

An Analysis of Ink Jet Ink and Untreated Vinyl Interactions

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Abstract

Over the past several years, the introduction of ultrawide format printers capable of printing on untreated and uncoated substrates, such as vinyls, have penetrated into the digital printing arena. Most of the current printer systems use glycol acetates and glycol ether acetates, especially in the systems using piezo drop-on-demand technologies. The few continuous printer systems used in this market are using MEK-based solvent inks. Such solvents are not considered “environmentally friendly”. In many instances, there is a strong demand for these imagers to use aqueous-based ink systems. This paper investigates the surface properties of solvent and aqueous inks and four commercially available vinyl substrates, as well as the inherent ink-substrate interactions.

The goal is to be able to predict how ink will spread on and adhere to a vinyl substrate. In theory, the vinyl and ink surface energies will determine the work of adhesion, W_a , between the two. Three approaches are used to determine W_a . The first two approaches involve directly monitoring the ink–vinyl interaction: the ‘Adhesion tape test’, which is currently in use for quality control of ink jet inks, and the application of Young’s equation, which involves the measurement of the ink surface energy and the ink–vinyl contact angle. The third approach attempts to derive W_a from solely the surface energies of the ink and vinyl. Two methods are used to calculate the vinyl surface energies: the polar-dispersive two component method and the acid base three component method. Both methods are based on the contact angles formed by pure liquids on the vinyl. The ink surface energies are measured directly using the modified Wilhelmy plate (static) and maximum bubble pressure (dynamic) methods. The ink–vinyl interfacial energies are calculated from the individual surface energies and the ink–vinyl contact angle by means of Young’s equation. Finally, we relate these results to the adhesion test of the inks on vinyl substrates.

Introduction

The work of adhesion W_a between a solid S and a liquid L is given by the Dupré equation¹

$$W_a = \gamma_s + \gamma_L - \gamma_{SL} \quad (1)$$

in which γ_s and γ_L are the surface energies of the solid and liquid, respectively, and γ_{SL} is the interfacial energy between the two. Physically, W_a represents the work required to separate one square centimeter of two surfaces²; in this case solid vinyl and liquid ink. Of the three energies in equation (1), only γ_L is easily measurable. However, Young’s equation³ relates these same three energies to another measurable value—the contact angle θ that the liquid forms on the solid.

$$\gamma_s = \gamma_{SL} + \gamma_L \cos \theta \quad (2)$$

Thus, by combining equations 1 and 2, W_a of the liquid film can be calculated from two measurable parameters, γ_L and θ

$$W_a = \gamma_L (1 + \cos \theta) \quad (3)$$

Equation (3) is referred to as the Young-Dupré equation. There are a number of models in the literature that attempt to define W_a as a function of the surface energies γ_s and γ_L , without the need to measure θ . Here, two such models are applied: the Kaelble, or Owens and Wendt, dispersive–polar method^{4,5} and the Good–Chaudhury–van Oss acid–base method.^{6,7} Both of these techniques redefine each surface energy as the sum of two additive components.

In the case of Kaelble, the γ of a surface is the sum of a dispersive component γ^d and a polar component γ^p .

$$\gamma = \gamma^d + \gamma^p \quad (4)$$

The γ_{SL} is then defined by the following:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2 [(\gamma_s^d \gamma_L^d)^{1/2} + (\gamma_s^p \gamma_L^p)^{1/2}]. \quad (5)$$

Comparing this to equation 1, it can be seen that:

$$W_{SL} = 2 [(\gamma_s^d \gamma_L^d)^{1/2} + (\gamma_s^p \gamma_L^p)^{1/2}]. \quad (6)$$

The Good–Chaudhury–van Oss method initially separates γ into a dispersive Lifshitz–van der Waals component γ^{LW} and a non-dispersive acid-base component γ^{AB} .

$$\gamma = \gamma^{LW} + \gamma^{AB} \quad (7)$$

However, γ^{AB} is further defined as the interaction between an acidic (electron acceptor) component γ^+ and a basic (electron donor) component γ^- .

$$\gamma^{AB} = 2 [\gamma^+ \gamma^-]^{1/2} \quad (8)$$

Because γ^{AB} is due to the interaction of γ^+ and γ^- , γ_{SL} is given by the following:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2 [(\gamma_s^{LW} \gamma_L^{LW})^{1/2} + (\gamma_s^+ \gamma_L^-)^{1/2} + (\gamma_s^- \gamma_L^+)^{1/2}] \quad (9)$$

and thus

$$W_{SL} = 2 [(\gamma_s^{LW} \gamma_L^{LW})^{1/2} + (\gamma_s^+ \gamma_L^-)^{1/2} + (\gamma_s^- \gamma_L^+)^{1/2}]. \quad (10)$$

Experimental Approach

Materials

Four commercial untreated vinyl substrates (1 to 4) and three cyan inks (A, B, and C) were used in all tests. Vinyls 1 and 2 are fiber reinforced substrates while vinyls 3 and 4 are pressure sensitive, adhesive backed substrates. Ink A is an experimental aqueous ink, ink B is similar to ink A with 0.2% of a wetting agent added, and ink C is a commercially available solvent based ink. All three inks have been successfully jetted using a piezo drop-on-demand ink jet printhead.

The standard liquids used for evaluating the surface energy components of the vinyls were water, diiodomethane, ethylene glycol, glycerol, and formamide. With the exception of water, the standard liquids were acquired from Fisher Scientific, all at +99.5% purity. The water was deionized tap water. The surface energy components of the standard liquids were taken from literature and are shown in Table 1.

Table 1. Surface energy components of standard liquids

Liquid	Dispersive-Polar		Acid-Base		
	γ^d	γ^p	γ^{LW}	γ^+	γ^-
Water ^a	21.8	51.0	21.8	25.5	25.5
Diiodomethane ^a	50.4	0.4	50.8	0.7	0.0
Glycerol ^a	33.6	29.7	34.0	3.9	57.4
Ethylene glycol ^b	29.3	18.6	29.0	1.9	47.0
Formamide ^a	28.0	29.3	39.0	2.3	39.6

(a) Correia 1997⁸

(b) Polar-Dispersive: Kwok 1994⁹ Acid-Base: Kwok 1994¹⁰

Methods

The surface energy, or surface tension, of the inks was measured both statically and dynamically. Static measurements were performed on a Cahn Dynamic Contact Angle Analyzer mounted with one of three different geometries: du Noüy ring, platinum plate, or glass rod (~2mm diameter). Each sample was tested a minimum of five times using each of the geometries at least once, and the results were averaged. Dynamic measurements were performed on a Krüss Bubble Pressure Tensiometer. Nitrogen gas was expelled through a silanized glass capillary (~225µm exit diameter) and the flow rate was varied so as to produce surface ages ranging from 50 milliseconds to 30 seconds. Each sample was tested with at

least three different capillaries and the results were averaged.

Contact angles, θ , were measured at room temperature (22±1°C) using an in-house built video goniometer attached to a Macintosh computer. For both the inks and the standard liquids, 1.5µL drops were suspended from a pipette tip and the sample substrate was raised from below until the drop contacted the substrate. In most cases the drop detached from the pipette tip on contact; however, in certain cases the surface was then lowered slightly until the drop detached. The drops were back lit and the profile of each was recorded at video rate (30 frames/second) for at least 10 seconds after contact/detachment. The collection and subsequent measurement of the drop images were automated using NIH Image software. The small drop volume allowed us to ignore the effects of gravity on drop shape and calculate the θ of each image using a circle fit routine. At least three drops of each liquid (standard and ink) were measured on each of the vinyls.

In order to define the components of the vinyls and inks, standard liquids with known surface energy components were used. First, the θ of each standard liquid was measured on each of the substrates. The W_{SL} for each liquid-solid pair was then directly calculated using equation 3, resulting in five W_{SL} values for each vinyl. By simultaneously solving equation (6) for any two of the liquids¹¹ or equation (10) for any three of the liquids,^{10,12} the individual surface energy components of each vinyl were calculated. Then, using the vinyl surface energy components, the same equations were used to calculate the surface energy components of the inks.

An additional issue that must be addressed in performing these calculations is the dynamic nature of both the surface tensions of the inks and the contact angles on the vinyls. The equations used to conduct the calculations assume equilibrium conditions; however, in practice both surface energy and contact angle are measured dynamically. Therefore, specific times must be chosen for these parameters, but it is unclear if or how the two time scales (surface age and time after contact) correlate.

Adhesion tests were performed according to ASTM D3359-97, Test Method B, the "Cross-Cut Tape Test". First, an ink film was applied to the substrate and allowed to completely dry. The solvent ink dried via evaporation and the aqueous inks by applying heat at 65°C for 5 minutes. The tested area was then scored with a crosshatch tool in two directions perpendicular to each other. A piece of adhesive tape was applied to the area, and then removed. Finally, the tape samples were digitally scanned and analyzed using imaging software to accurately determine the percent area removed. The results of three tests were averaged for each ink-vinyl pair.

Results and Discussion

Surface Energies

The static and dynamic surface energy results for the inks are tabulated and graphed below. The γ_s (static) of all

three inks are quite similar at between 26 and 30 mN/m. However, the γ_d (dynamic) results indicate that at shorter time scales the aqueous inks have a significantly greater γ_d than the solvent based ink. It is clear that surface active ingredients are more important in determining the γ_s of the aqueous inks than that of the solvent based ink.

Table 2. Ink surface tensions (γ_s and γ_d)

Ink	Description	γ_s mN/m	γ_d at 1s mN/m	γ_d at 10s mN/m
A	Aqueous	29.8	42.8	40.4
B	Aqueous; 0.2% wetting agent	29.1	35.0	30.9
C	Solvent based	27.7	28.5	28.3

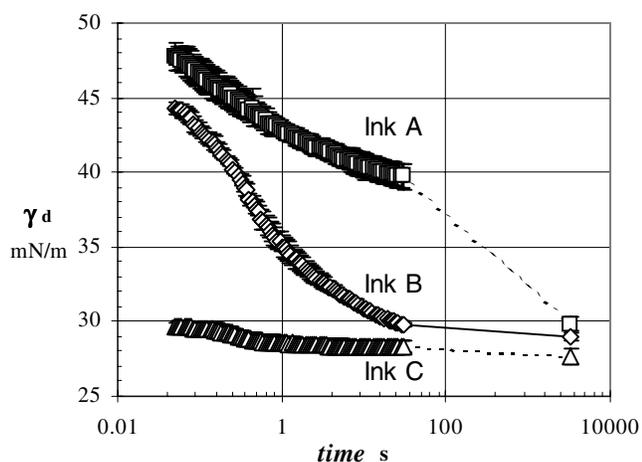


Figure 1. Ink surface tensions (γ_s and γ_d)

On all four vinyls, the standard liquids (with the exception of glycerol on specific vinyls) spread during the initial 0.5 to 1 second of contact and then maintained essentially constant θ during the remaining time. On vinyl 2 glycerol continued to spread for several seconds while on vinyl 1 glycerol spread throughout the 10 seconds of measurements. The contact angles at three times after contact were chosen for subsequent calculations: zero (initial measurement), one and ten seconds.

Each set of contact angles (0, 1, and 10s) were used to calculate surface energy values using both the dispersive-polar and acid-base methods. With 5 liquids this resulted in 10 possible combinations of liquids for both methods.

A large number of the calculations produced results that were deemed illogical and were thus discarded. These unreasonable results fell in one of the three following categories:

- (1) The square root of one of the components less than -1 .
- (2) A dispersive component (γ^d or γ^{LW}) that was greater than 50% of the total surface energy (the vinyls are assumed to be primarily dispersive in nature).
- (3) A total surface energy of less than 30 mN/m (assumed to be the lower limit for such substrates).

Note that when the square root of a component was found to be between -1 and 0 , that component was assumed to be zero and the results were kept.

First we examine the results from the polar-dispersive method. After eliminating the data according to the above categories, the remaining results all included diiodomethane as one of the standard liquids. The results calculated from the initial θ and steady θ are shown in Table 3. (The results for 1 and 10 seconds did not vary significantly; therefore the θ at 10 seconds were used for the steady results.)

Table 3. Calculated vinyl dispersive-polar surface energies (mN/m)

Vinyl	Liquids	Using initial θ		Using steady θ	
		γ^d	γ^p	γ^d	γ^p
1	D W	33.8	14.4	40.8	11.8
1	D G	-	-	42.4	4.5
1	D E	37.5	0.1	43.2	1.9
1	D F	34.8	7.8	41.3	9.2
2	D W	40.4	0.4	47.2	0.9
2	D F	42.1	(0)	49.2	(0)
3	D W	33.0	1.9	37.5	2.4
3	D G	34.9	(0)	38.6	0.4
3	D E	34.5	(0)	39.0	0.0
3	D F	33.6	0.7	38.1	1.2
4	D W	37.9	1.7	42.5	1.7
4	D G	-	-	43.6	0.1
4	D E	39.6	(0)	44.2	(0)
4	D F	38.8	0.2	43.0	0.7

Key to liquids: D diiodomethane W water
G glycerol E ethylene glycol F formamide

In the table above, (0) indicates the square root of a component was found to be between -1 and 0 . The results for the different pairs of liquids agreed within approximately 10%. Small differences were apparent between the initial and steady measurements with the steady being slightly larger—as the contact angle of the liquid decreased, the surface energy components increased. Overall, the vinyls were dispersive in nature with the value vinyl showing a slight polar component (Polar components less than 5% of the total surface energy can be disregarded). We used the results calculated from water and diiodomethane for subsequent calculations.

Now we consider the acid-base component method. We calculated the solution for each possible set of liquids (10 possible combinations), but the only set of liquids that gave plausible solutions was water, diiodomethane, and formamide. Even so, this group did not solve meaningfully for vinyl 2. The components calculated are shown below in Table 4.

Notice that the vinyls 3 and 4 showed an entirely dispersive surface energy ($\gamma^{AB}=0$) while vinyl 1 showed a small non-dispersive component. These results are consistent with the dispersive-polar method. Both techniques indicated that vinyl 1 has the largest non-

dispersive/polar component, while the other samples are entirely dispersive. Also, all the vinyls showed an entirely basic non-dispersive component, which has been observed in literature. Most studies of this method indicate that all solid surfaces are basic.¹³ However, this result seems questionable and may indicate a flaw in the theory.¹²

Table 4. Calculated vinyl acid–base surface energies using Water, Diiodomethane, Formamide (mN/m)

Vinyl	Using Initial θ			Using steady θ		
	γ^{LW}	γ^-	γ^+	γ^{LW}	γ^-	γ^+
1	30.7	24.3	0.5	38.2	17.5	0.8
2	-	-	-	-	-	-
3	30.6	7.1	0.0	34.9	8.1	0.0
4	34.7	9.3	0.0	39.5	7.4	0.0

Next, the vinyl surface energy results were used to determine the ink surface energy components. We followed the same method as above, only with the vinyls as the standards. To find the ink polar-dispersive components, we used the vinyl surface energies calculated from the initial contact angle of water and diiodomethane. The success of this technique depends on the vinyl pair chosen; one standard should have a significant polar and the other entirely dispersive. Thus, vinyl 1 was used in each pair because of its polar component. Table 5 shows the calculated results for both the initial and steady ink contact angle.

Table 5. Calculated ink dispersive polar surface energies (mN/m)

Ink	Vinyl Pair	Initial θ		Steady θ	
		γ^d	γ^p	γ^d	γ^p
A	1,2	7.5	25.0	17.6	25.1
A	1,3	3.1	42.3	-	-
A	1,4	6.6	27.6	16.1	28.2
B	1,2	11.8	11.5	20.3	29.4
B	1,3	7.0	21.4	-	-
B	1,4	11.4	12.3	16.0	38.3
C	1,2	22.1	6.3	35.2	12.5
C	1,3	13.7	16.5	20.7	32.0
C	1,4	17.6	10.9	28.8	19.4

Vinyl pairs 1,2 and 1,4 yielded consistent results for inks A and B, while pair 1,3 gave lower values and failed to solve at a steady contact angle. Results varied for ink C, but pairs 1,2 and 1,4 both predicted a larger γ^d than γ^p . As expected, the aqueous inks, A and B, have a large polar component, while the solvent based ink, C, is more dispersive. The disagreement of pair 1,3 is probably because vinyl 3 has a smaller polar component (Slightly greater than 5%) while 2 and 3 are entirely dispersive (Less than 5%).

The acid-base method provided no meaningful results for the ink components. Every solution yielded at least one component with negative square root. Similar difficulties when inverting the acid-base technique to calculate liquid surface energy components have been reported.¹¹

Work of Adhesion

To calculate W_a , we started with the simplest method using equation (3). The γ_L at a surface age of 1s was used to provide the greatest differentiation of W_a . Longer surface ages and the static value of γ_L gave W_a values that were all very similar. Table 6 shows the calculated W_a between ink and vinyl using the initial (0s) and steady (10s) ink contact angles.

Table 6. Ink-Vinyl W_a from Young-Dupré equation (3)

Vinyl	W_a (mN/m) – Ink A	
	Initial θ	Steady θ
1	74.0	68.1
2	79.9	73.8
3	78.9	73.2
4	78.2	71.7

Vinyl	W_a (mN/m) – Ink B	
	Initial θ	Steady θ
1	61.9	54.3
2	64.0	59.5
3	63.4	59.0
4	62.9	58.4

Vinyl	W_a (mN/m) – Ink C	
	Initial θ	Steady θ
1	49.5	44.8
2	49.4	45.2
3	49.5	45.3
4	49.6	45.1

For inks A and B, vinyl 1 showed the lowest W_a , followed by vinyls 4, 3, and 2. Ink C showed nearly identical results for every vinyl. Ink A showed the greatest W_a , followed by B and C. Also, the work of adhesion is lower with the steady contact angle than with the initial contact angle. A lower W_a indicates less energy required to separate the two phases. Hence, a lower work of adhesion equates to less attraction between ink and substrate.

The second method used to calculate W_a uses either the polar-dispersive or acid-base surface energy components with equation (6) or (9). Because the ink acid-base calculations failed to yield reasonable solutions, we were limited to only the polar-dispersive method. Table 7 shows the work of adhesion between each ink and vinyl combination using equation (6).

This method showed surprisingly different results than the Young-Dupré technique. These values indicate that W_a is largest for vinyl 1, with 2, 3, and 4 about 15 - 35% lower. Additionally, the work of adhesion is larger with the steady contact angle than with the initial contact angle.

Table 7. Ink-Vinyl W_a from Kaelble equation (6)

Vinyl	W_a (mN/m) – Ink A	
	Initial θ	Steady θ
1	69.8	87.9
2	40.2	66.2
3	44.6	66.3
4	46.1	67.0

Vinyl	W_a (mN/m) – Ink B	
	Initial θ	Steady θ
1	65.8	94.4
2	47.7	69.6
3	48.6	70.2
4	50.9	70.7

Vinyl	W_a (mN/m) – Ink C	
	Initial θ	Steady θ
1	74.1	99.7
2	60.3	85.3
3	59.3	81.7
4	62.5	84.2

Obviously, W_a values depend strongly on the method used. The Young-Dupré equation calculates W_a from the direct interaction between the ink and the substrate. On the other hand, the polar-dispersive or acid-base approach calculates W_a from the individual surface energies of the inks and vinyls. The Young-Dupré results are more reliable simply due to the number of measured parameters. To apply equation (3) only two parameters are needed, the ink contact angle and the ink surface energy. The polar-dispersive technique uses the contact angle of standard liquids, the contact angle of ink and the surface energy of the ink. Clearly, there is less room for experimental error with the Young-Dupré method. Also, the theoretical basis of combining the polar components of the surface energy as in equation (6) has been questioned.^{8,11}

Next, we consider the results of the adhesion test. Figure 2 shows the percent area removed for each ink-vinyl pair.

In figure 2, the y-axis shows the percent of ink area removed from the substrate. The error bars show one standard deviation of the results. A larger percent coverage means more ink was pulled off the substrate, hence less adhesion. Notice the two aqueous inks (A and B) showed substantially more area removed on vinyl 1 compared to the other samples. Vinyl 2 showed no area removed for all the inks and Ink C showed no area removed on all the vinyls.

Finally, we relate the calculated work of adhesion to the physical adhesion tests. Unfortunately, the adhesion test did not show significant differentiate between vinyls 2, 3, and 4. We can compare the difference between the aqueous inks on vinyl 1 compared to the aqueous inks on the others. With the Kaelble method, the aqueous inks showed significantly higher W_a with vinyl 1, but this is opposite of what is

expected. More area removed should equate to lower work of adhesion. The Young-Dupré equation did show the correct relationship— inks A and B had the lowest W_a on vinyl 1, but the differences were not large. Ink C showed the lowest W_a , which clearly does not agree with the physical test.

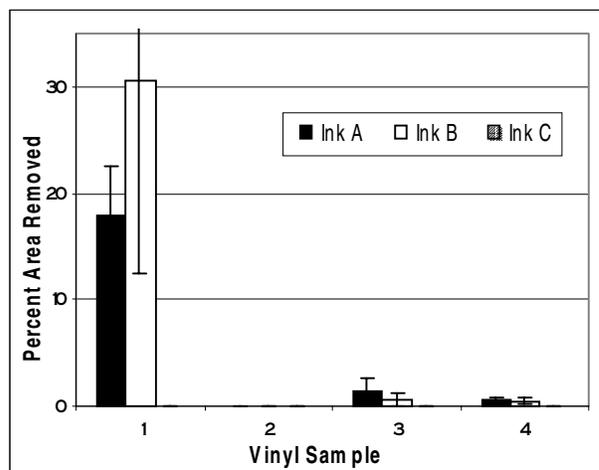


Figure 2. Adhesion Test Results

Overall, using work of adhesion to predict how well a dried printed ink will adhere to a vinyl substrate appears to be limited. There was no clear relationship that predicted the results of the physical adhesion tests. But, to confirm this finding, additional testing should be done with vinyl substrates that show a wider range of physical adhesion behavior. Our samples showed limited differentiation of adhesion behavior.

It should be realized that the work of adhesion we calculated is between the liquid ink and solid substrate. However, the physical adhesion test was performed after the ink dried, between solid ink and solid substrate. The adhesion properties and dynamics of these systems are very different. Although our W_a results did not correlate to the physical adhesion test, these results are more likely related to printing issues involving wet ink.

Conclusions

The following conclusions have been made from this study:

1. Measuring the surface energy components of vinyl substrates and inks is strongly dependent on the standard liquids used. The best results were obtained using diiodomethane-water for the polar-dispersive method and diiodomethane-water-formamide for the acid-base method.
2. Although the acid-base method provided real results for the vinyl surface energy, it failed to obtain real results for the ink surface energy.

3. Work of adhesion results calculated using the Young-Dupré equation did not agree with results from the polar-dispersive method. The Young-Dupré method is likely more accurate.
4. Neither method of calculating work of adhesion correlated to physical adhesion testing.
5. Work of adhesion results are better suited to predict phenomena between wet ink on the substrate.

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