Validation of Ink Media Interaction Mechanisms via Microscopic Analysis

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Abstract

For ink jet printing processes the ink media interaction has been described frequently in the literature. Most of the time a microscopic analysis has been done on printing results, sometimes in situ visualisation techniques have been used.[1-3]

In situ visualization techniques are not easily amenable for small droplet sizes, while practical printing experiments typically are done using these small dot sizes but the transient behaviour of the fundamental underlying processes has been lost in the final printout.

In this paper a combination of numerical simulations and real small size impingement studies are compared with microscopic analyses of the resultant dot patterns on the receiver.

The results of the microscopic analyses on individual dots can be used and compared with older data in the literature,[1-3] and can be related to the theories that can describe the spreading, absorption, and evaporation phenomena, and that can explain the influence of the media design on the ultimate image quality.

Introduction

Drop on Demand ink jet has gained a lot of attention for printing digital color documents. Good image quality can be achieved using a rather cheap apparatus for a wide variety of substrates, ranging from plain paper, over cast-coated paper, to high-end photo quality paper and specialties.

Most photo quality papers found on the market are characterized by non-absorbing substrates, coated with rather thick absorbing coating layers or microporous receptive layers.

The coating layers comprising polymer blends (such as gelatin, polyvinyl alcohol, polyvinyl-pyrrolidone) perform extremely well using printers with moderate printing speeds and dye based inks, delivering an excellent color gamut, but also showing slow drying times and poor water fastness.

Coating layers comprising microvoids work according to the principle of capillary wicking and show much faster drying times with high image quality,[1-2] but are much more sensitive to light fading and gas (ozone) fading.

Pigment based inks, showing a reduced color gamut as compared to dye based inks, perform much better for lightfastness and water fastness, but the compatibility with microporous coatings is not always very good.

For industrial applications eco-solvent inks (i.e solvent inks comprising low amounts of VOC's) or UV-curing inks are much more preferred due to their ability to be printed directly on cheap untreated substrates. The way in which these inks interact with many different substrates is still not well understood.

In this study microscopical techniques were used to get more insight in the interaction mechanisms. Special printing techniques were used in combination with microscopy. The results of the microscopic analyses were compared with simulation results and in situ visualisation information.

Optimum image quality and printing performance can only be gained by simultaneous optimization of both ink and media properties. A better understanding of the interaction mechanisms is therefore a welcome help.

Experimental

The basic experimental setup used in this work is built around droplet generating devices (commercially available printheads), an illumination source, an optical system coupled to an image recording system, and triggering electronics, as described earlier.[1]

Drop Ejection Devices

Droplets with a volume of 3 to 200 picoliters were created using driving electronics developed by Ardeje,[4] coupled to printheads from Hewlett Packard, Microdrop, Ink Jet Technologies, Spectra, or Xaar. The speed was determined by dual-exposure shot measurements using a Sensicam short shutter-time camera.

Inks

The inks that were used in this study were commercially available inks especially tuned for piezoelectric printheads (AgfaJet Sherpa Dye ink, AgfaJet Sherpa Pigment ink, Mutoh Eco solvent plus ink, Dotrix UV-curing ink).

Receiving Substrates (AgfaJet)

Different substrate materials were used throughout this work, ranging from ink jet polymeric blend materials, microporous and macroporous materials, to thin packaging materials comprising PE, PET, or ALU bases.

Visualization Devices

A short shutter time video camera from PCO, Sensicam, was used to capture a high-resolution single image of 1280 x 1024 pixels with a shutter time comprised between 500 ns and 1 µs, to assemble a "video movie" according to the pseudo-cinematography technique that has been described elsewhere.[5]

A high-speed camera, Kodak HG2000, was used to capture images of 51x 356 pixels at a real high speed frame rate of 1000 fps[1].

Analytical Techniques

For the analysis of dots printed on the various substrates "ImageXpert" coupled with a camera was used to do dot-quality analysis. Optical microscopy and scanning electron microscopy (SEM: JEOL JSM-6500) or field emission gun SEM (FEG-SEM: FEI Sirion) were used to characterise the optical and physical characteristics of the printed dots. The porosity of the substrates was measured using the technique of Hg-porosimetry (Auto IV 9500, from Micromeritics Instrument) and gas adsorption (Micromeritics ASAP2400). The BET-model was used to determine the specific surface area while the BJH-model was used to determine the pore size distribution.

Results and Discussion

To fulfill the objectives listed in the introduction part, drop-impinging experiments were performed using dye and pigment based inks on different substrates. The obtained dots were analyzed using microscopic techniques and the results are discussed in terms of the different time scales associated with these processes.

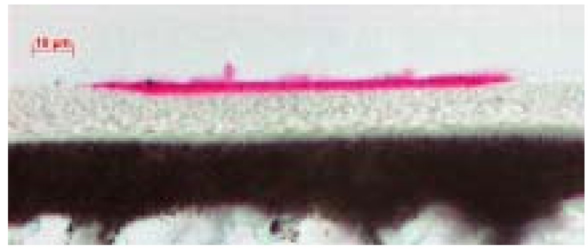
Evaluation of Absorption Kinetics

As soon as there is contact between a drop and a solid surface, the liquid generally starts spreading. In the limiting case i.e. when the drop is carefully placed onto the surface, the process of spreading is dominated by intermolecular forces. The dependence on time of the radius of the wetted spot and of the contact angle can be described by universal scaling laws as shown in detail first by de Gennes.[6]

Polymer Blend Based Media

It is generally accepted that the interaction process for an aqueous dye based ink on a polymeric blend material is govered by the diffusion law of Fick.[7] The typical time scale is a few seconds before the wet ink completely disappears into the receptive coating. In order to verify this, an experiment was set up where after printing a single dot, the remaining fraction of the ink was removed after a controlled time-delay via a doctor blade system or an air flux. The depth of ink penetration and its profile were measured by cross-sectional optical microscopy through a single dot. The results that could be obtained for a Sherpa Dye based ink printed onto an AgfaJet polymeric blend material are shown in figure 1.

25 ms after impact: 0.6 micron deep penetration



333 ms after impact: 2.7 micron deep penetration

1s after impact: 3.2 micron deep penetration

Figure 1. Cross sectional microscopy through single dot with varying times between impact and analysis

It is clear that in the first phase after impact a rather slow penetration of ink into the coating takes place. The wetting front is only 0.6 micron deep 25 ms after impact. If the time-interval after impact is taken rather large (1 second = almost full absorption), then the wetting front has reached a 3.2 micron deep penetration. These results are in good agreement with the expectations on the basis of a diffusion process,[7] as expressed in equation 1.

$$V(t) = V(0) - 2\pi R^2 \sqrt{\frac{D.t}{\pi}} \qquad (1)$$

Here V is the volume of ink on top of the receiver, R is the radius of the droplet in the form of a truncated sphere on top of the receiver, D is the diffusion coefficient of the ink.[7]

Microporous Media

In order to describe the imbibition process for dye and pigment based inks on microporous media, simplified numerical models based on Darcy's law[8] and the Davis-Hocking[9-10] model were used. The first model describes the vertical absorption of a drop initially at rest into a porous layer. It is based upon the simplification that the capillary wicking process happens as in one cylinder, for which the basis is the contact radius of the drop when the absorption starts. As a result the wet spot in the porous material has the shape of a cylinder.

The Davis-Hocking model[9-10] states that during sorption, the wet spot, and hence the available surface for sorption, diminishes. This model leads to a wet spot in the porous material in the form of a paraboloid with a depth (D) equal to the initial droplet height (h) divided by the porosity. The kinematics of the flow are described by the Lucas Washburn equation, giving the depth *d* as a square root of time:

$$d(t) = \sqrt{\frac{R_p \sigma \cos(\theta) t}{2\mu}} \tag{2}$$

The pore radius is given by R_p. The wet spot inside the porous material has the shape of a truncated paraboloid with a volume described at any time by:

$$V(t) = \frac{\pi R_p^2}{2}\left(2d(t) - \frac{d(t)^2}{D}\right) \tag{3}$$

All other parameters like droplet radius, droplet volume, droplet height and absorbed volume can then easily be calculated.

Both models were tested and compared with experiments. Three different classes need to be distinguished: dye based inks, pigment based inks, and inks which contain both pigments and dyes.

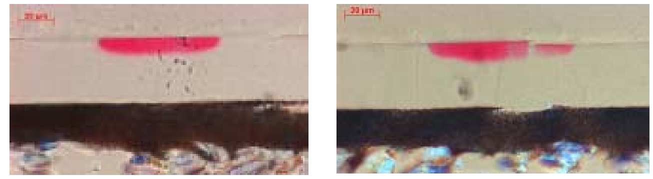
For the dye based inks good agreement was found between the Davis-Hocking model and the experiments. An example of the absorption speed of 45 pl of AgfaJet Sherpa Dye ink on microporous media is shown in figure 2.

In the beginning the penetration is vertical, later on the parabolic shape is formed. Compared to the case of the polymeric blend material the speed of penetration is much faster. Also the depth of penetration is much larger.

The microscopic image is in good agreement with the prediction of the Davis-Hocking model, suggesting a parabolic shape is obtained at equilibrium condition.

For a pigment based ink, the printing process leads to the creation of a filter cake on top of the receiver. This was already explained earlier.[3] Figure 3 gives the result of a microscopic analysis for an eco-solvent based pigment ink on a microporous medium. The results are very similar to the case of pigment based aqueous inks that have been described earlier.[3]

For inks which contain both pigments and dyes, a special situation is found. Figure 4 shows this case for the Sherpa Pigment Black ink: most colorant (i.e. the pigment) stays on top of the receptive coating, a bit of colorant (i.e. the dye) penetrates into the coating, and here it can be seen that the diffusion/capillary wicking of the dye based part leads to a broadening of the dot diameter.



25 ms after impact: 9.3 micron deep penetration

1000ms after impact: 11.7 micron deep penetration

Figure 2a. Microporous medium / dye ink

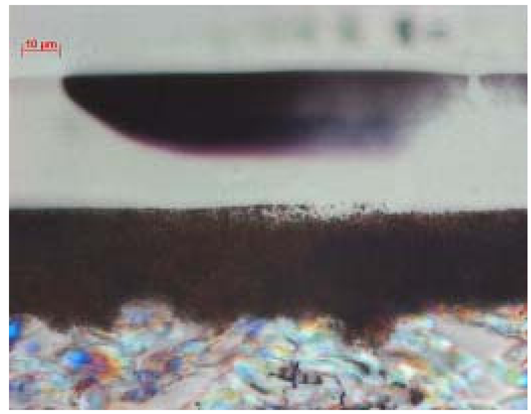


Figure 2b. Microporous medium / dye ink: final penetration profile (parabolic shape)

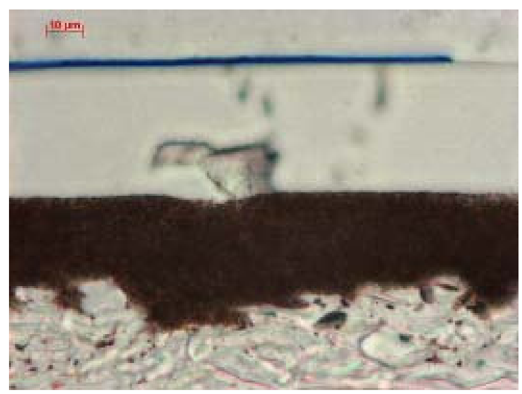


Figure 3. Microporous medium / pigment based solvent ink: formation of filter cake on top of receiver in final penetration profile

It is clear that the pigment filter cake is limiting the penetration speed, and that the penetration into the receptive coating is NOT fully vertical. This leads to a moderate dotgain and some halo-effect around the resulting dot (only visible in the microscopic image). The pigment filter cake in figure 4 has been detached from the substrate during the sample preparation process.

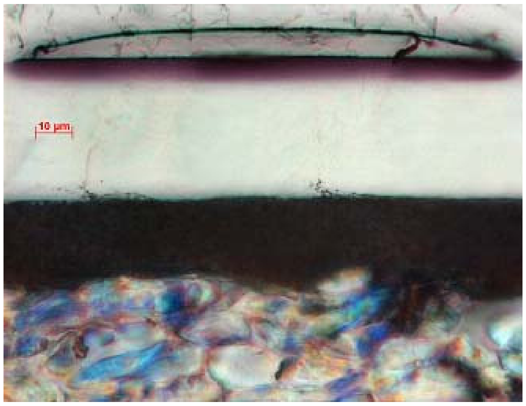


Figure 4. Microporous medium / mixed pigment/dye ink showing both pigment cake and dye penetration in final penetration profile

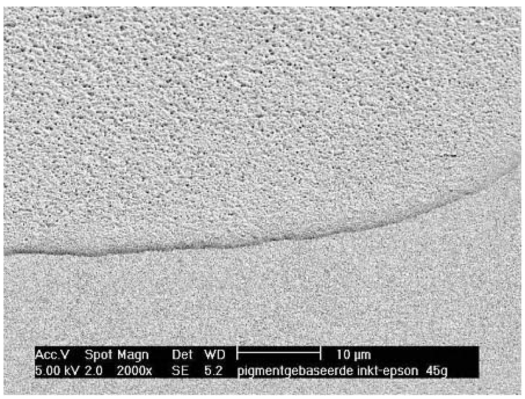


Figure 5a. Microporous medium / pigment ink: formation of pancake on surface

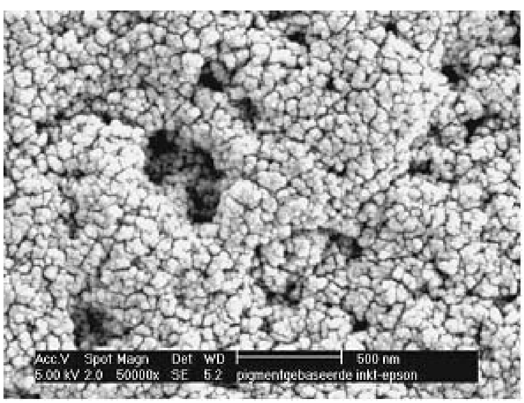


Figure 5b. Detail of pancake of figure 5a. The coagulated pigment particles are easily visible

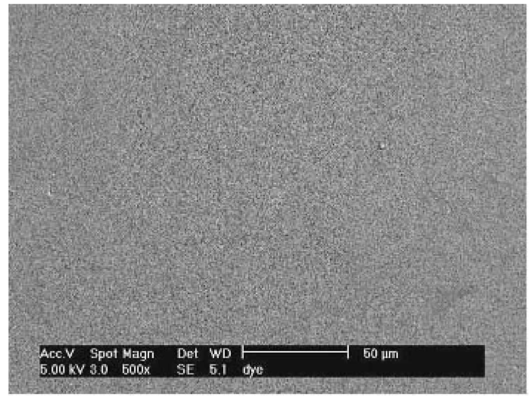


Figure 6a. Microporous medium / dye ink: no dot on top of receiver after penetration period

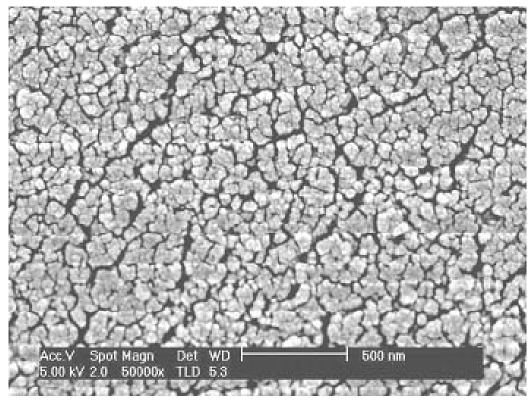


Figure 6b. Detail of top surface of figure 6a. The microporous nature of the original coating is easily visible

Evaluation of Dot Quality and Form

SEM has been used in order to elucidate the interaction mechanisms of aqueous/eco-solvent/UV-curing inks with substrates. A large variation is possible. It is shown in figures 5-7 that a lot of the SEM micrographs are consistent with the accepted interaction models.

As shown earlier,3 the pigments of a pigment based aqueous ink printed on top of a microporous receiver, stay as a pancake on top of the receiver.

For a dye based ink the SEM analysis cannot reveal the dot any more. As it can be expected that all the ink components have penetrated into the receptive layer, it is obvious that only the characteristics of the microporous layer itself can be visualised using the SEM technique.

The case of a pigment based eco-solvent ink is shown in the following images.

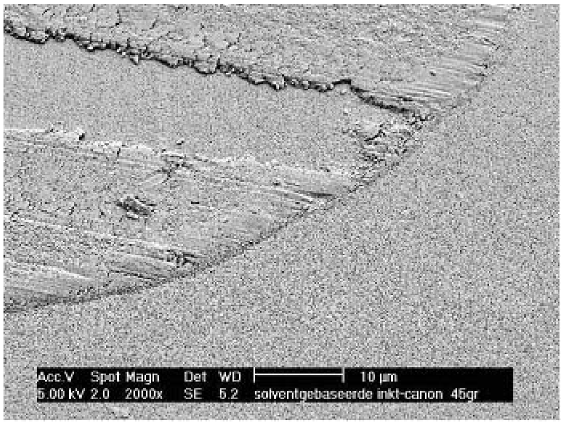


Figure 7a. Microporous medium / pigment solvent ink: filter cake on top of receiver

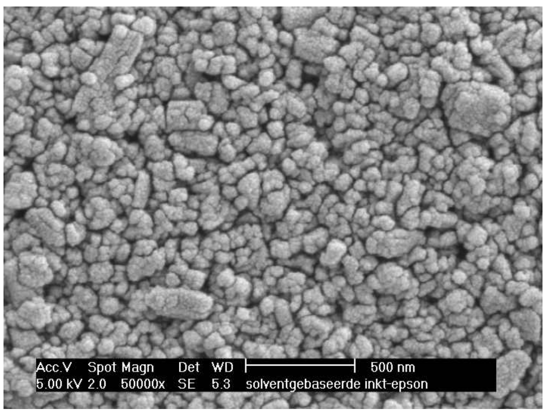


Figure 7b. Detail of pancake of figure 7a. The coagulated pigment particles are easily visible

It is clear that again the pigment stays on top of the receptive coating as a separate pigment filter cake. The eco-solvent ink is NOT chemically altering the receptive coating very strongly, as can be seen on the SEM image where part of the dot has been removed via scraping means. There is clearly an adhesive break between the receptive coating and the ink.

Ink-Ink Interactions for UV-Curing Inks

The process of wet-on-wet printing using the printer "The . Factory"® from Agfa/Dotrix, is illustrated in the following pictures.

Using the first color bar an image is printed using cyan inks at full density. Using a second color bar a second color (magenta) is printed on top of the first (still wet) UV-ink layer. After these 2 inks have had the opportunity to interact, the full image layer is cured and fixed.

Optical and SEM techniques have been used to verify what has been going on in the time phase before curing.

Two distinct cases can be found, as illustrated in the figures. If a single dot is printed in the wet layer, there is only ink-ink interaction of the type ink_2 with ink_1.

If a lot of ink_2 is printed into the wet layer of ink_1 the interaction mechanism must be much more complicated since now ink_1-ink_2 but also ink_2-ink_2 interactions can take place.

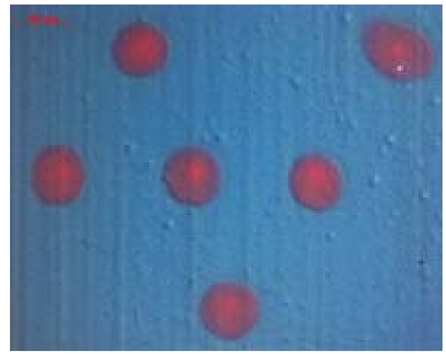


Figure 8a. Top-view microscopic image of magenta ink printed at low image density in an area of full density cyan ink

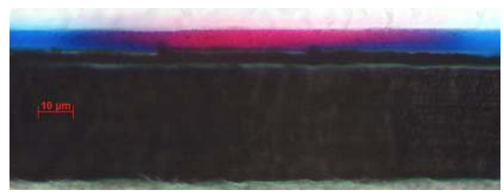


Figure 8b. Cross sectional microscopy of magenta ink printed at low image density in an area of full density cyan ink

Figure 9a. Top-view microscopic image of magenta ink printed at high image density in an area of full density cyan ink

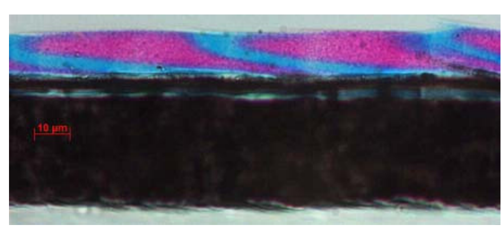


Figure 9b. Cross sectional microscopy of magenta ink printed at high image density in an area of full density cyan ink

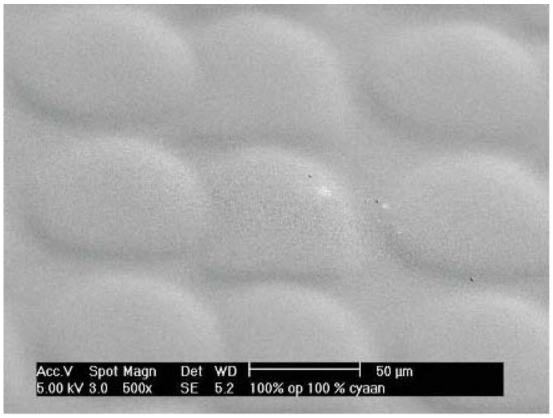


Figure 10. SEM image of magenta ink printed at high image density in an area of full density cyan ink

It is clear that the spreading of the ink_2 printed into the ink_1 layer is larger if the amount of ink_2 is low. If the amount of ink_2 is very high, the dots are limited in spreading, even so much that the typical circular form is disappearing. It can be seen in the SEM images that this squared dot form remains some surface roughness variation. The UV-curing inks are not merging to such an extent that only a single flat layer is obtained. On the other hand, it is also very clear that no compilation of "lens"-alike dots are obtained.

Conclusions

In this paper, it was shown that analytical techniques in combination with special printing conditions can gain a lot of insight into the ink media interaction model.

For dye based inks penetrating into polymeric blend receivers, a diffusion process according to the model of Fick is compatible with the obtained microscopic images.

For dye based inks penetrating into microporous receivers, a capillary wicking process according to the model of Davis-Hocking is compatible with the obtained microscopic images. The typical parabolic shape is clearly visible.

For pigment based inks penetrating into microporous receivers, a filter cake is formed on top of the surface of the microporous receiver. The pigment particles of the ink (both aqueous based as solvent based) are coagulating on top of the receiver and cannot penetrate the pores that are too small for the agglomerated particles.

For UV-curing inks in a wet-on-wet process the second droplet impinging into the first one is considerably interacting with this first one. This has considerable effects on the coalescence of different color dots and the resulting mottle in the printout.

It is clear that microscopic analysis of well-created test samples can teach us a lot on the interaction mechanisms in the ink jet printing process.

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Biography

Guido Desie got a Ph.D. at the K.U.Leuven, in the field of physicochemical analysis of enzymatic systems. In 1987, he joined Agfa Gevaert, Belgium, where he was involved in R&D of physical properties of film materials. From 1991, he was involved in R&D of Ink Jet and Toner based digital printing techniques. He is co-author of about forty granted patent families mainly in the fields of Ink Jet and Toner Jet printing. E-mail: guido.desie@agfa.com