Control Spreading Approach For Ink Jet Computer-To-Plate

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Abstract

Several studies have been published on Ink Jet Computer-To-Plate. Some authors described a “Mask approach”,[1] where they jet a fluid that block UV radiation on a conventional photopolymer plate, and further UV expose and process the plate. Some recent studies described “Direct imaging” on the plate substrate.[2-4] The main concern for direct imaging is to control resolution by limiting spreading of the droplets (poor wetting) whereas obtaining excellent adhesion of the image to get high press run-length during printing. A way to partially achieve both requirements could be to jet a hot melt fluid onto the plate substrate directly:[5] spreading is controlled by fluid phase-change. The drawbacks are a 10 to 20 times thicker image than on a conventional plate and low press run-length because of poor resistance properties of the wax-based fluid. In this study, a cationic copolymer (resp. anionic), partially neutralized by formic acid (resp. amonia) is solubilized in water and jetted through a piezo Ink Jet printer on a basic (resp. acidic) plate substrate. Water is evaporated and the copolymer forms the image area of the printing plate. The purpose of this paper is to show how to reconcile good image resolution (or “poor wetting”) and long press run-length (or “good adhesion”) by an Acid-Base interfacial matching approach.

Background

Spreading Control Issue

The real challenge in this project is to control drop spreading on treated aluminum oxide surfaces, which are high surface energy solids. Actually, these surfaces are well known for promoting “free spreading” and “zero contact angle” of a majority of liquids.[6-9] This phenomenon is actually the driving force for the use of treated aluminum oxide as the non-image area of the conventional plate, in order to favor dynamic spreading of the water-based fountain solution on the non-image area and preventing scumming of the printing plate.[10,11]

Model Prediction For Dot Spreading

Sheller and Bousfield did an extensive study on “Newtonian drop impact with solid surfaces”.[12] They proposed a model based on their experimental study of macro-drop (mm range) spreading, which gives a good prediction of maximum spreading of liquids on solid surfaces during impact and was found to fit several experimental data from the literature, even outside the range of the experimental correlation (ie micro-drop). The spreading ratio R_{max}/R is used to quantify the spreading behavior, R being the initial droplet radius and R_{max} the maximum dot radius observed during drop impact.

According to this model, the parameters of major importance to control drop spreading are droplet size, liquid viscosity and droplet speed. The surface tension of the ink has a rather small effect. This is due to the fact that the model describes “impact” in term of hydrodynamics only, and does not include the physico-chemical interactions at the liquid/solid interface that happened after the impact. For example, it did not take into account the nature of the substrate, postulating that it will not affect spreading after drop impact. As ink formulators, we have no control on the hydrodynamic parameters (speed, diameter and viscosity), because they are imposed by the head technology. But this work will show some unique and innovative ways for controlling spreading.

Experimental Evidence of the Substrate Effect on Long-Term Spreading

Even if a drop impact is a hydrodynamic process, it seems rather obvious that the substrate will play a role in the spreading phenomenon that happened after impact and therefore in the final dot size. This seems even more obvious for a high surface energy surface as aluminum oxide, on which zero contact angle and free spreading can be observed.[13] In order to show the substrate effect, an Epson printer Stylus ESC/P2 was used to print on several kind of substrates, with Epson black water-based ink.). The dot size was measured by microscopy on a paper (100-110 µm) and on a polymer substrate (80-90 µm) (Figure 1). When printed on an aluminum plate (Figure 2), dramatic spreading was observed and the dot size was not measurable under those conditions. It become rather obvious that the nature of the substrate had a tremendous effect on spreading and that spreading control on aluminum oxide was a real challenge.

Spreading Phenomenon: The “Primary Film”

Dynamic spreading of pure liquids or liquid mixtures onto solids is important in a large number of industrial processes like textile cleaning, detergency, spray painting and floatation and there are therefore some pertinent studies related to the complex phenomena involved in dynamic spreading.[14-20] There is a consensus among these authors concerning the fact that the phenomenon of droplet spreading onto solids is always preceded by the advancing of a so-called "primary film", ahead of the bulk of the droplet. Depending on the specific characteristics of this primary film and of the physical phenomena that can take place in it (evaporation or adsorption of one component), the overall spreading behavior can vary greatly from enhancement, to stopping and even to recession. Most of the solid surfaces studied in the literature were steel, clean glass or freshly cleaved mica.

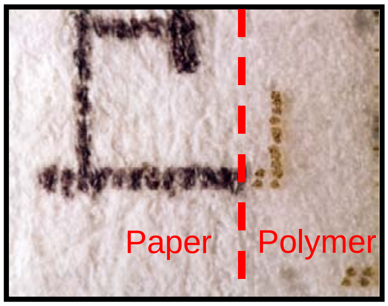

Figure 1: Paper vs. polymer

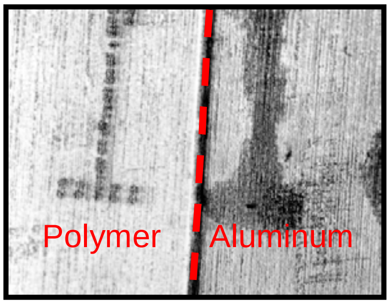

Figure 2: Polymer vs. aluminum

Adhesion Issue

Our goal is to control and minimize ink spreading on the plate during and after drop impact in order to obtain "high resolution" image. On one hand, we want a bad wetting of the substrate by the ink, on the other hand, the ink must have a very good adhesion to the aluminum oxide, so that the "press run-length" of the plate could meet 20,000 to 100,000 impressions, depending of the market addressed. In other words, we need bad surface wetting of the wet ink and high adhesion of the dry ink.

Experimental

A water-based ink system was originally investigated, because of non-toxicity, low boiling point and high surface tension of water. The plate will be easy to dry in an oven at moderate temperature (120°C). The high surface tension of water will give us room to formulate without falling below 35-40 mN/m.

Spreading Control Acid-Base Approach

It is well known by the printing plate manufacturers, that the aluminum oxide surface will behave acidic or basic, depending on the surface chemical treatment. We therefore thought that an acid/base approach could help "interfacial matching" between the plate and the polymer present in the ink and may help control spreading and adhesion of the dry ink.

Preliminary Results: Drop Test

We will first show this theory with macro-drops and without impact, by the "drop test" technique.

Acidic vs. Basic Plate Substrates: Several acidic and basic plates were supplied by KPG (Table 1). The mechanical and chemical treatments applied to them will results in different roughness, different topologies and different surface chemistry.

Table 1: Plate samples used for study

Plate substrate	Surface Treatment	Interlayer	Acid/ Base
CHB-Silicate	Chemically + Basic etched + Anodized	Silicate	B
PG-Silicate	Pumice grained + Anodized	Silicate	B
EG-Silicate	Electro-grained + Anodized	Silicate	B
DS-silicate	Etched + Desmut + Anodized	Silicate	B
G20	Electro-grained + Anodized	Vinylphos. acid /acrylamide copolymer	A
AA	Quartz grained + Anodized	None	A

Cationic vs. Anionic Ink. Two inks were formulated identically (Table 2), based on:

- an amine-containing copolymer partially neutralized with formic acid, referred as the "cationic ink".
- an acid-containing copolymer partially neutralized with ammonia, referred as the "anionic ink".

The chemical structure of these copolymers are the following: the cationic resin is a copolymer of MMA (Methyl Methacrylate)/DMAEMA (Di-Methyl Amine Ethyl Methacrylate) in a ratio 72/28, 75% neutralized with formic acid. The anionic resin is a commercially available styrene-acrylic copolymer, Joncryl 678, 85% neutralized with ammonia.

The amount of surfactant was chosen in order to achieve the same static and dynamic surface tension for both inks, i.e. 37.6, respectively, 39.2 mN/m.

"Drop Test" Results. In order to achieve a first screening of the spreading behavior of a liquid on a plate, a very simple "Drop Test" was designed. A 10 µl chromatographic micro-syringe with a flat needle was filled with the liquid to be studied. A droplet was formed at the needle extremity and dropped on the surface from a height of about 3 mm. As the drop falls, only the surface tension controls the drop volume (liquid density is almost constant, for a given system). Since part of this work is to control the surface tension in the range 35-40 mN/m, we can postulate an almost constant drop volume, during this test. This was verified by weighting 10 drops generated according to this procedure and with various formulations. A standard deviation of ±10 % was observed, which was acceptable for that kind of test.

Table 2: formulation and physical properties of cationic and anionic inks

Ink Formula and properties	**R2702-1581**	**R2702-1582**
R2737-188-75 Cationic MMA/DMAEMA (32 % sol)	9 %	-
R2737-197 Anionic Joncryl 678 (33 % sol)	-	9 %
Glycerol	2 %	2 %
DI Water	88.7 %	88.45 %
Surfynol 465	0.3 %	0.55 %
Ph	5.8	7.6
Stat. Surf. Tens (Du Nouy)	37.7	37.6
Dyn. surf. Tension (5 b/s)	39.1	39.3
Drop volume (Drop Test)	5 µl	5 µl

After deposition of 4 to 5 drops, the plate was dried in the oven or at room temperature and the resulting dot diameter was measured manually and averaged. In case of "ovoid" spreading (machine direction for CHB-plates) the smaller diameter is recorded and in case of heterogeneous spreading, either no value or a best estimate value was recorded. The drop test was applied to the substrate described above and results are shown on Figure 3.

Basic-plates: The cationic ink spreads much less than the anionic one, which seems to confirm a more basic surface.

Acidic-plates: The trend is less dramatic here, but the anionic ink spread a little less than the cationic one.

Interpretation. The presence of sodium silicate on silicated plates confers a basic character to the plate surface. Therefore, considering spreading by "primary film", the presence of an excess of free amine groups in the primary film (presumably because of formic acid evaporation from a very thin ink layer) would have a bad affinity for the basic plate surface, and will therefore minimize spreading. On the other hand, in the bulk of the drop, we have an excess of neutralized amine, which would react with sodium silicate through ionic exchange. This mechanism (Figure 5) would explain low spreading but strong adhesion of the polymer on the silicated plate.

Validation of the theory: effect of the % neutralization of the cationic resin. In order to verify this effect, we used the same polymer but with a percentage of neutralization of 50 % (half neutralized) and 100 % (no free amine groups). The resulting ink are respectively R2702-1631 and R2702-1580.

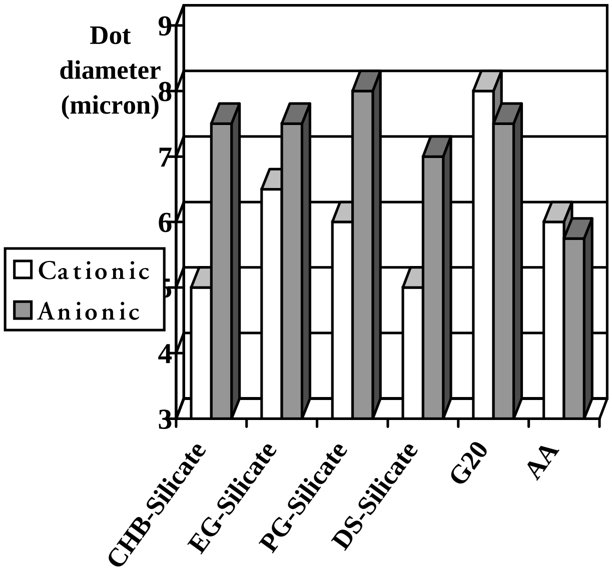

Figure 3: Ink drop test: Cationic vs. Anionic

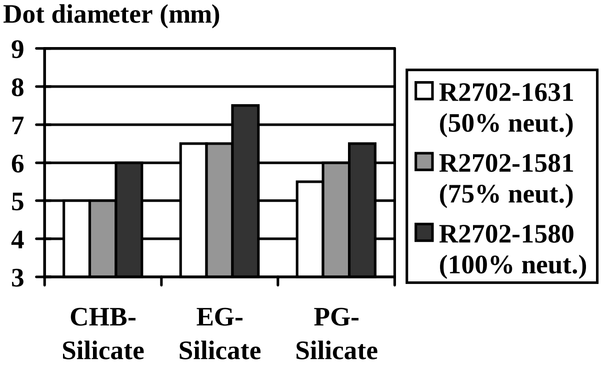

Figure 4: Effect of the % neutralization of the cationic ink on the basic subtrates.

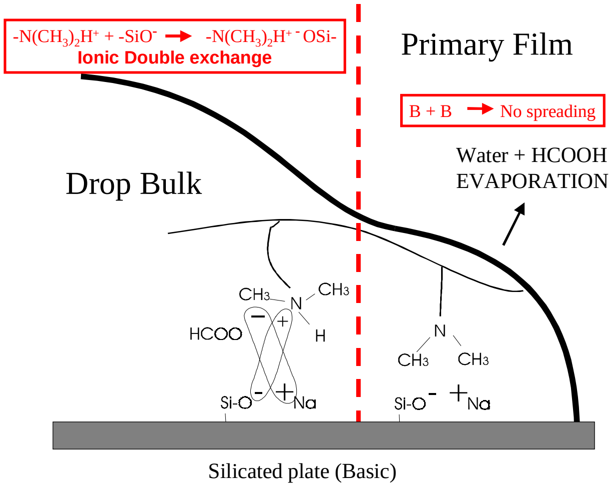

Figure 5: Schematic representation of the drop edge; "Acid/Base interfacial matching" in the case of a basic plate with a cationic ink

Results (Figure 4):

A significant increase in spreading was observed on the basic silicated plates when the cationic copolymer became more and more neutralized. When 100% neutralized, no free-amine groups were present in the ink, and spreading became more pronounced. This seems to confirm again that the free-amine groups in the primary film are responsible for spreading control.

"Ink Jet" Test

In order to test the concept in real conditions, three inks were formulated according to Table 3 and were all based on the cationic polymer R2737-188-75, which was proven above to give the best results in terms of spreading control.

Table 3: Ink formulations for the Ink Jet test

Formulations	**R2702-1343**	**R2702-135-1**	**R2702-1381**
R2737-188-75 (34% solid.)	9	9	13.5
Glycerol	2	-	-
Tri-Propylene Glycol	-	1.5	2.25
Surfynol 465	0.6	0.2	0.2
DI Water	88.4	89.3	84.05

The different inks were jetted with Epson printer 1 (Epson ESC/P2) and Epson printer 2 (Epson 800), on several plate substrates supplied by KPG and according to the following procedure:

For both printers we selected the highest resolution available from the printer driver (720 dpi for the Stylus ECP/P2 and 1440 dpi for the Epson 800) along with the "printing on film or transparency" option. Such a set-up will deliver a drop volume close to 35 and 14 picoliters respectively.

Results are reported in Table 4. All silicated plates are considered basic. Several ink were formulated based on the cationic resin R2737-188-75 and jetted on a large number of plates. Each ink/plate system is referenced with a number reported in Table 4. The "resistance" properties is a first indication of adhesion of the polymer to the substrate, during the manual plate inking step. The final resistance test will be the run-length of the imaged plate on a printing plate. The quality of the resolution (bad, fair or good) was evaluated visually, but the dot diameter (in micron) is more relevant. It is an average value over more than 30 dots which was determined by optical microscopy and the Image-Pro software. Figure 6 shows an example of the image obtained with the same ink R2702-1343 on a basic plate (silicate treatment) vs the same plate but with an acidic treatment.

Table 4: Ink Jet test; examples of Acid/Base matching

Substrate	Ref.	Printer	Resol.	Dot diam.	Resistance
CHB Silicated (Basic)	1a	1	GOOD	84.0	YES
CHB Silicated	1b	2	GOOD	62.3	YES
PG X-88 #1 Silicated	2a	2	GOOD	57.8	YES
PG X-88 Silicated/8g/B	2	2	GOOD	-	YES
PG X-88 Silicated/8g/A	3	2	GOOD	60.3	YES
PG X-88 Silicated/6g/Int	4	2	BAD	-	YES
PG X-88 Silicated/6g/Ext	5a	1	GOOD	84.2	YES
PG X-88 Silicated/6g/Ext	5b	2	GOOD	61.9	YES
PolyEster Silicated	6	1	FAIR	106.3	NO
EG Silcated	7a	2	GOOD	57.4	YES
EG Silcated	7b	2	GOOD	62.0	YES
DS Silicated (no graining)	12a	1	GOOD	74.2	NO
DS Silicated (no graining)	12b	2	GOOD	55.3	NO
EG PVPA (acidic)	8	2	BAD	-	YES
T71 PVPA (acidic)	9	2	BAD	134.0	YES
CHB PVPA (acidic)	10a	1	BAD	112.0	YES
CHB PVPA (acidic)	10b	2	GOOD	-	YES
EG as Anodized (acidic)	11	1	NO	205.0	YES

Results:

Our Acid/Base theory is confirmed. In fact, apart from 2 exceptions, an ink containing the cationic resin R2737-188-75 will not spread on a silicated substrate and will spread on an acidic substrate, during plate imaging through Ink Jet.

Spreading Control By Drop Volume Control

Model Prediction

Sheller's model[13] was used to predict the effect of drop volume on the resulting maximum dot size on the plate during impact (Figure 7). Droplet speed, surface tension and viscosity were arbitrarily fixed at 10 m/s, 40 mN/m and 3.5 mPa.s respectively.

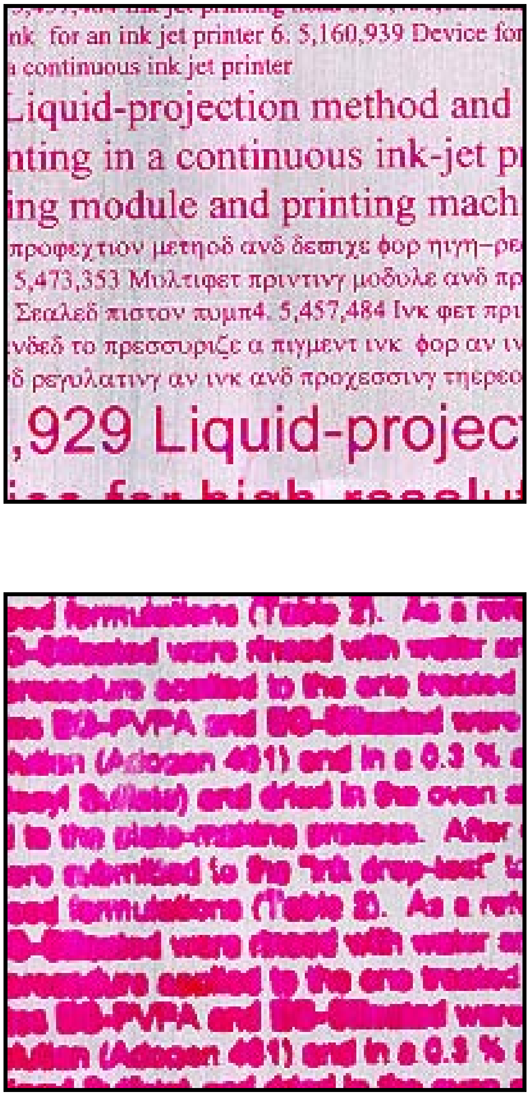

Figure 6: IJ imaged plates; results of A/B interfacial matching: Cationic Ink R2702-1343 on Basic CHB-silicate plate on top (ref. 1a in Table 4) vs. Acidic CHB-PVPA plate on right (ref 10a in Table 4).

Experimental Results

This trend was confirmed with our "controlled spreading" cationic ink R 2702-1343 on a CHB-silicated plate and with 2 Epson printers. The Epson stylus ESC/P2 delivers drop volume around 35 pl and the Epson 800, 14 pl. A decrease in dot size is observed on Figure 8 from 85-90 µm for the former Epson Stylus ESC/P2 to 50-60 µm for the Epson 800. These values have been reported on Sheller's model curve for spreading (Figure 7), and were found to match the curve exactly, indicating that there is no more "free-spreading" with our acid/base interfacial approach, which contrasts advantageously with a "non-controlled spreading" ink as shown on Figure 2 .

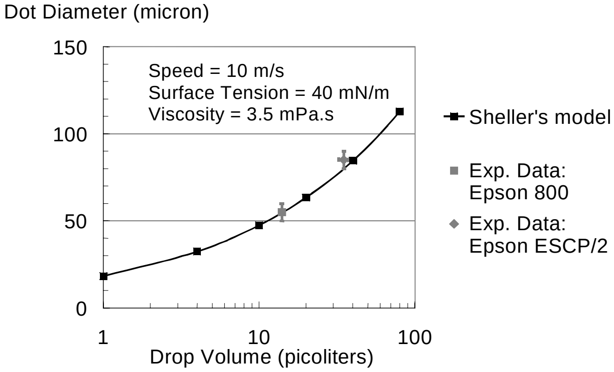

Figure 7: Drop volume effect on dot diameter according to Sheller's model

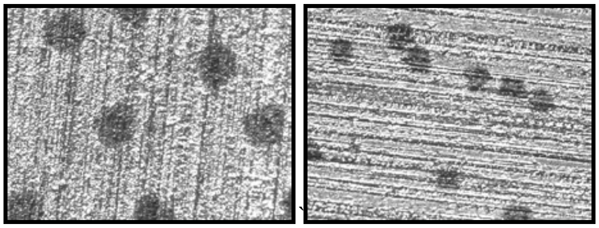

Figure 8: Epson Stylus ESC/P2 (left) and Epson 800 (right)

Table 5: Run-length of IJ plates

Ref	Substrate	Ink	Run-length
1	CHB-Silicated (Basic)	"Cationic" (MMA/DMAEMA)	>100,000
2	CHB-Silicated (Basic)	"Cationic" (MMA/DMAEMA)	>100,000
3	AA (Acidic)	"Anionic" (Stryene Maleic Anhydride)	>15,000*
4	EG-Silicate (Basic)	"Anionic" (Joncryl 678)	100*
5	EG-Silicate (Basic)	"Anionic" (Stryene Maleic Anhydride)	500*

(Artificially accelerated press runs)*

Litho Press Trial with IJ Plates

Several plates were imaged with different Epson printers with different ink formulations illustrating our "acid/base interfacial matching" theory (Table 5). After drying in an oven at 120 °C for 1 minute, they were put on the press and run for 100,000 impressions under normal conditions for the 2 first ink/plate systems and 15,000 impressions under accelerated conditions for the last 3 systems. No decrease in density was observed on the 10, 50 and 90% rasters during press run for the first 3 systems.

Results:

The cationic ink on basic plate and the anionic ink on acidic plate showed excellent press run-length. The anionic inks on basic substrate showed very poor press run-length. This high resistance to press run-length of the basic plates imaged with a cationic resin or of the acidic plate imaged with an anionic resin is characteristic of a very good adhesion of the polymer to the substrate. This may confirm the ionic bond anticipated in & 0 resulting from the ionic double exchange.

Conclusion

This study clearly showed that Ink Jet drop spreading is a combination of complex phenomena, and is not only controlled by hydrodynamics but also by interfacial chemistry. The “acid-base interfacial matching” approach described here was proved to control both drop spreading and adhesion, giving good resolution and press run-length when jetting a water-based ink on an aluminum oxide surface of high energy. The application of this theory was the topic of several patent applications[21-23] and has numerous applications in the field of ink jet. Several studies are undergoing at the moment and will be the topic of further publications.

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Biography

Dr. P. Aurenty is Director of Research at Sun Chemical Technical Center in Carlstadt, NJ. He joined Sun Chemical in 96 as a scientist in the Pioneering Technology department, where he was involved with digital printing. Engineer in Paper Making, Printing Processes and Converting, he obtained his Ph.D. in Material Science in 1996, at the Polytechnique Institute of Grenoble, France, where he was involved with rheology and physical chemistry of the Offset Lithographic process. Dr. Aurenty published 16 papers, presented 10 papers at international Graphic Arts conferences and has 11 patents pending.