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 how the profile of an inkjet printed layer can be influenced. Inkjet printed layers on glass have often non-uniform layer thicknesses. Commonly known as the Coffee-Stain Effect, the profile shows higher thickness at the edges, but agglomerations in the center of a cross section are also possible. Especially for the functional printing industry these structures might lead to issues in subsequent processes, defects in top coatings or even to short circuits in electric components. One of the key goals of this paper is to control the uniformity of the profile. Therefore, a better understanding of the influence of solvents, evaporation and drying conditions is necessary. Different ratios of ethylene glycol and butanol mixtures were pipetted onto a glass substrate and were measured with a confocal microscope during drying. With a confocal microscope drying droplets were 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.

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 Pas) 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.

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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. In figure 1 two typical structures of dried inkjet ink on glass are shown. The printed lines are 3mm in width and have a maximum height of 9µm.

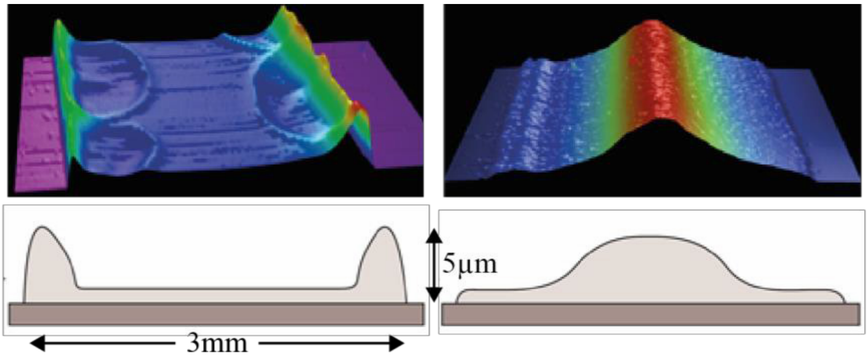

Figure 1: *Two different conductive inkjet inks printed and dried on glass. The left structure shows high agglomerations at the three-phase contact line (Coffee-Stain Effect). The right structure shows high agglomerations at the center.*

A specific profile of a Coffee-Stain Effect is shown in figure 1, left. The cross section has a characteristic shape of a M, so 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. The 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 et al., 2010), the drying parameters (Janßen et al., 2015) the solvent-mixture (Park et al., 2005), electrowetting (Eral et al, 2011) or changes of the atmosphere (Majumder et al., 2012) have an influence on the Coffee-Stain Effect. But 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, 2005).

In addition to the Coffee-Stain Effect high agglomerations at the center of the printed ink can also occur (Fig.1, right). In this paper high agglomerations in the center are defined as hill-profile. In the literature these structures are often explained by Marangoni Convections. While drying the inkjet ink, the evaporation of the solvent can cause concentration or temperature gradients in the ink which lead to gradients of surface tension (Hu et al., 2006). This effect is also known as “tears of wine” (Fournier, 1992). Higher layer thickness in the center can arise for solvent mixtures with one solvent of high boiling point and low surface tension and one solvent of lower boiling point and higher surface tension (Park, 2005) Sometimes 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 be present 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 previous studies a lot of conductive inks where printed, dried and measured with a profilometer. Most of the inks showed a Coffee-Stain Effect or agglomerations in the center (Janßen, 2012). In this study, the solvent mixture of a conductive copper ink which shows higher agglomerations in the center than at the three-phase-contact line (Fig.1, right) is chosen as a reference.

- ethylene glycol
- 1-butanol
- 1-methyoxy-2-propanol

Solvent	Surface Tension [mN/m]	Evaporation Rate
Ethylene glycol	47,3	0,01
1-butanol	26,2	0,46
1-methyoxy-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.

The liquid drop is observed during drying with a 3D laser scanning microscope. The 10x-objective is chosen because it does the fastest measurements and shows the biggest 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. So a fast measuring time is necessary and the size of the objective is limited due measuring time. One 3D image with the 10x-objective takes about 20 seconds. But the 10x-objective has a higher distance to the substrate as the other objectives. A high distance between objective and object can lead to artifacts induced by weak signals to the receiving element of the laser at steep flanks. Depending on the drying time a 3D-image is made every 40 seconds for up to 15 minutes. The resulting images could be evaluated in terms of the drying characteristics, drying time and profile of the dried drop. The color area of the 3D-images is leveled to the same vertical range. So 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 could be transformed into an .avi-file, so there are videos of the drying fluid.

Results and Discussion

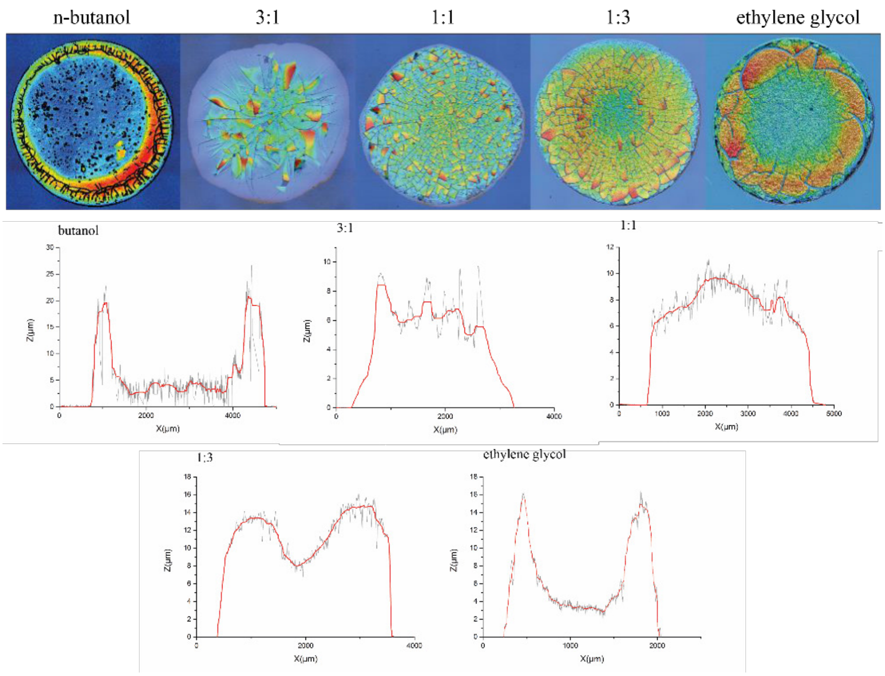

Figure 2: *Overview of the variation of 1µl butanol- ethylene glycol mixtures on glass which show different profiles of height. Coffee-Stain Effect: 1-butanol, 1:3 and ethylene glycol; aggregation at the center: 3:1; uniform profile:1:1*

In figure 2 an overview of the variation of 1-butanol with ethylene glycol is given. 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. The different shapes are only varied by different ratios of the solvent mixture. So 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 leads to the question of whether it is possible to create a forecast of the shape. The cracks of the dried ink are caused by the simple ink formulation.

While the profiles of 1-butanol and ethylene glycol look quite similar, the formations developed quite differently. The drying time of 1µl 1-butanol specimen takes 15 minutes and the drying time from 1µl ethylene glycol specimen 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 3 a 1µl 1-butanol drop is shown. 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 of the fluid is higher than the outer region. The gradient is uniform. Only a few seconds later the fluid shows an M-profile. The layer is thicker at the three-phase contact line than in the center. 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.

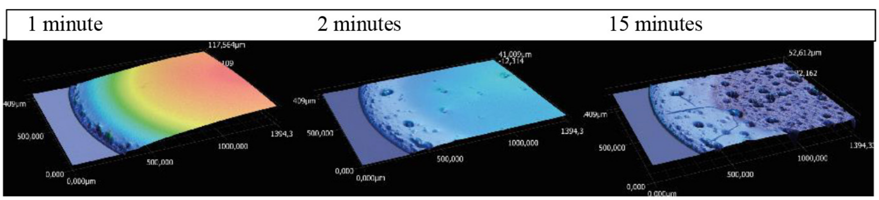

Figure 3: *Time dependence images from the laser scanning microscope of a drying 1µl 1-butanol drop on glass after 1, 2 and 15 minutes. (Image size: 1,4x1mm²)*

Ethylene glycol and 1-butanol show higher agglomeration at the three-phase contact line then in the center (M-profile). But the drying behavior from ethylene glycol shows 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 due to an error of measurement caused by the weak signal of the laser at steep flanks (Fig. 4, left). This can be also seen at the image from the microscope. The black area does not give any signal. The high flanks are 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 150µm, 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.

0 hours	12 hours	24 hours	36 hours

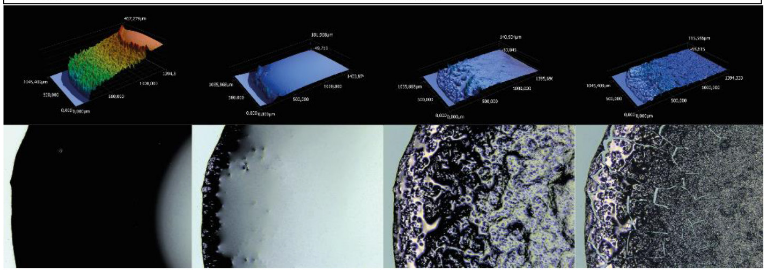

Figure 4: Time dependence images from the laser scanning microscope of a drying 1µl ethylene glycol drop on glass after (Image size: 1,4x1mm²)

The moving three-phase contact line is stronger with the mix ratio of solvents than with 1-butanol or ethylene glycol. In figure 5 the moving contact line is shown 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 5. 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. But a Coffee-Stain Profile can exist while the three-phase contact line is unpinned.

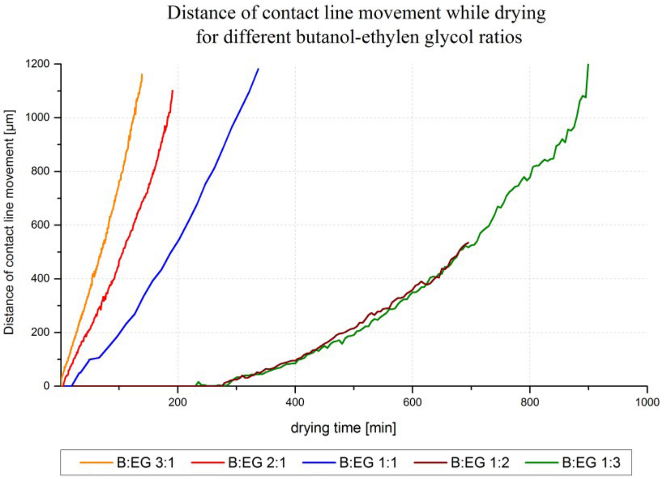

Figure 5: Distance of the moving 3-phase-contact-line from the outer region to the inner region.

In figure 6 the drying fluid of butanol and ethylene glycol in a ratio 3:1 is shown. 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. So after the fluid is dry it is not detectable if the three-phase contact line was pinned or unpinned. After t > 1000 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 butanol than ethylene glycol. If the gradient of tension were great enough then a flow from lower surface tension to higher surface tension would 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 a Coffee-Stain Effect, which would lead to an M-profile and not to a hill-profile. To realize a flow from the outer region into the inner region one solvent should have a lower boiling point and higher surface tension and one solvent should have a higher boiling point and a lower surface tension (Park, 2005). This combination is not given in the 1-butanol:ethylene mixture. So the influence of gradients of concentration are not dominating this scenario.

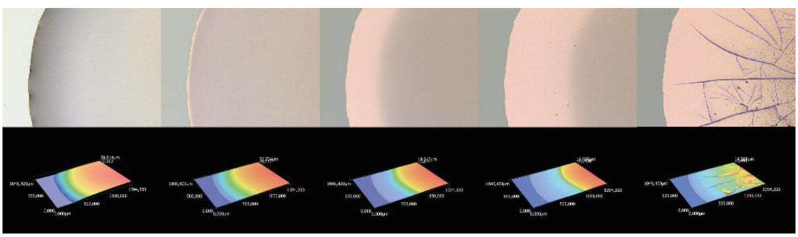

Figure 6: *Moving Contact line can be seen during the drying process. (e.g. butanol: ethylene glycol 3:1) While the contact line moves a film of dried ink is left over. The moving contact line does not affect the size of the dried area. The layer thickness is higher in the center than in the outer region. (Image size: 1,4x1mm²)*

To determine the influence of thermal gradients measurements of surface tension at different temperatures were done. The surface tension of three different model fluids where measured from 15°C to 30°C (Figure 7). 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 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.

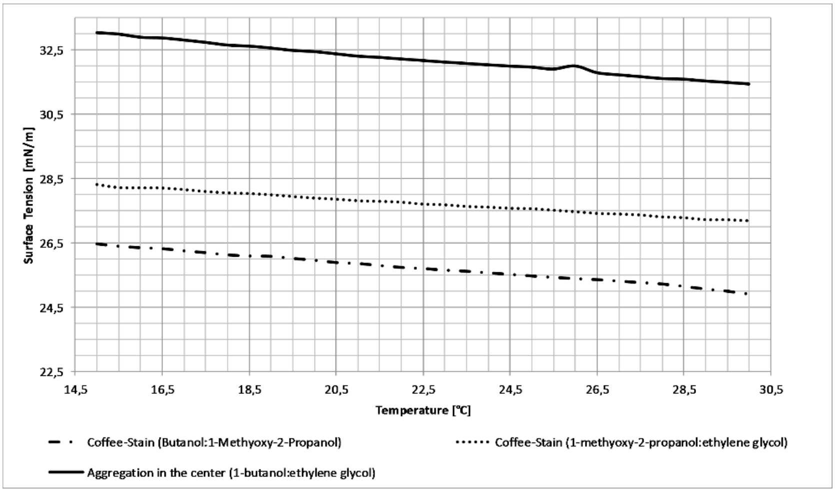

***Figure** 7: Influence of temperature on surface tension.*

Conclusion

It is shown on the basis of one example which kind of barrier has to be taken to formulate an ink with a homogenous layer thickness. Even in one combination of solvent three different shapes can be found – M-profile induced by the Coffee- Stain Effect, homogenous layer thickness, or agglomeration in the center (hill- profile), just by changing the mix ratio of solvent. All mixed ratios have in common that the three-phase contact line is unpinned. The moving contact line could be evaluated by using a 3D laser scanning microscope. Because a dried layer of ink deposits on the glass while drying, the size of the drying droplet is affected by the moving contact line. The drying behavior of the droplet cannot be explained by the dried model ink alone. To generate a Coffee-Stain the three-phase contact line does not to be pinned and low evaporation rates are possible. Aside from the known influence of Marangoni Convections, high agglomerations in the center can occur without gradients in concentration or temperature. The 3D laser scanning microscope is a useful tool to gain new insights into the drying behavior of fluids in particular to observe the behavior of three-phase contact line. In further evaluations new mixtures of solvents need to be tested. To create an overview of solvents and their influence into the homogeneity of layer thickness might be quite ambitious and not achievable. Still, a better understanding of solvents and their impact on homogeneity is important for the status of the inkjet in the functional printing industry.

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