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Free dispersing agent impact on latency issue for water-based inkjet inks

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Short abstract

The formulation of water-based pigment inkjet inks constitutes a major challenge: in addition to be perfectly stable colloidal suspensions, water-based pigment inks should strictly meet all the requirements imposed by the printhead specifications regarding flow properties, surface tension and density. The nature and the quantity of dispersing agent used to stabilize the pigment particles in suspension are crucial issues that can significantly impact the ejection phase. Inkjet inks must be stable over time and during jetting whatever the ejection duration and cycle imposed by the digital printing flow. Each nozzle can be activated according to different ejection cycles. All the nozzles are not jetting at the same time. Some idle nozzles do not jet for a certain duration which can lead to ejection disturbances when they are restarted after this period. The latency refers to this negative behaviour after periods of sitting idle in the printhead. So far, solutions for minimizing the impact of latency have been proposed by adjusting the formulation but no scientific research tried to understand precisely the causes behind this phenomenon. This paper tries to show the significant influence of the dispersing agent on the latency issue for the jetting of water-based and pigmented inks.

Keywords: water-based pigment inkjet inks, latency, dispersing agent, drop formation

1. Introduction and background

Inkjet printing is a non-impact printing method in which picoliter droplets of ink are jetted onto different substrates such as paper, textile or non-porous substrates. This method of printing allows an infinite choice of printed images. Drop on Demand (DoD) systems including a piezoelectric element are the most common in the industry for the moment. This jetting process saves ink, cleaning time and offers an excellent printing quality at high speeds. Typically, DoD systems with a piezoelectric element can jet at high frequencies (above 10kHz). The inks should meet strict requirements imposed by the printhead manufacturer in terms of physico-chemical and rheological properties such as viscosity, density and surface tension as explained by Hoath (2016).

The use of water-based and pigmented inks can induce different defect while printing such as latency of the nozzles. Latency appears when a nozzle cannot jet correctly after a certain time without jetting. This can be critical for graphical applications: unprinted zones may appear in the printed image. This phenomenon is often explained by the drying of components at the meniscus at rest, as described by Magdassi (2010). In fact, the use of water as the main solvent induces water evaporation at the meniscus and implies the rise of concentration of other components such as pigments as suggested by Thakkar and Sun (2003). This leads to an increase in viscosity and elasticity. However, this hypothesis has never been demonstrated. Another explanation is made by Jackson (2016) with the use of different counter-ions to neutralize the dispersing agent. The larger the hydration radius (or Stern layer) of those counter-ions is, the lower is the possibility of pigment particles to retract from the ink vehicle (Kabalnov and Wennerstrom, 2006) and would imply latency. Jackson (2016) provided a solution to slow this possible drying by the addition of humectants such as glycerol or mixes of counter-ions including lithium. A higher number of patents exists on this subject as for example the work of Brust, et al. (2009).

Only the hypothesis of drying of the meniscus is raised. However, if only this drying is the reason of latency, why different inks with approximatively the same water content can show latency or not?

It is a big challenge to explain what really happens at the nozzle meniscus. In this paper, latency phenomenon for water-based and pigmented inkjet inks is highlighted through different ink formulations and printing tests. A focus is made on the role of the dispersing agent. Jackson (2016) made the hypothesis that the extra free dispersing agent contained in the initial pigment dispersion may be the cause of latency issues. Different formulations will be prepared with or without pigment and with or without dispersing agent in order to show its impact on jetting.

2. Materials and methods

2.1 Materials

Four cyan dispersions were used in the ink formulations. Those dispersions were prepared with polystyrene-acrylic dispersing agents with different molecular weights: 8 500 $g.mol^{-1}$; 11 500 $g.mol^{-1}$ and 16 500 $g.mol^{-1}$ and PB15:3 phtalocyanine blue pigment from an external supplier (dispersions respectively called D1, D2 and D3). The fourth one, Projet ADP 1000 Cyan, was provided by Fujifilm. A dye supplied by Clariant (Direct Blue 199, Duasyn Cyan FRL-SL liquid) was also used. Three different humectants including glycol(s) and diol(s) were bought from Sigma-Aldrich. A silicon surfactant was also added into the ink formulations. Deionized water was prepared in laboratories. The type of printhead used to perform the drop observations and printing tests is a non-recirculating piezoelectric printhead including more than 2 000 nozzles with a 10 µm orifice diameter and a temperature of use between 30 °C and 32 °C. In total, seven inks were implemented, and the details of their composition are presented in Table 1. No binder was added into those inks' formulations. The addition of a binder may hide the impact of the dispersing agent.

Table 1: Formulations of the pigment-based inkjet inks

Component (wt %)	Ink 1	Ink 2	Ink 3	Ink 4	Ink 5	Ink 6	Ink 7
Colourant type	D1	D2	D3	Projet ADP 1000	Projet ADP 1000	DB 199	DB 199
Colourant	3	3	3	3	3	1	1
Dispersing agent contained in the dispersion	3	3	3	?	0	0	0
Free dispersing agent at 16 500 $g·mol^{-1}$	0	0	0	0	1	0	3
Humectant 1	24	24	24	24	24	24	24
Humectant 2	2	2	2	2	2	2	2
Humectant 3	3	3	3	3	3	3	3
Silicone surfactant	1	1	1	1	1	1	1
Deionized water	64	64	64	?	66	69	67

2.2 Methods

2.2.1 Preparation of the pigment dispersion

PB15:3 pigment (15 wt %) and a dispersing agent (15 wt %) are mixed with water (60 wt %) for one night. Then the mixture is poured into a grinder at 4 000 rpm for approximatively 6 hours. The desired mean particle size is less than 150 nm.

2.2.2 Preparation of the inkjet inks

Pigment and dye-based inks are prepared according the same procedure. Their formulations are listed in Table 1. Deionized water, humectants, silicone surfactant and free dispersing agent (if one is added) are mixed under stirring until homogenization. Then, the pigment dispersion or the dye is added. The mixture is stirred until homogenization. Finally, the ink is filtered through a WHATMAN 1 µm GF/B w/GMF filter thanks to a peristaltic pump. This step permits to avoid the presence of large particle aggregates, if necessary. The inks are directly used to do drop ejection observations and printing tests.

2.2.3 Measurement of physico-chemical properties of the inkjet inks

The particle size of the inks was measured by Dynamic Light Scattering at ambient temperature. pH measurement was made thanks to a pH-meter (Checker Portable pH Meter, Hanna Instrument) at ambient temperature. The rheological analysis was performed thanks to a TriPAV (Piezo Axial Vibrator) rheometer, provided by TriJet Limited. The measurements were made at 32 °C from 1 Hz to 10 000 Hz. In this case, measured values are valuable up to 5 000 Hz. The dynamic surface tension of the inks was measured with a bubble pressure tensiometer (BP100 from Krüss) between 10 ms and 10 000 ms at 32 °C. Static surface tension was then read at the equilibrium.

2.2.4 Drop formation observation

The observation of the drop formation is possible thanks to a JetXpert set up. The drop watcher is placed in a controlled atmosphere at 23 °C and a humidity rate between 40 % and 50 %. Drops of 4 pL targeted volume are jetted and their volume, speed and trajectory can be measured. A printing station includes a conveyor belt to allow to print on different substrates.

2.2.5 Printing test: evaluation of the latency

In order to evaluate the latency of the different inkjet inks, a printing test including a specific test form is performed on non-coated white paper with 80 gm^{-2}. The printhead is cleaned and a specific pattern (Figure 1) is printed one time at time 0. The printhead is then stopped and started again to print the same pattern 1 min after. The same process is repeated at several times: 3, 5, 10 and 30 min. The idea is to know if the ink can be printed without latency after a certain idle duration. To evaluate the latency, the index I_{latency} was defined (Equation [1]). In Figure 1, 16 lines are printed at first. The number of missing lines indicates the level of latency. If $I_{\text{latency}} = 0$, the ink can be jetted perfectly without delay, if $I_{\text{latency}} = 1$ none of the 16 lines is printed, the ink shows a latency issue.

$$I_{\text{latency}} = \frac{\text{number of missing lines}}{16} \quad [1]$$

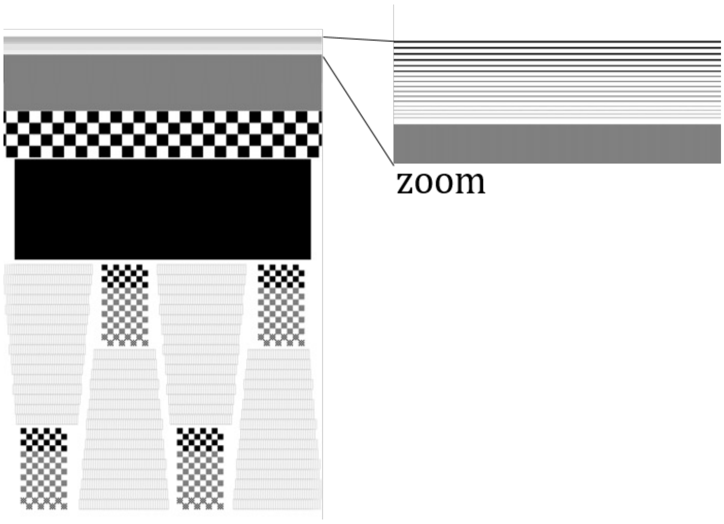

Figure 1: Printed pattern to evaluate the latency of an inkjet ink

The observations of the different printed patterns are made with the help of a Keyence numerical microscope using the objective ZS20.

3. Results and discussion

3.1 Physico-chemical properties of the inkjet inks

Different properties of the inks such as pH, viscosity, mean particle size (D_{50}), the static and dynamic surface tensions and density were characterized. Data are shown in Table 2. The dynamic surface tension was determined at 1 ms thanks to the model established by Hua and Rosen (1991). The Z number is also calculated in Table 2 with a nozzle diameter set at 10 µm. Z (Equation [2]) is used as ejectability criterion for inkjet.

$$Z = \frac{1}{Oh} = \frac{\sqrt{\rho \sigma L}}{\mu} \quad [2]$$

With:

- ρ the density of the ink in kg·m^{-3};
- σ the static surface tension of the ink in N·m^{-1};
- μ the complex viscosity of the ink in Pa·s, at 100 Hz;
- L the diameter of the nozzle in µm.

Table 2: Physico-chemical properties of the water-based inkjet inks

Sample	Colourant type	pH	Viscosity (Pa·s)	D_{50} (nm)	Static surface tension (N·m^{-1})	Dynamic surface tension (N·m^{-1})	Density (kg·m^{-3})	Z
1	Home-made	7.76	$9.68 \cdot 10^{-3}$	110	$27.07 \cdot 10^{-3}$	$48 \cdot 10^{-3}$	1 031	1.70
2	Home-made	8.30	$5.40 \cdot 10^{-3}$	119	$21.01 \cdot 10^{-3}$	-	1 060	2.76
3	Home-made	8.21	$8.66 \cdot 10^{-3}$	134	$25.61.10^{-3}$	$59 \cdot 10^{-3}$	1 025	1.87
4	Commercial	-	$3.22 \cdot 10^{-3}$	118	$26.35 \cdot 10^{-3}$	$47 \cdot 10^{-3}$	1 013	-
5	Commercial	-	$3.98 \cdot 10^{-3}$	-	$23.63 \cdot 10^{-3}$	-	1 041	-
6	Dye	8.05	$2.46 \cdot 10^{-3}$	-	$23.19 \cdot 10^{-3}$	-	1 019	6.25
7	Dye	7.91	$4.15 \cdot 10^{-3}$	-	$24.02 \cdot 10^{-3}$	-	1 028	3.77

All the inks Z numbers seen in Table 2 are in the range establish by Reis and Derby (2000): $1 < Z < 10$. Which means that, according to them, all the listed inks are printable. Viscosities were measured at 100 Hz at 32 °C. The viscosity of samples 1 and 3 are above 6 mPa·s. This is certainly due to instabilities between components of the ink. In fact, the targeted viscosity is around 5 mPa·s at 32 °C. Some dynamic surface tension curves were not “S-shaped”, this is why the Hua and Rosen model did not fit those measurements. In fact, S-shaped dynamic surface tension curve is needed to apply this model.

3.2 Drop watching results

Drop watching is performed for 5 out the 7 inks formulated. There are two main differences between pigment-based inks (1, 2 and 3) and dye-based inks (6 and 7). Firstly, the length of the tail when the drop comes out the nozzle seems longer for dye-based inks. Secondly, only ink 7 presents satellite drops (Figure 2). This ink is made with the addition of extra free dispersing agent. This component may disturb the jetting of the ink.

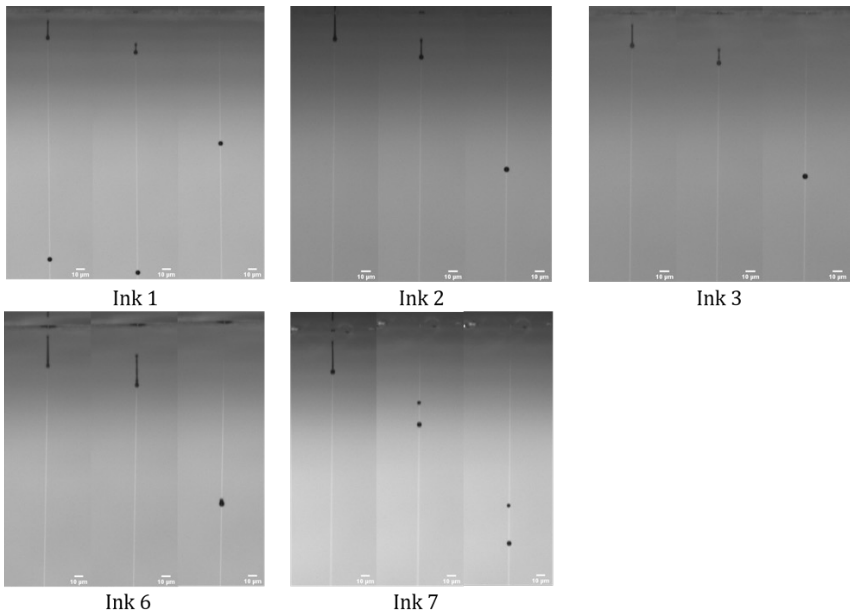

Figure 2: Images of drop watching for water-based inkjet inks

In Table 3 the different characteristics of the drops are listed. For the greyscale selected, a speed of 6 m·s^{-1} and a volume of 4 pL is expected. The trajectory from the nozzle plate is also measured in order to evaluate the position of the ink on the substrate. The drops for inks 1 to 3, made with dispersions, have characteristics close to the expected ones. Regarding the dye-based ink 6, volume and speed are higher than expected but there was no satellite during jetting. This is not the case for ink 7 which was impossible to analyse.

Table 3: Characteristics of drops ejected

Sample	Colourant type	Drop volume (pL)	Drop speed (m·s^{-1})	Drop trajectory (°)
1	Home-made	3.118	5.047	90.395
2	Home-made	4.534	5.956	90.723
3	Home-made	4.744	6.187	90.608
6	Dye	6.837	7.458	90.912
7	Dye	*unstable jetting*		

3.3 Latency test

The latency of the different inks is represented in Figure 3 thanks to the latency index described in 2.2.5.

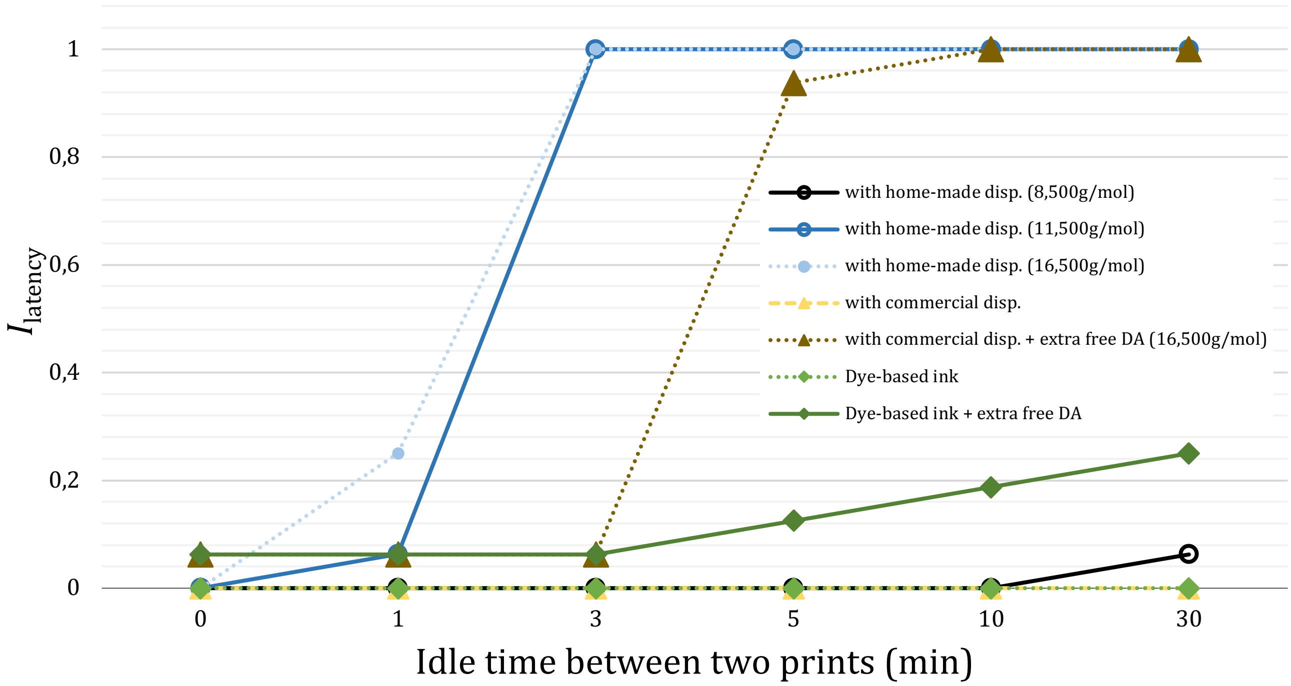

Figure 3: Latency for water-based inkjet inks for different times without printing, inks 1,2 and 3 are made with own made dispersions; inks 4 and 5 are made with a commercial dispersion and a free dispersing agent is added to ink 5; inks 6 and 7 are dye-based inks and a dispersing agent is added to ink 7

Inks 1, 2 and 3, respectively made with the dispersions D1, D2 and D3 show latency phenomenon. Latency issue increases faster with higher molecular weight of the dispersing agent. The Figure 4 shows that the first lines are not printed correctly for ink 3 after 1 min without printing. Ink 5 is the ink made with the Fujifilm dispersion. This dispersion has no excess of dispersing agent. By adding extra free dispersing agent, latency issue begins to appear distinctly after 5 min without printing. For the dye-based inks, the same observation can be made. Without free dispersing agent, the ink 6 does not show any latency. However, when a certain amount of free dispersing agent is added into the formulation, the pattern cannot be entirely printed since the time zero.

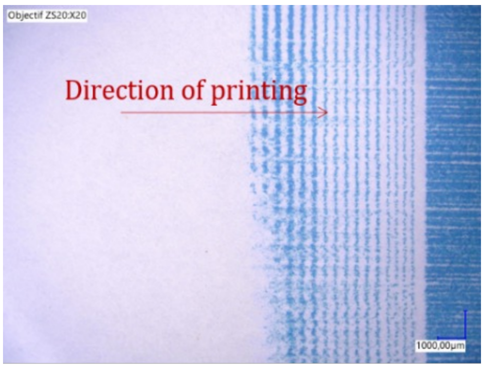

Figure 4: Photo of latency apparition for the ink made with the dispersion with molecular weight of 16 500 g·mol^{-1}, after 1 min without printing

4. Conclusions

This paper aimed to demonstrate how the extra free-dispersing agent may be involved in the latency phenomenon. All the inks prepared with home-made dispersion have this latency issue. It is assumed that all those dispersions include extra free-dispersing agent. Moreover, the latency index increases faster when the molecular weight of the dispersing agent is higher. The ink prepared with the commercial dispersion from Fujifilm does not have latency. This dispersion is prepared with the aim of removing the extra dispersing agent not anchored to the pigment particles after the grinding process. Dispersing agent with the highest molecular weight used in this study (16 500 $g \cdot mol^{-1}$) is added directly to this last ink. Surprisingly, latency appeared quite fast. To avoid any interactions between dispersing agent and pigments, dye-based inks were also tested: one without dispersing agent and another one with the addition of 3 wt% of dispersing agent with a molecular weight of 16 500 $g \cdot mol^{-1}$. The dye-based ink with no dispersing agent jetted perfectly even after 30min without printing. This was not the case of the one containing dispersing agent because the ink presented latency after few seconds without printing.

The conclusion of this study is that extra free-dispersing agent may have a strong impact on jetting and induce latency issue. Nevertheless, the hypothesis needs to be confirmed by the measurement of concentration changes at the meniscus.

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