Image Quality and Surface Tension of Digital UV Curable Inks

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Abstract

Surface tension of a digital ink can affect substrate wetting, print resolution and jet stability. Digital printing with UV curable inks is a dynamic process involving droplet formation/ejection, substrate wetting and UV cure, which occurs on the order of milliseconds. Dynamic surface tension (DST) measurements can provide information in 10 to 1000 millisecond timeframe. This paper will focus on the effect of surfactant type and concentration on print image quality. Surface tension difference between the substrate and ink was found to affect drop size and image quality. This difference for various substrates places constraints in providing good image quality with a single ink on all substrates. Information from DST measurements can be used to match ink and substrate surface tension. This helps an ink formulator to choose the optimum ink to provide the effective image quality to end user.

Introduction

The printing industry has seen huge strides in development of UV curable digital inks.[1] Ink properties crucial for good performance include low viscosity, optimum surface tension, nanometer particle size, fast print speed, good jettability and long-term storage stability.[2] The cured inks also needs to provide physical properties such as good substrate and intercoat adhesion, flexibility, hardness, chemical resistance, color gamut, and durability.

In addition to viscosity, surface tension is an important property of a digital ink.[3] It can influence ink meniscus recovery and drop formation from the printhead nozzle. For example, low surface tension can result in excessive nozzle faceplate wetting leading to poor ink ejection thereby affecting jet reliability. On the other hand, a high surface tension can lead to insufficient face plate wetting, which can also impact droplet formation and ejection.

Substrate	*Surface Energy (Dynes/cm)*
Polytetrafluoroethylene	*18-20*
Polypropylene (PP)	*29-31*
Polyethylene (PE)	*30-31*
Polyvinyl chloride (PVC)	*33-39*
Polycarbonate (PC)	*46*

Table 1. Surface energy of commonly available substrates.

Surface tension also affects substrate wetting, print quality and adhesion and it needs to be optimized to improve jet stability and performance.[3,4] Hence, an ink formulator needs to balance the demands of good jettability, substrate adhesion, print image quality and drop spread.

Substrate surface energy plays an important role in determining drop spread. Table 1 shows the surface energy of several substrates. Good substrate wetting can be achieved when surface tension of ink is much lower than the substrate.[6] However, if the ink surface tension is too low, it can increase drop spread reducing resolution. Although it is desirable to use a universal ink for all substrates, the different substrate surface energies make it quite difficult to achieve it since a proper balance of surface tension is required for each substrate.

UV curable digital inks cure rapidly, often before completely wetting out on the substrate. Hence, static surface tension, as measured by techniques such as du-Noüy ring or Wilhelmy plate is not useful in predicting jetting properties of an ink as it is only relevant to substrate wetting on a larger time scale. In a jettable ink, the timeframes involved between newly created surfaces at droplet ejection and contact with substrate followed by UV cure is very rapid on the order of micro to milliseconds. It is influenced by drop velocity, carriage velocity, reactivity of the ink to UV lamp, and distance of printheads to UV lamps. The surface active components need to migrate to the newly formed interface in these short timescales in order to influence surface tension.

For a dynamic process such as inkjet printing, ink surface tension measurement at extremely short time intervals is critical rather than at longer equilibrium values. The process can best be described using dynamic surface tension (DST) measurements, which allow a time dependent characterization within milliseconds.[5] However, ink drops are formed in a much shorter timescale compared to the measured surface ages. Although the time interval is much shorter, DST measurement provides useful information in the timeframe wherein the ink drop resides on the substrate prior to UV cure.

This paper analyzes the effect of surfactant type and concentration on DST of digital inks and the kinetics of surfactant migration. The information will be used to correlate image quality of a digital print on substrates with different surface energies. This will be useful in choosing the ink with optimum substrate wetting characteristics.

Digital UV inks have several components such as monomers, oligomers, pigments, and additives. However, the surfactant, by far has the highest impact on the surface tension. It is desirable to rapidly lower dynamic surface tension with a suitable surfactant to promote substrate wetting without affecting face plate wetting and image quality.

DST was determined using a Kruss BP2 Tensiometer, which measures the rate at which bubbles are formed. The theory of DST measurement using a bubble tensiometer is explained by Fies *et al.*[6] Gas is bubbled through a 0.3 mm glass capillary immersed in the liquid and the bubble pressure related to surface tension at maximum radius (radius of the capillary tip) is measured. We carried out the measurement at 25°C for a surface age range from 10 milliseconds to 30 seconds.

Static surface tension measured by the Wilhelmy plate method is an equilibrium surface tension measurement, and it represents the minimum value recorded by dynamic testing. It shows that the surface tension of each sample decreases with time, due to surface active materials in the sample migrating to a freshly developed surface and reaching an equilibrium. However, the surface tension will not decrease below the static (equilibrium) surface tension at any of the surface ages studied by the bubble pressure DST technique.

If we consider the complete process of ink drop ejection to curing or pining of the ink drop, there are three time segments. The summation of these individual segments is the time that the drop has to wet-out on the substrate before curing after which its form will not change. (1) Drop ejection time: Firing frequencies can range from 1-40 kHz in a piezoelectric printhead. A typical frequency is 16 kHz; which is represented on a time scale of 0.063 milliseconds per drop.[7] (2) In-flight travel time: The substrate is recommended to be placed at a distance of 1 mm from the printhead faceplate otherwise drop velocity decreases significantly due to air drag force. Assuming a typical drop velocity of 6 meters/sec from the printhead, the drop will take approximately 0.17 milliseconds per drop[8] to strike the substrate. (3) Dwell time: Distance between the printhead to the UV lamp varies by printer and will also depend on the number of printheads and their arrangement. In one UV inkjet printer, the closest printhead to a UV lamp is 3.5" away and the furthest printhead is 15.5" away. The carriage speed varies by printer, but a typical speed would approximately be about 24 inches/second. Dwell time for the ink droplet on the substrate prior to UV cure can be calculated based on the above lamp distances and print speed and would range from 146 to 646 milliseconds.[9] It is evident that the ink drop from the printhead that is furthest away from the UV lamp (646 millisecond) will have the largest time to change its surface tension (contact angle or drop shape on the substrate) compared to the ink drop closest to the UV lamp (146 millisecond).

The sum of drop ejection and in-flight travel time is about 0.23 milliseconds. It is difficult to reliably measure dynamic surface tension experimentally with a tensiometer at this time scale since the lowest surface age measured by the tensiometer is about 10 milliseconds. This surface age range relates to the dwell time wherein the ink drop has ejected from the printhead nozzle and reached the substrate and is in the process of spreading on it before UV cure. Information on surface tension for longer surface ages of above 1000 milliseconds would not be meaningful for the inkjet UV cure process unless it is an extremely slow printing system.

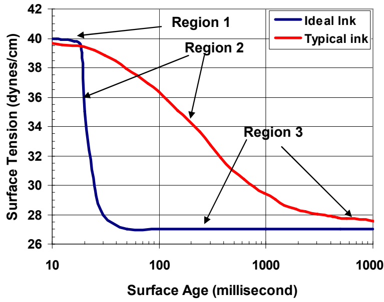

Figure 1. Dynamic surface tension of an ideal and typical ink.

Figure 1 shows the DST curve of a typical and ideal ink sample. It can be divided into three parts: (1) An initial plateau (Region 1) representing values at low surface age; (2) a rate limiting stage due to migration of surface active materials (Region 2), and (3) an equilibrium stage represented by the static surface tension (Region 3).

For an ideal ink, the plateau (Region 1) needs to be short followed by a quick drop[10] (Region 2) upon which the ink should reach the static surface tension. After reaching this value, it is not expected to change further (Region 3). All three stages, described above will largely be dependent on the type of surfactant and its migratory process at different time scales after the moment the gas is bubbled out of the capillary. The surface tension curve of a typical ink also shows three distinct regions, however, the rate of drop in surface tension is not as rapid as an ideal ink. For an ideal ink, surface tension change in region 2 should occur in a time interval of less than 0.10 milliseconds, so it is not influenced by any of the three timeframes. However, in reality the surfactant migration to the interface boundary limits the surface tension decrease. Hence, DST drop for a typical ink rarely mimics the ideal behavior.

Effect of Surfactant Concentration

DST curve for cyan inks with varying amounts of surfactant are shown in Figure 2. The curves have an initial short plateau (Region 1) followed by a rapid decrease upon which the inks decay to an equilibrium state represented by the static surface tension. The decrease (Region 2) is observed around 20 milliseconds for the inks. The magnitude of surface tension difference between surface age of 10 milliseconds and 10000 milliseconds increases with an increase in surfactant concentration. However, the magnitude of this difference starts to plateau at [surfactant] greater than 250 ppm. Surfactants help substrate wetting before UV cure and result in a much better print quality. However, excess surfactant can lead to poor print resolution. Hence, an ink formulator needs to carefully consider type of substrate and the time to cure on the printer prior to optimizing surfactant concentration.

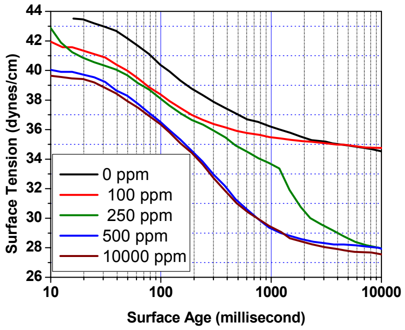

Figure 2. Effect of surfactant on dynamic surface tension for a cyan ink.

Effect of Surfactant Type

For this study, a silicone surfactant and a non-silicone leveling agent were used. Figure 3 shows the DST curve for a white ink without surfactant, compared to ink with leveling agent, and silicone surfactant. Ink with leveling agent is similar to the pure ink since it does not reduce the surface tension in the dynamic and static range.

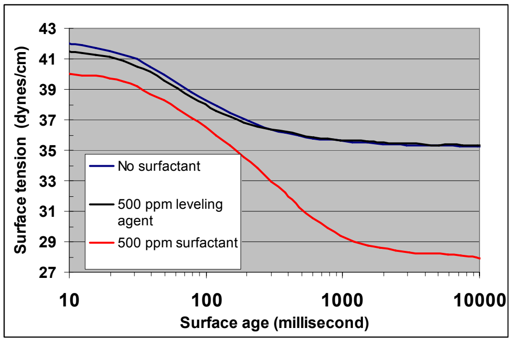

Figure 3. DST curves for white ink a) without surfactant; b) with 500 ppm silicone surfactant; c) with 500 ppm leveling agent.

The DST curve for ink with silicone surfactant shows a large drop in region 2 and the surface tension value in region 3 is also lower. It is expected to provide better substrate wetting compared to leveling agent. Although it is desirable to have a white ink with low surface tension to aid in substrate wetting, applications where it is used as a bottom layer to enhance opacity of the colors require it to have higher surface tension relative to the colors. In this scenario, a white ink with a leveling agent would be useful. The colors on top need to be formulated with silicone surfactant since the surface tension difference can lead to good wetting of the top ink layer. Conversely, white inks are also used in second surface printing where it is printed on top of the colors. This would necessitate use of leveling agent for the colors and a white ink with high levels of surfactant.

Kinetics of Surfactant Migration

The kinetics of surface tension change for the inks was studied by using a first-order exponential decay fit to the data for all plots. The fits were made according to the following equation: $_t$ = $_{eq}$ + exp(-t/k) where $_{t=}$ the surface tension at any given time, $_{eq}$ = surface tension at 700 milliseconds, = the decrease in surface tension over the time frame of testing, t = time, and k = the rate constant for the first order decay.

[Surfactant] ppm	$_{eq}$ (dynes/cm)	Rate Constant, k (millisec)
50	35.9	99
100	35.8	106.4
125	35.46	107.4
250	34.7	131.2
500	29.8	233.8
10000	29.7	236.4

Table 2. Kinetics data for the different ink samples.

DST curves for cyan inks with varying amounts of a silicone surfactant (Figure 2) were used for this analysis. A surface energy range of 10 msecs to 700 msecs was chosen since this range reflects the dwell time range i.e. the time when ink droplet has been ejected out of the printhead nozzle and is in the process of spreading on the substrate before UV cure. The rate constant values for different surfactant concentrations are listed in Table 2. The rate constant apparently follows a linear increase until 500 ppm and then plateaus off with further increase in surfactant. As the rate constant increases the inks ability to spread on the substrate is expected to increase.

Effect of Surfactant on Print Dot Spread

The effect of surfactant and DST on image quality in a printing process was studied. Black inks with different levels of silicone surfactant were used. The DST curves of the inks are shown in Figure 4. The dwell time *ca.* 700 milliseconds is the time for the ink drop to spread prior to UV cure. A large magnitude of difference exists between the three inks in the dwell time region. The effect of this difference on the drop spread of a print was investigated.

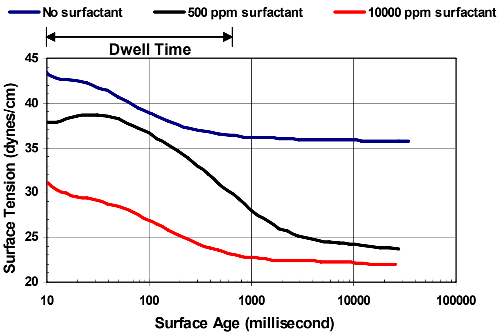

Figure 4. DST curves for black inks. a) Ink 1 without surfactant; b) Ink 2 with 500 ppm silicone surfactant; c) Ink 3 with 10000 ppm silicone surfactant.

The inks were printed using a Spectra S class SE 128 printhead, which has a typical drop size of 30 picoliters. Printed inks were pinned with an Omnicure S2000 H lamp and then cured with a Fusion UV mercury vapor (H) lamp at an energy density of 700 mJ/cm^2. The pinning occurs in a time frame of 0.5 to 1 second. Three substrates viz., polycarbonate, PVC, and parafilm with surface energies in the range of 42-46, 30-34 and less than 30 dynes/cm, respectively, were used for the prints. The surface energies were measured with a dyne pen. The large range of ink and substrate surface tension is expected to provide insight on selecting an appropriate ink for printing on these substrates.

Substrate	*Surface Energy [dynes/cm]*	*Dot Diameter [microns/dot]*		
		Ink 1	*Ink 2*	*Ink 3*
Parafilm	*< 30*	*62.8*	*60.2*	*77.2*
PVC	*30 - 34*	*83.8*	*84.1*	*103*
Polycarbonate	*42 - 46*	*121*	*127*	*149*

Table 3. Drop diameter for black inks on parafilm, PVC and polycarbonate. a) Ink 1 without surfactant; b) Ink 2 with 500 ppm surfactant; c) Ink 3 with 10000 ppm surfactant.

The ink drop diameter was measured using a Leica DMRX optical microscope. Table 3 lists the ink drop diameters on the three substrates at various surfactant loadings along with their respective surface energies. Drop spread is directly proportional to surfactant concentration and substrate surface energy. The highest resolution is defined by the smallest drop size. Inks 1 and 2 have similar drop spread for parafilm and PVC. Ink 3 has the largest drop spread for all substrates, and is very high on polycarbonate. For all the inks, PVC prints have intermediate drop spread when compared to other substrates. Figure 5 shows microscope images of the drops for black ink with 0 and 10000 ppm surfactant on polycarbonate. The larger drop spread is obvious for the ink with surfactant.

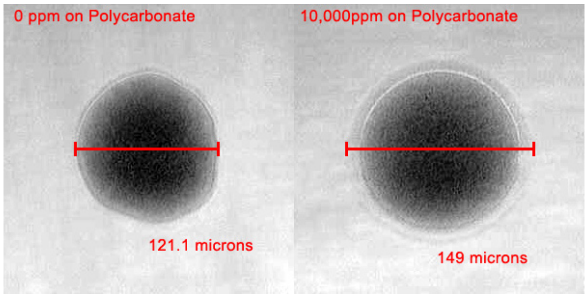

Figure 5. Microscope images showing the drop spread on polycarbonate for cured black ink with a) Ink 1 No surfactant, b) Ink 3, 10000 ppm surfactant.

In order to interpret the data, we need to consider the ink surface tension in the dwell time range and compare it to the substrate surface energy. Ink surface tension has to be significantly lower than substrate surface energy in order for the ink to effectively spread on a substrate. A large drop spread results in a high gloss and better adhesion.

If we consider ink surface tension in the dwell time range up to 700 milliseconds (Figure 4), it is apparent that ink 1 has a surface tension of about 36 dynes/cm. Hence, it has difficulty spreading on parafilm and PVC. Ink 2 has a surface tension of about 30 dynes/cm, therefore, it has difficulty spreading on both parafilm and barely spreads on PVC, but is able to spread well on higher surface energy polycarbonate.

Ink 3 has a surface tension of *ca.* 23 dynes/cm in the dwell time and hence spreads well on all PVC and polycarbonate. Although the drop diameter of ink 3 on parafilm is higher than ink 1 and 2, it is still not sufficient to spread on it. The data suggests that an ink with high amount of surfactant is desirable to increase drop spread. We investigated if excess surfactant can lead to nozzle face plate wetting affecting jet reliability. It was found that ink with 10000 ppm surfactant retains a wide jetting window.

The data from the DST curve can be used to predict drop spread on different substrates. Currently the graphic and industrial arts printing market are demanding faster print speeds. This lowers dwell time even further and provides less time for ink to spread on substrate before UV cure. Hence, an ink formulator needs to carefully consider factors such as dwell time, jet reliability, ink and substrate surface tension in designing an appropriate ink system.

Conclusion

The timescales in DST measurements allow one to predict ink droplet spread on the substrate. Ideal inks are expected to have a rapid drop in surface tension before contacting the substrate. However, in reality the kinetics of surfactant migration to the interface of a liquid drop is dependent on surfactant type and its concentration leading to much slower drop in surface tension. In order to achieve good print speed, ink formulation needs to balance jet reliability, drop spread and dot gain. Difference in surface energies of substrate makes it difficult to provide good image quality for all substrates. Information from DST measurement can be used to correlate surface tension and drop spread in a printing process and aid an ink formulator to choose the ink with optimum substrate wetting characteristics.

References

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7. 16 kHz = 16,000 drops/second or inverting it to get $6.25\text{x}10^{-5}$ sec/drop or 0.063 millisecond/drop.
8. 1 mm x (1 m/1000 mm) x (1 sec/6 m) = $1.67 \text{ x } 10^{-4}$ sec = 0.167 millisecond/drop.
9. a) T_1= 3.5 inch x (1 sec/24 inch)=0.146 sec (146 millisecond). b) T_2 = 15.5 inch x (1 sec/24 inch) = 0.646 second = 646 millisecond.
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Author Biography

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Dan Wilson received a B.S. in Chemistry from University of Missouri at Rolla. Since 1995, he has been involved in the development of UV curable inks, coatings, adhesives for telecom, optical media, digital printing markets.