Ink Jet: Ink Properties and Ink Drop Spreading at Paper Surface

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Abstract: Since the beginning of the use of SOHO (small office, home office) ink jet processes, the aim of any development is to improve print quality on plain paper. Indeed, the use of water-based inks generates problems of ink spreading, which deteriorate the visual quality of prints.

To better understand these phenomena, we focused on the physicochemical properties of commercial inks. 23 inks were selected among the commercial suppliers. The following properties were analysed:

- pH,
- Conductivity,
- Charge density,
- Viscosity,
- Surface tension,
- Contact angle.

Finally, the behaviour of the 23 inks on four different kinds of paper was observed to connect ink properties to ink spreading.

The results presented in this paper constitute the first step of a wider study on ink / paper interactions in ink jet printing.

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Introduction

Although scientists investigated the physics underlying inkjet technology during the nineteenth century, inkjet printers are widely used only since the last decade. This new non impact process allows to print in colour on many kinds of substrates with a low cost. Inkjet printing is therefore very indicated to meet the new needs of graphic industries which are short length run and personalization.

In our study, we focused on the drop-on-demand inkjet technology used in office printers. Since the beginning of the use of SOHO (small office, home office) ink jet processes, the aim of any development is to improve print quality on plain paper. Indeed, the use of water-based inks generates problems of ink spreading, which deteriorate the visual quality of prints.

Many studies have been conducted on ink spreading with dye-based or pigmented solutions and seldom with real commercialised inks. But, at the present time, inkjet inks are very complex mixtures of several components which all play a crucial role in establishing the overall ink properties. Therefore, we focused on the physicochemical properties and the spreading of 23 commercial inks

Experimental - Materials

• Inks

In this paper, the commercial names were replaced by anonymous references.
For colours, we selected:
- 6 cyan inks (codified from C1 to C6),
- 6 magenta inks (codified from M1 to M6),
- 5 yellow inks (codified from Y1 to Y5).

For black inks, we selected:
- 3 dye-based inks (codified NB1, NB4 and NB5),
- 3 pigmented inks (codified PB1, PB2 and PB3).

• Papers

Four different papers were used:
- a plain paper,
- a common offset coated paper,
- a special inkjet coated paper,
- a high grade photo paper.

• pH
pH was measured with a Bioblock pHmeter.

• Conductivity
Measurements were performed with a WTW ProfiLine LF197 Conductimeter on diluted inks (dilution by 100) because of the available amount.

• Charge Density
Inkjet inks are all anionic. To compare their charge density, a polyelectrolite titration was done with polyethylene Imine (PEI). Titrations were performed with a MÜTEK PCD 02 Particule Charge Detector.

• Viscosity
The rheological behaviour of inks is evaluated through shear flow analyses of inks conducted on a rotating rheometer (Texas Instrument Carri-med CSL^2 500) with the cone-plate geometry (diameter = 6 cm, top angle = 1°). The measurements of viscosity were made at a shear rate of 2500 s^{-1} and a temperature of 20°C. Values of viscosities, given in mPa.s, are means of 3 measurements.

• Surface Tension
Measurements were carried out with the ring method on a Krüss K10ST digital tensiometer. Values, given in mN/m, are means of 5 measurements.

• Contact angle
Contact angles were measured with a GBX Digidrop Device. Values are means of 10 measurements.

• Ink Spreading
To study ink spreading, we have deposited with a syringe ink drops of 0.7 µl, 10 drops per ink, on the 4 kinds of papers mentioned above. An image analysis enables us to get area, perimeter, equivalent diameter and circularity of the dots. Results, means of the measurements of the 10 drops, are given either in area values (mm^2) or in spread factor value. The spread factor is the ratio between the equivalent diameter of the dot on the substrate over the diameter of the drop, which is supposed to be spherical, before impact.

• pH

	Black NB	Black PB	Cyan C	Magenta M	Yellow Y
1	8.6	9.5	7.5	6.5	6.4
2		8.6	7.6	6.7	6.3
3		7.5	10.0	10.5	10.4
4	9.5		9.2	9.4	9.1
5	9.5		9.4	9.3	9.5
6			9.2	9.3	

Table 1: pH measurements

When looking at pH measurements obtained on coloured inks, it is possible to make a classification in 3 groups:
- A group: inks have an index of 1 or 2; pH is neutral or slightly acid.
- B group: all inks have index 3; pH is basic, slightly higher than 10.
- C group: inks have an index of 4, 5 or 6; pH is ranging between 9.1 and 9.5.

All coloured inks of the same group have similar pH.
Concerning black inks, these groups are more difficult to distinguish. Only dye-based black inks of the C group have pH similar to coloured inks.

• Conductivity

	Black NB	Black PB	Cyan C	Magenta M	Yellow Y
1	144	27	597	556	757
2		30	570	599	802
3		77	126	199	158
4	301		84	136	64
5	287		104	135	171
6			37	78	

Table 2: conductivity measurements (µS/cm)

Concerning coloured inks, the A group is clearly distinguished: the values of conductivity oscillate between 550 and 800 µS/cm whereas values do not exceed 200 µS/cm for the two other groups.
With regard to black inks, pigmented inks have an extremely low conductivity compared to dye-based inks.
For A and B groups, coloured inks have a higher conductivity than black inks. It's the opposite for the C group: dye-based black inks have a higher conductivity compared to coloured inks.

• Charge Density

	Black NB	Black PB	Cyan C	Magenta M	Yellow Y
1	93	31	75	141	196
2		41	64	115	99
3		23	107	238	180
4	392		97	159	86
5	407		132	157	226
6			33	80	

Table 3: charge density measurements (µeq/ml)

With regard to coloured inks, no tendency can be released: the very dispersed values lie between 30 and 240 µeq/ml.
Concerning black inks, dye-based inks have a very higher charge density than pigmented inks.
Finally, for the C group, black inks are more than two times more anionic than coloured inks.

• Viscosity

The 23 inks present a similar Bingham behaviour. We can even say that 21 of the 23 present a Newtonian behaviour (*Figure 1*) because of the very low yield stress. Only the M5 and J3 inks have a yield stress of about 2 Pa.

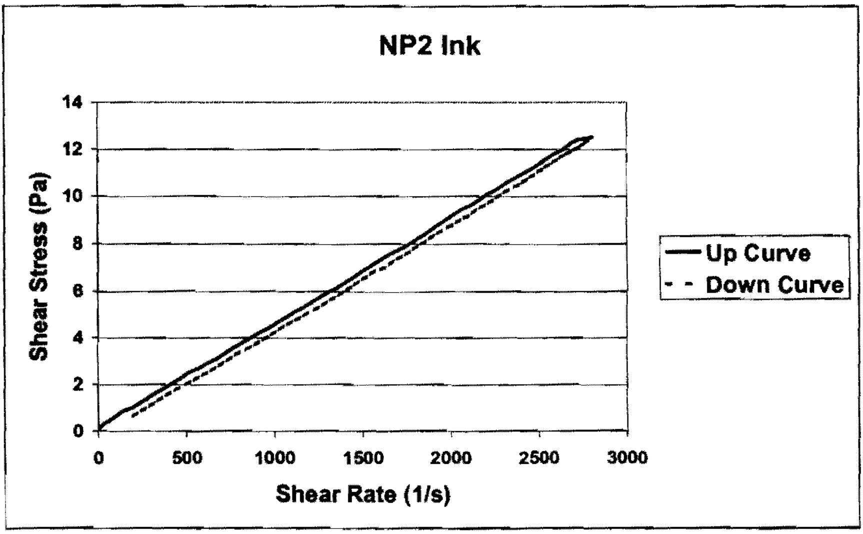


Figure 1: flow curve of NP2 ink

However, the slope of the curve is constant for shear rates higher than 2000 s^{-1}. So we did the calculations of viscosities for a shear rate of 2500 s^{-1}.

	Black NB	Black PB	Cyan C	Magenta M	Yellow Y
1	2.4	3.5	14.1	4.2	3.8
2		4.5	3.9	3.5	4.4
3		2.7	2.3	3.3	4.4
4	4.6		4.8	4.2	4.1
5	4.6		4.1	6.4	5.7
6			2.1	4.4	

Table 4: viscosity measurements (mPa.s)

With regard to *Table 4*, it is impossible to distinguish the inks according to viscosity. Except for the C1 ink, all inks have a viscosity ranging between 2 and 5 mPa.s.

• Surface Tension

	Black NB	Black PB	Cyan C	Magenta M	Yellow Y
1	44,6	55,8	25,2	31,0	26,6
2		49,0	25,5	31,8	25,8
3		38,3	32,6	35,2	34,3
4	30,6		26,8	27,3	28,6
5	31,0		29,6	30,1	33,3
6			29,8	34,0	

Table 5: surface tension measurements (mN/m)

With regard to coloured inks, surface tension values are in the same range, between 25 and 35 mN/m.
For the C group, all inks, black and coloured, have quite the same surface tension. But for the A group, black inks have higher surface tension for both dye-based and pigmented inks but the highest values are reached for pigmented inks with 49 or even 56 mN/m.

• Drop Impact on Porous Surface

The impact of an ink drop on paper is a complex process involving three phenomena: penetration, spreading and evaporation. These three phenomena depend on many parameters concerning both ink and paper (Juntunen and Virtanen, 1991):
- ink drop characteristics (size, impact velocity),
- ink properties (surface tension, viscosity),
- paper properties (roughness, porosity, surface energy).

Many studies have been conducted on drop impacting on non porous substrates. In this case, we can find different models in the literature.
In the case of spontaneous spreading, Gu and Li developed a model to predict drop radius (Gu and Li, 1998):

$$R(t) \approx 1.86\left(\frac{5\sigma V^3}{12\pi^3\eta}\right)^{0.1} t^{0.1}$$

with η: ink viscosity
σ: ink surface tension
V: volume of the drop before impact
R(t): radius of the ink/substrate contact zone according to time

In the case of spreading with impact velocity, models (Chandra and Avedesian, 1991) (Pasandideh-Fard *et al.*, 1996) (Mao *et al.*, 1997) give a predicted spread factor (ratio between the diameter of the dot on the substrate over the diameter of the drop before impact) according to two dimensionless numbers:

- Reynolds number $\mathrm{Re} = \frac{\rho u_i D}{\eta}$

- Weber number $We = \frac{\rho u_i^2 D}{\sigma}$

with ρ: ink density
u_i: impact velocity
D=2R: diameter of the drop
η: ink viscosity
σ: ink surface tension

But, in the case of porous substrate, there is an additional parameter that plays a crucial role: the porosity of the substrate, in our case paper. The mechanism can then be divided into two steps: first, ink is forced to spread and penetrate into the paper because of impact velocity (Chandra and Avedesian, 1992), and then there is spontaneous spreading of ink.
Therefore, theories developed for non porous substrates have to be modified. The penetration of ink into paper capillaries can be modelled by the Lucas-Washburn theory (Oliver *et al.*, 1991):

$$h = \sqrt{\frac{r\sigma \cos\theta}{2\eta}} \cdot \sqrt{t}$$

with h: distance covered by the ink front in a capillary
r: capillary radius
σ: ink surface tension
θ: ink contact angle on the capillary surface
η: ink viscosity

However, no model considering both impact and penetration could be found in the literature.

• Comparison Between Syringe and Printer Dot Areas

In order to make a comparison between spread factors of the different inks, we must be sure to have the same initial conditions, mainly the same technology (thermal or mechanical), the same impact velocity and the same drop size, which is not the case with the different printers. The best way of controlling the initial conditions is to use a syringe, even if the drop sizes are not the same between syringe and printer. So, we first look at the correlation between syringe and printer dot area for 6 inks on the 4 papers.
Figure 2 shows a difference between the behaviours of pigmented and dye-based inks. We saw that printer spreading occurs in two steps: forced penetration and spreading due to impact velocity and spontaneous spreading. For dye-based ink, spontaneous spreading is preponderant (Bouchon, 2000). We can observe large differences in the ink spreading according to the papers. And a correlation does exist between syringe and printer dot area for the five dye-based inks. It's going clearly in the same way: when syringe dot areas are growing, printer dot areas are doing the same. Ink spreading occurring during printing can then be studied through the use of drops emitted by a syringe. For pigmented inks, the variations in the surface of the dot areas obtained either through the syringe or the printer are not so wide, according to the papers. The correlation between syringe and printer dot areas is not so obvious. The impact velocity is more important than spontaneous spreading. The laboratory equipment to use for

studying pigmented ink behaviour has to take into account the influence of the impact velocity.

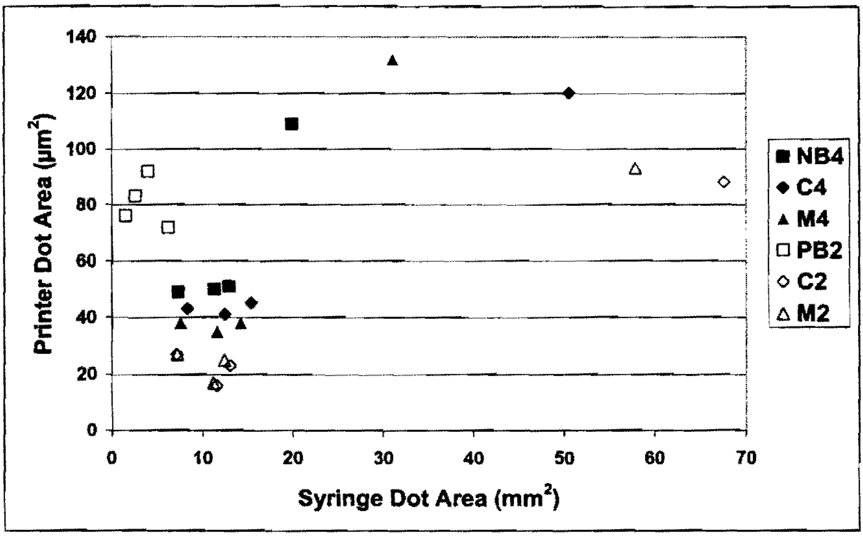


Figure 2: comparison between syringe and printer dot area

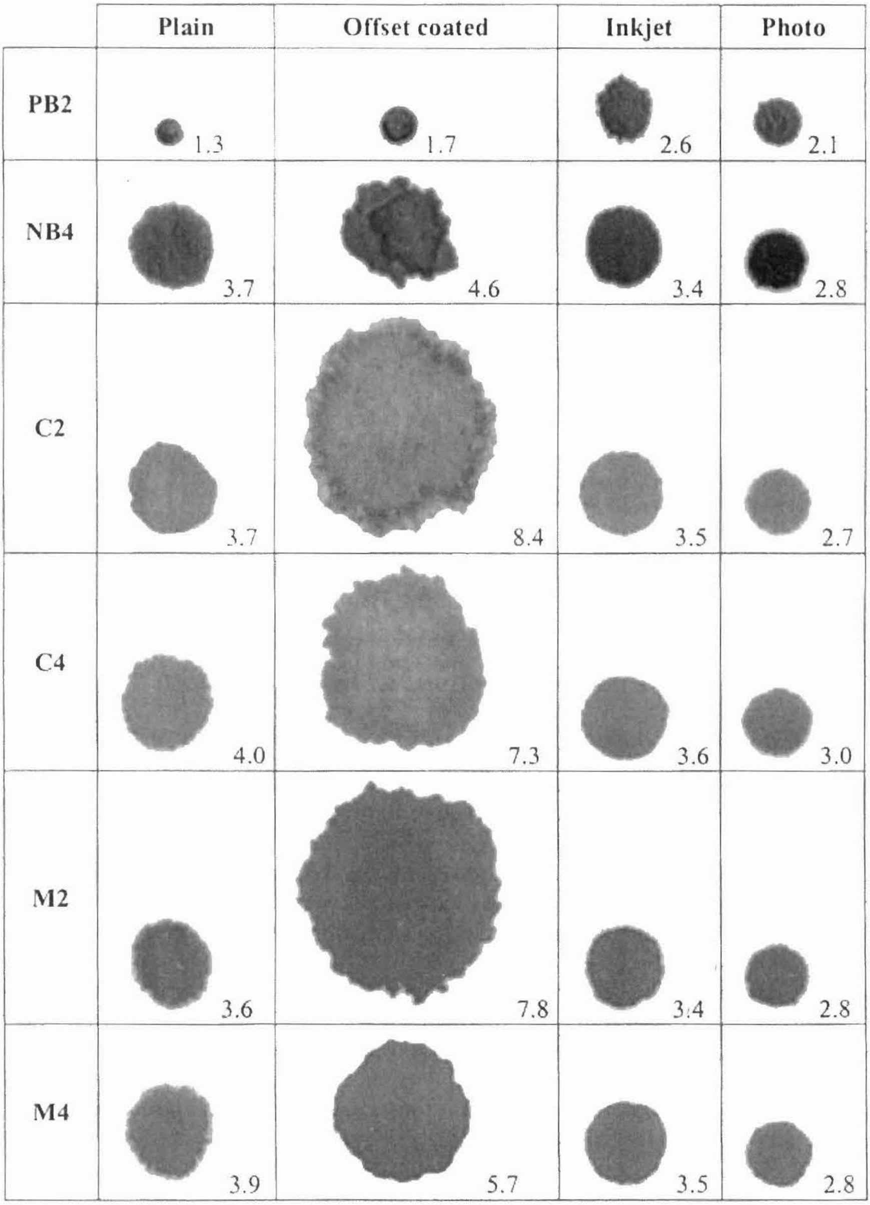
• Comparison Between Papers

Visually, the difference of behaviour of inks on the 4 different papers is very clear. Some photos of dots are given *Table 6*.

Table 6 shows that, the offset coated paper tested here is not adapted at all to ink jet dye-based inks. Spread factors obtained on this paper are very high and very different from one ink to another: values are ranging between 2.5 and 9 for the 20 dye-based inks. Although spread factors are nearly the same for plain paper and inkjet paper, it can be expected that print quality will be better on inkjet paper because circularity is better and optical density more uniform. Finally, for photo paper, spread factor is very small (not higher than 3) and circularity is quite perfect.

All dye-based coloured inks show a similar spontaneous spreading behaviour, but there is a great difference between the behaviour of dye-based and pigmented inks. Dye-based inks dry when they spread on every kind of paper. On the contrary pigmented inks do not spread a lot on plain and offset coated paper: they dry by evaporation and it can be very long. On inkjet and photo paper, they spread a little more and it can therefore reduce the drying time.

To have a good print quality, the aim is to reduce spreading for dye-based inks and to find a good compromise between spreading and drying time for pigmented inks.



	Plain	Offset coated	Inkjet	Photo
PB2	1.3	1.7	2.6	2.1
NB4	3.7	4.6	3.4	2.8
C2	3.7	8.4	3.5	2.7
C4	4.0	7.3	3.6	3.0
M2	3.6	7.8	3.4	2.8
M4	3.9	5.7	3.5	2.8

Table 6: syringe dots of some inks with spread factors

• Correlation Between Spread Factor and Ink Properties

As it is found in the literature, either pH, conductivity or charge density do not seem to have any influence on final spreading of ink. On the contrary, we could expect that spread factor is correlated to surface tension.

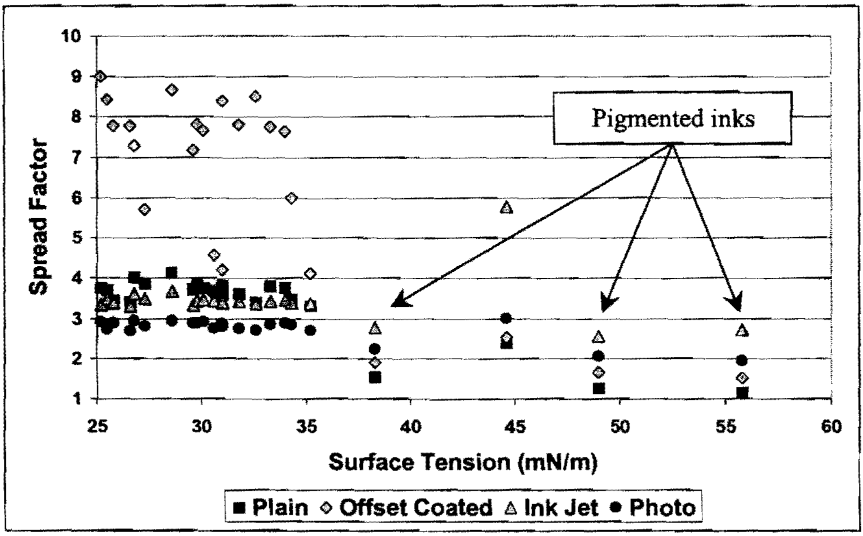


Figure 3: correlation between spread factor and ink surface tension

No real clear correlation was found between the spread factor and the ink surface tension. The slight trend observed in the decrease of the spread factor for the highest surface tension values has to be looked carefully. These values correspond to the pigmented inks. The spreading is probably limited not only because of the value of the surface tension. Phenomena linked to pigments deposition will probably be responsible for the decrease in the spread factor.

As we saw, every models of spontaneous spreading or penetration involves viscosity of inks through the ratio surface tension over viscosity. But *Figure 4* shows that the correlation with the ratio surface tension over viscosity is not better than the correlation with surface tension. To find a correlation between spreading and ink properties we must not forget the interactions between ink and paper and so paper properties.

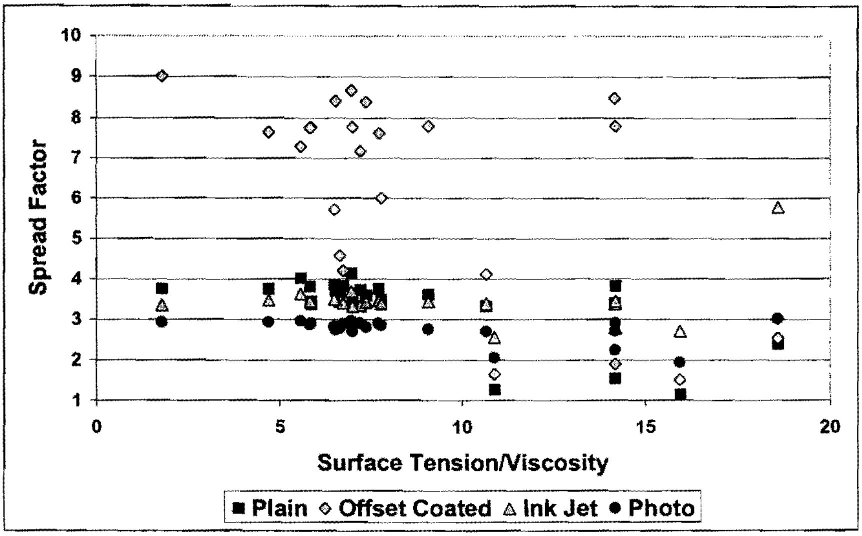


Figure 4: correlation between spread factor and ink surface tension/viscosity

To take into account both ink and paper properties, we have measured contact angle between each ink and each paper. The measurement of contact angles were carried out with a GBX Digidrop device. Given values are contact angle at 25 ms that is to say just after the drop had been completely deposited.

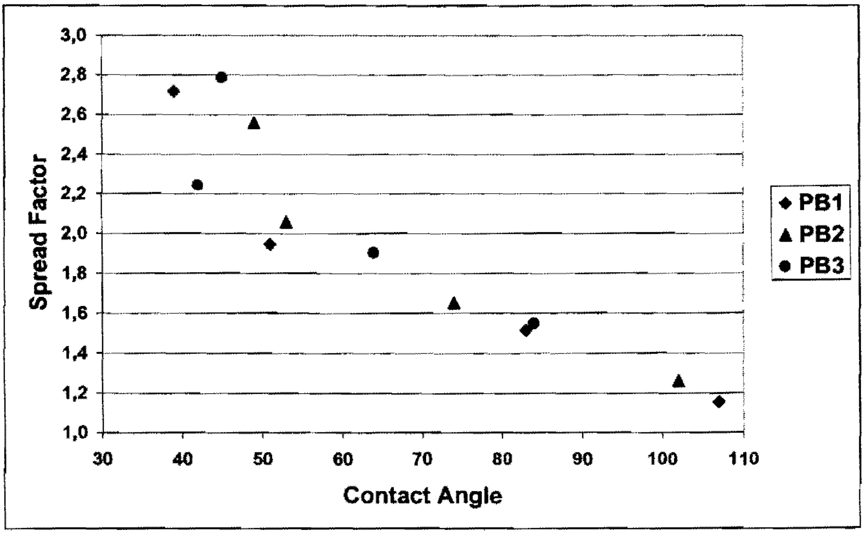


Figure 5: correlation between spread factor and contact angle for pigmented inks

The correlation between spread factor and contact angle shown *Figure 5* is very good for pigmented inks. Indeed, contact angles for pigmented inks are constant during almost one second, they can be considered as static contact angles and their values can be considered as reliable.
But, we must not forget that this correlation represents only the spontaneous spreading. To find the complete relation between ink spreading and contact angle for pigmented ink, it would be necessary to understand the effect of impact velocity. That will be taken into account in the continuation of our study.

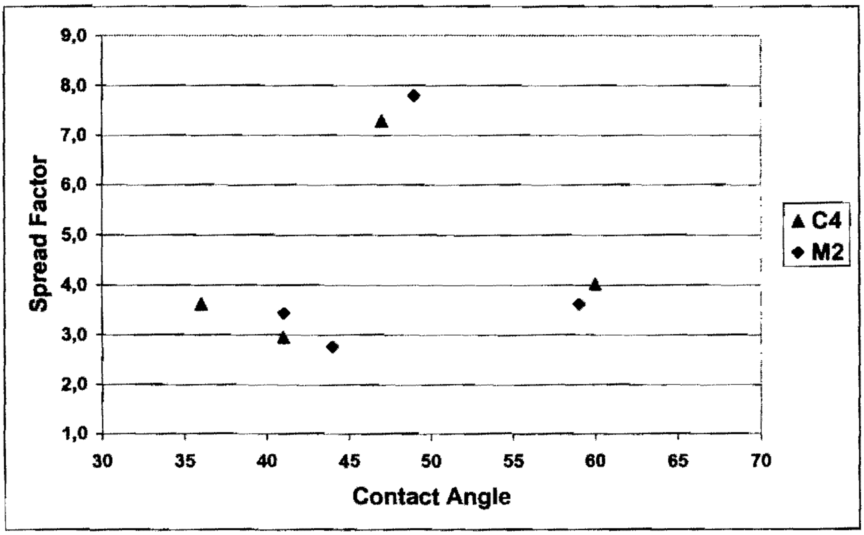


Figure 6: correlation between spread factor and contact angle for dye-based inks

The results obtained with dye-based inks are more complicated to analyse than those with pigmented inks.
For dye-based inks, it is impossible to have static contact angle, it is decreasing very rapidly in only 100 or 200 ms according to inks and papers. We made the choice to measure contact angles just after 25 ms, that is to say the very beginning of the spreading.
Figure 6 shows two examples representative of the results obtained with the 20 dye-based inks. No conclusion can be drawn from such a graph. The values obtained at 25 ms are representative of inks under unstable conditions. To get reliable explanation and understanding on the relation existing between spread factor and ink surface tension, we have to study the entire behaviour, spreading and penetration, of the ink at paper surface, as soon as the ink gets into contact with the paper surface. This is the continuation of the study.

Conclusion

In this study, many inkjet inks properties were analysed. Surface tension and viscosity are those which seems to influence the most the final spreading of inks. But, if we want to find a modelisation of final spreading, paper properties must be taken into account. In this way, contact angle seems to be a good indicator but a thorough study of the influence of paper properties will have to be carried out. That will be the next step of our study.

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