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Printing of Dye and Pigment-Based Aqueous Inks Onto Porous Substrates

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In this article, the dynamics of droplet impingement and absorption into microporous materials for pigment based aqueous inks and dye based aqueous inks are compared. For dye based inks it was shown earlier that three main phases could be resolved: 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, and is easily amenable to dimensionless analysis. The absorption phase could be well described by a capillary wicking process according to imbibition models. Evaporation is the slowest process only being finalized after many seconds. These results are now compared with droplet impingement and absorption of pigment based inks on microporous receivers. It is shown that these inks behave totally differently 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 stays on top of the microporous layer. Most polymer stabilizers in the pigment based inks create a colored polymer layer having polymeric blend characteristics limiting considerably the penetration of water compared to the capillary wicking process. The capillary imbibition models are not valid any more because now the build-up of the filter cake changes not only the receding contact angle but also introduces a diffusion process changing as a function of time during the drying of the wet ink.

Introduction

Drop on Demand ink jet technology has gained a lot of attention for printing digital documents. Good image quality can be achieved with cheap devices 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, and deliver an excellent color gamut, but also show slow dry times and bad lightfastness. Coating layers comprising microvoids and working according to the principle of capillary wicking² show much faster drying times with high image quality,¹ but are much more sensitive to light and dark 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 understand better the interaction mechanisms between pigment based aqueous inks and microporous receivers, in order to be able to develop systems with a much better performance. The full ink media interaction model is composed of the behavior immediately after impact of the ink on the substrate, which in the case of low to moderate impact velocities is mainly determined by the kinetic energy, the viscosity and surface tension of the droplet,¹ and the behavior on the longer time scale dealing with the penetration in the medium²⁻⁴ and being investigated in more detail in this article. The penetration of the pigment based inks in microporous media is 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.⁵ The results are related to the ink and media properties.

These results are compared with a model including 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 found experimentally. After printing using pigment based aqueous inks a dot is formed on top of the

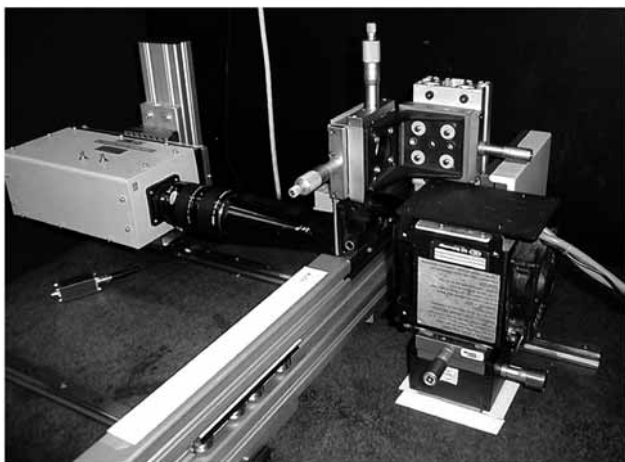


Figure 1. Experimental set-up with Xe-light, HP500 printhead, Kodak HG2000 high speed video camera

microporous layer. This dot has been analyzed using optical, microscopic and surface analysis tools to determine different parameters such as porosity, roughness, etc. The absorption phase can be explained by combining two separate physical behaviors: a diffusion process⁶ for the 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 elsewhere.^{1,5}

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 μ s 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.⁷ The main components of the experimental set-up are shown in Fig. 1.

Visualization Devices

A short shutter time video camera from PCO, SensiCamTM, was used to capture a high resolution single image of 1280 \times 1024 pixels with a shutter time comprised between 500 ns and 1 μ s, to assemble a “video movie” according to the pseudo-cinematography technique that has been described elsewhere.⁷ A highspeed camera, Kodak HG2000, was used to capture images of 512 \times 356 pixels at a real high speed frame rate of 1000 fps.^{1,5} The camera was equipped with a Mitutoyo long working distance objective (type M Plan Apo 20x), mounted on a 123 mm extension tube for appropriate

TABLE I. Properties of the Inks

	Viscosity (mPa.s)	Surface tension (mN/m)
Thermal black dye ink (HP)	1.1	43.1
Piezo cyan dye ink (Agfa)	3.2	33.2
Piezo cyan pigment ink (Agfa)	3.6	32.0
Piezo black pigment ink 1 (Agfa)	4.0	40.7
Piezo black pigment ink 2 (Agfa)	3.2	41.3
Piezo cyan dye ink 2 (Agfa)	4.5	30.2

magnification. Light illumination was provided by a high intensity Xenon lamp from ILC Technology, (model LX300F) with a 300 Watt collimated Cermox Xenon lamp with peak intensity of 515.000 candelas.

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 (AgfaJetTM SherpaTM Cyan Dye ink, AgfaJetTM SherpaTM 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 of the inks was also varied. The characteristics were measured using a Brookfield DVII viscometer and a Krüss K9 digital tensiometer. The properties of the test inks for the printing tests on paper are given in Table I.

Receiving Substrates (AgfaJet) and Characteristics

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 as detailed below.

For the analysis of dots printed on the various substrates a system available from “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 were used to characterize the optical and physical characteristics of the printed dots. The porosity of the substrates was measured using the Hg porosimetry technique (Auto IV 9500, from Micromeritics Instrument) and the gas adsorption technique (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.¹¹ The mean pore size diameter of the tested substrates is given in Table II.

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.⁸

In the case of a finite velocity, which is obvious for printing, the drop first spreads radially into a “pancake” shape before taking on a truncated sphere shape. The rate of spreading depends on a combination of parameters, as described previously.^{1,5} It was found that the inertial spreading phase of the pigment based inks, analyzed according to the models that were presented elsewhere,²⁻⁴ corresponds rather well with the behavior of that of dye based inks.⁹ The big difference in practical behavior between pigment and dye based inks on microporous layers therefore cannot be attributed to the inertial spreading phase. More details on the inertial spreading phase are described elsewhere.^{5,10}

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 Fig. 2, 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 two carbon black pigment model inks of varying viscosities have been jetted on top of different ink jet receptive substrates. The penetration speed of the thermal ink jet ink (HP 51625a) into the different receivers is depicted in Fig. 3. The mechanism of ink absorption of dye based inks into these substrates has been described elsewhere.⁹

Three big classes could be found among these substrates: cast-coated papers and macroporous outdoor materials showing a very short absorption time, polymeric blend materials in which all the liquid has to be absorbed via a diffusion process, and microporous materials showing good glossy characteristics and a much faster drying time than the polymeric blend materials.

TABLE II. Properties of the Substrates

Substrate	Mean pore size diameter (nm)
Microporous 1	16
Microporous 2	35
Microporous 3	100
Microporous 4	140
Microporous 5 = Macroporous	1000
Microporous 6	20
Microporous 7	26

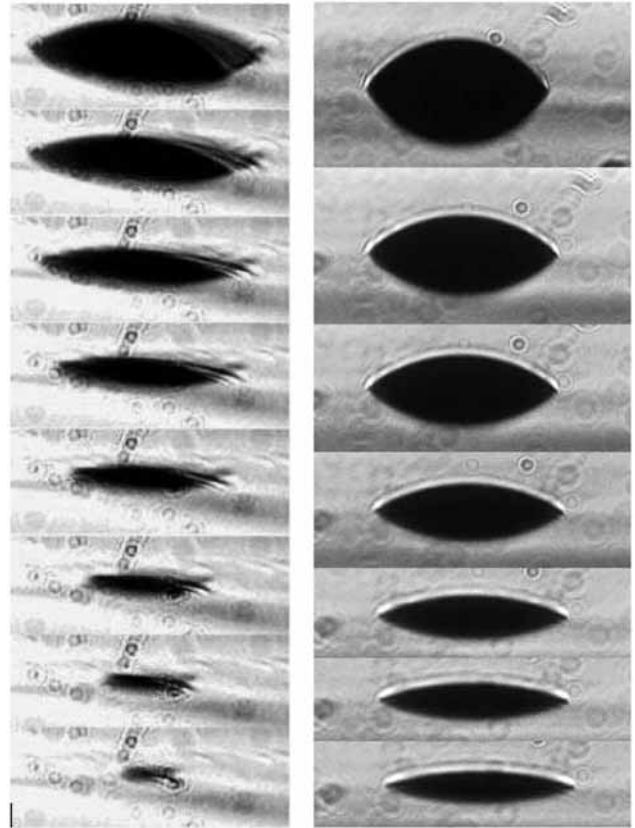


Figure 2. Microphotographs taken during the course of the imbibition phase: left = dye, right = pigment based ink.

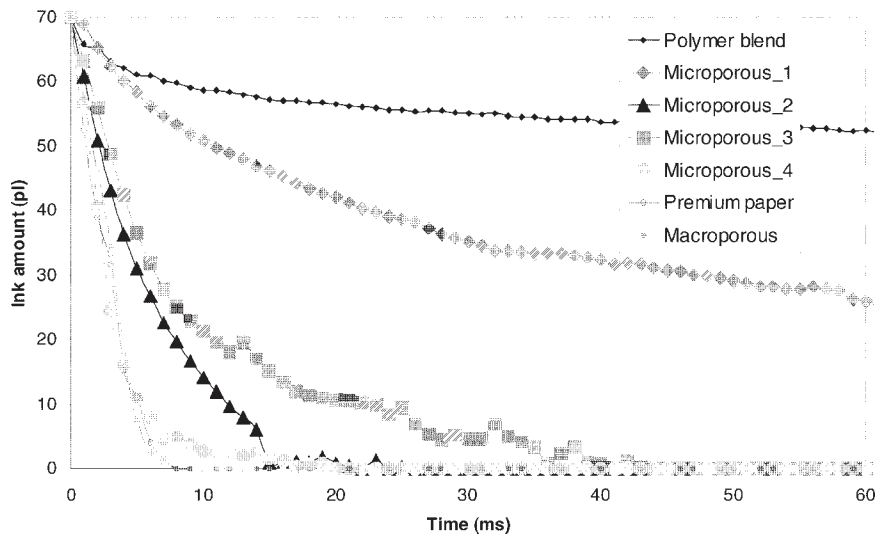


Figure 3. Imbibition of HP51625a inks into different receivers

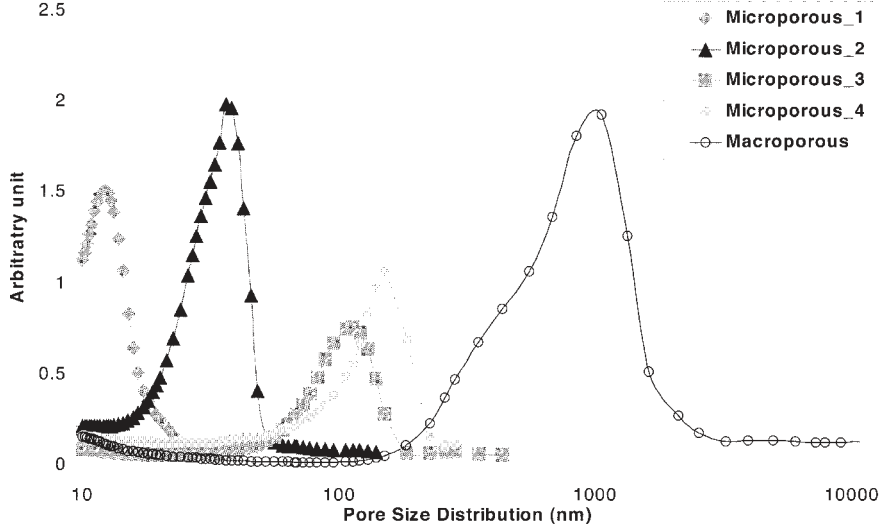


Figure 4. Porosity distribution of different samples

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 Fig. 4. Four main classes were investigated having pore sizes in the ranges of 16, 35, 100 and 140 nm. For comparison the very big pores found in a macroporous material (1000 nm) are also shown in Fig. 4.

In order to describe the imbibition process for dye and pigment based inks, simplified numerical models based on Darcy's law² and the Davis–Hocking^{3,4} model were used. Darcy's law 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 (Eq. (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,⁹ so all other can be neglected. The flow through the capillary is assumed to follow Poiseuille's law:

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

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:

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

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:

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

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^{3,4} 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^{3,4} are shown in Fig. 5.

The Davis–Hocking model^{3,4} can be considered valid for describing porous media. In the case of polymeric blend materials it was shown that a diffusion law is much more appropriate.⁶

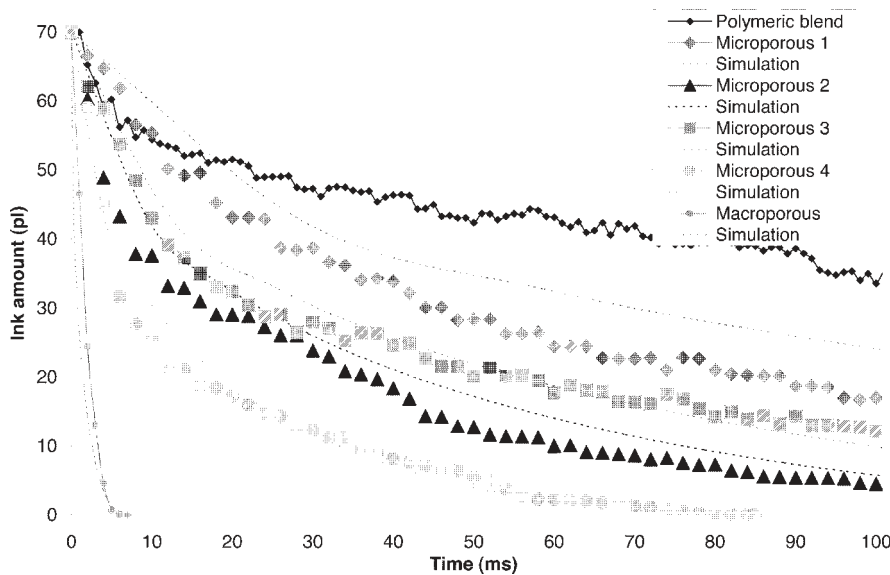


Figure 5. Piezo dye-based ink drop imbibition for different receiving layers.

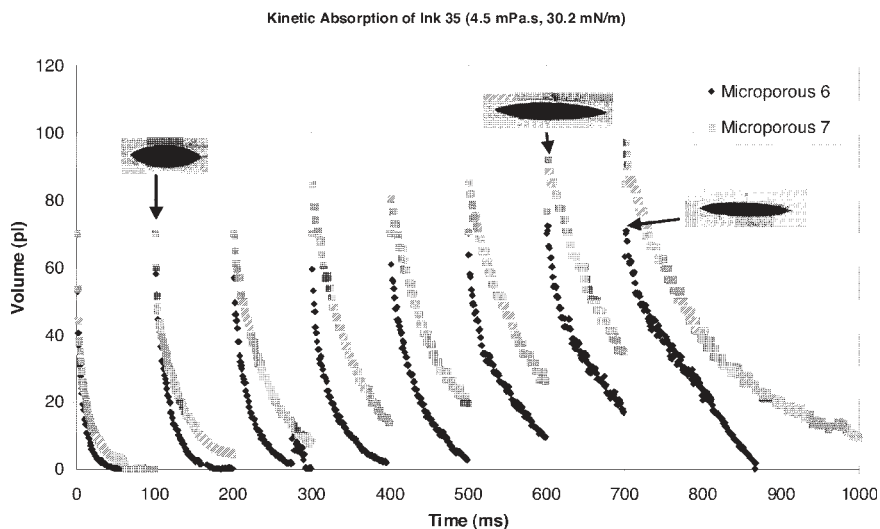


Figure 6. Piezo dye-based ink drop imbibition for different receiving layers.

If a larger amount of ink is printed upon the microporous media it could be observed that the penetration speed is decreasing as a function of applied ink volume. This is shown in Fig. 6 for a Dye based ink with viscosity of 4.5 mPa.s and surface tension of 30.2 mN/m.

The evolution of the volume and of the diameter of a pigment ink drop (Carbon Black model ink with 3.2 mPa.s, 41.3 mN/m) on top of a microporous receiver (microporous_6) is depicted in Fig. 7.

The main differences between dye and pigment based inks are visible in Figs. 3 and 7: 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.

For the pigment based inks very big deviations were found compared to dye based inks, so none of the two previously described models (Darcy², Davis–Hocking^{3,4})

can represent the process accurately. Taking a closer look at the Fig. 7 we see that the dot diameter remains constant during the full wicking process for the pigment based inks, so the Darcy model² 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 the 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 captured of printed dots are shown in Figs. 8 to 10.

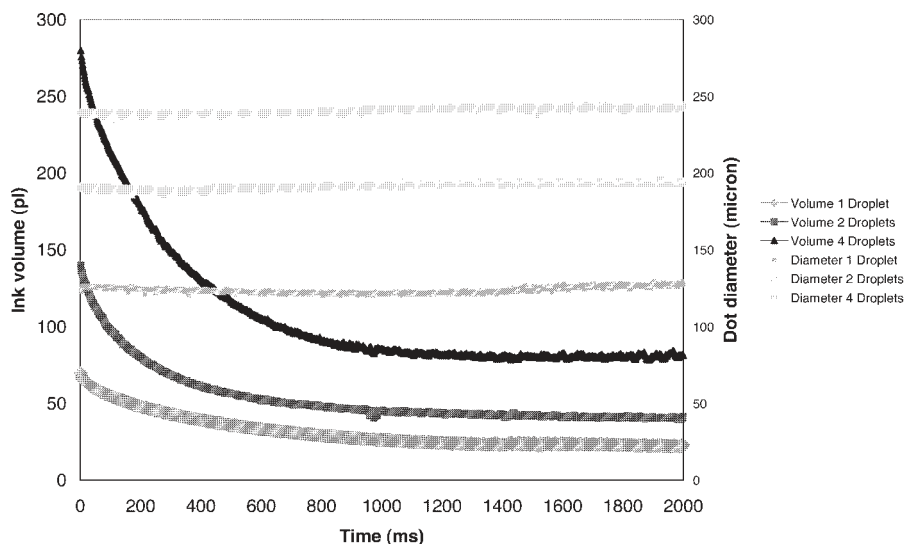


Figure 7. Evolution of drop volume and diameter for a Carbon Black pigment ink on a microporous coating

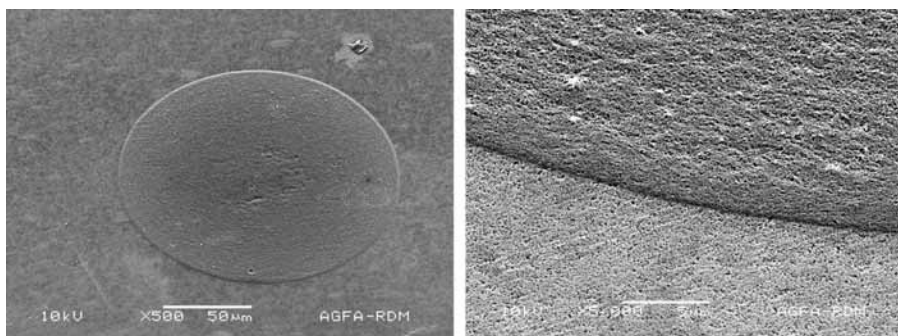


Figure 8. SEM pictures of carbon black test ink 1 printed on microporous 6 medium

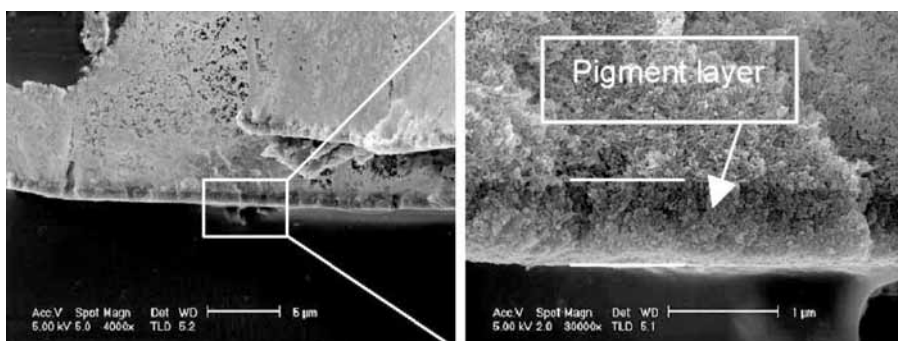
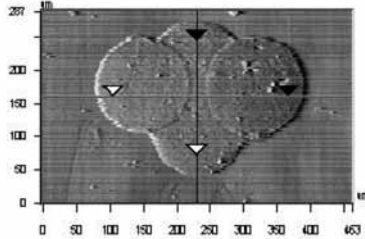


Figure 9. FEG-SEM picture of AgfaJet Sherpa Black Pigment ink printed on microporous 6 material

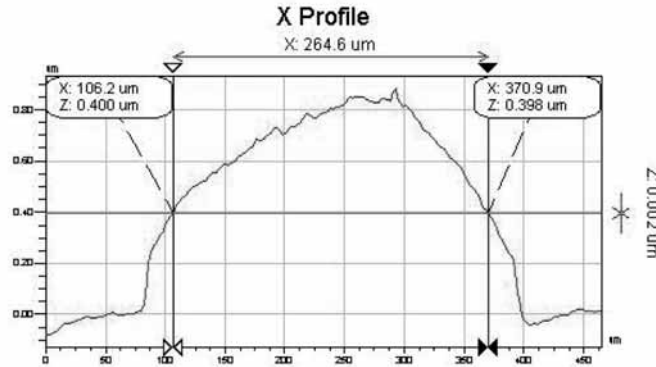
It is clear that the pigment ink has formed an additional layer on top of the microporous layer having a rougher surface characteristic. This additional layer has a thickness of 600 to 800 nm as visible in a FEG-SEM picture of the microporous coating layer, shown in Fig. 9 and also on the scan using optical profilometry as shown in Fig. 10.

The microporous layer with printed pigment layer on top of its surface was characterized via gas adsorption

and mercury porosimetry: no significant additional porosity could be found, neither 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 considerably lower contact

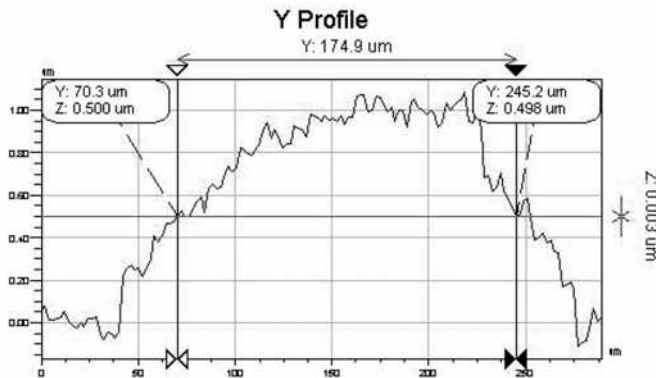


X	229.54	-	-	um
Y	157.68	-	-	um
Ht	0.77	-	-	um
Dist	-	-	-	um
Angle	-	-	-	°



Rq	0.13 um
Ra	0.12 um
Rt	0.49 um
Rp	0.88 um
Rv	0.40 um

Angle	-8.37 urad
Curve	-20.75 mm
Terms	User Fit
Avg Ht	0.68 um
Area	179.14 um2



Rq	0.17 um
Ra	0.15 um
Rt	0.58 um
Rp	1.08 um
Rv	0.50 um

Angle	-15.94 urad
Curve	-7.80 mm
Terms	User Fit
Avg Ht	0.86 um
Area	148.68 um2

File: WYK2B

Figure 10. Optical profilometry on printed dots of pigment ink (pigment ink 1) on microporous media (**microporous 6**)

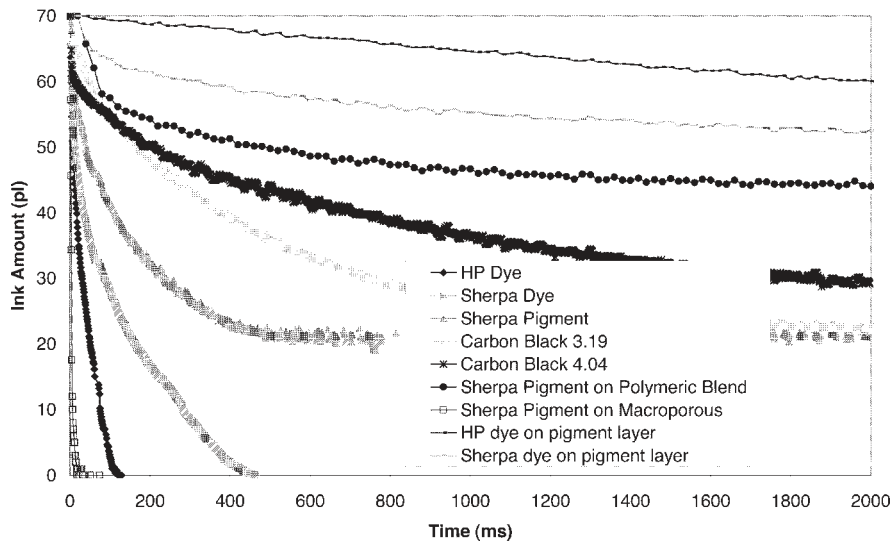


Figure 11. Absorption kinetics of Dye and Pigment inks on different receivers, and of Dye inks printed on top of microporous material first printed with an AgfaJet Cyan Pigment ink

angles were measured if compared with raw microporous receivers.

It is clear that during the absorption process a filter cake is being formed making the absorption characteristics of the receiver time-dependent. To prove this assertion 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 plot of imbibed ink versus time is shown in Fig. 11. It is clear that under these circumstances the absorption speed of the dye based ink is consider-

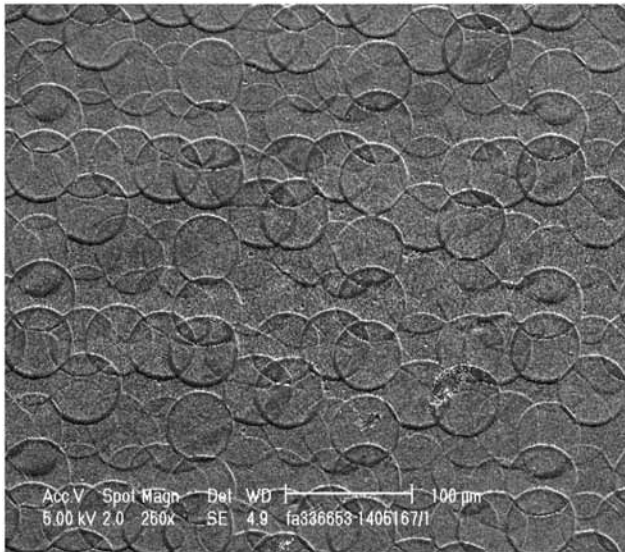


Figure 12. SEM picture of a printout at maximum density using 45 pl droplets of pigment ink deposited in a 4 × 4 shingling algorithm on the **microporous 6** receiver

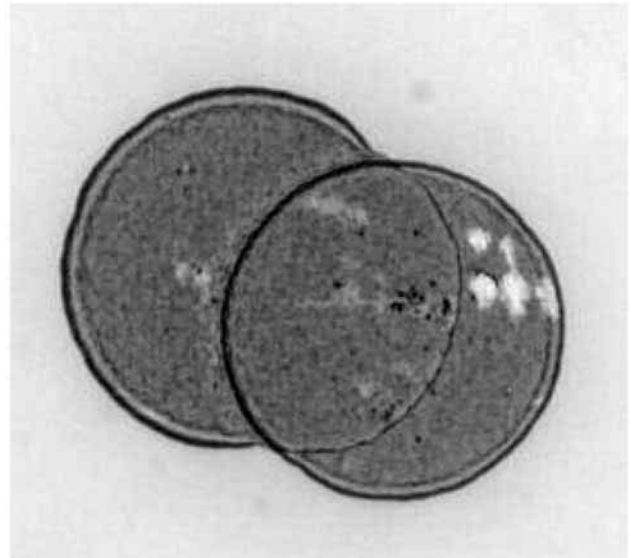


Figure 13. Optical microscopic analysis of 2 droplets of pigment ink printed upon the **microporous 6** receiver with a delay of 100 ms between the 2 impact times of the droplets

ably 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. Indeed, on the macroporous medium having pores with a diameter larger than the pigment particles an additional pigment layer is not built up due to the ratio of sizes of pores compared to pigments.

A printout was made using Agfa cyan pigment ink on microporous media **microporous 6** using a 45 pl Xaar head operated in a 4 × 4 shingling algorithm. The result of a SEM analysis with the resultant image is shown in Fig. 12. It is clear that in this printout where neighboring droplets are time-separated by 10 seconds a collection of different independent “pancakes” can be found.

The impact delay between two consecutive droplets of pigment ink has been reduced to 100 ms as shown in Fig. 13, and here too it could be demonstrated that the two ink droplets are not merging together and are not forming a single large dot. For dye based inks this coalescence has been shown to lead to a single large dot with dye molecules intruding into the pores of the microporous medium.⁹

Model for the Description of the Absorption Phase

Taking into account that there is no significant deviation in the inertial spreading regime⁵ between the dye and pigment based inks as explained elsewhere,⁵ and that during the absorption phase a filter cake is being built up, having polymeric blend characteristics and lower receding contact angle values, it seems plain that a model describing the absorption phase should start with Darcy’s law² and as a function of time add diffusion limits based on Fick’s law⁶ to the overall behavior. This is the topic for further work.

Conclusions

In this article, 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 absorbed 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 the top of the surface. These sedimenting and clustering particles are forming a pigment filter cake having a polymeric blend character and limiting the imbibition by a diffusion process. The full description can be best explained with a Darcy model at the beginning of the absorption, followed by a diffusion trend 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 which is reduced as a function of the drying time.

If the time difference between two neighboring pigment ink droplets is small enough, overlapping “pancake” structures are visible in the final image. 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 in the inks leads to better rub resistance but it reduces significantly absorption times thus hampering higher printing velocities. ▲

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