Imbibition of Dye and Pigment-based Aqueous Inks into Porous Substrates

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Abstract

In this article, the dynamics of droplet impingement and absorption into microporous materials are investigated for pigment based aqueous inks and compared with dye based aqueous inks.

For dye based inks it was shown earlier that three main phases could be resolved which are essentially: inertial spreading, absorption, and evaporation of the liquid, leading to the final equilibrium condition on which the typical customer is evaluating the image quality. For the inertial spreading phase it could be shown that the spreading behavior is largely determined by the hydrodynamic properties such as Weber and Reynolds number, and is easily amenable to dimensionless analysis. The absorption phase could be well described by a capillary wicking process according to the theory of Davis-Hocking. Evaporation is the slowest process only being finalized after many seconds.

These observations are compared in this article with droplet impingement and absorption of pigment based inks on microporous receivers. It can be shown that these inks behave totally different from dye based inks. Immediately after impingement and initial spreading the pigment particles start to coagulate on the surface of the microporous layer, creating a filter cake limiting the passage of carrier liquid. As a result much longer absorption times are observed and the equilibrium dot is staying on top of the microporous layer. Most polymer stabilizers in the pigment based inks create a colored polymer layer having polymeric blend characteristics limiting the penetration of water considerably compared to the capillary wicking process. The Davis Hocking model is not valid any more because now the build-up of the filter cake changes the receding contact angle and introduces a diffusion process changing as a function of time during the drying of the wet ink.

Introduction

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

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

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

It is important to better understand the interaction mechanisms between pigment based aqueous inks and microporous receivers, in order to be able to develop systems with a much higher performance.

The final image quality that can be obtained using an ink jet printing process is not only related to the absorption phenomenon. Immediately after impact of the ink on the substrate, interactions and deformations can take place. In the case of low to moderate impact velocities, the inertial spreading phenomenon is determined by the kinetic energy, the viscosity and surface tension of the droplet.[1]

In this study the impact behavior for pigment based inks is compared with the results of dye based inks. Maximum spreading factors and spreading dynamics are analyzed and compared with data on dye based inks. A proprietary pseudo-cinematography method[2] where the evolution of the drop dynamics is reconstructed with photographs of different droplets taken at successive stages of the impact process, is used to record the inertial spreading phase experimentally. The data are compared with models describing spreading in terms of the variational principle indicating that droplet kinetic and potential energy is counterbalanced by the work of spreading.

On the longer time scale the penetration of the pigment based inks in microporous media is analyzed and compared with data on dye based inks. The evolution of the droplet diameter and volume on top of the microporous layer is followed as a function of time using high speed video techniques. The results are related to the ink and media properties.

These results are compared with a model of transient filter-cake buildup during the absorption process. Both physical and physicochemical analyses are done on the filter cake to determine its typical properties, and explain why the drying process is evolving as determined experimentally.

After printing using pigment based aqueous inks a dot is formed on top of the microporous layer. This dot has been analyzed using optical, microscopic and surface analysis tools to determine the porosity, roughness, etc.

The absorption phase can be explained by combining 2 separate physical behaviors: a diffusion of liquid through a filter cake on top of the microporous layer and a capillary wicking into this microporous layer.

Optimum image quality and printing performance can only be gained by optimization of both ink and media properties.

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 about 70 picoliters were created by using a Hewlett Packard HP500 printhead, cartridge HP51625a. Signals of 4 µs in duration and of 19V in amplitude were sent to a single connecting point of the resistor element in this head. The velocity of the drops was found to be a function of the ink composition and was varied between 5 and 12 m/s. The speed was determined by dual-exposure shot measurements using a Sensicam short shutter-time camera. Droplets with a volume of 80 to 200 picoliters were created using an Ink Jet Technologies 64 ID2 printhead coupled to driving electronics developed by Ardeje.[3]

Ink Composition

The inks that were used in this study were commercially available aqueous inks especially tuned for thermal printheads (Hewlett Packard HP500 Black ink), and for piezoelectric printheads (AgfaJet Sherpa Cyan Dye ink, AgfaJet Sherpa Cyan Pigment ink) and other prototype pigment type aqueous inks. Viscosity and surface tension was set to ranges of 1-4 mPa.s and 30-40 mN/m, while pigment type and stabilization was also varied. The characteristics were measured using a Brookfield DVII viscometer and a Krüss K9 digital tensiometer.

In Table 1 the properties of the test inks for the printing tests on paper are given.

Table 1. Properties of the Inks

	Density (kg/m^3)	Viscosity (mPa.s)	Surface tension (mN/m)
Thermal black dye ink (HP)	996	1.14	43.1
Piezo cyan dye ink (Agfa)	997	3.20	33.2
Piezo cyan pigment ink (Agfa)	997	3.56	32.0
Piezo black pigment ink (Agfa)	1001	4.04	40.7
Piezo black pigment ink (Agfa)	1000	3.19	41.3

Receiving Substrates (AgfaJet)

Different substrate materials were used throughout this work, ranging from ink jet polymeric blend materials to ink jet microporous and macroporous materials. These materials (AgfaJet) were obtained by coating pigment/binder compositions on PET and measuring the resulting porous characteristics using mercury porosimetry, gas adsorption, and scanning electron microscopy techniques.

Visualization Devices

A short shutter time video camera from PCO, Sensicam, was used to capture a high-resolution single image of 1280x1024 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.[2]

A high-speed camera, Kodak HG2000, was used to capture images of 512x356 pixels at a real high speed frame rate of 1000 fps[2].

Analytical Techniques

For the analysis of dots printed on the various substrates “ImageXpert” coupled with a camera was used to do dot-quality analysis, while SEM (JEOL JSM-6500), or field emission gun scanning electron microscopy (FEG-SEM: FEI Sirion) and optical microscopy was 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 results are discussed in term of the different time scales associated with these processes.

Inertial Spreading

As soon as there is contact between a drop and a solid surface, the liquid generally starts spreading out. 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.[4]

In the case of a finite velocity, which is obvious for printing, the drop spreads radially into a "pancake" shape.

The rate of spreading depends on a combination of parameters, as described previously.[1] It was found that the inertial spreading phase of the pigment based inks, analysed according to the models that were presented elsewhere,[1] corresponds rather well with the behavior of that of dye based inks. The big difference in practical behavior between pigment and dye based inks on microporous layers therefore can't be attributed to the inertial spreading phase. More details on the inertial spreading phase can also be found in a separate paper to be presented on NIP19.[5]

Drop Imbibition

After a certain period of time a pseudo-equilibrium condition is reached, determining the final shape of the liquid on top of the receiving substrate prior to penetration or absorption into the receptive coating.

Most experiments regarding the drop imbibition phase were conducted using the HP500 print head and the HG2000 fast video capturing of the droplet impinging upon the substrates. An example of photographs taken by this camera is shown in figure 1, where a dye and a pigment-based ink droplet disappear into a microporous paper.

HP black thermal dye ink, AgfaJet Sherpa Cyan Dye ink, AgfaJet Sherpa Cyan Pigment ink, and 2 carbon black pigment model inks of varying viscosity have been jetted on top of different ink jet receptive substrates.

The mechanism of ink absorption of dye based inks into these substrates has been described elsewhere.[6]

Three big classes could be found among these substrates: the very fast ones are cast-coated papers and macroporous outdoor materials showing a very short absorption time, the slowest ones are the polymeric blend materials in which all the liquid has to be absorbed via a diffusion process. The third class is the intermediate one of the microporous materials showing good glossy characteristics and a much faster drying time than the polymeric blend materials. The microporous test samples were made by changing the fillers, binders and filler to binder ratio of the porous coating layers. The porosity characteristics were evaluated using Hg-porosimetry. The main difference between the samples shown was the pore size distribution, with variations in pore volumes and mean pore sizes as represented in figure 2. Four main classes were investigated having pore sizes in the ranges of 15, 40, 100 and 150 nm. For comparison the very big pores found in a macroporous material (1000 nm) are also shown in figure 2.

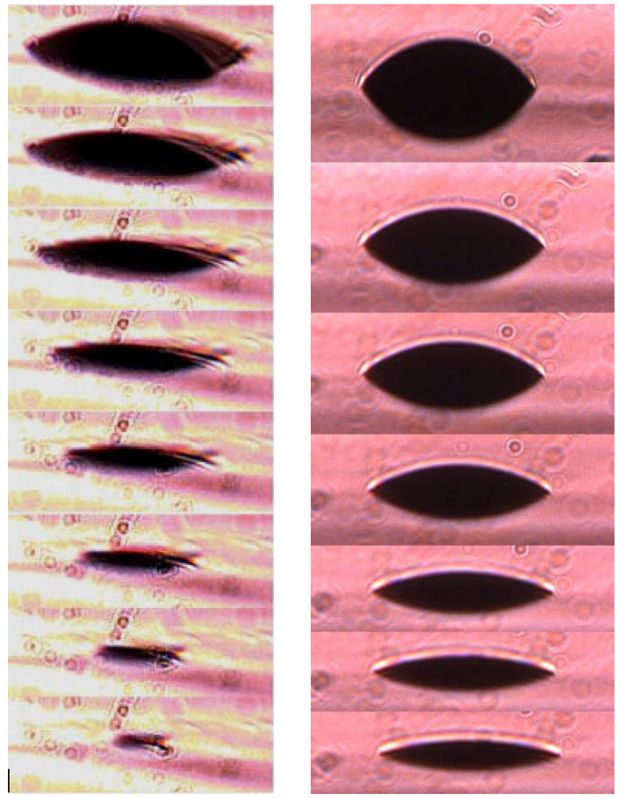

Figure 1. Experimental results of the imbibition phase: left = dye, right = pigment based ink

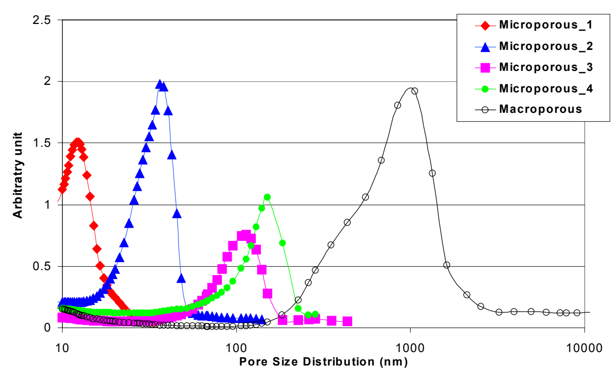

Figure 2. Porosity distribution of the different samples

In order to describe the imbibition process for dye and pigment based inks, simplified numerical models based on the Darcy's law[7] and the Davis-Hocking[8-9] model are presented. 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 is given by four different contributions (equation 1) among which the first one, which represents the suction pressure, is by far the largest.

$$\Delta P = \frac{2\sigma\cos\theta}{R_p} + \rho g h_d + \frac{2\sigma}{R_d} - \Pi_{VDW} \quad (1)$$

In this equation, σ is the surface tension, θ the internal contact angle, R_p is the pore radius, R_d the contact radius of the drop with the substrate and h_d its height. Only the first term has a significant contribution,[6] so all other can be neglected. The flow through the capillary is assumed to follow Poiseuille's law:

$$U = \frac{dx}{dt} = \frac{R^2 \Delta P}{8 \mu x} \quad (2)$$

where x is the wetted length in the capillary. Finally, solving this equation and assuming that the contact area of the drop is independent of time, the final absorption time, or the so-called capillary wicking time is given by:

$$t_w = \frac{2 \mu V_0^2}{\sigma R_p \cos\theta \pi^2 R_d^4 \varepsilon^2} \quad (3)$$

where V_0 is the initial drop volume and ε is the fractional open area depending on the capillary size and the porosity of the material. This model considers that absorption 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.

Another description of the absorption phenomena, again based on Darcy's law, which can be found in the literature, is the Davis-Hocking model.[8-9] 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 well-known Lucas Washburn equation, giving the depth *d* as a square root of time:

$$d(t) = \sqrt{\frac{R_p \sigma \cos(\theta) t}{2\mu}} \quad (4)$$

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:

$$V(t) = \frac{\pi R_p^2}{2}\left(2d(t) - \frac{d(t)^2}{D}\right) \quad (5)$$

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. For the dye based inks good agreement was found between the Davis-Hocking model and the experiments. An example of the absorption speed of 70 pl of AgfaJet Sherpa Dye ink on different microporous media, and the results of a Davis-Hocking analysis are shown in figure 3.

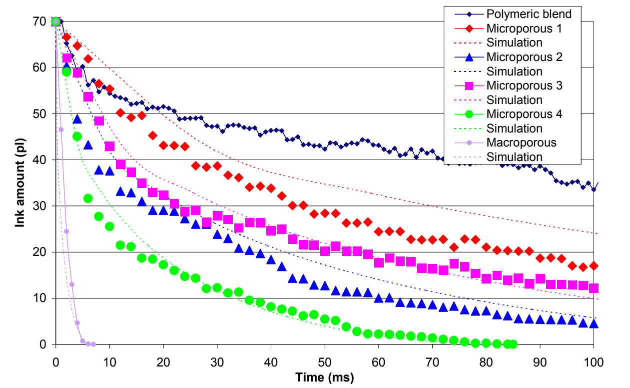

Figure 3. Piezo dye-based ink drop imbibiton for different receiving layers

The Davis-Hocking model can only be used for analysing porous media, for polymeric blend materials it was shown on NIP18 that a diffusion law has to be used.[10]

The evolution of the drop volume and diameter of a pigment ink (Carbon Black model ink with 3.19 mPa.s, 41.3 mN/m) on top of a microporous receiver (microporous_2) is depicted in figure 4.

The main differences between dye and pigment based inks are visible in figures 3-4: the overall absorption speed is much higher for dye based inks, while the evolution of the dot diameter remains much more constant as a function of time for the pigment based inks.

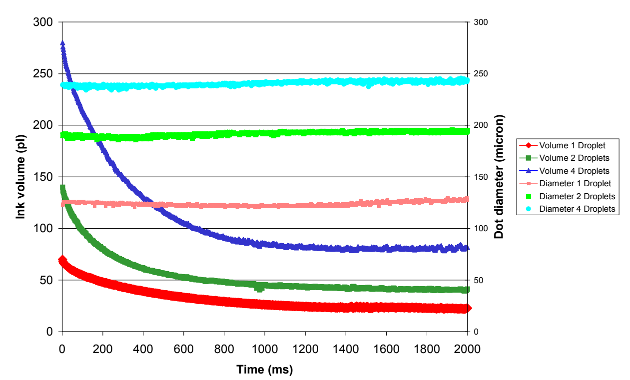

Figure 4. Evolution of drop volume and diameter for a Carbon Black pigment ink on a microporous coating

For the pigment based inks very big deviations were found compared to dye based inks, so neither of the 2 models (Darcy, Davis-Hocking) can describe the process accurately. Taking a closer look at the figure 4 it is evident that the dot diameter remains constant during the full wicking process for the pigment based inks, so the Darcy model should be a better description. However, during the wicking process the pigment particles from the ink are coagulating at the top of the receptive coating, creating a barrier layer limiting the penetration of carrier liquid into the coating. Therefore, the properties of this additional barrier layer were analyzed.

Evaluation of Filter Cake Layer

In a first set of experiments single dots and areas of full ink load were printed using the dye and pigment based inks and analyzed using optical and physicochemical tools.

Images using microscopic techniques on printed dots are shown in figures 5-7.

It is clear that the pigment ink has formed an additional layer on top of the microporous layer having a rougher surface characteristic.

This is clearly visible in a FEG-SEM picture of the microporous coating layer, shown in figure 6. A profilometric scan based on SEM analysis is shown in figure 7.

The microporous layer with printed pigment layer on top of its surface was characterised via gasadsorption and Mercury porosimetry: no significant additional porosity could be found, not on polymeric blend material, nor on different microporous media. It is clear that the pigment filter cake is composed of pigment particles stabilized via polymeric dispersants, leading to a typical “polymeric blend” type of coating having almost no porosity.

Contact angle measurements on these pigment layers were also performed, using AgfaJet Sherpa Cyan Pigment ink as liquid, and considerbly lower contact angles were measured if compared with raw microporous receivers.

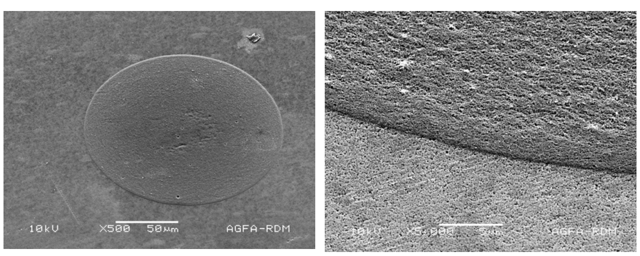

Figure 5. SEM pictures of carbon black test ink 1 printed on microporous_2 medium

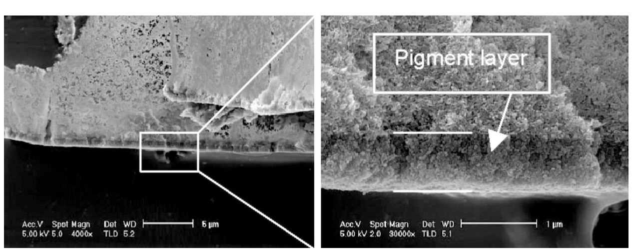

Figure 6.FEG-SEM picture of AgfaJet Sherpa Black Pigment ink printed on microporous_2 material

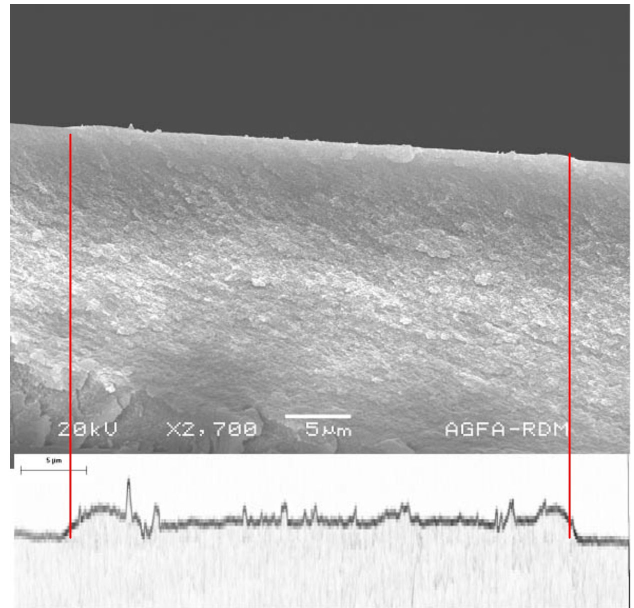

Figure 7. SEM picture and its derived thickness profile of AgfaJet Sherpa Black Pigment ink on microporous_2 material: note that the height-scale is enlarged by a factor of 7 compared to the width scale

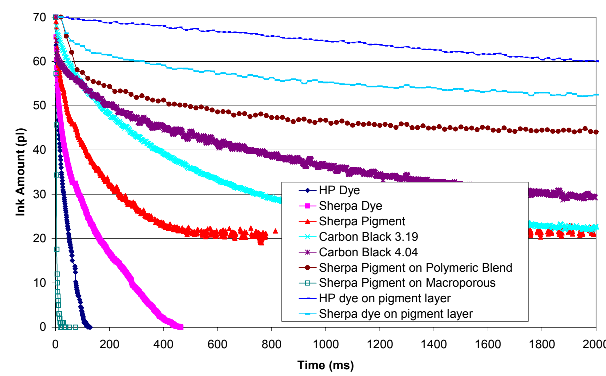

Figure 8. Absorption kinetics of Dye and Pigment inks on different receivers, and of Dye inks printed on top of microporous material first printed with a AgfaJet Cyan Pigment ink

It is clear that during the absorption process a filter cake is being formed changing the absorption characteristics of the receiver on a transient way. To prove this a full-area printed microporous medium was overprinted with individual droplets of AgfaJet Sherpa Cyan Dye ink, and the absorption speed was recorded and compared with the original dye and pigment ink experiments. A graph is shown in figure 8. It is clear that under these circumstances the absorption speed of the dye based ink is considerably longer than on the raw microporous medium, proving that the formed pigment filter cake considerably limits the absorption speed. It is also evident from this figure that not only the pigment ink properties have a big influence on the absorption times, but also the receiver properties. On the macroporous medium having pores with a diameter larger than the pigment particles an additional pigment layer is not built up.

Model to Describe the Absorption Phase

Taking into account that there is no significant deviation in the inertial spreading phase between the dye and pigment based inks, and that during the absorption phase a filter cake is being built having polymeric blend characteristics and lower receding contact angle values, it is clear that a model describing the absorption phase should start with Darcy's law and as a function of time add diffusion limits based on Fick's law to the overall behavior.

Conclusions

In this paper, the absorption process of dye and pigment based aqueous inks on different receivers has been compared.

In the inertial spreading phase both inks behave quite similarly.

In the imbibition phase the dye based inks are mainly disappearing into the microporous coating due to a capillary wicking process which can best be described by the Davis Hocking model. The pigment based inks show initial imbibition into the microporous layer with aggregation of pigment particles on top of the surface. These sedimenting and agglomerating particles are forming a pigment filter cake having polymeric blend character and limiting the imbibition by a diffusion process. The full description can be attributed to a Darcy model at the beginning of the absorption, followed by a diffusion limit according to Fick's law as the absorption continues as a function of time. The filter cake layer has better wetting properties leading to constant dot diameters, which is in contrast to the dot diameter of a dye based ink that is reduced in function of the drying time.

It is clear that the process of absorption for pigment based inks leads to more constraints in the printing process with regard to drying times and coalescence. Pigment stabilization by polymers leads to better rub resistance but reduced absorption times.

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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