, Brenda Hutton and Fuping Liu

Keywords: Conventional offset lithography, ink transfer mechanism, interfacial adhesion strength, film splitting

Abstract

In conventional offset lithographic printing, it has been well established that the existence of a continuous layer of fountain solution (FS) on the surface of the non-image area is an essential condition to ensure correct operation of lithography. However, the mechanistic function of FS in preventing the ink from being transferred onto the non-image area has not been fully understood. Several major mechanistic interpretations can be found in the literature, which are based either on comparing of static works of adhesion and cohesion of ink and FS, or on the splitting of the "weaker" FS layer. Although the latter becomes more accepted, *direct* experimental evidence is difficult to find in the literature. On the other hand, confusing information found in the literature showed that the ink transfer (or non-transfer) observations reported in many case studies correlate well with simple comparisons of works of adhesion, cohesion and spreading data of ink/FS, ink/plate and FS/plate obtained under the static condition. These results therefore imply that, in explaining the function of FS in preventing ink transfer to the non-image area, the ink/FS interfacial adhesion failure would be the dominant mechanism.

This study presents results obtained from some novel experiments using Teflon or ice as a substrate, the work of adhesion and cohesion were not able to predict ink transfer in some cases. Instead, the adhesion force and ink tack force may be more useful for the prediction of ink transfer to onto a substrate. This work also provided direct experimental evidence which shows that the splitting of the FS layer was involved in the prevention of ink-transfer to the non-image areas and the thickness of the FS layer is critical in allowing the splitting to occur.

Introduction

Lithographic printing is a planographic printing process. The image areas, which transfer ink, and the non-image areas, which do not transfer ink, are differentiated by their surface chemical properties [1,2]. The ink transfer condition is controlled by the surface properties of the plate, and also by the properties of the ink and fountain solution (FS) [1 – 3]. Comprehensive descriptions of surface properties of the lithographic plate

---

* Australian Pulp and Paper Institute (APPI), Department of Chemical Engineering, Monash University, Clayton Campus, Vic. 3800, Australia.
Email: wei.shen@eng.monash.edu.au

and the practical working principle of lithography can be found in references [1 – 3].

Lithographic inks are oil-based paste inks; they are not miscible with water to any substantial degree. In order for the image area to transfer ink, the image area must be wettable by the ink. At the same time, ink must not transfer onto the non-image area. To ensure this, fountain solution (FS), an aqueous solution containing a number of functional components, is used.

The FS is designed to fully wet the non-image area and to cleanse ink and other contaminants that deposit on the non-image area during printing. Inks and most other hydrocarbon-type contaminants accidentally introduced onto the non-image area can, therefore, be removed by FS [3]. However, if a contaminant bonds too strongly to the non-image area of the plate, it cannot be removed by the normal cleansing function of FS. If this adsorbed contaminant changes the surface chemical properties of the non-image area, the area may start to accept and transfer ink.

The focus of this study was on further understanding the prevention mechanism of ink transfer to the non-image area by FS. To assist the result presentation and discussion, the terms ‘surface free energy’ and ‘surface tension’ will be used interchangeably. New ideas are proposed and discussed regarding the relationship between surface free energy, wetting and ink transfer. New experimental results are also presented providing deeper insights into the prevention mechanism by FS of ink onto the non-image area. The surface free energy interpretation is exploited further in attempts to transfer ink onto other substrates (Teflon and ice). It shows that, in some cases, it is difficult to use changes in surface free energy alone to clearly explain and predict ink transfer. Instead, it requires alternative considerations to explain the observed results. The discussion offered was confined within the classical adhesion theory, although the concepts of disjoining pressure and hydrophobic force may also be able to explain some aspects of the transfer and non-transfer mechanisms involved. The interpretations using these concepts will be offered in future work in this line.

Summary of previous research work on lithographic principles and ink transfer

Several previous investigations have addressed the interactions between ink, FS and plate in attempts to clarifying the principle of lithography. Wilkinson et al. [1] used a model system in which the image and non-image areas of a lithographic plate were simulated by Teflon and aluminium patches vacuum-deposited on Teflon, respectively. A low-viscosity mineral oil and water were used to simulate ink and FS, respectively. The authors found that spreading of oil from the Teflon area into the aluminium area was dependent upon the thickness of the water layer in the aluminium area. Likewise, the spreading of water from the aluminium area into the Teflon area was also dependent upon the thickness of the water layer. They then concluded that in order to keep the non-image area free of ink, the fountain solution in the non-image area must have a certain thickness [1].

Work by Wilkinson et al. [1] presented a view, using low viscosity oil, of a likely scenario at the border of the image and non-image areas of a lithographic plate under near-static conditions. However, these authors did not address the ink transfer (non-transfer) under a dynamic condition or by forced wetting.

De Grace and Mangin [4] reported a study on the influence of surface energetics of printing substrates to the transfer of lithographic ink. Although their study did not focus on the interactions of ink and FS with the printing plate, their results and interpretation on ink transfer onto substrates of different surface energies were relevant to this study. The substrates they chose were Teflon, polyethylene and polyester. They showed that there was no significant difference in ink receptivity of substrates of different surface free energies (measured by the weight of ink transferred per unit area), although it was noted that the ink film on the Teflon surface broke and receded into patches shortly after the transfer. This was not observed on the polyester surface [4]. This means that ink wetted the polyester surface to a greater degree than it did the Teflon surface under ambient conditions. The difference in substrate wettability by the ink had little influence on ink transfer (measured by the weight of ink transfer per unit area) [4].

De Grace and Mangin [4], however, assumed that, in order for ink to transfer onto the Teflon surface in a similar way onto the polyester surface, wetting of the Teflon surface by the ink was required. They postulated that the surface tension of ink could have been depressed significantly under the pressure in the printing nip. They also cited an early study that showed it was thermodynamically possible for the liquid surface tension to drop under high pressure [5]. De Grace and Mangin, however, did not check whether it was also possible to transfer ink onto Teflon under zero pressure.

Kato et al. [12] proposed that the ink transfer condition could be predicted by comparing the works of adhesion and cohesion obtained under static conditions. They stated that in order for the non-transfer condition of ink on the non-image area to be satisfied, the works of cohesion of FS ($W_{c(FS\text{-}FS)}$) and of ink ($W_{c(ink\text{-}ink)}$) needed to be greater than the ink and FS work of adhesion ($W_{a(ink\text{-}FS)}$). If these criteria are satisfied, the work and adhesion between ink and FS ($W_{a(ink\text{-}FS)}$) is the weakest and Kato et al. suggested that the interface between the ink and FS would split during printing, thereby preventing the transfer of ink onto the non-image area. To support their theory, they performed a series of contact angle measurements and interfacial energy calculations [12]. Their results were in agreement with their theory, as they used octane, a low viscosity hydrocarbon, to simulate ink in their measurement.

It is possible that the criteria proposed by Kato et al. [12] be modified to predict ink transfer under different experimental conditions. For example, if a neat lithographic ink is used to test the ink transfer onto a substrate (without involving FS), then the ink transfer criterion would be the comparison of the work of adhesion between the ink and the substrate ($W_{a(ink\text{-}substrate)}$) and the work of cohesion of the ink ($W_{c(ink\text{-}ink)}$).

Kaelble et al. [6] characterized surface energetics of several lithographic plates and other substrates and proposed some surface free energy criteria for ink transfer on the image and non-image areas of a printing plate. Their approach was also based on a static consideration. A major difference of their work to those of others was that they considered the inability of ink to transfer onto the non-image area of a plate as a result of adhesion failure between the ink and non-image area, caused by the intrusion of a mono-molecular layer of water or FS [6]. They did not, however, further consider the effect of the thickness of the water layer on the ink adhesion to the non-image area of the plate.

MacPhee [7] analyzed the ink transfer in a lithographic printing process. Ink transfer from an inking roll to the plate was via the splitting of the ink film. If there were two layers of immiscible liquids between the rolls, splitting occurred within the liquid that was less viscous [7]. This view may be compared with the situation of ink on an inking roll contacting a FS layer on the plate's non-image area, and concluding that the FS layer will split, since it is less viscous than the ink. Under this condition, ink will not transfer onto the non-image area. Since the FS does not fully wet the image area, ink transfer to this area would be allowed. MacPhee's point of view is that in order to stop ink transfer to the non-image area, a layer of FS that is much thicker than a monomolecular dimension is required. In practice, several studies showed that under normal printing conditions the FS on the non-image area has a thickness of 0.2 [8] – 0.7 μm [9].

Vanderhoff [3] emphasized the role played by gum Arabic in preventing the adhesion of inks to the non-image area of the plate. He proposed that the effectiveness of gum Arabic was due to the adsorption of the gum onto the surface of aluminium oxide. Riddell and Davies [10] investigated the adsorption of gum Arabic on various metal oxides and concluded that the gum did indeed adsorb on the surface of aluminium oxide, and that the adsorbed layer was readily swellable in water [10]. Tritton [11] experimentally estimated that the thickness of adsorbed gum Arabic on an aluminium plate surface was about 1000 molecules thick. However, the adsorption of gum Arabic on surfaces of bone charcoal and other aliphatic organic substrates was very weak, leading to less than one monomolecular layer being adsorbed [11]. Results reported by these authors implied that the adsorption of highly water-swellable gum Arabic on the non-image area of the plate formed a barrier with a thickness much greater than one mono-molecular layer. It was also suggested that a thick barrier layer formed only on the non-image area, not on the image area.

Other reports in the literature [13,14] have presented analysis of ink transfer conditions using thermodynamic wetting and spreading criteria. Some researchers, however, pointed out that thermodynamic analysis based on comparison of the work of adhesion between the ink and plate, and the work of cohesion of ink, could not successfully explain ink transfer under a dynamic printing condition [15]. This is understandable, since the interactions between ink, FS and plate occur under a non-equilibrium condition, and it is difficult for this interaction to be described using thermodynamic quantities such as the work of cohesion and work of adhesion.

The above review shows quite clearly that the principle of lithography requires further clarification. Consideration of wetting, forced wetting, rheological properties of ink and adhesion of ink to image and non-image areas of the plate is required. The current study attempts to address some of these issues.

Experimental

Materials and chemical reagents

Liquids used for contact angle measurements were water (MilliPore, 18 MΩ) and diiodomethane (>99%, Aldrich). The diiodomethane (DIM) was used without further purification.

Mineral and vegetable oils for ink formulation were obtained from Sicpa Ink (Australia). News ink samples, listed in Table 1, were also obtained from Sicpa ink (Australia). Fountain solution (EuroFount N) was obtained from DS Chem Port (Australia), and was diluted with MilliPore water to 2 wt% before use. The surface tension values of oil samples and their interfacial tension values with water and FS were determined using the pendant drop method with an OCAH 230 instrument (DataPhysics) and listed in Table 1. This experimental interfacial tension data will be used in the discussion below.

Table 1 Surface and interfacial energy values (in mJ/m^2) of ink, water, FS, oil/water and oil/FS.

Samples	CAS No.	Density (g/cm^3)	$\gamma_{sample/air}$	$\gamma_{sample/water}$	$\gamma_{sample/FS\ (2\%)}$
Water	-	1	71.7	0	-
FS (2%)	-	1	44.1	-	0
Magiesol 60	8042-47-5	0.83	23.1	39.7	22.5
Conosol 260	64742-46-7	0.83	23.0	39.7	22.9
Drakesol 260	8042-47-5	0.81	22.4	40.7	21.5
Paraset	-	0.83	21.8	22.6	19.7
Veg. Oil	-	0.92	30.5	34.4	26.4
Sicpa Ink (black)	-	1.08	25	-	-

Process news ink samples were also obtained from Sicpa Ink. The surface tension of the ink was also determined using the pendant drop method. Since ink samples are highly viscous, a stable surface tension reading could only be obtained by allowing sufficient time (typically 2 – 5 minutes) for the drop to reach an equilibrium shape.

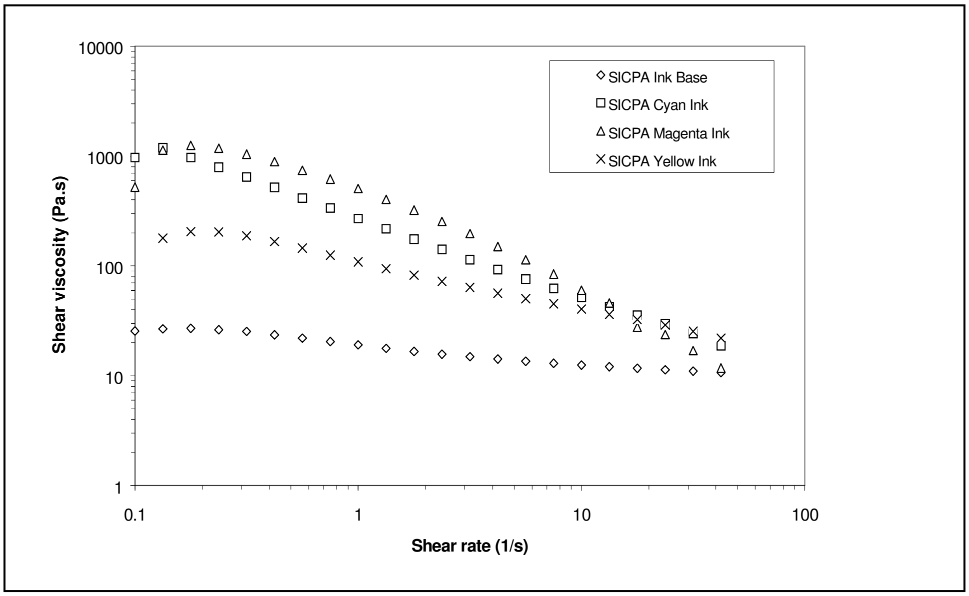

Figure 1. Ink viscosity as a function of shear rate.

Since the density of news ink is very close to 1.0 g/cm^3, it is not possible to measure its interfacial tension with FS using the pendant drop method without introducing a large error. For this reason, $\gamma_{ink/FS}$ was not measured. The ink viscosity was measured in a low shear-rate range (0.1 – 40 1/s). The purpose of collecting the ink viscosity data was to estimate the influence of ink viscosity to the ink surface tension measurement through calculating the capillary number (Ca) of the ink (see below).

Lithographic plates were obtained from Pageset Digital Pre-press, Melbourne, and cut into suitable sizes for surface analysis and contact angle measurements. Teflon sheets of 0.5 mm thickness were obtained from Goodfellow. Samples of 25×25 mm^2 squares were cut from the sheet, and were again blown with nitrogen to remove any loosely-bound dust. Some samples were further washed with the non-ionic surfactant solution followed by exhaustive rinsing with water, while others were not. However, contact angle measurements using water and DIM suggested that washing made no difference to the contact angle results.

Preparation and analysis of substrates

Lithographic plates

Pressurized high purity nitrogen was used to remove any loosely-bound dust form the plate surface prior to use. Measurements of water and diiodomethane on the plate surface were also made using the OCAH-230 instrument (Data Physics). Surface energy data calculated using equation (7) (see below) are listed in Table 2.

Table 2 Contact angle data (in degrees) and surface energy parameters (in mJ/m^2) of the plate samples

Samples	H_2O	DIM	γ^d	γ^p	γ
Non-image	4.8	45.4	36.8	38.1	74.9
Image	58.6	48.4	37.9	13.9	51.8

Teflon sheets

No further preparation of the Teflon sheets was performed, as further cleaning of the Teflon surface did not change the contact angles of probe liquids on it. When the Teflon substrate was used to investigate ink transfer at near-zero pressure, a microbalance (DCA 322, Cahn Instruments) was employed. The force curve for ink-Teflon contact was recorded, and is shown in Figure 5.

Ice substrates

A low temperature freezer cabinet (QUIRK'S, Australia) was used to make ice. Polystyrene foam boxes were used to house both ice and ink samples (Figures 2 and 3) to minimize temperature fluctuations within the cabinet. A temperature data logger (T-TEC 7, U-lab Instruments) was used to record the actual temperature inside the polystyrene foam box, and Figure 4 shows a typical record of temperature variation inside the box, being around ±0.3 ºC.

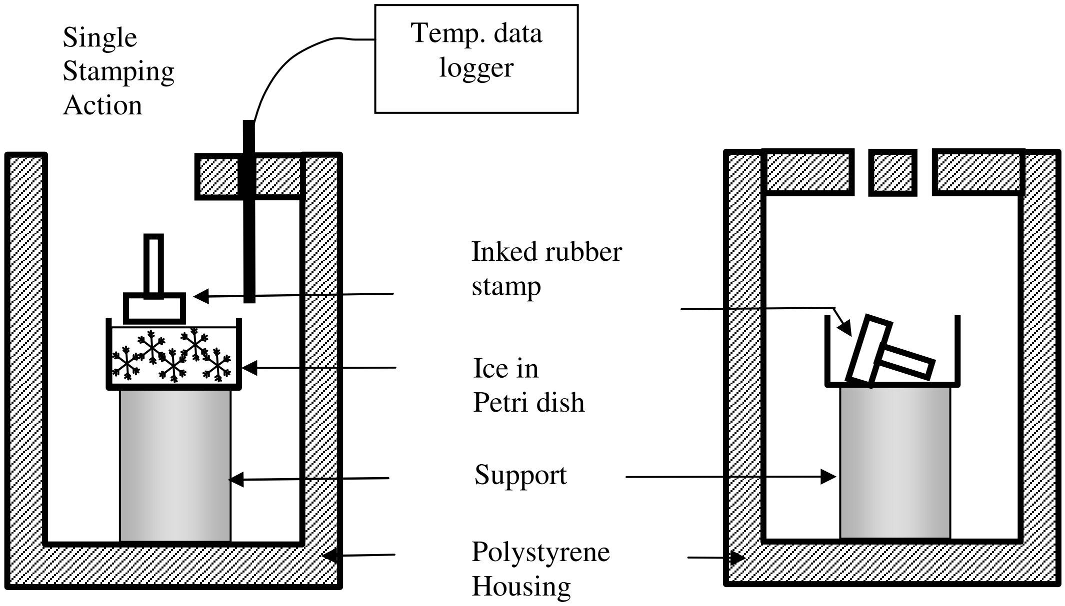

Figure 2. Schematics of the ink transfer test method using a rubber stamp.

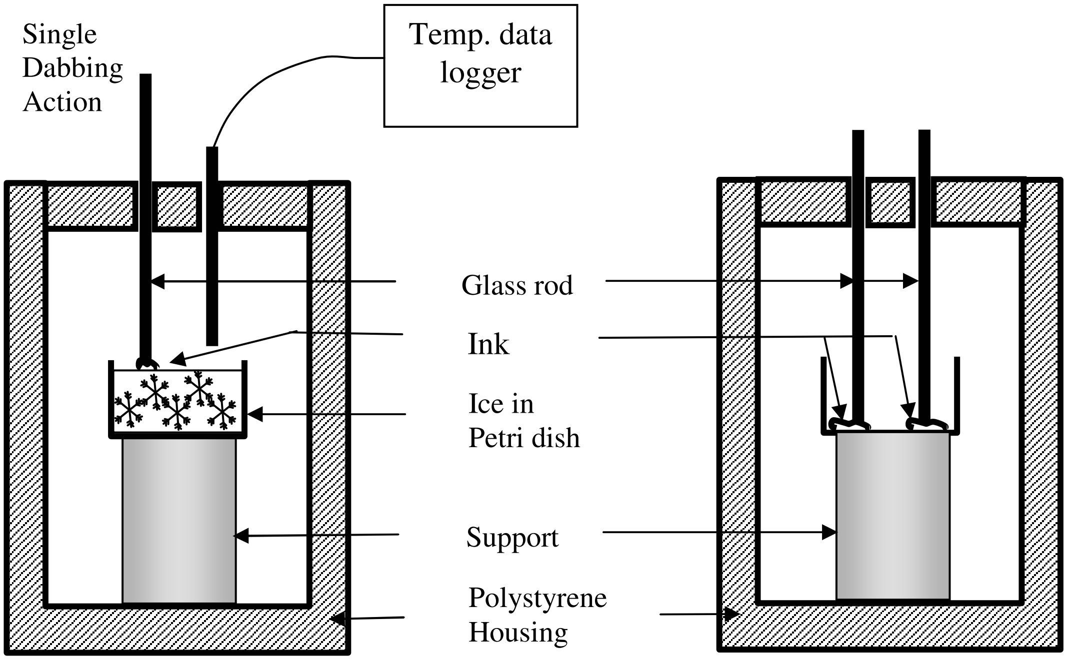

Figure 3. Schematics of the ink transfer test method using a glass rod.

MilliPore water was placed in a clean Petri dish within the foam box at –7^{o}C for 2.5 days, to prepare the ice substrates for experiments conducted at subzero conditions. For those conducted at 0^{o}C, water was frozen at –5^{o}C for one day followed by 0^{o}C for 1.5

days, to ensure that the substrates were solid water rather than liquid water at this temperature. A digital camera was used to record the results of ink transfer onto these substrates.

Ink transfer methods

Ink was uniformly transferred onto a hand roller and subsequently transferred to lithographic plates and Teflon substrates.

Ink transfer onto Teflon at near-zero pressure used a microbalance as mentioned previously. To eliminate any effect of gravity on the ink transfer process, the Teflon sample was allowed to approach a patch of ink from above (depicted in Figure 5). The approaching speed of Teflon towards the ink patch was 16 µm/s. The instrument was programmed to stop Teflon advancing as soon as it touched the ink. This method minimized the impact force on Teflon. The Teflon was then allowed to remain in contact with the ink for 16 seconds before being retracted back at the same speed (Figure 5).

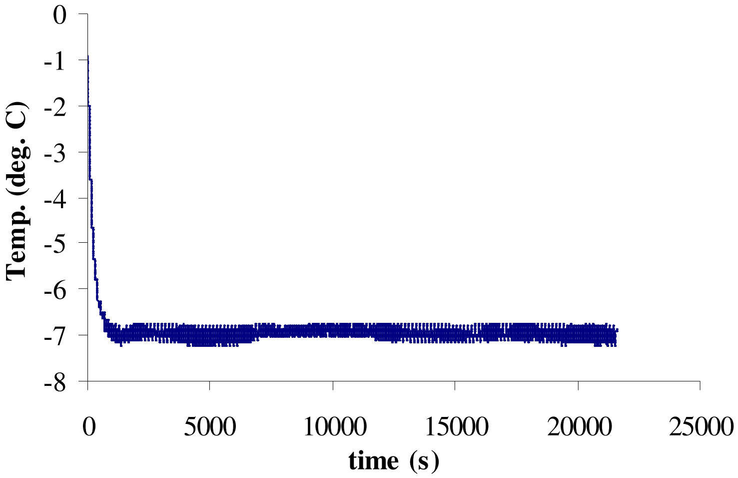

Figure 4. Typical temperature fluctuation inside the foam box used for conducting ink transfer test on ice.

Transfer of ink onto ice surfaces used either a rubber stamp pressed against a uniformly rolled patch of ink, or a glass rod covered by a relatively thick layer of ink. Both stamp and rod were refrigerated with the ice in polystyrene foam boxes, and the ink was transferred at the appropriate time by a single stamping (or dabbing) action.

Results and discussion

Basic wetting and adhesion theory

Since classical theory of adhesion is used extensively in the discussion of these results, it is appropriate to review the relevant definitions, which will be used in later sections.

Wetting and adhesion under a static condition

The principles of lithography are often explained using interfacial energetics. The work of adhesion (W_a) between two entirely immiscible liquids (A and B) is defined as:

$$W_a = \gamma_A + \gamma_B - \gamma_{AB} \tag{1}$$

where γ_A and γ_B are the surface tension values of liquid A and B, respectively, and γ_{AB} is the interfacial tension [16]. The work of cohesion of a liquid (A) is defined as:

$$W_c = 2\,\gamma_A \tag{2}$$

If one phase in equation (1) is solid (assuming perfect smoothness) and the other is liquid, which forms a contact angle with the solid, the work of adhesion between them can be written by substituting Young's equation into equation (1), as follows:

$$W_a = \gamma_L(1+\cos\theta) \tag{3}$$

where γ_L is the surface tension of the liquid and θ is the contact angle between the liquid and the solid surface [16].

If the interfacial interaction is considered to be the sum of contributions of different types of intermolecular forces, and assuming that these intermolecular forces are not appreciably influenced by one another, the surface free energy can be written as the sum of different components [17]. There are several different models in the literature that link the interactions of these components with the work of adhesion [18]. In the present study, the semi-empirical model that was first proposed by Girifalco, Good and Fowkes and later modified by Owens and Wendt [19] is chosen for simplicity. The assumptions of this model are:

$$\gamma = \gamma^d + \gamma^p \tag{4}$$

$$\gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A^d \gamma_B^d} - 2\sqrt{\gamma_A^p \gamma_B^p} \tag{5}$$

where γ is the surface free energy, and γ^d and γ^p are its dispersion and polar components respectively. Subscripts A, B and AB indicate surfaces and the interface between the two phases, respectively. According to Owens and Wendt, γ^p includes contributions from dipole, induced dipole and hydrogen bonding interactions [19].

Between these two types of intermolecular interactions, the dispersion force is universal and always attractive [20-21]. The range of dispersion interaction is estimated to be ≤ 10 nm. Beyond this distance, dispersion interaction decays rapidly [20-21]. The dispersion force contributes significantly to adhesion. Considering two immiscible phases in intimate contact, the work of adhesion due to the dispersion force can be estimated using the semi-empirical rule proposed by Fowkes [22] as follows:

$$W_a = 2\sqrt{\gamma_A^d \gamma_B^d} \tag{6}$$

If polar molecular interaction also contributes to the work of adhesion, an additional term ($2\sqrt{\gamma_A^p \gamma_B^p}$) can be added to equation (6). This can then be substituted into equation (3) to write:

$$W_a = \gamma_L(1+\cos\theta) = 2\sqrt{\gamma_A^d \gamma_B^d} + 2\sqrt{\gamma_A^p \gamma_B^p} \tag{7}$$

Many research results suggest that, provided sufficiently intimate intermolecular contact is achieved at the interface, the dispersion force alone is sufficient for the establishment of strong adhesion [23]. Good [21] proposed that the ideal adhesive strength at an interface could be written as:

$$\sigma_{AB}^a = \frac{16}{9\sqrt{3}} \frac{W_a}{z_{0,AB}} \tag{8}$$

where $\sigma^a{}_{AB}$ is the ideal adhesive strength at an interface separating A and B phases, W_a is the work of adhesion (mJ/m^2) and $z_{0,\mathrm{AB}}$ (Å) is the equilibrium separation between molecules A and B.

Adamson and Gast [24] indicated that although the representative values for the work of adhesion due to dispersion forces were small and usually only a few tens of mJ/m^2, the fact that molecular interaction operated over a very small distance, the separation force (or ideal adhesion strength) was usually surprisingly large. By way of example they showed that while the work of adhesion between water and benzene was only 56 mJ/m^2, the separation force was as high as 560 kg/cm^2, taking the effective intermolecular distance to be 10 Å [24].

Wetting and adhesion under a dynamic condition

The wetting and spreading of a liquid on a solid surface is governed by the balance of three types of forces: gravity, viscous and interface (i.e. the liquid/solid and liquid/vapour) forces. The most relevant force in considering wetting of a plate (or other substrate) by a lithographic ink is the influence of the viscous force on interfacial tension driving force, which is best appreciated with the dimensionless capillary number ($Ca = \eta U/\gamma$) [26]. Where η is the viscosity, γ is the surface tension and U is the ink droplet front line velocity. Figure 1 shows the ink viscosity data measured at low shear rate. When a drop of ink is place on a substrate for contact angle measurement, the shear rate, generated by the interfacial tension driving forces, is very low. The viscosity and the surface tension of a typical lithographic ink at a low shear rate (i.e. during a wetting process) are around $10^2 - 10^3$ Pa.s and 25 mN/m, respectively. The capillary number calculated from these figures is $\geq 4\times10^3$ U. Even if a very low initial ink spreading speed (say 0.01 m/s) is taken, Ca is still quite large, being ≥ 40. A large Ca means that viscosity of the ink will have a significant influence on its spreading (For a comparison, Ca for H_2O is 0.014, assuming the front line velocity, U, is 1 m/s).

The kinetic treatment of a wetting process of a solid by a liquid considers that the initial stage of the process is transient [24]. Zhmud [25] shows that a time dependent wetting process can be treated using the classic Navier-Stokes equation. When the viscosity of the liquid is high, the rate of wetting is determined by the rheological properties of the liquid. For a highly viscous liquid like lithographic ink, the surface tension does not have a dominant influence on the wetting dynamics during the transient period. As a dynamic wetting process is approaching a static equilibrium state, surface tension and contact angle can be used to describe the interfacial energetics of the final state.

Surface and interfacial tension measurements of oils and news ink varnish

Surface tension values of four mineral and one vegetable oil samples were determined and are listed in Table 1. The surface tension values of the four mineral oils fell into a narrow range of 21.8 to 23.1 mJ/m^2. Their interfacial tension values with water were, however, very different, with Paraset being much lower than other oil samples. Among the oil samples selected, Paraset contained the highest aromatic content, according to the supplier's specification. This was confirmed qualitatively by UV-Vis spectrometry. This may be one of the reasons why this sample has a low interfacial tension with water [16]. Another reason may be that there are some surface active functional groups either on the aromatic rings or on the aliphatic chairs of the oil molecule.

The interfacial tension values for mineral oils and FS (2 % (v/v)) were lower than the values for these oils and water. This reduction was obviously due to the presence of surfactant(s) in the FS. The fact that the oil/FS interfacial tension for the mineral oils fell into a narrow range (from 19.7 – 22.9 mJ/m^2) suggested that surfactant(s) could have adsorbed on all oil/FS interfaces. News ink vegetable oil had a higher surface tension and interfacial tension with water and FS. However, the vegetable oil sample showed the same trend as did the mineral oil samples, i.e., its interfacial tension with FS was lower than that with water. The work of adhesion of these oil samples with water can be estimated using equation (1) [16].

Plate surface free energy measurements and ink transfer tests

Surface energy data of the plate

The dispersion and polar components of surface free energy of the image and non-image areas of the plate are listed in Table 2. The dispersion component (γ^d) of surface free energy for the untreated non-image area was 36.8 mJ/m^2. This value is higher than that reported by Bassemir and Shubert (21 mJ/m^2) [14] and Kaelble et al. (25.5 mJ/m^2) [6] for the non-image area of commercial lithographic plates, but lower than the value by Kato et al. (50.3 mJ/m^2) [12]. Kato et al. commented that the γ^d value for several metal oxides determined by Fowkes using gas adsorption were much higher than values reported by Kaelble et al. [6]. It is reasonable to assume that the surface free energy of a clean anodized Al_2O_3 surface is also quite high. The poor agreement in the γ^d values was most likely attributable to different surface conditions of the plate. In particular, the adsorption of organic materials such as the surface protective "gum" on anodized Al_2O_3 surface is expected to reduce its surface free energy. The image area of the plate has a similar dispersion component to that of the non-image area, but has a much lower polar component than the non-image area. This trend is in agreement with the results reported by Bassemir and Schubert [14].

An ink transfer test using a hand roll on the plate showed fully expected results: Ink transferred on both the image and non-image areas if FS was not applied to the plate; ink only transferred on the image area if FS was applied to the plate first. Further studies using these plate samples were focused on surface contamination induced non-image area scumming and will be reported separately.

The splitting mechanism of the FS layer in lithography

An important question of the fundamental mechanism of lithography is whether the splitting occurs at the FS – ink interface or within the FS layer. Some researchers assumed that in order for the FS to prevent ink transfer to the non-image area, the splitting should occur within the FS layer, since it is much "weaker" than the ink layer. Process modeling analysis of the possible location of splitting can be found in the literature [7], but direct experimental evidence is lacking. The apparent success of Kato's concept of comparing the works of adhesion and cohesion in describing ink transfer events in some cases [12] and Wilkinson's approach of using low viscosity oil and water to simulate the ink/FS/plate interactions [1] imply that the equilibrium surface free energy data can be used to predict the highly dynamic ink/FS/plate interactions in lithographic printing. However, these studies did not consider the fact that an equilibrium condition cannot be established in a highly dynamic printing process. It is appropriate to ask whether those studies based solely on equilibrium surface free energy data have adequately addressed the fundamental mechanism of lithography.

Teflon substrates

Ink transfer onto Teflon surfaces

De Grace and Mangin [4] have demonstrated that the amount of ink transferred onto three polymeric films of different surface free energies is largely independent of the surface free energy. These authors noted that shortly after the ink transfer, ink film started to break, receding into patches. The current study also tested ink transfer onto a Teflon surface, and it was found that a film of ink could be readily transferred. Shortly after the transfer, however, the ink film started to break, gradually receding and leaving some parts of the Teflon surface completely free of ink. This confirms the observation reported by De Grace and Mangin [4]. Interestingly, but not surprisingly, the ink film did not recede after being transferred onto a glass surface when the same test was repeated on a glass substrate.

The surface free energy of Teflon was experimentally determined in this work to be 19 mJ/m^2 and is exclusively due to dispersion forces. Taking the surface free energy of ink as 25 mJ/m^2 (the value determined using the Pendant drop method), the work of adhesion between the ink and Teflon can be determined ($W_{a(ink/Teflon)} \approx 2\times(19\times25)^{1/2} = 43.6$ mJ/m^2). However, since lithographic inks also have a small polar component [6,12], the dispersion component of the ink surface free energy is thus smaller than 25 mJ/m^2. This means that the actual work of adhesion between the ink and Teflon is lower than 43.6 mJ/m^2. On the other hand, the work of cohesion ($W_{c(ink-ink)}$) of the ink calculated using equation (2) is 50 mJ/m^2. In this case, Kato's concept failed to predict the transfer of the ink to Teflon. Clearly, ink transfer cannot always be predicted by comparing the equilibrium surface free energy data.

De Grace and Mangin indicated that at the moment of ink transfer, the ink must completely wet Teflon. These authors suggested that in order for this to occur, the surface tension of the ink must have dropped to below the critical surface tension of Teflon under the high nip pressure [4]. Following the same line of thought, one would expect no ink transfer under very low transfer pressures. This theory, however, was refuted in the experiment shown in Figure 5, where ink was transferred onto the Teflon surface under near-zero pressure.

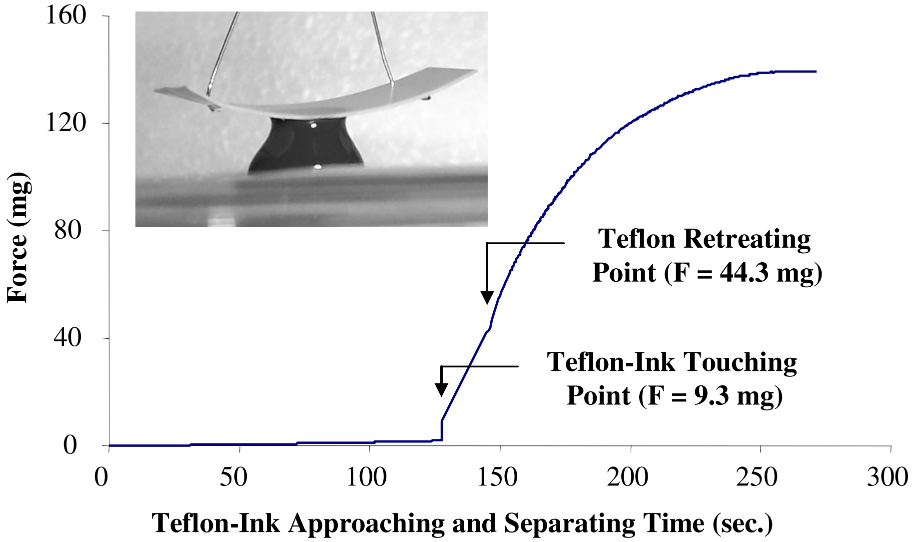

Figure 5. The force, reflecting the adhesion between ink and Teflon under near-zero pressure, recorded over time. The result shows that ink transfer onto Teflon does not require a high external pressure.

The force curve showed that at the Teflon and ink contact point, the total force measured was 9.3 mg or 9.3×10^{-5} N. The diameter of the circular contact area between ink-Teflon was estimated to be 0.8 cm. This information leads to a calculated absolute value of 2 Pa for the contact pressure. Interestingly, such a pressure was negative, since an increase in the measured force indicated that the ink "pulled" the Teflon towards itself via the surface tension force. As is shown in Figure 5, this force increased in magnitude, apparently linearly with time, as the Teflon sample was allowed to dwell for 16 seconds after the contact with ink was made. Such an increase in force during the dwell time was caused by ink wetting the Teflon substrate. Therefore, the adhesion between Teflon and ink did not require any positive pressure. This again suggests that equilibrium surface free energy data alone do not sufficiently describe every ink transfer process. Ink transfer does not require the ink to completely wet the substrate surface.

The slow receding of the ink film from the Teflon surface is due to the high viscosity of the ink dominating the initial stage of the receding process [25]. In this initial stage, the interfacial tension forces stated in Young's equation, which are the driving forces for ink receding, do not dominate the receding process. This can be appreciated on a qualitative basis by examining ink spreading, the reverse process of ink receding. Figure

6 shows the contact angle change as a function time of an ink drop on a Teflon surface. Equilibrium could not be established until 250 seconds after the ink drop contacted the Teflon surface. Figure 7 shows the evolution of ink drop shape onto Teflon. In the initial 80 seconds, the viscosity effect prevents any meaningful measurement of contact angle (as observed by the non-hemispherical shape of the ink drop).

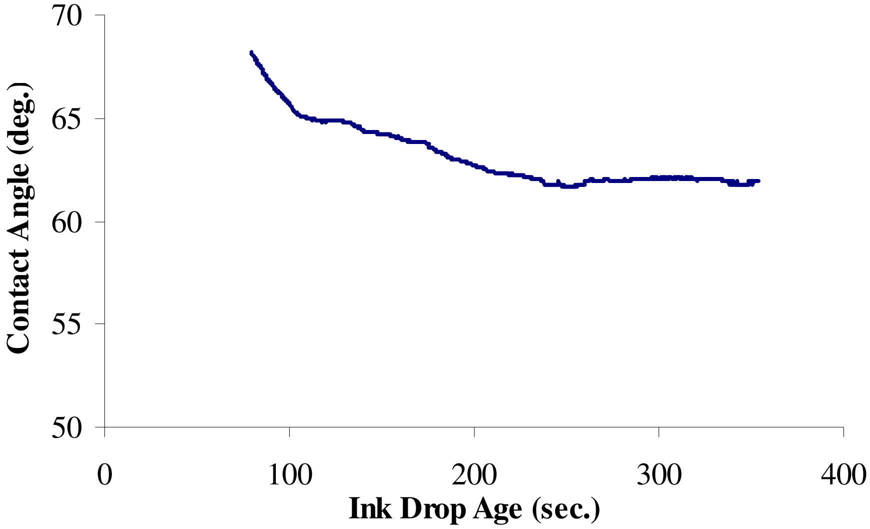

Figure 6. Contact angle of the Sicpa process news ink (Cyan) on Teflon as a function of time.

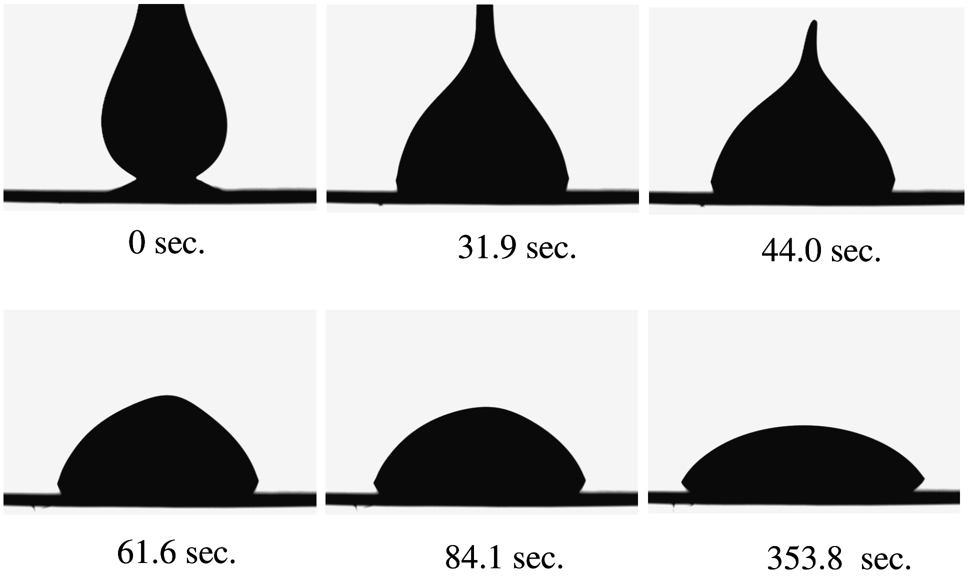

Figure 7. Evolution of the ink drop shape on Teflon.

The transfer of the ink film onto Teflon surfaces reported by De Grace and Mangin was due to forced (non-equilibrium) wetting. The initial stage of the ink receding process from Teflon is dominated by the rheological properties and not by the surface free energy of the ink. In this context, the splitting of the ink or fountain solution layer should be investigated by considering both forced wetting [6] and forced splitting; however, the relative magnitudes of ink adhesion strength to the plate surface and ink tack force should also be considered [12,15,27]. Ink tack force is defined as the maximum tensile stress exerted on the ink film that causes it to split in the printing nip [3].

It is generally agreed that dispersion interactions between the two phases alone are sufficiently strong to provide good adhesion performance if sufficiently intimate intermolecular contact can be achieved at the interface. It is expected that forced wetting brings ink molecules into close contact with Teflon, and the dispersion interaction between molecules of the two phases is established. (It is possible that various other forces could be involved. However, only the dispersion force will be considered, since the focus of this work was to address the non-transfer condition of ink onto the plate's non-image area using classical adhesion theory). The ideal adhesion strength between the ink and Teflon can then be calculated using equation (8) from the work of adhesion value ($2(19\times25)^{1/2} = 43.6$ mJ/m^2) and the intermolecular distance between the two phases. If the separation between ink and Teflon is assumed to be 10 Å, an ideal adhesion strength of 457 kg/cm^2 is obtained. Although the real adhesion strength is likely to be more than an order of magnitude lower than the ideal adhesive strength [28], the real adhesion strength between ink and Teflon would still be about 4.6 kg/cm^2, assuming that the real adhesion strength is two orders of magnitude lower than the ideal adhesion strength.

Aspler et al. [29] measured the ink tack force in a printing nip directly using apparatus built in-house. These authors built a pressure transducer in a printing cylinder that was inked. When ink was transferred onto the surface of a substrate, a negative force caused by the splitting of the ink film was recorded. These authors controlled the thickness of the initial ink film at about 4.5 μm, and printed onto a Mylar film at a relatively low speed of 5 m/s [29]. Their measurements indicated that the ink film splitting force typically fell in the range of 0.7 – 1.4 kg/cm^2.

Comparing ink tack forces reported by Aspler et al. [29] with the estimated adhesion strength between ink and Teflon, it can be concluded that there should not be any difficulty in transferring ink onto a Teflon surface.

Factors influencing ink transfer

Kaelble et al. [6] proposed, from the surface energetics point of view, that the intrusion of a single molecular layer of water at the interface between ink and the plate could generate a de-bonding force, which is strong enough to reduce the adhesion interaction between the ink and the plate surface, thus preventing ink from being transferred onto the plate surface.

Such a concept, based on a single molecular layer of water, may overlook some other factors. If it is assumed that adhesion between the ink and water involves only dispersion interactions, one can easily conclude using equation (6) that the work of adhesion between ink and water is greater than that between Teflon and ink ($2(21.8\times25)^{1/2} = 46.7$ mJ/m^2 for ink/water, compared to 43.6 mJ/m^2 for ink/Teflon). If ink can be transferred onto Teflon, it should also be transferred onto a substrate that is covered by single molecular layer of water.

Another problem with the concept is that the thickness of a single molecular layer of water is smaller than the range of van der Waals interactions, which is around 10 nm. Adamson and Gast [20] cited a number of surface chemistry works that provided evidence for long-range van der Waals forces occurring far beyond the thickness of a monolayer of some small molecules. It is possible that there would still be van der Waals interactions between the plate and ink even though a monolayer of high dielectric water molecules intrudes the ink-plate interface.

McGill [30] suggested that a failure or cleavage along the interface between two phases was highly improbable. Instead, failure almost always occurred within one of the two phases. MacPhee [7] assumed that a complete release of the ink film from the non-image area under normal printing conditions was due to splitting of the FS film. McGill and MacPhee's opinions suggested that under the extensional stress of ink film splitting, it was most likely the failure of the low viscosity FS layer that contributed to the prevention of ink transfer onto the non-image area. Optimum surface energetics of the plate, fountain solution and ink contributed indirectly to ink splitting, since a good match of surface energetics of these materials promoted the formation of a sufficiently continuous FS film on the non-image area.

The two hypotheses more likely reflecting the non-transfer mechanism of ink to plate non-image area in conventional lithography may be stated as follows. Firstly, the molecular level adhesion strength at the interface between ink and FS is stronger than the ink tack as well as the force required split the FS layer. Therefore, failure at ink-FS interface will not occur under printing conditions. Secondly, in order for FS to stop ink transfer to the non-image area of the plate, the FS layer must be thick enough so that failure will occur within this layer and not within the ink layer. As will be discussed in the following section, the force required to split a liquid film is sensitively dependent upon its thickness. To experimentally demonstrate these points, one should ask, first, what will happen if water is solid and can only engage in interfacial interactions with ink, but cannot be split? And second, is it a sufficient condition to stop the ink transfer to a substrate if there is a layer of FS which is just thick enough to eliminate any van der Waals interactions between the ink and the substrate?

Ice substrates

Characteristics of ice substrates and van der Waals forces

Water is the major component in FS, which selectively controls the ink transfer to different areas of the plate. Choosing water in its solid state to test the above hypotheses has revealed some fundamental phenomena that would otherwise be difficult to observe. However, ice cannot be seen simply as solid water if the focus is on its surface. Faraday [31] first proposed that a thin layer of liquid-like water covered the surface of ice, which was in equilibrium with the bulk of ice at temperatures below the bulk melting point. This thin layer of water gives ice an unusual slipperiness. The existence and thickness of the liquid-like layer on ice has been of interest to many researchers [27, 32 - 34]. Studies showed that the thickness of the liquid-like water layer on ice varied with temperature. Good agreement on the thickness of such a layer was found between models proposed by several authors [32-34, 35] and the available experimental data [32, 34]. Gilpin [34] summarized the thickness of the liquid-like water layer on an ice surface predicted by various models. All models predicted that the thickness of this layer is less than 10 nm if the temperature is at or below -5˚C, but is equal to or greater than 10 nm when the temperature approaches 0˚C. Based on these literature data, it is hypothesized that the thickness of the water layer on ice is less than the van der Waals force range at the temperature below -5˚C, and equal to or greater than the van der Waals range at 0˚C.

Ketcham and Hobbs [36] reported that the contact angle of water on ice at 0˚C was 20±2˚. Knight [37] reported that the receding contact angle for water on ice was 12˚. These contact angle values suggest that the surface free energy of ice is higher than that of water at 0°C. Water has a value of 75.7 mJ/m^2 at 0˚C, while there is, however, no unanimous value of the surface free energy for ice at 0˚C.

Ketcham and Hobbs [36] briefly summarized some early values of ice surface free energy, which lie between 85 and 122 mJ/m^2 at 0˚C. These early works did not separately report the dispersion and polar components. From the CS_2 contact angle data on polycrystalline ice reported by Adamson et al. at -5˚C [27], a Lifshitz-van der Waals surface free energy component of 34 mJ/m^2 can be calculated using the model proposed by van Oss et al. [38]. Kloubek [39] reported surface free energy value from a calculation using contact angle data of water, carbon disulphide and chlorobenzene. He employed a model similar to equation (7) and obtained a total surface free energy value of 106 mJ/m^2 at 0˚C, with the dispersion component being 94.6 mJ/m^2. van Oss et al. [38] reported, based on their own contact angle data, that the total surface free energy of ice at 0 ˚C was 66.5 mJ/m^2, with the Lifshitz-van der Waals and the acid-base components being 26.9 mJ/m^2 and 39.6 mJ/m^2, respectively. Despite the poor agreement in these data, it seems that the dispersion component of ice is greater than that of water, which is 23.3 mJ/m^2 at 0˚C [38].

If, as suggested, the surface of ice near 0˚C is not much different in structure from that of liquid water [27,31,34], the higher dispersion component of ice surface free energy compared with liquid water could be due to the contribution of van der Waals forces from the subsurface region, which may still have an effect on the surface when the thickness of this water-like layer is smaller than the van der Waals range.

Ink transfer onto ice

In order to test the hypotheses proposed in the previous section, ink transfer experiments onto ice were conducted under three conditions: a) the assumed existence of van der Waals interactions between the ink and solid ice beneath the liquid-like layer at temperatures ≤ -5°C, b) the elimination of van der Waals interactions at temperatures ~ 0°C, and c) significantly thicker liquid-like films between ink and ice at > 0°C.

Based on the previous discussions, it can be predicted that ink should easily be transferred onto ice at temperatures below -5˚C. Figures 8 and 9 show the successful ink transfer results of three inks onto ice at -7˚C. A relatively thick layer of ink was present on the glass rods during the rod transfer method, resulting in low ink tack [7], and hence easy transfer of ink onto the ice substrate. However, use of the rubber stamps allowed a much thinner and more uniform ink film thickness to be delivered, again without difficulty, even though the ink tack was expected to be greater, since tack is related to ink film thickness and is higher when the ink film decreases [7]. The non-uniform transfer of ink observed by the stamp method was due to curvature of the substrate surface resulting from expansion during freezing.

The existence of the liquid-like water layer on ice allows the results to be interpreted as follows. The literature data indicate that the thickness of the liquid-like water layer on ice at -7˚C is less than 10 nm, and this is also the generally accepted van der Waals range. Therefore, it is possible that some direct van der Waals interactions between the ink and the ice underneath the liquid-like water film are still effective. Since the water film is very thin at this temperature (< 10 nm), the required splitting force for the water layer is also stronger than the ink tack. This point will be further discussed below. Since the failure did not occur at the ink-water interface or within the thin water layer, this result is consistent with the first hypothesis that the adhesion strength between the ink and FS is stronger than ink tack or splitting force for the FS layer (although not totally proven). This result is also consistent with the predictions of ink tack being weaker than the

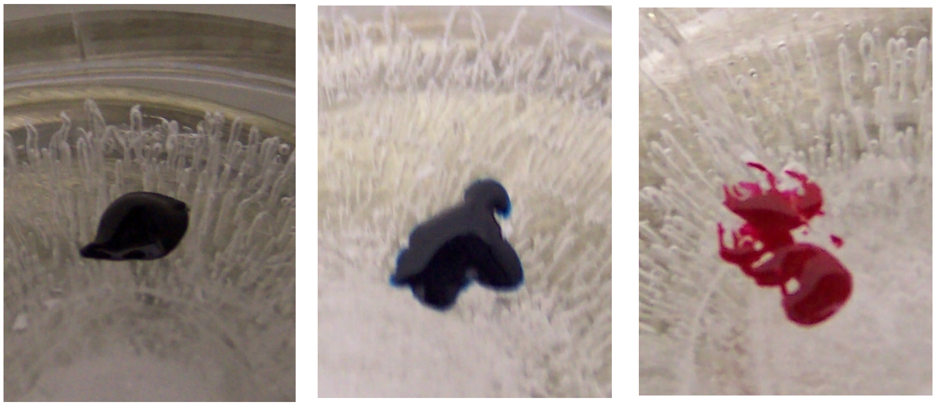

Figure 8. Photographs of the transfer of ink onto ice surface at -7 ºC using the glass rod dabbing method (See Figure 3). From left to right are black, cyan and magenta inks.

Figure 9. Photographs of the transfer of ink onto ice surface at -7 ºC using the rubber stamp method (See Figure 3). From left to right are black, cyan and magenta inks.

interfacial adhesion strength between the ink and water, and it is weaker than that between ink and Teflon.

The results of ink transfer experiments conducted at $0^{o}C$ are shown in Figures 10 and 11, and indicate that inks can also be successfully transferred onto ice substrates with either rod or stamping methods. Since photos had to be taken sometime after the ink transfer test (typically 2 minutes), melting of the ice occurred during this time. A slight spreading of ink on ice can be seen for the magenta ink, but such ink spreading was not observed at the time of ink transfer.

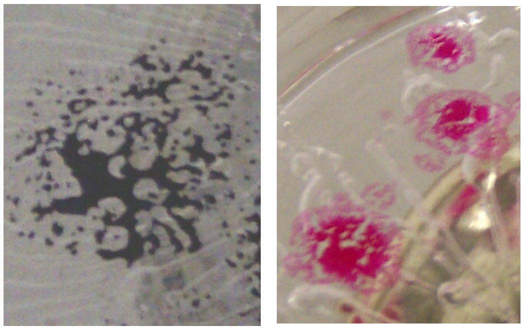

Figure 10. Photographs of the transfer of ink onto ice surface at 0 ºC using the rubber stamp method (See Figure 2). From left to right are black and magenta inks.

Literature data suggest that the thickness of the liquid-like water layer on ice surface is ≥ 10 nm at or higher than 0 ˚C. At this distance, intermolecular van der Waals interactions between the ink and the ice (beneath the liquid-like water layer) decay rapidly [20]. It is reasonable to assume, therefore, that if the thickness of the liquid-like water layer was not reduced by mechanical and chemical impacts of the ink during the test, the adhesion strength due to the van der Waals interactions between the ink and ice underneath the liquid-like water layer would be quite weak. However, since ink transfer was still possible at near-zero van der Waals interactions, this suggests that the water layer may still not be thick enough to allow film splitting.

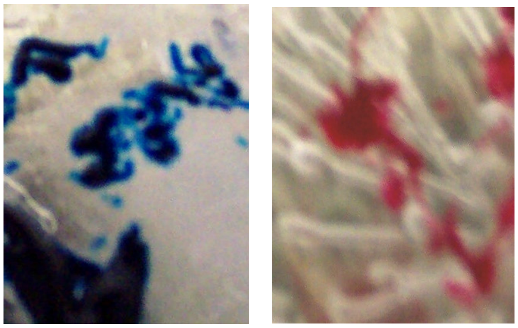

Figure 11. Photographs of the transfer of ink onto ice surface at 0 ºC using the glass rod dabbing method (See Figure 3). From left to right are cyan and magenta inks.

Further investigation into the 'desirable' thickness of the film that allows film splitting may be found upon consideration of Stefan's equation (9). This equation links the force required to split a liquid film held by two parallel flat plates. MacPhee [7] used this equation to explain the splitting of a liquid film or a composite liquid film of two layers:

$$\frac{F}{A} = \frac{C\eta v}{\mathrm{t}^3} \tag{9}$$

where F is the force, *C* is a constant, η is the viscosity of the liquid, v is the speed at which the plates are separated, A is the plate area and t is the thickness of the liquid layer. He used equation (9) to explain that the splitting of a composite film of two liquid layers should occur within the layer of lower viscosity [7]. It should, however, be noted that while equation (9) shows that the liquid film splitting force relates linearly to the viscosity of the liquid, the equation also shows that the splitting force is inversely proportional to the third power of the thickness of the film. Therefore, the force required to split a thin liquid film increases rapidly as the thickness of the film decreases. In the situation where such a force is applied to a composite film of ink and water, with splitting occurring in the latter, an estimation of the thickness of the water layer can be made using equation (9). Assuming the values of viscosity for ink and water are 100 Poise and 0.01 Poise, respectively, and the ink layer thickness is 2 μm, to ensure the splitting occurs in the water layer, the thickness of the water layer must be at least 0.2 μm.

In the experiments conducted, it was difficult to control the water layer thickness on ice to 0.2 μm. However, a qualitative test was carried out instead to demonstrate that the water layer thickness affected its splitting. Ice samples prepared at –7^{o}C were removed from the refrigerator and placed at room temperature (21.6^{o}C) to initiate a temperature rise. Ice samples were maintained within the foam box to reduce the rate of temperature increase, and the internal foam box temperature was recorded as a function of time. Ink transfer onto ice was successfully demonstrated until a temperature of about 8^{o}C was achieved, when ink transfer was no longer possible. At this point in time, the water film thickness would have become large enough to induce splitting of this layer. Qualitatively, the second hypothesis, stating that water layer thickness affected the ink transfer, was proven to be realistic.

These results show that it is not the failure of the interfacial molecular adhesion between the ink and water (or FS) that prevents the ink transfer to the non-image area of the plate. Instead, the splitting of the water (or FS) layer contributes to the prevention of ink transfer to this area. The thickness of the water layer is critical to its splitting, and certainly requires a much larger thickness than a single molecular layer as proposed by Kaelble [6].

Conclusion

The fundamental mechanism of conventional offset lithographic printing was revisited in this study; specifically, the function of FS in preventing ink transfer onto the non-image area of the plate. It is shown in this work that the thermodynamic data used in the context of classical theory of works of adhesion and cohesion failed to predict ink transfer onto the substrates of Teflon and Kealble's model of the intrusion of mono-molecular layer of water into the interface of plate and ink failed to predict ink transfer onto ice.

Ink transfer experiments onto Teflon and ice substrates has shown that splitting of the FS layer is the mechanism that prevents ink from being transferred onto the non-image area. It is not the adhesion failure at the ink/FS interface, as previously suggested by some researchers. While the mechanism of film splitting in the FS layer has been suggested before, this work demonstrates new and *direct* experimental evidence. The thickness of the FS layer, however, must be large enough to allow splitting to occur within that layer, and the present study has shown that it needs to be significantly thicker than the van der Waals interaction range.

In a highly dynamic printing situation, forced wetting brings different materials into intimate molecular contact. The adhesion strength at the interface is remarkably large. It is, therefore, very unlikely that an adhesion failure at the interface of ink and FS could occur under the printing conditions. The analysis in this work showed that ink/FS adhesion strength was greater than the ink tack force as well as force required to split a FS layer.

Acknowledgements

This work was carried out as part of the research program for the CRC Smartprint. Funding received from the Federal Government and Norske-Skog via the CRC program is gratefully acknowledged.

We would like to thank Sicpa, DS ChemPort and Penreco for the ink, fountain solution and oil samples, respectively, they kindly supplied for this work.

Special thanks are due to Mr. R. Urquhart, CEO of the CRC Smartprint for many valuable discussions on lithography.

References

[1] M.C. Wilkinson, M.P. Aronson, J.W. Vanderhoff and A.C. Zettlemoyer, in: *Adhesion Sci. Technol. Part B*, L.H. Lee (Ed.), pp. 725 – 734. Plenum Press, New York (1975).

[2] R.H. Leach, R.J. Pierce, E.P. Hickman, M.J. Mackenzie and H.G. Smith, (Eds), *The Printing Ink Manual*, 5th edn, pp. 342 – 452. Chapman & Hall (1993).

[3] J.W. Vanderhoff, *Amer. Ink Maker*, **51**(3), 25 - 27 (1973).

[4] J.H. De Grace and P.J. Mangin, *Adv. Printing Sci. Technol.* **17**, 312 – 332 (1984).

[5] J.C. Eriksson, *Acta Chem. Scand.* **16**, 2199 - 2211 (1962).

[6] D.H. Kaelble, P.J. Dynes and D. Pav, in: *Adhesion Sci. Technol.* Part B, pp. 735 – 361. L.H. Lee (Ed.), (1975).

[7] J. MacPhee, *Technical Association of the Graphic Arts Proceedings*, pp.237-277 (1979).

[8] U. Lindqvist, A. Karttunen and J. Virtanen, *Adv. Printing Sci. Technol*. **16**, 67 - 96 (1982).

[9] P. O. Trollsas, *Tappi J*. **78**(1), 155 - 160 (1995).

[10] G.L. Riddell and C.W. Davies, *J. Phys. Chem*. **35**(2), 2722 - 2731 (1931).

[11] F.J. Tritton, *J. Soc. Chem. Ind*. **51**, 299 - 313 (1932).

[12] Y. Kato, F.M. Fowkes, and J.W. Vanderhoff, *Ind. Eng. Chem. Prod. Res. Dev*. **21**, 441 – 450 (1982).

[13] R.W. Bassemir and F.G. Shubert, *Technical Association of the Graphic Arts Proceedings*, pp.555 - 567 (1984).

[14] R.W. Bassemir and F.G. Shubert, *Technical Association of the Graphic Arts Proceedings*, pp. 290 - 310 (1982).

[15] P. Ottinen and H. Saarelma, *Printing*, Chap. 5, pp. 132 – 168. Fapet Oy, Helsinki, Finland, (2000)

[16] D.J. Shaw, *Introduction to Colloid and Surface Chemistry*, 4th edn, p.66, Butterworth-Heinemann (1992).

[17] S. Wu, *Polymer Interface and Adhesion*, p.98, Marcel Dekker, New York (1982)

[18] J.C. Berg, in *Wettability*, J.C. Berg (Ed.), pp. 75 - 148. Marcel Dekker, New York (1993).

[19] D.K. Owens and R.C. Wendt, *J. Appl. Polym. Sci*., **13**, 1741 – 1747 (1969).

[20] A.W. Adamson and A.P. Gast, *Physical Chemistry of Surfaces*, 6th edn, Chapter VI, pp. 225 – 256. Wiley-Interscience, New York (1997).

[21] R.J. Good, in *Treatise on Adhesion and Adheives*, Vol. 1, R.L. Patrick, (Ed.) pp. 9 – 68. Marcel Dekker, New York (1967).

[22] F.M. Fowkes, *Ind. Eng. Chem. Prod. Res. Dev*. **56**(12), 40 - 52 (1964).

[23] J.R. Huntsberger, in *Treatise on Adhesion and Adheives*, Vol. 1, R.L. Patrick, (Ed.) pp. 119 - 149. Marcel Dekker, New York (1967).

[24] A.W. Adamson and A.P. Gast, *Physical Chemistry of Curfaces*, 6th edn, Chap. XII. Wiley-Interscience, New York (1997).

[25] B. Zhmud, Pira Conference, paper 7, Brussell, Belgium (2003).

[26] G. Garnier, J. Wright, L. Godbout, and L. Yu, J. *Colloids Surfaces. A: Physcochem. Eng. Aspects* **145**, 153 (1998).

[27] A.W. Adamson, F.P. Shirley and K.T. Kunichika, *J. Colloid Interface Sci*. **34**, 461 – 468 (1970).

[28] S. Wu, *Polymer Interface and Adhesion*, p. 339. Marcel Dekker, New York (1982).

[29] J.S. Aspler and Y.-H. Zang, L. Larrondo and L. Perron, *Technical Association of the Graphic Arts Proceedings*, pp.162 – 178 (1997).

[30] W.J. McGill, *Trans. Communic. Oil & Colour Chemists' Association J*. **60**, 121 - 126 (1977).

[31] M. Faraday, *Proc. Roy. Soc*. (London), **10**, 440 - 450 (1860).

[32] D. Beaglehole and D. Nason, *Surface Sci*. **96**, 357 - 363 (1980).

[33] N.H. Fletcher, *Philos. Mag*. **66**, 109 - 115 (1992).

[34] R.R. Gilpin, *J. Colloid Surf. Sci*. **68**, 235 - 251 (1979).

[35] M.J.M. Romkens and R.D. Miller, *J. Colloid Interface Sci*. **42**, 103 - 111 (1973).

[36] W.M. Ketcham and P.V. Hobbs, *Philos. Mag*. **19**, 1161 – 1173 (1969).

[37] C.A. Knight, *J. Colloid Interface Sci*. **25**, 280 - 284 (1967).

[38] C.J. van Oss, R.F. Giese, R. Wentzek, J. Norris and E.M. Chuvilin, in *Contact Angle, Wettability and Adhesion*, K.L. Mittal (Ed.) pp. 677 - 690. VSP, Utrecht, (1993).

[39] J. Kloubek, *J. Colloid interface Sci*. **46**, 185 - 190 (1974).