

Influencing the profile of an inkjet printed layer on glass by using optimized solvent mixtures

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Abstract

In this paper it is shown that variations of layer thickness of a dried inkjet printed layer on non-porous substrates can be affected strongly by simple variation of ink solvents. Inkjet printed layers on substrates like standard glass have often non-uniform layer thicknesses. One known reason for this is referred as the Coffee-Stain Effect. In such a case the layer thickness is up to four times higher at the edges than at the center. An extended evaporation rate at the edge is driver for that effect. In other cases, agglomeration of particles in the center of a printed layer can also be found. Marangoni Convection driven by thermal gradients are often referred as the main cause. Both deviations of layer thickness are common in functional printing applications if low viscous inks with a high amount of solvents are used. This variations of structures might lead to issues in subsequent processes, e.g. defects in top coatings or even short circuits in electric components. One of the key goals of this paper is to identify one parameter to control the uniformity of such printed structures. Therefore, a better understanding of the influence of solvents, evaporation and drying conditions is goal of this work. The drying mechanism is observed by printing model inks of a well-known and simple composition of ethylene glycol (EG) and 1-butanol and the colorant solvent black 29. For a simplified application the layers were generated by pipetting the layers onto a glass substrate. To observe the variation of layer thickness during drying the pipetted layers are measured by utilizing a confocal microscope. Drying of droplets are measured in a period from 15 minutes up to 36 hours. The results show new aspects of profile characterization and provide insights into the major impact of solvent composition due to the final film uniformity and their formation during the drying process. On the basis of gained 3D pictures the phenomenon of non-moving, called pinned, and moving, called unpinned, of the three-phase contact line can be visualized. To quantify this pinning or unpinning a measure, so called three phase contact line movement, was introduced. The resulting drying characteristics of each solvent ratio together with the examination of thermal gradients indicate that the uniformity of the layer thickness is strongly affected by the ratio of solvents and not by Marangoni Convection. The Coffee-Stain Effect can be observed with pinned and unpinned contact line movement.

Introduction

Aside from good solubility of the colorant or a stable dispersion of particles, the most important parameters for the inkjet ink chemistry are viscosity (8-12 Pa-s) and surface tension (~28mN/m) (Magdassi, 2010). These parameters ensure that the ink can pass the nozzle, build a drop in the air and adhere on the substrate without spreading or dewetting. It is well known that the parameter window is small and the variation of solvents is limited. To guarantee an optimized fluid flow in the printing head and a good wettability on the substrate, other quantities like the uniformity of the dry layers are often insufficient and less controlled. Next to the ink formulation, the surface energy of the substrate, the temperature and the ambient atmosphere also have a strong impact on the uniformity of the layer. As a result, ink formulation often bases on an empiric time-consuming approach.

The functional printing applications demand new specifications in comparison to conventional inkjet printing. Smaller dimensions in thickness and width, uniform layers and new substrates are only a few examples. Especially the uniformity on nonporous substrates like glass or foils is becoming increasingly important. In this paper a homogenous thickness is defined as dome-profile.

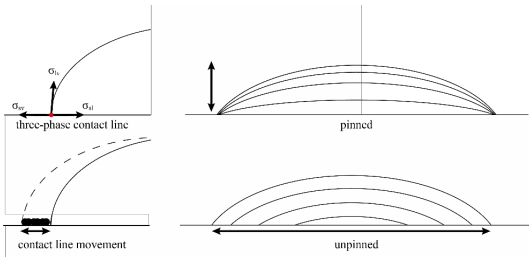


Figure 1: Overview of the different drying characteristics. The three-phase contact line is the contact line between the ink, substrate and air. The three-phase contact line can be pinned and the volume loss gets compensated by a decreasing of contact angle. The three-phase contact line can be unpinned. The volume loss gets compensated by a decreasing contact radius. If the contact line is unpinned a contact line movement can be measured. It is the distance between the origin of the contact line and the current contact line.

There are three interfacial tensions if a fluid is in contact with a solid substrate: σ_{LV} (liquid-vapor), σ_{SL} (solid-liquid) and σ_{SV} (solid-vapor). The three-phase contact line is the contact line between the liquid phase (ink), solid phase (glass substrate) and the vapor phase (air) (Brutin, 2015). At the three-phase contact line the contact angle can be measured. During drying of a fluid on a nonporous substrate the volatile portions like solvents evaporate. The loss of volume in the liquid phase leads to a decrease of the contact angle (pinned contact line) or decrease of the wetted area with constant contact angle (unpinned contact line). If the contact angle gets smaller the height of the fluid gets smaller and the radius is constant. The three-phase contact line does not move and is pinned. If the contact radius gets smaller the height of the fluid is changing slightly as well as the contact angle. The three-phase contact line moves and is unpinned. (Figure 1)

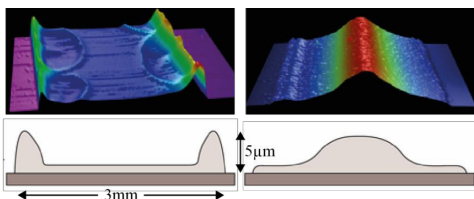


Figure 2: Two different conductive inkjet inks printed and dried on glass. The left structure shows high agglomerations at the three-phase contact line (Coffee-Stain Effect). The right structure shows high agglomerations at the center.

A specific profile of a Coffee-Stain Effect is shown in figure 2. The printed lines are 3mm in width and have a maximum height of 9μm. The cross section has a characteristic shape of a M. In this paper the Coffee-Stain will also be described as M-profile. The Coffee-Stain Effect provokes a non-uniform layer thickness. During the evaporation of solvents, the Coffee-Stain Effect causes aggregations of particles at the three-phase contact line. The dispersion evaporates faster at the three-phase contact line than in the center of the liquid. The different losses of solvent at the outer regions of the fluid cause a compensating flow of solvent towards the three-phase contact line driven by a gradient in solvent concentration. For homogeneity in the ink the remaining solution flows toward the contact line. Particles can stream outward along the solvent flow and aggregate at the contact line (Deegan et al., 1997). It is known that, among others, different shapes (Yunker et al., 2011) and sizes of particles (Weon & Jung, 2010), the drying parameters (Janßen & Jung, 2015) the solvent-mixture (Park & Moon, 2005), electrowetting (Eral et al., 2011) or changes of the atmosphere (Majumder et al., 2012) have an influence on the Coffee-Stain Effect. Those solutions do not homogenize the printed layer ideal. It is assumed that, to generate Coffee-Stain Effects, the solvent needs to evaporate very fast, the temperature gradient needs to be latent and the three-phase contact line needs to be pinned (Park & Moon, 2005).

In addition to the Coffee-Stain Effect, high agglomerations at the center of the printed ink can also occur (Fig.1). In this paper high agglomerations in the center are defined as hill-profile. In literature, these structures are often accounted as Marangoni Convections. While drying inkjet ink, the evaporation of solvent can cause concentration or temperature gradients in the ink which lead to gradients of surface tension (Hu & Larson, 2006). This effect is also known as "tears of wine" (Fournier & Cazabat, 1992). In some cases, the Marangoni Convection is also called "Reversed Coffee-Stain Effect" (Innocenzi, 2013). This leads to the impression that the shape of the profile is only driven by Coffee-Stain Effects and Marangoni Convection. A homogenous thickness is defined as dome-profile.

In this paper it is shown that

- the Coffee-Stain Effect can also be observed for unpinned contact line
- the Coffee-Stain Effect can also occur for low evaporation rates
- high agglomerations in the center can arise without gradients in solvent concentration and temperature
- both structures can occur in one solvent mixture by changing their ratio

Methods

In an extensive study by Janßen (2012) conductive inks where printed, dried and subsequently measured by utilizing a profilometer. Most inks had an M-profile caused by the Coffee-Stain Effect as evidenced by agglomerations of particles at the outer region or showed a hill-profile by agglomerations of particles in the center. In the present study, a solvent mixture of a conductive copper ink, which has higher agglomerations of particles in the center than at the three-phase-contact line (Fig.1, right), is chosen as a reference. The copper ink is solvent based on ethylene glycol, 1-butanol and 1-methoxy-2-propanol. In this paper it is assumed, that the most impact of the uniformity of the layer thickness is the evaporation rate and the surface tension of the solvent. Therefore, the complexity of the copper ink was reduced. For the examination of the drying mechanism a model ink is used, based on two solvents and one colorant.

In table 1 the surface tension and the evaporation rate of the three solvents are listed.

Solvent	Surface Tension [mN/m]	Evaporation Rate
Ethylene glycol	47,3	0,01
1-butanol	26,2	0,46
1-methoxy-2-propanol	27,7	0,71

Table 1: Surface tension and evaporation rate of the solvents

A model ink consisting of 1-butanol and ethylene glycol in the ratios 1:0, 3:1, 2:1, 1:1, 1:2, 1:3, 0:1 is mixed with 10% colorant solvent black 29 (Valifast Black 2808). To get an understanding of the solvents the model fluid is as simple as possible and a conscious decision to work without binders and additives is given.

A drop of 1µl volume gets pipetted on a glass substrate. The glass substrates are cleaned with Isopropanol and clean room grade wipers.

Next, the liquid drop is observed during drying with a 3D laser scanning microscope. A moderate magnification of 10x has been chosen. This magnification enables a maximum scanning speed and shows the largest image section. The image section has a size of 1,4x1mm². Fast laser scanning is important due the fact that the ink is measured while drying. Higher evaporation rates lead to faster drying times and a faster change in layer thickness and uniformity. The faster the fluid dries, the more likely it is that a blurring in measurements might appear. One 3D image with the 10x-objective

tive takes about 20 seconds. Depending on the drying time a 3D-image is made every 40seconds for up to 15 minutes. The resulting images are evaluated in terms of drying characteristics, drying time and profile of the dried drop. The color area of the 3D-images is leveled to the same vertical range. The color already provides an insight as to how the height of the drying fluid changes over time. The 3D images and the microscope images are transformed to video-files. Therefore, videos of the drying fluid exist.

Results and Discussion

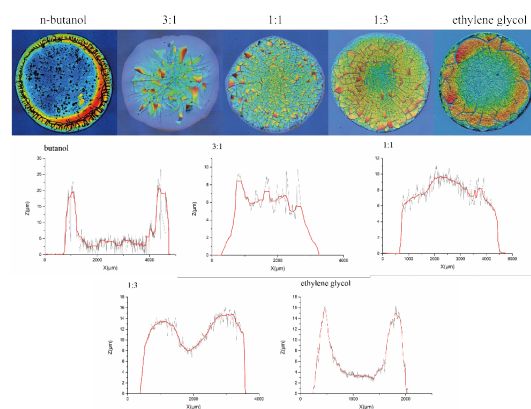


Figure 3: Overview of the variation of 1µl butanol-ethylene glycol mixtures on glass which show different profiles of height. Coffee-Stain Effect: 1-butanol, 1:3 and ethylene glycol; aggregation at the center: 3:1; uniform profile:1:1

An overview of the variation of 1-butanol with ethylene glycol is given in figure 3 and gives an insight into the sensitivity of the drying behavior of different solvent ratios. 1-butanol, 1-butanol-ethylene glycol 1:3 and ethylene glycol show different characteristics of an M-profile which is the result of the Coffee-Stain Effect. 1-butanol-ethylene glycol 3:1 shows a hill-profile due agglomerations in the center. And 1-butanol-ethylene glycol 1:1 shows a uniform profile like a dome shape. Different shapes are only achieved by different ratios of the solvent mixture. With the butanol-ethylene glycol mixture it is possible to influence the shape of the profile from non-uniform layer thickness to uniform layer thickness only by changing the ratio. This demonstrates that the solvent ratio can be used to optimize the uniformity of the layer

thickness and should not only be used to adjust the optimal surface tension. It is to expect, that the uniformity varies with different substrates and has to be tested and adapted with newsubstrates.

While the profiles of 1-butanol and ethylene glycol are quite similar, the formations developed quite differently. The drying time of 1µl 1-butanol specimen takes 15 minutes while the drying time of the 1µl ethylene glycol specimen takes 2300 minutes (Table 2).

Solvent Ratio	Drying Time [Min]
butanol	15
butanol:ethylene glycol 3:1	180
butanol:ethylene glycol 2:1	300
butanol:ethylene glycol 1:1	480
butanol:ethylene glycol 1:2	840
butanol:ethylene glycol 1:3	1080
ethylene glycol	2300

Table 2: Drying time of 1µl fluid.

In figure 4 the drying fluid of butanol and ethylene glycol in a ratio 3:1 is shown and serves a good understanding of the efficacy of the 3D measurement over the drying time and the visualization of the moving contact line. The grey area of the microscope picture represents wet areas, the lighter areas represent dry areas. The distance between the three-phase contact line at one minute and the current three-phase contact line is described as contact line movement. In this example the three-phase contact line is unpinned. While the contact line moves from the outer region to the inner region, a film of dried ink with a thickness of about 8µm is left behind. This can be seen in the images of the microscope as a brighter grey and in the 3D images in blue. The size of the dried ink is not affected. After the fluid is dry, it is not detectable if the three-phase contact line was pinned or unpinned. After $t > 180$ minutes the model ink is dry and has higher thickness in the center than in the outer region (hill-profile). The ink dries uniformly from the outer to the inner region. The higher agglomeration in the center might not be affected by gradients in concentration. While the butanol evaporates faster at the outer region than in the inner region, the fluid is unbalanced and higher surface tensions at the outer regions might occur caused by the lower surface tension of the more volatile butanol than the less volatile ethylene glycol. If the gradient of surface tension is big enough a flow

from regions of lower surface tension towards regions of higher surface tension should arise. Because the outer region might have a higher surface tension the flow should be from the inner to the outer regions and this would strengthen the M-profile instead of hill-profile. According to this reason it can be assumed that the influence of gradients of concentration are not dominating this scenario.

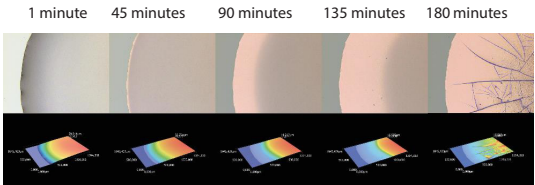


Figure 4: Moving Contact line can be seen during the drying process. (e.g. butanol: ethylene glycol 3:1) While the contact line moves a film of dried ink is left over. The moving contact line does not affect the size of the dried area. The layer thickness is higher in the center than in the outer region. (Image size: 1,4x1mm²)

In figure 5 a 1µl 1-butanol drop is presented. The time dependence measurement gives an insight into the drying behavior of the droplet. In picture 1 a typical drop shape of a dome can be seen. The center (red) of the fluid is higher than the outer region (blue). Only a few seconds later the fluid has changed to a M-profile. The layer is thicker at the three-phase contact line (light blue) than in the center (darker blue). A typical Coffee-Stain can already be predicted. After 15 minutes 1-butanol is dry. The dried profile is a Coffee-Stain. This drying behavior is consistent with the theory of Coffee-Stain Effects.

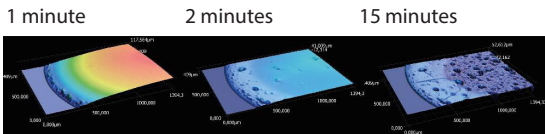


Figure 5: Time dependence images from the laser scanning microscope of a drying 1µl 1-butanol drop on glass after 1, 2 and 15 minutes. (Image size: 1,4x1mm²)

Ethylene glycol and 1-butanol have higher agglomeration of particles at the three-phase contact line then in the center (M-profile). The drying behavior from ethylene glycol has different characteristics then the drying behavior from 1-butanol. In the first minute of drying the model fluid ethylene glycol has the shape of a dome. The noticeable edge and the rough section between three-phase contact line and center are expected to be a measurement error caused by

the weak signal of the laser at steep flanks (Figure 6). This can be also seen in the microscopic image. The black area does not give any signal. The high flanks are likely caused by the high contact angle of ethylene glycol. After 12 hours the contact angle is at its lowest point. Until this point the three-phase contact line is pinned. The loss of ethylene glycol due to evaporation can only be seen in the height of the fluid and the contact angle. After 12 hours the drop starts to build dry edges and the three-phase contact line moves from the outer to the inner region. The contact line is unpinned. The distance between the first 3-phase-contact-line and the last three-phase contact line is about $150\mu\text{m}$, which is very small. With the moving of the contact line the contact angle decreases too and the combination provokes a smoother Coffee-Stain Effect than the 1-butanol.

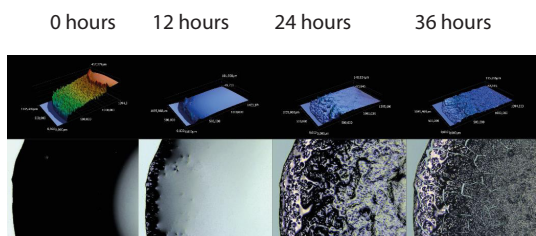


Figure 6: Time dependence images from the laser scanning microscope of a drying $1\mu\text{l}$ ethylene glycol drop on glass after (Image size: $1,4\times 1\text{mm}^2$)

The moving three-phase contact line is much stronger with the mix ratio of solvents than with 1-butanol or ethylene glycol. In figure 7 the moving contact line is presented for each mix ratio of solvent. Because 1-butanol has a pinned contact line and the unpinned contact line from ethylene glycol is very small, they are not listed in figure 7. The more 1-butanol in the mixture and the faster the evaporation time is, the faster the border of the three-phase-contact line moves. The contact line moves for all three kinds of profiles – M-profile, uniform layers, and hill-profile. Which kind of profile the dried fluid has cannot be predicted by the pinned or unpinned contact line. A Coffee-Stain Profile can exist while the three-phase contact line is unpinned. Probably the velocity of the contact line movement might give an idea of the characteristic of the profile.

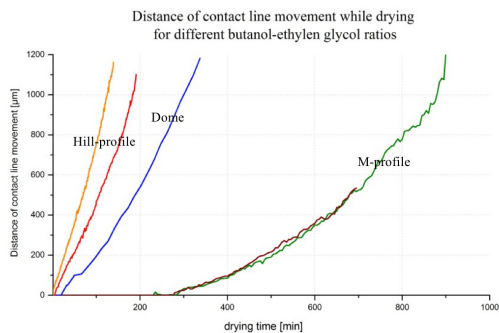


Figure 7: Distance of the moving 3-phase-contact-line from the outer region to the inner region.

Beside the contact line movement thermal gradients inside the fluid while drying might also lead to higher agglomerations at the center. To determine the influence of thermal gradients measurements of surface tension at different temperatures were performed. The surface tension of three different model fluids was measured from 15°C to 30°C (Figure 8). Two fluids show the characteristics of a Coffee-Stain and one shows agglomerations in the center (butanol: ethylene glycol 3:1). The temperature has nearly the same effect on every model fluid. All three mixtures have a decrease from $1,5\text{ mN/m}$ from 15°C to 30°C . If the model fluid has a large gradient in temperature, high gradients in surface tensions can occur and the fluid can flow from low surface tensions to high surface tensions. Because M-profiles and hill-profiles have the same small temperature gradient the temperature gradient might not affect the drying behavior of butanol: ethylene glycol-mixtures.

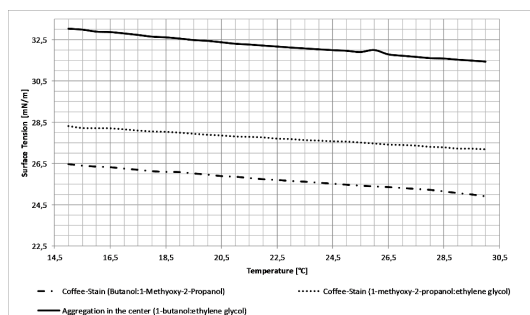


Figure 8: Influence of temperature on surface tension.

Conclusion

In this paper it is presented that one solvent mixture can result different characterizations in layer thickness just by changing the ratio of solvents. To distinguish the drying characteristics three different variations of layer thickness, called profiles, were postulated. The M-profile with high agglomeration of particles, e.g. colorant, at the outer region, the hill-profile with higher agglomeration of particles at the center and the dome-profile with a uniform layer thickness. To observe the contact line movement a 3D laserscanning microscope is used to measure the layer thickness at different drying times. This new method of measuring the layer thickness of fluids during drying period results in an extended observation of the three-phase contact line movement. This leads to differentiation between the determination of pinned and unpinned contact lines during drying time. Therefore, the 3D scanning microscope is an appropriate tool as an extended in situ method for observation of the drying behavior.

The major influence of solvent composition on the layer thickness could be demonstrated by an example of the solvent system of 1-butanol and ethylene glycol with different ratios. In one combination of solvent three different shapes can be found only by varying the ratio. The final layer thickness after drying of butanol:ethylene glycol in a ratio of 3:1 shows a hill-profile, the butanol:ethylene glycol of a ratio 1:1 shows uniform layer thickness (dome-profile) and the butanol:ethylene glycol mixture with ratio of 1:3 shows M-profile. All 3 different layer variations occur with a movement of 3 phase contact line, called unpinned contact line. This is in contradiction to other surveys where the pinned status is described as on precondition for Coffee-Stain like M-profiles.

An example of 3 model inks based on different solvents with different types of layer variation (two M profiles and one hill profile) have similar thermal gradient of surface tension below 0.1 mN/m K indicates the minor importance of Marangoni convection to the final dried layer thickness.

The results show how difficult ink formulation is relating to the uniformity of layer thickness. Beside the major parameter of viscosity and surface tension the uniformity of dried layer thickness should become more important for functional printing applications. It might be necessary for uniform layer thickness that the ink formulation need to be adapt for every substrate.

In further works extended mixtures of solvents are suggested to be observed by 3D Scanning observation. A better understanding of solvents and their impact on homogeneity of layer thickness is crucial for the application of inkjet inks in the functional printing industry.

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