Fundamental Mechanisms in Ink Media Interactions for Aqueous, UV-Curing and Solvent Based Inks

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Abstract

In this article, the dynamics of droplet impingement, spreading, absorption, penetration, curing and/or 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, and UV-curing 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 can not be easily separated into different independent time-scales.

For UV-curing inks, a polymerisation reaction leads to solidification of the ink. For that reason the absorption or diffusion is not important, and has to be replaced by a reaction process.

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 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. When printed with dye based inks they show very fast drying times with high image quality and good water fastness,[1] but are much more sensitive to light fading and especially gas (ozone) fading.

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. UV-curing inks can – in principle – be printed on any substrate. Immediately after impact of the ink on the substrate the kinetic energy of the droplet is converted to forced spreading. In the case of low to moderate impact velocities this inertial spreading phenomenon is mainly determined by the kinetic energy, the viscosity and surface tension of the droplet.

In this study the impact behavior of aqueous-, solvent- and UV-curing inks on different substrates was analyzed. The pseudo-cinematographic method was used to record the inertial spreading phase experimentally.[2] 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. The results were related to the ink and media properties.

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]

Drop Ejection Devices

Droplets with a volume of 20 to 200 picoliters were created using driving electronics developed by Ardeje.[3]

coupled to printheads from Hewlett Packard (HP51625a), Microdrop (AD-K-501), Ink Jet Technologies (64 ID2), or Spectra (SL128). 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, SunJet UV-curing ink).

The ink 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

	Viscosity (mPa.s)$^{\$}$	Surface tension (mN/m)
Piezo dye ink (Agfa)	3.20	33.2
Piezo pigment ink (Agfa)	3.56	32.0
Piezo pigment eco-solvent ink (Mutoh)	3.73	30.4
Piezo pigment UV-curing ink (SunJet UGE5570)	9.50	31.6

$^{\$}$: Viscosity at jetting temperature (45 C for UV curing ink)

Table 2 Properties of the Microporous Receivers

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

Receiving Substrates (AgfaJet)

Different substrate materials were used throughout this work, ranging from non-absorbing 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.[4-5]

Also some commercially available reference micro-porous 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 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.[2]

A high-speed camera, Kodak HG2000, was used to capture images of 512 x 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. 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 a variety of inks on different substrates. The results are discussed in terms of the different time scales associated with these processes. An example of the evolution of the ink on the substrates is shown in figure 1.

Dye Based Aqueous Inks on Polymeric Blend Receivers

As already indicated earlier[1,6] the absorption speed of a dye based ink in a polymeric blend material is slow, taking about 2 seconds 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 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.[6]

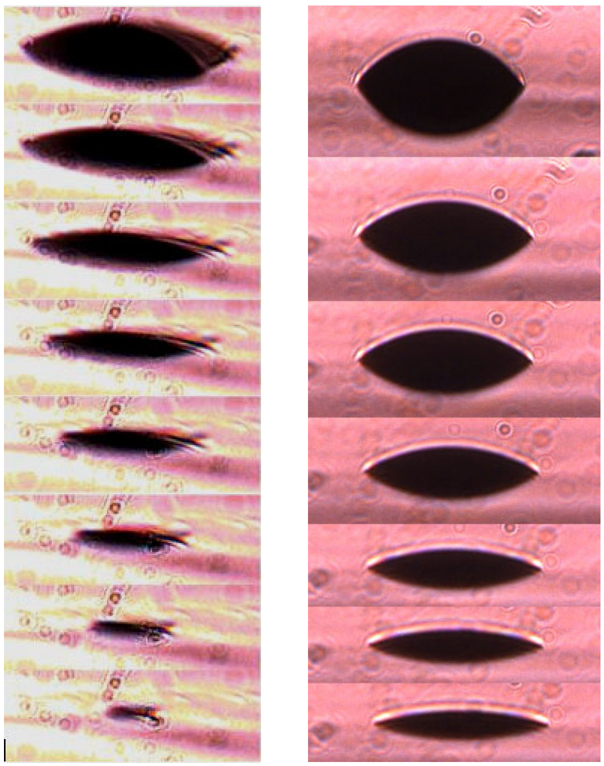

Figure 1. Experimental results of the imbibition process: left = dye, right = pigment based ink jetted onto a microporous receiver

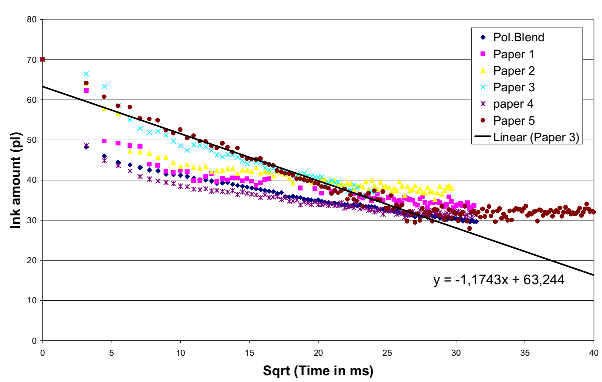

Figure 2. Absorption speed of Sherpa dye ink printed on polymeric blend and conventional papers with low porosity

The results are shown in figure 2. 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.

Dye Based Aqueous Inks on Microporous Receivers

The evolution of a droplet of 70 pl of pigment based aqeous ink on a microporous receiver is shown in figure 1.

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, the rate being largely dependent upon the porous properties of the receivers.[5]

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[7] and the Davis-Hocking[8-9] 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[8-9] 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:

$$d(t) = \sqrt{\frac{R_P \, \sigma \cos(\theta) t}{2\mu}} \qquad (2)$$

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:

$$V(t) = \frac{\pi R_P^{\,2}}{2}\left(2d(t) - \frac{d(t)^2}{D}\right) \qquad (3)$$

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 & Raszillier.[10]

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.

Pigment Based Aqueous Inks on Microporous Receivers

The evolution of a droplet of 70 pl of pigment based aqeous ink on a microporous receiver is shown in figure 1.

More details on the absorption process of this class of inks can be found in the literature.[4]

The pigment particles in the pigment based ink are forming a filter cake on top of the microporous layer. 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.

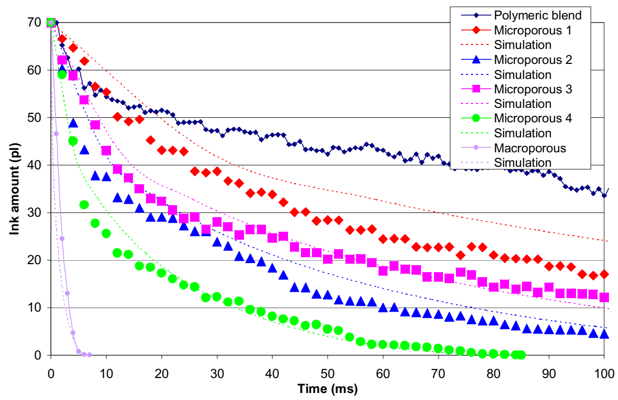

Figure 3. Piezo dye-based ink drop imbibiton for different receiving layers

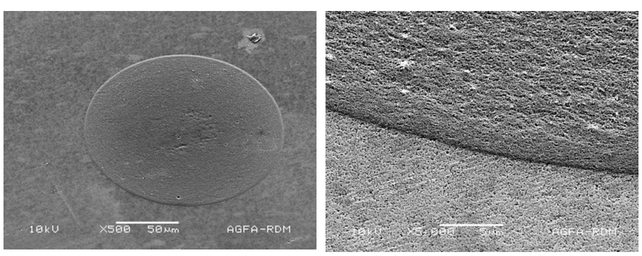

Figure 4. SEM pictures of Sherpa pigment ink printed on microporous_2 medium

Pigment Based Solvent Inks on Microporous Receivers

The evolution of a droplet of 70 pl of pigment based solvent ink on a microporous receiver was comparable to the behaviour of the pigment based aqueous ink on top of the microporous receiver. Here also a filter cake was formed, limiting the penetration of liquid into the receptive coating. The solvent ink, however, has a different composition and the penetration of this ink into the receptive coating may be faster that that of the aqueous ink. The printed dot has been scratched with a hard pin, making it even better visible that the filter cake is on top of the microporous coating and can be more easily damaged than the microporous coating itself.

Pigment Based Aqueous Inks on Papers

The evolution of a droplet of 70 pl of pigment based aqueous ink on different conventional papers is shown in figure 6. Three classes of papers can be identified: very fast ones, moderate ones, and very show 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.

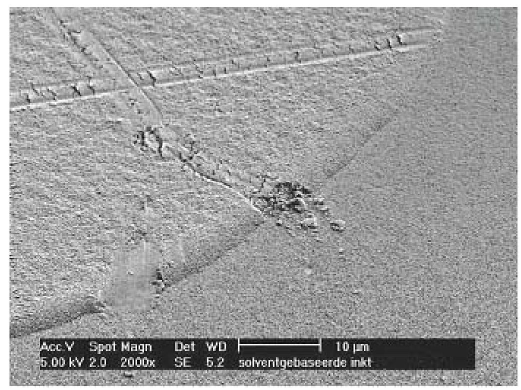

Figure 5. SEM picture of solvent based ink printed on microporous_2 medium

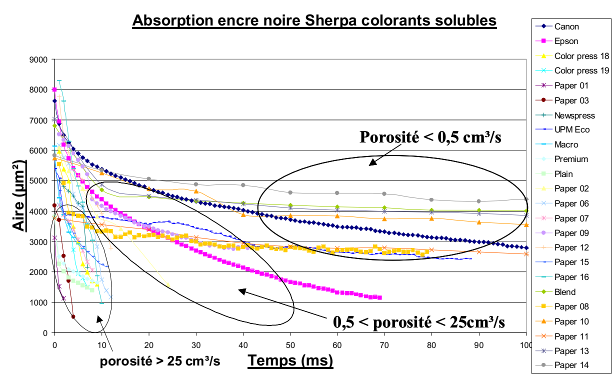

Figure 6. Absorption kinetics of Pigment inks on different papers

Pigment Based Solvent Inks on Vinyls

The evolution of a droplet of 70 pl of dye and pigment based solvent ink on vinyl substrates is shown in figure 7.

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.

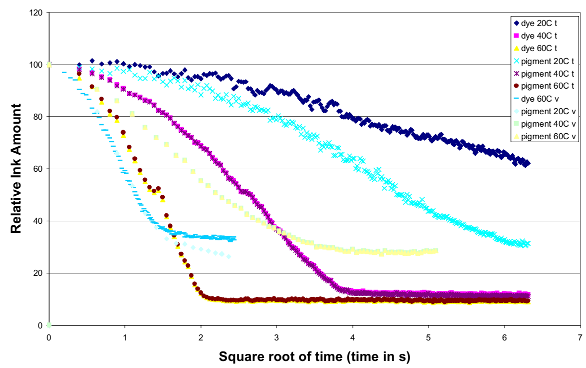

Figure 7. Absorption kinetics of Dye and Pigment based solvent inks on different receivers

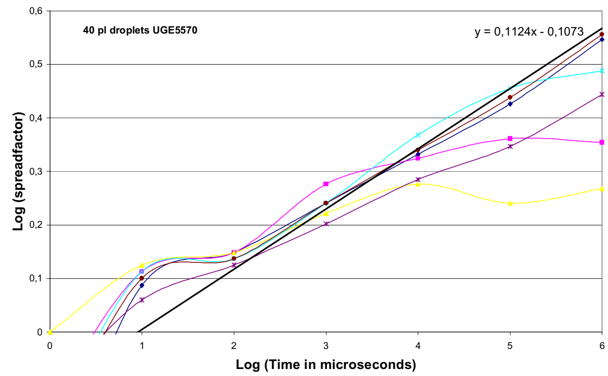

Figure 8. Spreading kinetics of Pigment based UV-curing inks on different receivers

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 largely enhanced. By increasing the temperature of the vinyl to about 55C a printing speed can be obtained that is equivalent to the printing speed that is feasible with aqueous based dye inks on polymeric blend materials.

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 2 separate and non interacting parts: hence modeling of the solvent based inks on vinyl substrates is much more difficult.

Pigment Based UV-Curing Inks on Plastics

The evolution of a droplet of 40 pl of pigment based UV-curing ink on different plastic substrates is shown in figure 8.

Now there is only spreading on the substrate and a very small absorption or capillary wicking. The spreading was continued until an equilibrium condition was reached, or until the UV-curing process stopped the spreading before the equilibrium was reached.

The full process can be divided into 3 parts. On the very fast scale there is an inertial spreading, after some time there is rearrangement of the droplet geometry to a truncated sphere form, and then the capillary spreading is related to the ink and substrate properties. The main driving forces driving this phase are the surface tension of the ink and the surface energy of the substrate. If the surface tension of the ink is much lower than the surface energy of the substrate, spontaneous spreading continues in a regime of perfect wetting. If the difference is smaller, then spreading only occurs till the equilibrium contact angle is obtained. After this moment no additional spreading takes place. It is obvious in figure 8 that a few ink-substrate combinations are fulfilling these requirements.

Conclusions

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

In the inertial spreading phase all inks behave quite similarly.

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 behaviour 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.

For UV-curing inks there is almost no absorption process. The dot characteristics are mainly determined by the spreading to equilibrium, unless the print-to-cure time is short enough the freeze the moving droplet.

References

1. G. Desie, S. Allaman, O. Lievens, K. Anthonissen and A. Soucemarianadin, Proceedings of IS&T NIP18, 360 (2002)
2. P. Pierron, S. Allaman and A. Soucemarianadin, Proceedings of IS&T NIP17, 308 (2001).
3. P. Pierron, E. Auboussier, C. Schlemer and N. Galley, Proceedings of IS&T NIP16, 56 (2000)
4. G. Desie, O. Pascual, T. Pataki, P. de Almeida, P. Mertens, S. Allaman and A. Soucemarianadin, Proceedings of IS&T NIP19, 209 (2003)
5. S. Allaman, G. Desie and A. Soucemarianadin, Proceedings of the 11th IPGAC, II5 (2002)
6. K. Yip, A. Lubinsky, D. Perchak and K. Ng, Proceedings of IS&T NIP18, 378 (2002)
7. S. Middleman, Modeling Axisymmetric Flows (Academic Press) 1995.
8. S.H.Davis, L.M. Hocking, Physics of Fluids, 11, 48 (1999).
9. S.H.Davis, L.M. Hocking, Physics of Fluids, 12, 1646 (2000).
10. N. Alleborn and H. Raszillier, Chemical Engineering Science, 59, 2071 (2004).

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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