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Validation of Ink Media Interaction Mechanisms for Dye and Pigment-based Aqueous and Solvent Inks

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Abstract. *In this article, the dynamics of droplet impingement, spreading, absorption, penetration, and evaporation are discussed for different ink jet ink classes. Both dye and pigment based aqueous inks are included, as well as solvent or eco-solvent inks. The fundamental physicochemical rules determining the dynamics can be very dependent from ink to ink, and are compared. After impact there is a fast spreading phase that takes into account the evolution of the kinetic energy of the droplet to forced spreading on the receiver. Later on, diffusion or capillary wicking is possible, and is depending upon the nature of the substrate. The speed of these processes can be influenced by the presence of dyes or pigments in the inks. After absorption / penetration, the carrier liquid can evaporate leading to the final equilibrium condition. For (eco)-solvent inks the evaporation is much more important compared to the other penetration/absorption processes, so that it cannot be easily separated into different independent time scales. In situ visualization of the dynamics for real size ink jet droplets is not easy, especially for the droplets of only a few pl volume. Comparison of large droplet impact dynamic studies with theory and extrapolation of the behavior to small droplet cases has some risks. Test experiments have been setup in order to simulate transient absorption phases on different receivers. Traditional microscopic evaluations have been done in order to verify whether the proposed models for describing the transient behavior are in agreement with the experimental observations for real small sized droplets.* **© 2006 Society for Imaging Science and Technology.**

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INTRODUCTION

Drop on Demand ink jet has become a leading technology 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 nonabsorbing substrates, coated with rather thick absorbing coating layers or microporous receptive layers.

The coating layers comprising polymer blends (such as gelatin, polyvinyl alcohol, and polyvinylpyrrolidone) 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. When printed with dye based inks they show very fast drying times with high image quality and good water fastness,[1,2] but are much more sensitive to light fading and especially 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. On special plastics such as vinyls solvent based inks can be used at more elevated temperatures. The overall printing speed is not very high but printing with moderate quality on very cheap vinyls is possible.

In this study the impact behavior of dye and pigment based aqueous- and solvent inks on different substrates was analyzed. The pseudo-cinematographic method was used to record the inertial spreading phase experimentally.[3] The data were compared with models describing spreading in terms of the variational principle indicating that droplet kinetic and potential energy are counterbalanced by the work of spreading. On the longer time scales the penetration and evaporation of the inks was evaluated using high speed video techniques.[3] The results were related to the ink and media properties.

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 the simulation results and the *in situ* visualization information.

Optimum image quality and printing performance can only be gained by optimization of both ink and media properties. A better understanding of the basic 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]

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Table I. Properties of the inks.

	Viscocity (mPa.s)	Surface tension (mN/m)
Piezo dye ink (Agfa)	3.2	33.2
Piezo pigment ink (Agfa)	3.6	32.0
Piezo pigment eco-solvent ink (Mutoh)	3.7	30.4

Table II. Properties of the Microporous Receivers.

	Pore size distribution peak (nm)
Microporous_1	16
Microporous_2	35
Microporous_3	100
Microporous_4	140
Macroporous	1000

Drop Ejection Devices

Droplets with a volume of 3–200 picoliters were created using driving electronics developed by Ardeje,[3,4] coupled to printheads from Hewlett Packard (HP51625a), Microdrop (AD-K-501), Ink Jet Technologies (64 ID2), Spectra (SL128), or Xaar (Omnidot). The speed was determined by dual-exposure shot measurements using a Sensicam short shutter-time camera.

Ink Composition

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).

The ink characteristics were measured using a Brookfield DVII viscometer and a Krüss K9 digital tensiometer.

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

Receiving Substrates (AgfaJet)

Different substrate materials were used throughout this work, ranging from nonabsorbing substrates (glass, teflon, PET), to absorptive ink jet polymeric blend, microporous and macroporous materials, conventional papers, and untreated vinyls. Some of these materials (AgfaJet) were obtained by coating pigment/binder compositions on clear PET support and measuring the resulting porous characteristics using mercury porosimetry, gas adsorption, and scanning electron microscopy techniques. The microporous receivers used were identical to the ones described earlier in the literature.[2,5]

Also some commercially available reference microporous media were used: The Canon PR101 and the Epson photo glossy paper. A selection of conventional papers was provided by the EFPG of Grenoble. For the sake of the comparitive study only the differences in porosity will be indicated.

Visualization Devices

A short shutter time video camera from PCO, Sensicam, was used to capture a high-resolution single image of 1280 × 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.[3,4]

A high-speed camera, Kodak HG2000, was used to capture images of 512 × 356 pixels at a real high speed frame rate of 1000 fps or 512 × 178 pixels at 2000 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 characterize 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.[5]

RESULTS AND DISCUSSION

To fulfill the objectives listed in the introduction part, drop-impinging experiments were performed using a variety of inks on different substrates. The results are discussed in terms of the different time scales associated with these processes.

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]

Dye Based Aqueous Inks on Polymeric Blend Receivers

As already indicated earlier[1,7] the absorption speed of a dye based ink in a polymeric blend material is slow, taking about 2 s for a 70 pl droplet to fully disappear.

It can be stated that the liquid is absorbed into the polymeric blend material by a diffusion process. The absorption speed can be expressed by plotting the remaining liquid on top of the receiver as a function of square root of time, and from this analysis the diffusion constant of the liquid in the polymeric blend material can be calculated.

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

Here V is the volume of ink on top of the receiver, R is

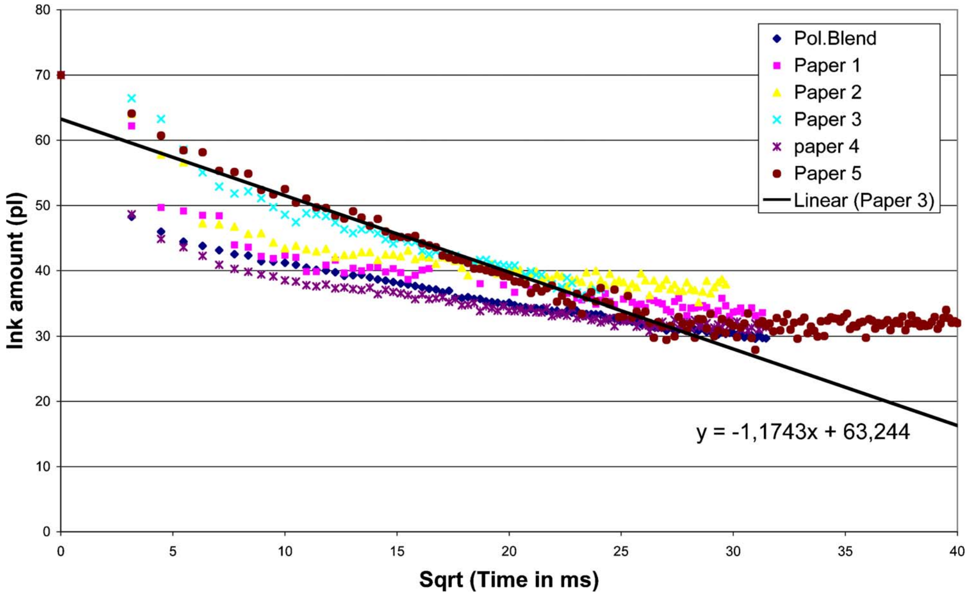


Figure 1. Absorption speed of Sherpa water-based dye ink printed on polymeric blend and conventional papers with low porosity.

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]

The results are shown in Fig. 1. A slope of about -1.2 is observed if 70 pl of ink is followed as a function of the square root of time, expressed in ms. The corresponding diffusion constant is about 1.8×10^{-11} m^2/s.

In order to verify these kinetic results as described by the law of Fick,[7] 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 Fig. 2.

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 μm deep 25 ms after impact. If the time-interval after impact is taken rather large (1 s = almost full absorption), then the wetting front has reached a 3.2 μm deep penetration. These results are in good agreement with the expectations on the basis of a diffusion process,[7] as expressed in Eq. (1).

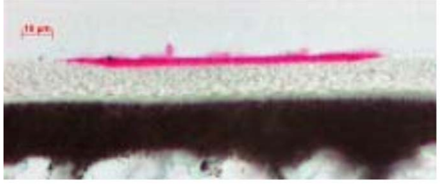
Pigment Based Aqueous Inks on Polymeric Blend Receivers

The absorption mechanism for pigment based inks on polymer blend receivers is rather similar to the case of dye based inks. As visible in Fig. 3 the absorption speed is slow (order of magnitude seconds). Again a model as developed by Fick is a good starting point to describe this drying process based on diffusion of the carrier liquid into the polymeric coating.

Dye Based Aqueous Inks on Microporous Receivers

The evolution of a droplet of 70 pl of dye based aqueous ink on a microporous receiver is shown in Fig. 4.

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 2. Cross sectional microscopy through single dot of Sherpa water-based dye ink printed on AgfaJet polymeric blend paper with varying times between impact and analysis.

Compared to the case of the polymeric blend material this process is much faster. It has been shown in the literature that the process can be described by a capillary wicking model and that the rate is largely dependent upon the porous properties of the receivers.[2]

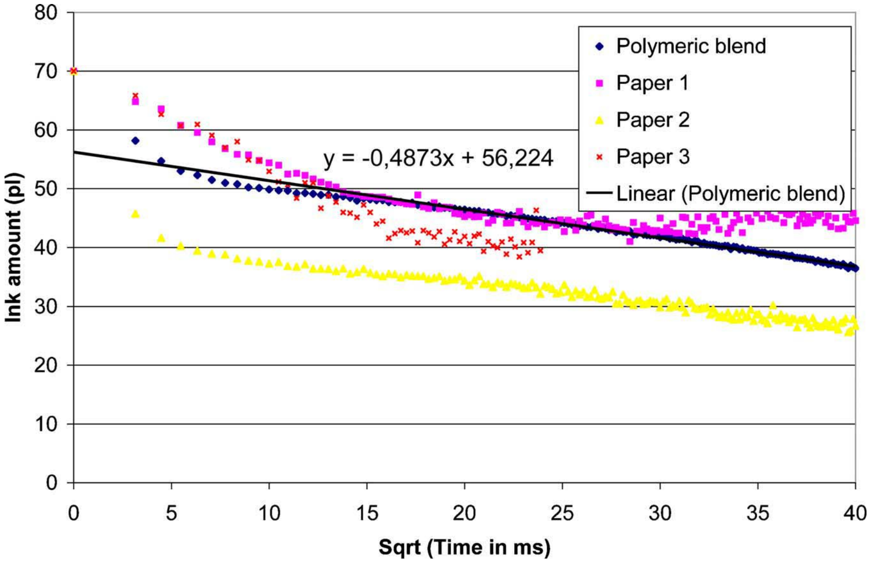


Figure 3. Absorption kinetics of Sherpa water-based pigment ink on polymeric blend and conventional papers with low porosity.

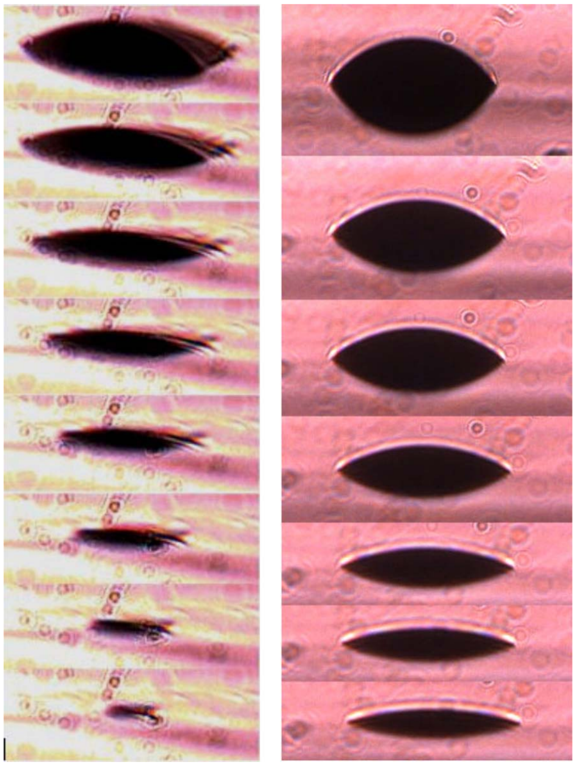


Figure 4. Experimental results of the imbibition process: Left=dye, right =pigment based ink jetted onto a microporous receiver.

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.

In order to describe the imbibition process for dye and pigment based inks, simplified numerical models based on the Darcy's law[8] and the Davis-Hocking[9,10] model were 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 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.

More details on the numerical analysis for dye based inks on microporous media are given in the paper of Alleborn and Raszillier.[11]

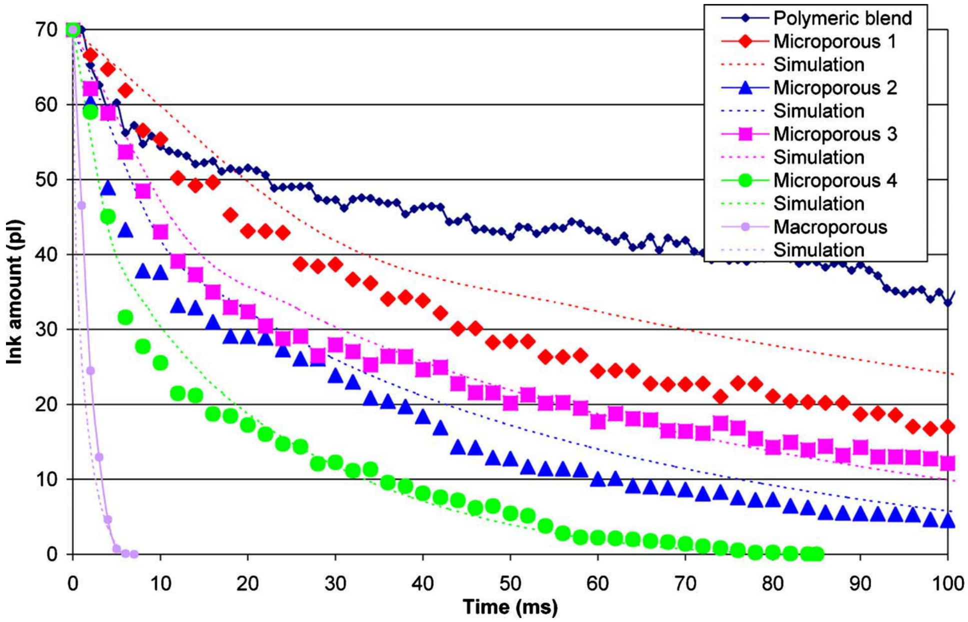
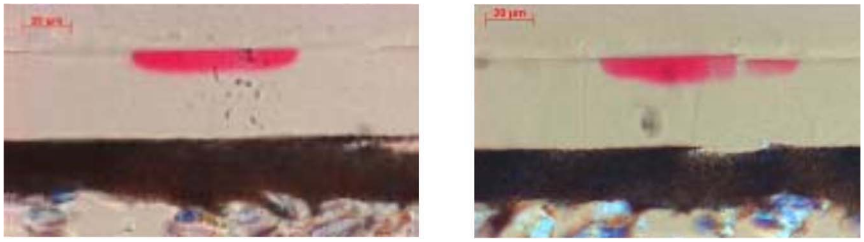


Figure 5. Aqueous dye-based ink drop imbibition for different receiving layers.

Both models were tested and compared with experiments.

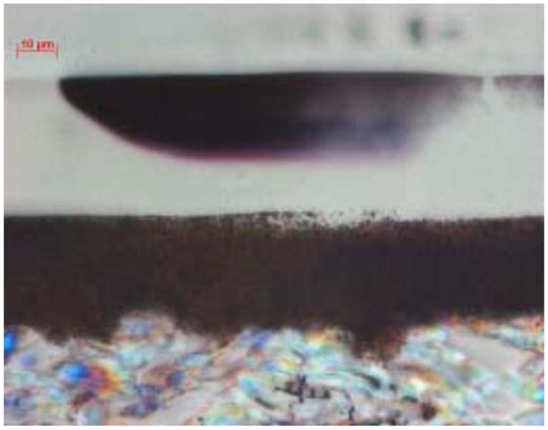
For the dye based inks good agreement was found between the Davis-Hocking model and the experiments. An example of the absorption speed of 70 pl of AgfaJet Sherpa Dye ink on different microporous media, and the results of a Davis-Hocking analysis are shown in Fig. 5.



25 ms after impact: 9.3 micron deep penetration

1000ms after impact: 11.7 micron deep penetration

(a)



(b)

Figure 6. (a) Microporous medium/dye ink. (b) Microporous medium/dye ink: Final penetration profile (parabolic shape).

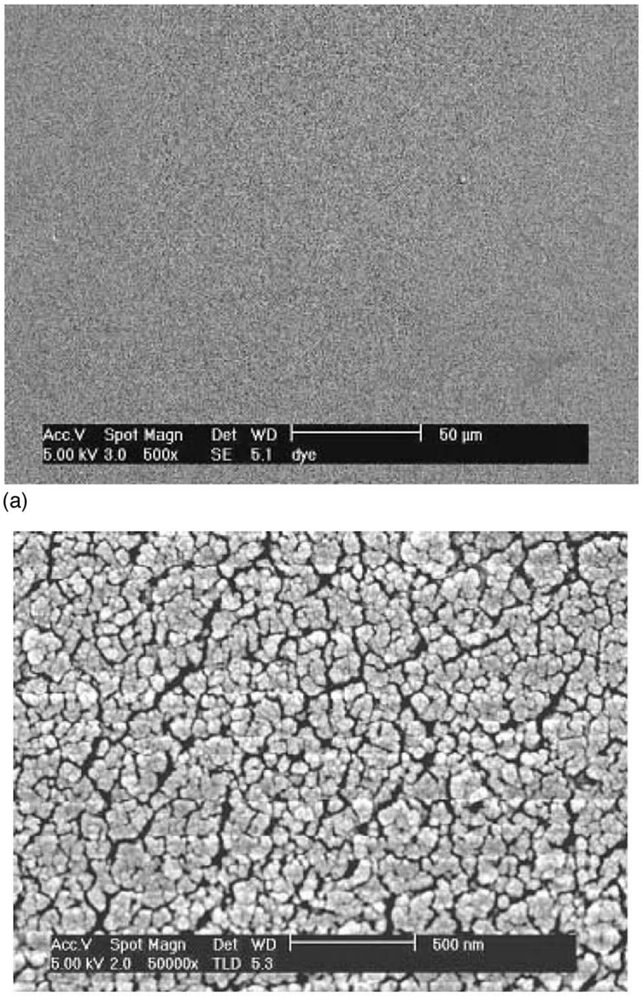


Figure 7. (a) Microporous medium / dye ink: No dot on top of receiver after penetration period. (b) Detail of top surface of Fig. 7(a). The microporous nature of the original coating is easily visible.

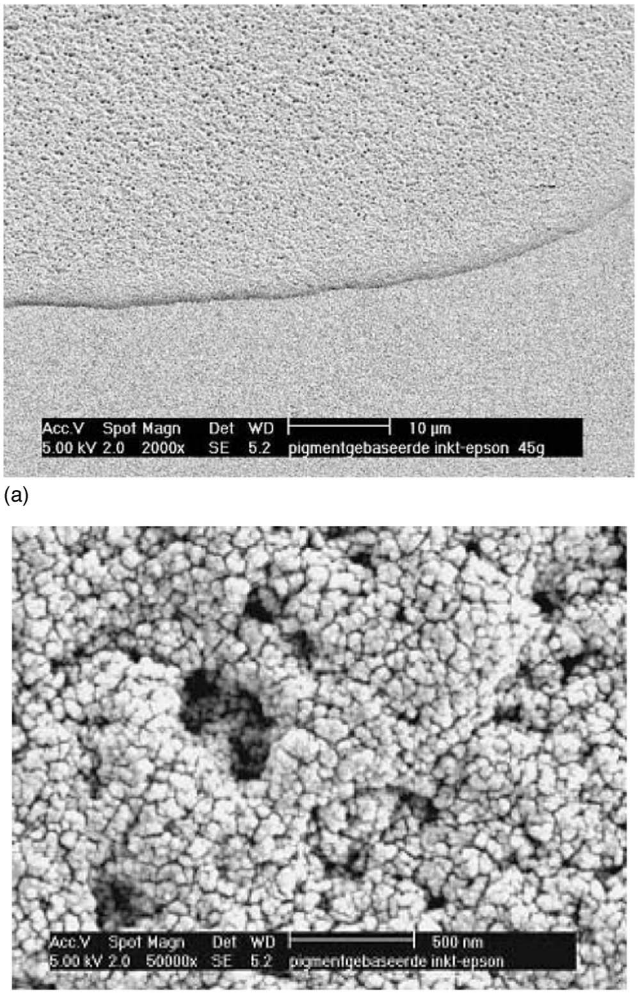
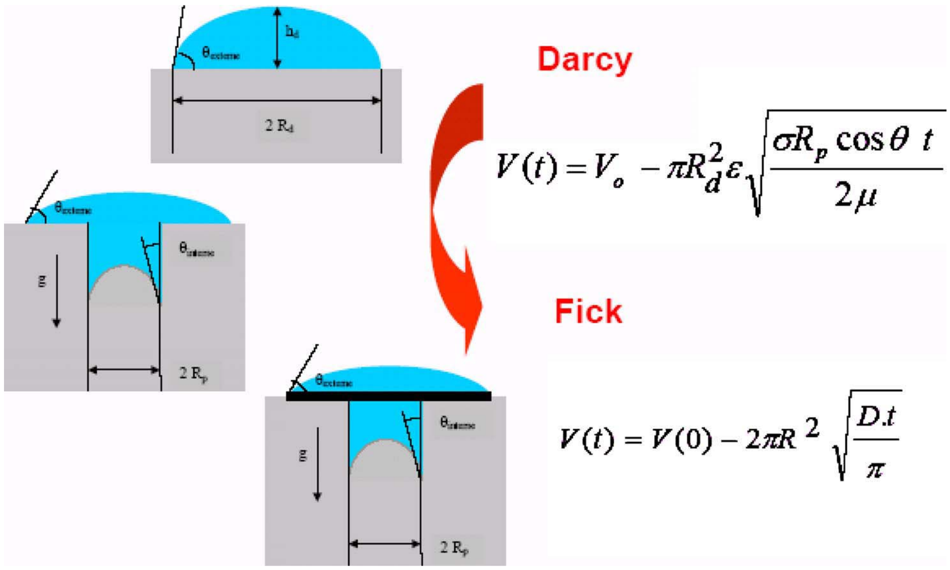


Figure 8. (a) Microporous medium / pigment ink: Formation of pancake on surface. (b) Detail of pancake of Fig. 8(a). The coagulated pigment particles are easily visible.



$$V(t) = V_o - \pi R_d^2 \varepsilon \sqrt{\frac{\sigma R_p \cos\theta\ t}{2\mu}}$$

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

Figure 9. Model for the absorption kinetics of water based pigment inks on microporous receivers.

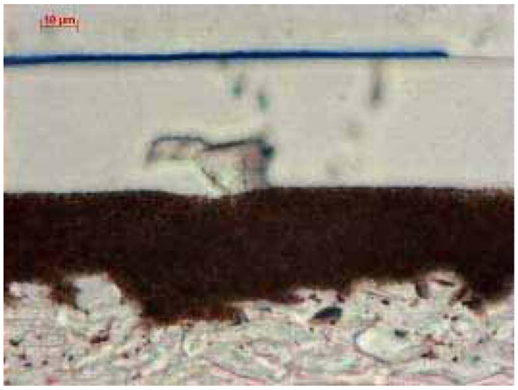


Figure 10. Microporous medium /pigment based solvent ink: Formation of filter cake on top of receiver in final penetration profile.

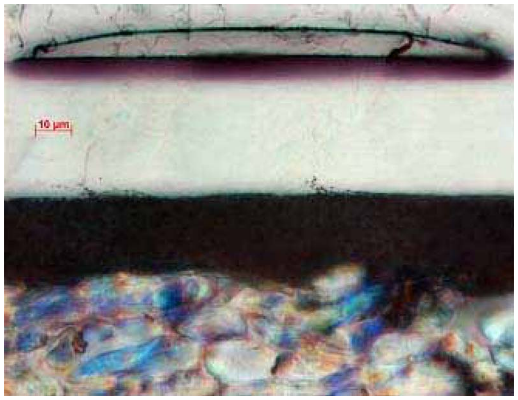


Figure 12. Microporous medium / mixed pigment/dye ink showing both pigment cake and dye penetration in final penetration profile.

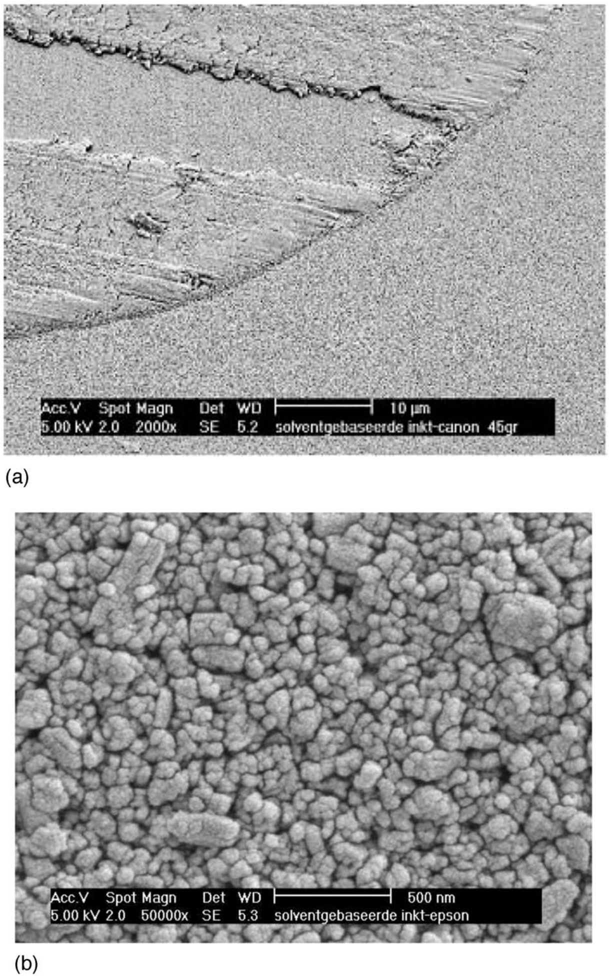


Figure 11. (a) Microporous medium/ pigment solvent ink: Filter cake on top of receiver. (b) Detail of pancake of Fig. 11(a). The coagulated pigment particles are easily visible.

An example of the absorption profile of 45 pl of AgfaJet Sherpa Dye ink on microporous media is shown in Fig. 6.

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 dye based ink the SEM analysis cannot reveal the dot any more, as shown in Fig. 7. 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 visualized using the SEM technique.

Pigment Based Aqueous Inks on Microporous Receivers

The evolution of a droplet of 70 pl of pigment based aqueous ink on a microporous receiver is shown in Fig. 4. More details on the absorption process of this class of inks can be found in the literature.[5]

The pigment particles in the pigment based ink are forming a filter cake on top of the microporous layer. As visible in Fig. 8 this filtercake layer may limit the penetration of liquid into the receiving coating. For that reason the drying time may be longer than that of dye based inks.

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

The model to describe the absorption process is depicted in Fig. 9: Starting with inertial spreading and penetration according to the law of Darcy, followed—once a filter cake is being formed—by a model of Fick.

Pigment Based Solvent Inks on Microporous Receivers

For a pigment based solvent ink, the printing process leads to the creation of a filter cake on top of the receiver too. This was already explained earlier.[5] Figure 10 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.[5]

The SEM pictures of pigment based eco-solvent ink printed onto microporous media are shown in Fig. 11.

It is clear that again the pigment stays on top of the receptive coating as a separate pigment filter cake. The eco-

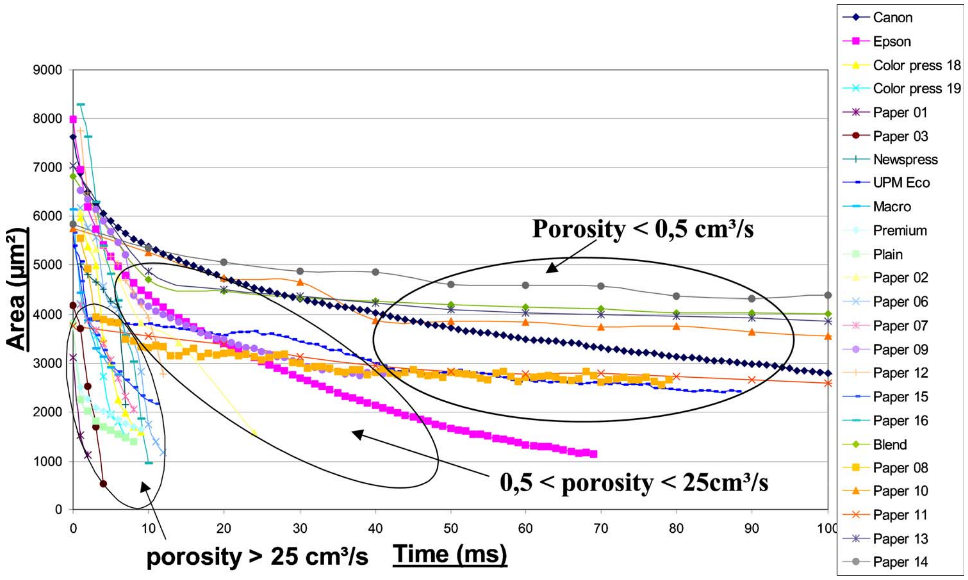


Figure 13. Absorption kinetics of water based dye/pigment inks on different conventional papers.

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.

For inks which contain both pigments and dyes, a special situation is found. Figure 12 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.

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 Fig. 12 has been detached from the substrate during the sample preparation process.

Pigment Based Aqueous Inks on Conventional Papers

The evolution of a droplet of 70 pl of pigment based aqueous ink on different conventional papers is shown in Fig. 13. Three classes of papers can be identified: Very fast ones,

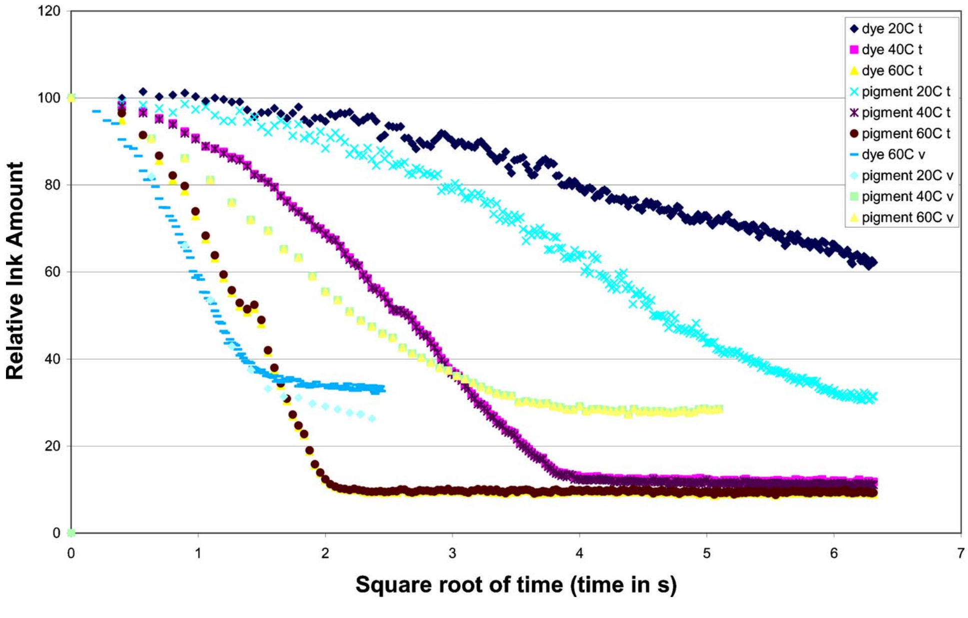


Figure 14. Absorption kinetics of dye and pigment based solvent inks on teflon and vinyl receivers.

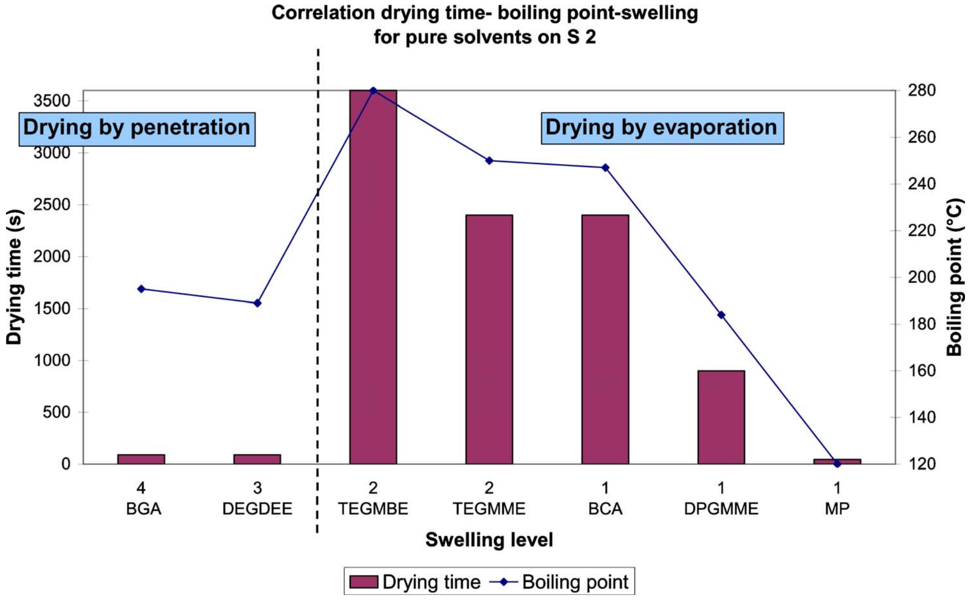


Figure 15. Absorption kinetics of dye and pigment based solvent inks on vinyl receivers.

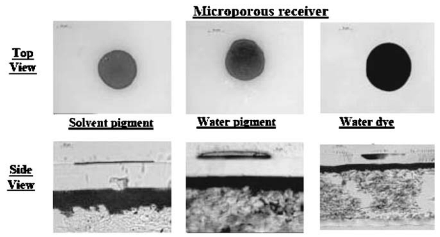


Figure 16. Microscopic analysis of dye and pigment based inks on a microporous receiver.

moderate ones, and very slow ones. The printing speed is largely correlated with the porosity of the papers.

So the behavior of the pigment based inks on conventional paper substrates is quite similar to that on microporous media: The diffusion law of Fick and the Davis-Hocking model being adequate starting points to model the absorption process.

Pigment Based Solvent Inks on Vinyls

The evolution of a droplet of 70 pl of dye and pigment based solvent ink on a vinyl substrate is shown in Fig. 14.

Here it can be seen that the dry times become extremely long—i.e., not useful for practical purposes. By increasing the substrate temperature the drying time can be shortened considerably.

It is obvious that by increasing the temperature of the substrate, the speed of diffusion into the vinyl can be increased, but also the evaporation speed is greatly enhanced. By increasing the temperature of the vinyl to about 55°C a printing speed can be obtained that is equivalent to the printing speed of aqueous based dye inks on polymeric blend materials.

As shown in Fig. 15 this ink media interaction process is not only determined by temperature and evaporation rate. Tests were done with test inks having chemical variation in carrier composition. Some inks are chemically interacting with the vinyl substrate leading to swelling of the polymer and diffusion of solvent into the receiver, while other inks are not penetrating into the vinyl and the solvent only disappears via an evaporation process. As shown in Fig. 15 the cases of drying by penetration lead to much shorter drying times.

The time scales of diffusion and evaporation are much closer together than the time scales of capillary wicking and evaporation for aqueous inks. Consequently it is not possible to divide the model for describing the drying time into two separate and noninteracting parts: Hence modeling of the solvent based inks on vinyl substrates is much more difficult.

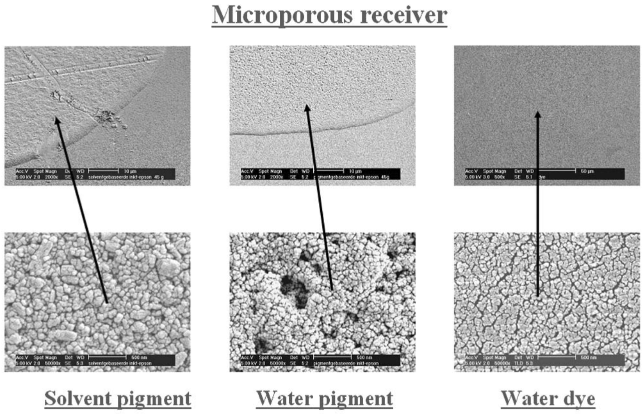


Figure 17. SEM analysis of dye and pigment based inks on a microporous receiver.

Summary of Ink Media Interaction Results

The conclusion of the ink media interaction study for dye and pigment based aqueous and solvent inks is summarized in Figs. 16 and 17.

All inks absorb slowly in polymeric blend materials. Pigment based inks absorb slower than dye based inks and a certain amount of colorant stays on top of the layer.

In Fig. 16 it is clear that the colorant of the pigment inks stays on top of the microporous medium, while for a dye based ink a parabolic shaped penetration zone within the coating is observed.

The same conclusions can be obtained from the SEM study as shown in Fig. 17. Solvent and water pigment inks result in pancake formation of a filter cake, while for the dye based ink the colorant has penetrated into the pores of the medium.

CONCLUSIONS

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

In the inertial spreading phase all inks behave quite similarly as explained in more details elsewhere.[12]

In the imbibition phase the dye based inks are mainly disappearing into the polymeric blend coating by a diffusion process, and 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 polymeric blend/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. The same behavior is found for pigment based (eco)solvent inks on microporous media. The solvent inks printed on vinyl substrates require an increased substrate temperature, and the diffusion process takes place at almost the same time scale as the evaporation process.

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

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