SURFACE FREE ENERGY OF PAPER AND INKS : PRINTABILITY ISSUES

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Abstract: A Wilhelmy plate apparatus (Cahn Dynamic Contact Angle Analyzer) has been used to measure surface free energies of paper and inks. The role of surface free energy in predictive print performance is discussed. The experimental methodology is described as are issues related to ink adhesion, penetration and wetting. The importance of variation in paper surface chemistry in determining printability is highlighted.

Introduction

In this paper, the relation of the surface chemistry of both inks and paper to printability is discussed. The main focus will concern ink adhesion in intaglio printing. The fundamental lessons are however useful to those employed in other types of printing.

Intaglio printing is used throughout the world for the printing of various security documents. Because of the nature of these documents durability is a major concern. The movement away from solvent based inks over the last several years has led to changes in ink formulations. These changes have brought with them many technical challenges. One of these challenges is the production of durable documents. Surface chemistry issues do not seem to have been adequately addressed by both the ink and paper maker.

In this study we have measured the surface free energies of various papers and varnishes used in intaglio printing with the hope of better understanding the mechanisms of adhesion failure. We believe that the application of modern adhesion science will lead to improvements in intaglio printing. The Wilhelmy plate method has been used to measure surface free energies.

Surface Thermodynamics and Adhesion

A more detailed discussion of the topics discussed here can be found in Adamson (1990). Here we give a brief introduction to adhesion science.

The differential energy expressions which govern the spreading of a liquid over a solid interface are as follows:

$$dE = TdS - PdV + \sigma dA + \sum_i \mu_i dn_i \qquad [1]$$

$$dG = -SdT + VdP + \sigma dA + \sum_i \mu_i dn_i \qquad [2]$$

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Here E and G are the energy and Gibbs free energy respectively; S, the entropy; σ, the surface tension and μ_i the chemical potential of the ith component. P, V, T have their usual thermodynamic meaning.

Surface tension is defined from Eqn. 2 as:

$$\sigma \equiv \left(\frac{\partial G}{\partial A}\right)_{T,P,n_i}$$ [3]

and the surface free energy, g^S, is :

$$g^s = \sigma + \sum_i \Gamma_i \mu_i$$ [4]

Here Γ_i is the Gibbs surface excess. For positive values of the surface excess, the component in question is preferentially selected into the interfacial zone. Bulk and surface concentrations are thus not generally equal. For 1 component systems $g^S = \sigma$. A more complete discussion of surface excess is given by Adamson (1990).

The principal equation which determines the extent of spreading of a liquid over a solid material is the Young equation.

$$\sigma_{SV} - \sigma_{SL} = \sigma_{LV} \, Cos\theta$$ [5]

Here σ is the interfacial free energy (surface tension) and the subscripts SV, SL and LV refer to the solid-vapor, solid-liquid and liquid-vapor interfaces respectively. θ is the contact angle.

When a drop of liquid is placed on a solid material the drop spreads until the interfacial forces are balanced. Typically such a drop appears as it does in the cartoon below. The contact angle, θ, is the angle defined by the intersection of the liquid-vapor and solid-liquid interfaces. Contact angle is related to thermodynamic quantities through the Young equation (Eqn. 5).
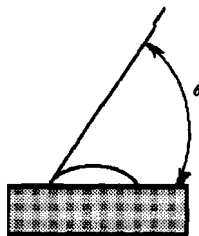

Figure 1. Cartoon of a drop of a liquid on a solid. Contact angle,θ, is shown.

Zisman, in numerous scientific articles (see Adamson 1990), has discussed the notion of a "Critical Surface Tension". The Zisman critical surface tension is determined by measuring the contact angles of a homologous series of liquids on a given solid substrate. A plot of Cos θ versus σ_{LV} is prepared. The intercept at Cos $\theta = 1$ is the Zisman critical surface tension.

Surface free energies of materials determine their adhesive properties. The ideal work of adhesion between surfaces 1 and 2 is given below.

$$W_{12} = \sigma_1 + \sigma_2 - \sigma_{12} \tag{6}$$

Combining Eqn 6 with Young's equation one finds

$$W_{12} = \sigma_2 [1 + \text{Cos } \theta] \tag{7}$$

A useful relation between the work of adhesion and the Zisman critical surface tension is the following:

$$W_{12} = \sigma_2 (2 + b \cdot \sigma_c) - b \cdot \sigma_c^2 \tag{8}$$

W_{12}, the ideal work of adhesion, applies to adhesion between atomically smooth surfaces. Real surfaces are rarely atomically smooth thus W_{12} is much larger than empirically determined adhesion strengths. Equations 6-8 none-the-less illustrate important issues. These issues are as follows:
1.   Wetting is important to adhesion.

2.   Contact angles less than 90° are required for good adhesion.

3.   Optimal adhesion, barring other factors, would occur somewhere between 0 and 90°.

Estimation of Contact Angle, Interfacial Energies, and Adhesion Strengths

Estimation of interfacial free energies and contact angles at the solid-liquid interface remains a forefront topic in surface and colloid science. Approaches for calculation such interfacial tensions are based on the axiom which states that the total surface tension can be expressed as follows.

$$\sigma_T = \sum_i \sigma_i \tag{9}$$

where the σ_i's result from specific classes of intermolecular forces. Separation of the surface energy components is possible using contact angle measurements employing appropriate probe liquids.

One strategy advanced by Good and Girifalco (1957) more than 30 years ago suggested division of surface energy into polar and non-polar (or dispersion) components. Thus

$$\sigma_T = \sigma^d + \sigma^p \tag{10}$$

Here σ^d is the surface free energy resulting from London dispersion forces. London Forces result from the polarizability of electron orbitals and are common to all intermolecular interactions. σ^P is the surface free energy resulting from Lewis acid-base (polar) interactions.

According to the Good-Girifalco theory

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^d \cdot \sigma_2^d} - 2\sqrt{\sigma_1^P \cdot \sigma_2^P} \qquad [11]$$

More recently Fowkes et al.(Fowkes, 1987; Fowkes et al. 1978 and Kato et al. 1982) and van Oss et al.(see van Oss et al., 1987 and Morra et al. 1990) have suggested separation of the polar component into separate Lewis acid and Lewis base terms. Thus

$$\sigma^P = 2\sqrt{\sigma^+ \cdot \sigma^-} \qquad [12]$$

According to the above model the polar contribution to the interfacial tension between two surfaces is given by the following:

$$\sigma_{12}^P = \sigma_{12}^{AB} = 2\left[\sqrt{\sigma_1^+} - \sqrt{\sigma_2^+}\right] \cdot 2\left[\sqrt{\sigma_1^-} - \sqrt{\sigma_2^-}\right] \qquad [13]$$

Eqn. 11 can be combined with the Young Equation in order to calculate contact angles. The resulting equation is

$$1 + Cos\ \theta = \left(\frac{1}{\sigma_1}\right) \cdot \left[2\sqrt{\sigma_1^d \cdot \sigma_2^d} + 2\sqrt{\sigma_1^P \cdot \sigma_2^P}\right] \qquad [14]$$

Accounting for Lewis acid-base interactions using Eqn. 12, Eqn. 14 becomes:

$$1 + Cos\ \theta = \left(\frac{1}{\sigma_1}\right) \cdot \left[2\sqrt{\sigma_1^d \cdot \sigma_2^d} + 2\left\{\sqrt{\sigma_1^+} - \sqrt{\sigma_2^+}\right\}\left\{\sqrt{\sigma_1^-} - \sqrt{\sigma_2^-}\right\}\right] \qquad [15]$$

Complete wetting occurs when $\theta = 0$ or $1 + Cos\ \theta = 2$. Non-wetting occurs when $\theta > 90°$ or $1 + Cos\ \theta < 1$. Eqn. 15 differs from Eqn. 14 in a significant manner. In Eqn. 14 polar interactions are always attractive and thus result in lowered contact angles. In contrast, Eqn. 15 says that polar interactions may either be attractive or repulsive. In other words, $1 + Cos\ \theta$ may either be increased or decreased depending on the relative magnitude of σ^+ and σ^-. Lower contact angles result when two interfaces have opposite acid-base character.

Wetting and Practical Adhesion

Real adhesion differs from ideal adhesion. This difference results from roughness of the surface. Surface roughness on a dimension greater than atomic results in reduced area of contact between solid surfaces. Also, some weak adhesion may be caused by capillary penetration of adhesives into pores and away from the bonding interface.

In order for a liquid adhesive to achieve the maximum area of contact, the liquid must wet the surface (zero contact angle). Adhesive bond strengths depend on:

1. Compatible surface energies such that zero contact angle is achieved;

2. Adequate contact of adhesive and substrate: Liquid adhesive must flow into crevices in order to maximize area of contact.

3. Cohesive energy of the adhesive must be adequate: (Ideally, the substrate should fracture under the load before the adhesive fails.)

Low contact angles that are necessary for good adhesion are achieved with:

1. Solid surfaces with large surface energies,

2. Surfaces with matching fractional polarities,

3. Surfaces with opposite acid-base chemistry.

Again, the above conditions ensure maximal values of W_{12} as predicted by Eqn. 15.

Experimental Approach for Determination of Surface Energies.

A Wilhelmy Plate apparatus was used to measure surface energies and contact angles. Specifically, a Cahn DCA-312 (Domingue, 1990) was used.

The Wilhelmy plate method measures the force required to either immerse or withdraw a solid object of known perimeter in a liquid. The measured force is determined by the following relation.:

$$F = p\sigma_L \ Cos \ \theta + A \ \Delta\rho \ g \left(x - x_{ZDOI}\right) \qquad [16]$$

Here p is the object perimeter, $\Delta\rho$ is the difference in the density between liquid and vapor, g the acceleration due to gravity (980 cm/sec^2), x the position of the plate and x_{ZDOI} the position of the plate at zero depth of immersion. Evaluating Eqn. 16 at $x = x_{ZDOI}$ gives

$$F_{ZDOI} = p \ \sigma_L \ Cos \ \theta \qquad [17]$$

Eqn. 17 may be used to evaluate σ_L when using a wetting liquid (Cos $\theta = 1$) or to evaluate Cos θ if σ_L is known.

For porous media such as paper, some liquid will be retained by the sample upon withdrawal. The force curve must be corrected for the extra force due to the retained liquid when either receding contact angles or σ_L are calculated. If the liquid does not wick at much greater velocity than the advancing meniscus then the receding force may be corrected as follows. (N.B. The Cahn software makes this correction.) During the receding part of the cycle

$$F_{rec} = p \ \sigma_L \ Cos \ \theta + Ag \ \Delta\rho \left(x - x_{ZDOI}\right)...$$
$$+ \Delta m \ g\left[1 - \left\{\frac{x - x_{ZDOI}}{x_{max} - x_{ZDOI}}\right\}\right] \qquad [18]$$

where Δm reflects the change in mass of the sample after complete withdrawal of the liquid. Thus

$$F_{rec,ZDOI} = p\,\sigma_L\,Cos\,\theta + \Delta\,m\,g \qquad [19]$$

and

$$F_{rec,ZDOI,corr} = F_{rec,ZDOI} - \Delta\,m\,g \qquad [20]$$

If the contact angles between a given solid and two different liquids (e.g. water and methylene iodide) are known then Equation 14 may be used to calculate σ^d and σ^p for the solid when corresponding properties for each of the liquids is known. The use of a third liquid allows calculation of σ^+ and σ^- via Eqn. 15.

Surface Free Energy of Various Paper Grades

The surface energies of various grades of papers were measured by the Wilhelmy plate method on the Cahn DCA-12. A strip of paper 2.54 cm wide was cut into sections of appropriate length. The paper strip is used as the Wilhelmy plate. The stage speed was 140 μm/sec. The surface energies were calculated from advancing contact angles using both water and methylene iodide as probe liquids. The results are shown in Fig. 2.

It is significant that the total surface energy of the tested grades varies over a broad range - roughly 25-60 mN/m. In an earlier as yet unpublished report where a large number of linerboard samples were tested: a similar range of surface energies was found. The range of observed surface energies is sufficiently large so as to suggest the need for different ink formulations for various papers.

The fractional polarity,(σ^p/σ_T) , also differs considerably between paper grades. The fractional polarity varies from about 0.01 to 0.6. This also suggests the need for various ink formulations. It appears that the substances added to the furnish for sizing and other purposes determine the surface chemistry. Papers having a sufficiently large fractional polarity may exhibit poor adhesion due to repulsive polar interactions.

Surface Tension of Intaglio Varnishes

The surface tensions were determined for various intaglio varnishes. In these measurements the stage speed used was 6 μm/sec. The Wilhelmy plate was constructed of either Platinum or Glass. Both materials give zero receding angles. It was necessary to correct for varnish which adhered to the plate. The results are shown in Fig. 3. It noteworthy that most of the tested Alkyd varnishes have significant polar contributions to the surface tension. Linseed oil used in less modern intaglio formulations does not have a significant polar contribution to its surface tension. Poly-ethylene was used to construct Wilhelmy plates in order to determine σ^p and σ^d. If the surface tension of the varnish and that of polyethylene ($\sigma = \sigma^d$) are known then the polar and dispersive components can be calculated for the liquid varnish.
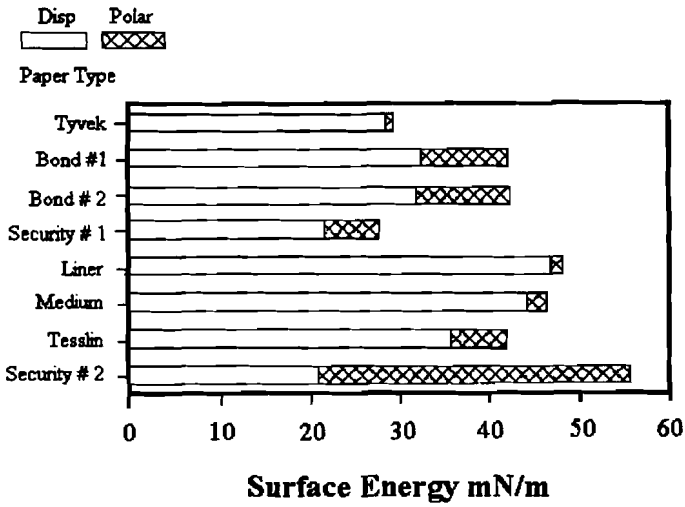
Paper Type

Surface Energy mN/m

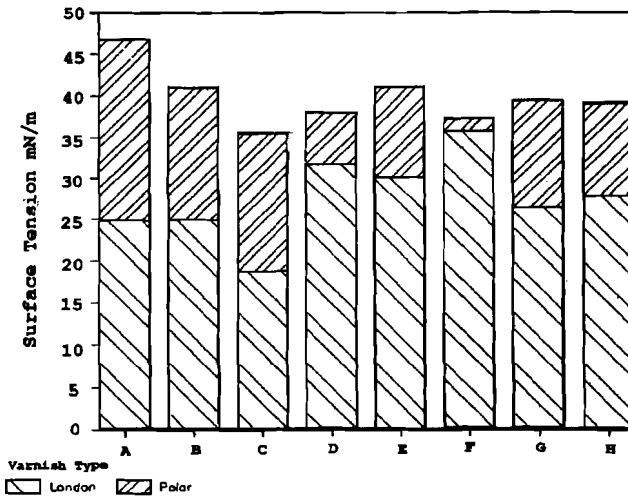Figure 2. Polar and dispersive surface energies of various papers.

Figure 3. Surface tensions of various alkyd intaglio varnishes.

Contact Angle of Intaglio Varnishes on a Security Paper

The advancing contact angles of four varnishes on security paper #2 were measured. The stage speed was 2 μm/sec. The data are shown in Fig. 4. The results suggest that as the polarity of the varnish increases then so does the contact angle. Eqn. 15 suggests that such a result might be the result of base-base or acid-acid interactions at the interface. It is significant to note that linseed oil which has essentially no polar component to its surface tension has a zero advancing contact angle.
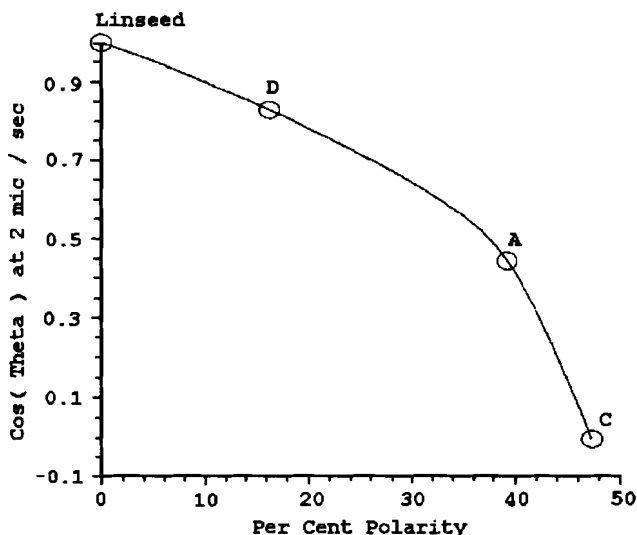

Figure 4. Cosine contact angle of intaglio varnishes on security paper # 2 versus surface polarity. Letters correspond to those of varnishes in Figure 3.

Time Dependent Contact Angle Phenomena

The contact angle of varnish on paper has been found to be time dependent. Measured values of varnish contact angle are shown in Fig.5. Contact angle has been plotted with the reciprocal of the stage speed as this variable is related to the interface lifetime. The observed time dependence may result from either the high viscosity of the alkyd varnishes, slow macromolecular rearrangements or diffusion processes. Measurement of the time dependence of contact angle using a goniometer with video processing equipment confirms the time dependence of the contact angle on paper. Typical results are seen in Fig. 6. The time dependence is not a peculiarity of the Wilhelmy method.

Cherry et al. and Newman (see Kinloch, 1987) have expressed the time dependent contact angle with the following equation

$$Cos\ \theta_t = Cos\ \theta_\infty \left[1 + k_1\ e^{-k_2 t}\right] \qquad [21]$$

where

$$k_2 = \frac{\sigma_{LV}}{\eta\ L} \qquad [22]$$

Here L is an adjustable parameter. Cherry et al.'s model agrees at least qualitatively with our data and further suggests that macromolecular rearrangements may be involved in time dependent contact angle phenomena. These authors have shown that the kinetic constants in Eqn. 21 are related to joint strength. Furthermore, print quality may show speed dependencies related to surface dynamics.

Yasuda (1991) has discusses the kinetics of reorientation of polymeric materials when wetted with water. His results also show reorientations occurring over similar time scales.

Discussion

The surface chemistry of paper has been explored by others in the past. (see for instance; Luner, 1969, Swanson, 1976; Borch, 1982 and Aspler et al., 1987). Borch, in particular, has explored the effect of surface sizing on adhesion. Triantafillopoulos et al. have discussed some aspects of acid-base chemistry at the interface and its relationship to printability. In general, earlier workers have used a contact angle goniometer to measure contact angles.

More recently the Wilhelmy method has been applied to cellulosic materials. Gardner(1991) has studied the wettability of various species of wood. Berg and co-workers (see for instance, Hodgen and Berg, 1988) have studied the wettability of single fibers.

Sharma (1991) as well as Bassimer and Krishnan (1991) have recently discussed the role of surface chemistry of inks and paper in printing. These other workers have not discussed ink adhesion of high viscosity intaglio inks. They did find that the surface chemistry of paper and ink are important to the printing process.

The work collected in this study and that of the other investigators above has established the importance of surface chemistry to printing.

It has been shown that the surface chemistry of paper varies considerably with paper grade. Other experiences of the authors suggests that the surface chemistry of a single grade may sometimes vary depending on the manufacturer as well as process variations which occur in a given mill. These changes in surface chemistry occur due to changes in the chemical nature of the furnish.

The data show that some grades of paper exhibit large polar contributions to their surface free energy. The tested alkyd varnishes frequently exhibit high polarity in contrast with linseed oil which is used in solvent based formulations. It has been shown that high polarity leads to poor wetting and presumably to poor adhesion of varnishes.

van Oss (1988) has noted that a large number of polar polymeric materials have large σ^- values. It is uncommon to find polar materials with large σ^+ values. This observation suggests that the adhesion between polar materials will often be poor. It will be an important future task to
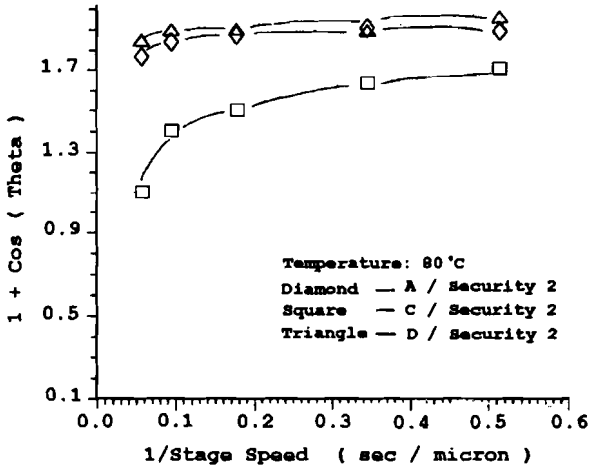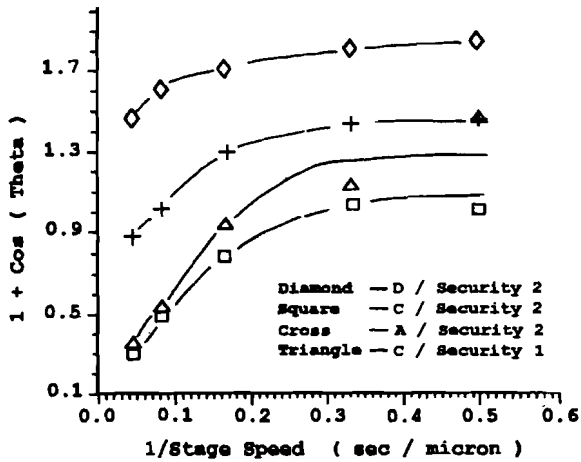
Figure 5. Contact angle varnish on paper versus stage speed for various paper/ varnish combinations. Top 20°C. Bottom 80°C
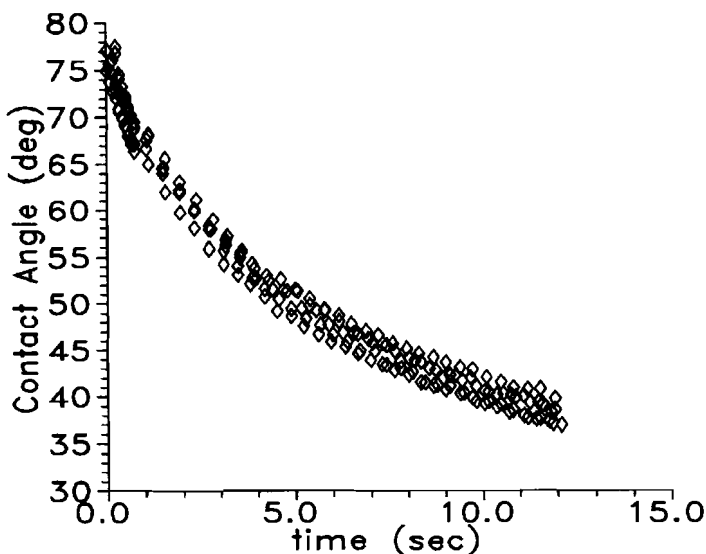
Figure 6. Contact angle of varnish C on security paper #2 as measured on a contact angle goniometer versus time drop is in contact with paper. Time dependence may be caused by either diffusional effects or by macromolecular rearrangements.

establish σ^+ and σ^- values for the relevant materials. In the past, linseed oil has been a good varnish material as it is non-polar and does not have polar repulsions.

The data collected in this study suggest that macromolecular rearrangements play an important role in the wetting of paper with alkyd varnishes. The precise nature of these rearrangements is unclear at this time. Yasuda (1991) has shown that polymeric surfaces can undergo slow structural transformations in order to minimize the interfacial free energy. In the printing process if an alkyd ink dries at the interface before good wetting can be achieved poor adhesion will result. Both kinetic and thermodynamic factors , thus, may play a role in the poor adhesion of intaglio inks.

It is important to note that linseed oil and other such natural oils used in solvent based formulations wet polar papers well, as they do not have significant polar repulsions nor do they seem to have any wetting delays caused by macromolecular events.

It will be an important task for future investigators to learn more about the conformation on alkyd polymers in the liquid state to learn what changes occur when these polymeric materials are brought to the interface. Molecular modeling studies might prove to be useful.

Conclusion

In this study the surface energies and appropriate contact angles have been measured using the Wilhelmy plate method. These data together with modern theories of adhesion have been used to shed light on durability problems for documents printed with the intaglio process. It has been

found that commonly used alkyd varnishes show poor wetting on typically used papers. The poor wetting appears to result from repulsive Lewis acid-base interactions at the interface. The poor wetting is further complicated by slow macromolecular events at the interface. Both factors are likely to contribute to poor adhesion. Theory suggests that it is possible to overcome these problems by minimizing the polar repulsions at the interface. A strategy which worked in the past is to use oil based varnishes. Environmental issues, however, are unlikely to make this option viable. In the future careful attention to the surface chemistry of both paper and ink must be given.

Acknowledgments

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