THE EFFECT OF WATER HARDNESS OF DAMPENING SOLUTIONS ON PRINTING QUALITY IN OFFSET LITHOGRAPHY

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Abstract : Even though water hardness is often mentioned in the literature as possibly disturbing the offset lithographic process, most of its effects have only been described qualitatively. The purpose of this study was to determine if water hardness actually affects print quality. A project led in 1995 by IFRA and EFPG had produced interesting results, especially when measuring contrast on samples printed on a newspaper press. Because of these results, showing a maximum contrast at intermediate levels of hardness, it was decided to look more closely into rheological properties of emulsions. Tests were carried out with 3 model inks and 5 model dampening solutions of increasing hardness. Printing tests displayed higher contrasts at 2 intermediate levels of hardness (70 and 140 PPM as $CaCO_3$). Viscosity measurements, out of flow curves plotted at various temperatures, showed a clear drop in viscosity at these same levels of hardness. These two phenomena are not necessarily connected, but do occur in the same range of hardnesses. Therefore, we can say that water hardness affects the lithographic process, as well as the resulting printed product.

Introduction

Offset lithography enables printers to produce high quality documents at relatively low costs per copy. However, increasing requirements in terms of quality and productivity enhance any weakness in one or several of the materials involved in offset lithography, namely ink, dampening solution, plate, blanket, or

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paper. Web presses now reach printing speeds of 15 meters per second, which leaves about 10 milliseconds for emulsification to take place and for the resulting emulsion to be transferred within the printing unit to the paper.

Therefore, accurate knowledge and monitoring of raw materials are necessary to maintain what is usually referred to as "ink/water balance". The latter, conditioning the quality and consistency of the emulsion, actually characterizes the compatibility between an ink and a dampening solution.

The dampening solution is made up of a mixture of all the necessary ingredients to reach proper wetting and protection of the non-image areas on a plate, as well as to form a stable and easy-to-transfer emulsion with the ink. This additive is diluted in the proportion of 2 to 3% in water (plus 3 to 15% isopropanol -or a substitute- when the dampening system makes it necessary).

This means that water constitutes the main ingredient in the dampening solution. Strangely, though, it is the least controlled of all parameters, so much so that indeed, many printers use tap water in their dampening solutions, without questioning its quality. However, aqueous solutions are very complex in terms of understanding their physical properties.

Naturally, any dampening additive manufacturer will analyze the tap water in the customer's printshop, then elaborate the additive with adequate ingredients. Moreover, natural water (which we shall call "raw" water in this paper) is fortunately usable in the offset process most of the time.

However, process problems due to the nature of raw water are regularly mentioned in the literature [MacPhee, 1988 ; Schmitt, 1993 ; Sirost, 1990 ; Zanon & al., 1990]. At the same time, manufacturers of water treatment systems insist on the importance of using a water of adjusted and constant quality in offset lithography [Bates, 1993 ; Zanon & al., 1990]. What is more, Mac Faul suggested defining a standard for raw water quality that would be suitable for a given offset lithography process [Mac Faul, 1992].

Aside of these effects, it is the often reported impact of the dampening liquid on printing quality that made us be interested in the relationship between properties of the print on the one hand, and properties of the ink and dampening solution on the other.

I. Water, dampening solution, and contrast

1.1. The dampening solution

1.1.1. Roles and tasks

Remark : we will only consider acidic dampening solutions in this paper.

The dampening solution is designed for several purposes:

- to wet the non-image areas of the plate;
- to protect them and maintain a hydrophilic film on them;
- to emulsify the ink, while keeping some liquid at the ink surface (in order to keep wetting the non-image areas);
- to cool off the form rollers, thus maintaining ink viscosity within an acceptable value;

While playing these roles, the dampening solution must not let its ingredients interfere with the process or have undesirable effects. This assigns supplementary tasks such as:

- avoiding corrosion;
- avoiding bacterial developments;
- avoiding foam;
- compensating for poor water quality, etc.

1.1.2. Composition

In order to achieve all these tasks, an acidic dampening solution will therefore hold a fair number of ingredients, viz. :

- an acid;
- a buffer;
- a desensitizer (such as gum arabic or glycerol);
- one or more surfactant(s);
- a corrosion inhibitor;
- one or more biocide(s);
- an anti-foaming agent (when necessary);
- a sequestrating agent (when the raw water is very hard).

Except for conventional dampening systems, the solution will also hold isopropanol or a substitute. The latter brings the useful viscosity at low speed, improves wetting and emulsification, and (in the case of isopropanol) cools the rollers by evaporating [Burris, 1993 ; Fuchs, 1994].

1.1.3. Water

Tap water, which has been treated to become drinkable, is still not pure water : it holds various solutes among which dissolved gases (such as oxygen or carbon dioxide), and mineral salts (anions such as chloride, carbonate, phosphate, nitrate and sulfate, and cations such as calcium, magnesium, sodium and iron).

In this study, we will consider water hardness only, that is, the amount of dissolved calcium and magnesium salts.

Total hardness, noted "TH", corresponds to the total amount of calcium and magnesium ions in a given raw water. It may be expressed in many units such as English, French, or German degrees. We chose to use "parts per million equivalent calcium carbonate" (PPM as Ca CO_3). One PPM as $CaCO_3$ corresponds to the amount of calcium carbonate which, if taken alone, would result in the same total hardness as obtained with the corresponding mixture of calcium and magnesium ions.

One can expect a very hard water to cause precipitation of calcium and magnesium ions with fatty acids present in the inks. Such precipitates will disturb the offset process by reducing transfer on the inking rollers and blanket ("glazing") or on the plate, resulting in non-inked parts in the image areas ("plate blinding") [Schmitt, 1993 ; Tosch & al., 1991 ; Zanon & al., 1990]. Deposits in the dampening pan and in pipes may also seriously disturb the dampening solution circulation [Burris, 1993 ; MacPhee, 1988].

As to very soft water, it will increase the dampening solution pick-up by the ink [Schmitt, 1993]. The resulting film of emulsion will have less cohesion and will split irregularly. One can also expect a decrease in ink density [Fuchs, 1994]. Very hard water will also tend to over-emulsify in the ink [Schmitt, 1993].

Because neither a very soft nor a very hard water are suitable for maintaining proper setting of the offset lithographic process, specialists will recommend intermediate levels of hardness to printers.

However, from one source to the other, the "proper" range will vary significantly without specific reason, e.g.:

- 50 to 150 PPM as $CaCO_3$ [Burris, 1993 ; Sirost, 1990] and 50 to 200 PPM as $CaCO_3$ [MacPhee, 1988];
- 145 to 180 PPM as $CaCO_3$ [Schmitt, 1987];
- 125 to 215 PPM as $CaCO_3$ [Fuchs, 1994].

1.1.4. Contrast and dampening solution

Since raw water affects emulsification, one should assume that it could affect printing quality as well. This is why, in the course of a one-year project dealing with the issue of water quality and supported by IFRA (INCA-FIEJ Research Association), we carried out tests on a newspaper press kindly made available by the French newspaper *Le Dauphiné Libéré* in Veurey, France [IFRA, 1996].

By plotting contrast* (measured at 50% dot coverage) as a function of water hardness (see figure 1), we obtained a maximum in contrast at an intermediate level of hardness, i.e., 145 PPM as $CaCO_3$.

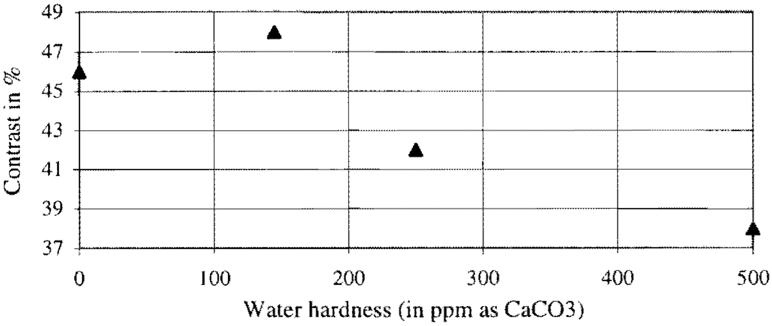

Fig. 1. Contrast as a function of water hardness : black newsink on newsprint at 40,000 copies per hour

* Contrast K is defined here by the following formula :

$$K = 100*(D_s - D_{50})/D_s$$

with,

D_s : solid ink density,
D_{50} : density measured on a 50% halftone.

Remarks:

- *we had to use 2 different papers for the tests (one for the first 2 hardnesses, the other for the last two). These papers were very similar in terms of optical and surface properties. All other printing parameters remained constant throughout the tests.*
- *With very hard water (500 PPM as CaCO3), we had to "overdamp" the plate in order to avoid serious scumming. This phenomenon agrees with reports*

mentioning an increase in water pick-up when hardness was high [MacPhee, 1988 ; Schmitt, 1993].

As the shifts in contrasts are significant when water hardness is altered, a closer investigation appears to be reasonable. What is more, we had picked our samples only several thousands impressions after the okay sheet, which indicated a short term effect.

It is conceivable that hardness may have somehow affected the emulsions, resulting in changes in tone values. This colorimetric effect (reduction in solid ink density when water content increases) has already been observed [Fadner & Doyle, 1985 ; Martin & Silver, 1976].

However, the nature of our dampening solutions varied, since the concentration in calcium carbonate was changed. Indeed, it was the only changing parameter in our printing tests (if it is accepted that paper was kept essentially constant). This is why we chose to investigate the rheological properties of our emulsions.

II. Experimental

2.1. Ingredients

The printing experiments reported were obtained using a sheetfed press dealing with heat set inks (formulated for sheetfed applications).

On finds a fair number of ingredients in both inks and dampening additives. In order to facilitate the interpretation of possible phenomena, we simplified the inks and the dampening additive as much as we could, while maintaining their ability to work correctly on the press.

Hartmann Druckfarben (based in Frankfurt, Germany) kindly provided 3 model inks (cyan, magenta and black) and a model dampening additive for our experiments.

The inks were made of	(i) a pigment, (ii) a resin, and (iii) a solvent
The dampening additive was made of	(i) an acid, (ii) a buffer, (iii) a desensitizer, and (iv) a surfactant.

Its pH was adjusted to 5.0 ± 0.05, and it was to be used at a 2% dilution with distilled water.

To vary water hardness, we used distilled water into which we dissolved calcium carbonate. The unit used to express total hardness (PPM as $CaCO_3$) therefore corresponds to the actual concentration of calcium carbonate in mg/l.

The selected levels of hardness were first 0, 70, 140, 200, and 350 PPM as $CaCO_3$.

2.2. Laboratory experiments

We adjusted pH to 5.0 *after* having added calcium carbonate, because by adding calcium carbonate to an acidic dampening solution, one increases the pH, and any effect on the printing process could either be attributed to the presence of calcium ions or to the variation in pH (our dampening additive being optimized for a 5.0 pH value).

We chose to keep the 5.0 pH value for all dampening solutions (that is, for all hardnesses) to make sure that the pH would not interfere with the dampening solution behavior.

However, we then could not fully reproduce the actual effect(s) of a change in raw water quality on the offset process, since we eliminated those due to the increase in pH.

We prepared emulsions in an emulsifier turning at 10,000 rpm. We put 20 g of ink in a 40 mm diameter beaker. The 20 mm wide fan was positioned in the middle of the beaker, 5 mm above its bottom. This geometry enabled us to reach a gradient comparable to those obtained in printing nips.

We added droplets of dampening solution into the ink until it reached 15% (in weight) and let emulsification take place for 5 minutes. The concentration of 15% allowed some of the solution to remain at the surface of the emulsion : such surface water is necessary to keep a printing plate free of ink [Rosenberg, 1985]. These emulsions were therefore comparable to those obtained in a press.

We carried out flow experiments on a controlled stress rheometer with a cone/plate geometry. The cone diameter was 2 cm, and its angle 4°. The distance between the base of the cone and the plate was 105 µm.

We applied the same procedure for each experiment, viz.:

- compression of the ink sample and removal of the amount exceeding the cone width;
- setting time (2 min);
- continuous increase of shear stress from 0 to 1000 Pa for 2 minutes;
- continuous decrease in shear stress from 1000 Pa to 0 for 2 minutes.

Reproducibility was good, except for low shear stresses at low temperatures.

All inks and emulsions (at 0, 70, 140, 200, and 350 PPM as $CaCO_3$) were tested at 5, 10 (15 for the cyan ink) and 20°C. Emulsions at 0, 200, and 350 PPM as $CaCO_3$ were also tested at 30, 40, and 50°C.

2.3. Printing experiments

Printing tests took place on the 2 color sheetfed press available at EFPG. It uses a direct, contact-type dampening system, requiring isopropanol or a substitute.

We printed with the exact same inks and additives as those we used in the laboratory. However, we added 5% isopropanol to the dampening solution in order to improve printing conditions. This extra ingredient was taken into account when adjusting the concentration of calcium carbonate in our solutions.

We chose an 80 g/m^2 uncoated paper in a 450 mm x 320 mm format, because coated paper might have held calcium carbonate, and thus interfered with our dampening solution. Indeed, variations in water hardness often result from too acidic a solution dissolving calcium carbonate from a coated paper.

The printing speed was 6000 impressions per hour. We printed 1200 documents after the okay sheet for each test.

We used the same unit for each test, thus making sure that roller settings would remain the same throughout the experiment.

The fountain pan was emptied, rinsed with distilled water and dried before each test. The refrigerating unit was also emptied, rinsed with distilled water and re-emptied before using each new solution.

Five plates were produced in a row, under the same exposure and development conditions. This allowed us to change the plate before each test, thus preventing any wearing or possible deposit. The test form held an image, highlights and shadows, as well as a GATF*/SWOP proofing bar [SWOP, 1986].

After having adjusted ink keys settings and obtained uniform inking, we decreased the general dampening until scumming appeared. We then increased dampening by 5% (on the machine scale). By proceeding so, we printed with minimum dampening, which is always advisable.

We recorded temperature in the fountain pan and, with an infra-red thermometer, on the first ink form roller (before the plate nip). Conductivity was also measured when we reached the okay sheet and at the end of each test, that is, after 1200 impressions.

The pH remained at 5.0 ± 0.1 throughout the experiment.

* GATF : Graphic Arts Technical Foundation

III. Results and discussion

3.1. Influence of temperature and hardness on the viscosity of emulsions

In a flow curve, one plots shear stress (in Pa) as a function of the obtained shear rate (in s^{-1}). The slope of the curve gives the viscosity (in Pa.s).

Because we could achieve good reproducibility at higher shear stresses, we chose the viscosity measured at 1000 Pa as our rheological parameter. We will then refer to the latter as "viscosity".

3.1.1. Activation energy

If we want to understand the results on a microscopic level, the concept of the activation energy may be helpful. In the case of viscosity, the activation energy is generally understood as a measure of the energy needed for an average particle in a liquid to change its position.

Eyring describes the elementary flow process of a liquid as the passing of an energetic threshold by an elementary unit of the compound. This transition is therefore favored when temperature increases [Eyring, 1935].

Viscosity will then be expressed by an Arrhenius-type relationship, viz.

$$\eta = A \exp (E_a/RT)$$

with,

η : viscosity,
A : constant related to molecular oscillation frequency,
T : absolute temperature,
R : gas constant,
E_a : activation energy for viscous flow.

Generally, E_a depends on interactions between molecules and on the microstructure of the liquid, as well as on the shear stress, in the case of non Newtonian flows (which will be the case with our inks) [Blayo, 1994].

This number has been used to interpret the forces distinguishing the strength of the local structure in a liquid [Angell, 1991].

The structure of the liquid analyzed here (a homogenous mixture between ink and the dampening solution) is extremely complex, and a lot of different forces are involved in stabilizing such a mixture. Therefore, we think a numeric interpretation of the activation energy might be overinterpreted. Thus, we understand this number not in a quantitative, but in a qualitative sense as a means for the relative forces between the particles in the mixture between ink and the dampening solution.

Figures 2 to 4 display the variation of viscosity as a function of temperature for each ink, in an Eyring plot.

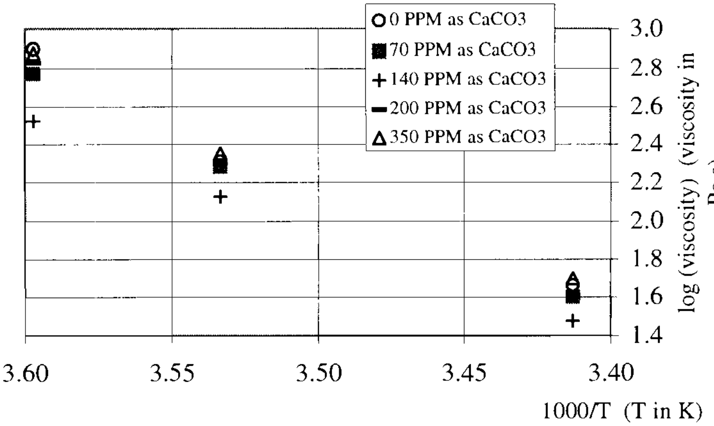

Fig. 2. **Viscosity of black emulsions as a function of temperature and water hardness**

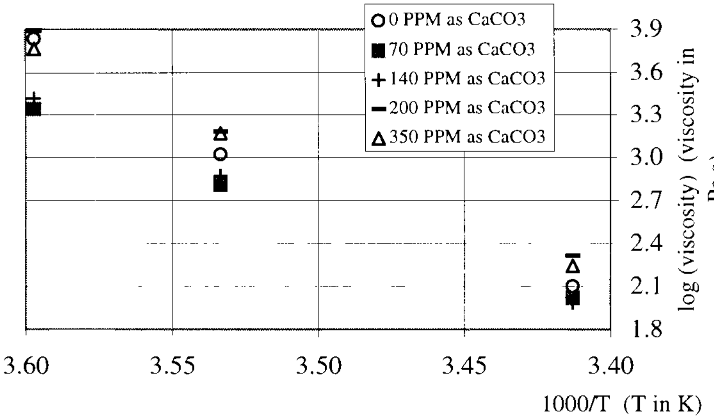

Fig. 3. Viscosity of magenta emulsions as a function of temperature and water hardness

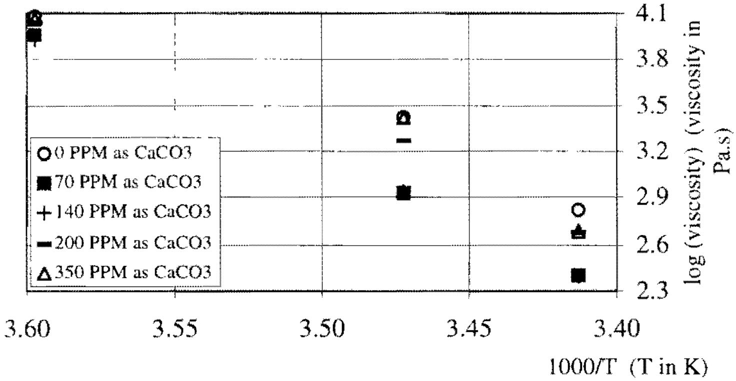

Fig. 4. Viscosity of cyan emulsions as a function of temperature and water hardness

A noticeable feature of these graphs was that viscosity reached at 70 and 140 PPM as $CaCO_3$ was always lower than the corresponding ones at 0, 200, or 350 PPM as $CaCO_3$. The cyan was the most viscous, and the black the least viscous of all three inks.

As for the "slope" of these lines, 3 experimental points were not enough to draw a straight line without risking an inaccuracy. However, for the black and magenta inks, the slope appears to be lower at 70 and 140 PPM as $CaCO_3$ than they are at other hardnesses, which would mean that the activation energy of the corresponding emulsions was reduced, meaning that flow in such emulsions was made easier.

Figure 5 shows viscosity as a function of temperature, for the emulsions with a 200 PPM as $CaCO_3$ hardness, in an Eyring plot.

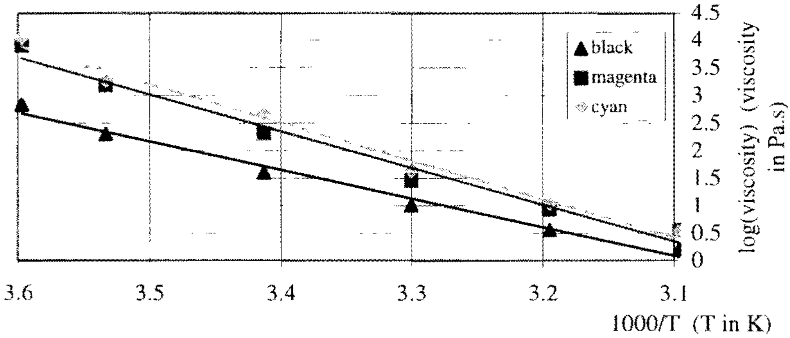

Fig. 5. Viscosity of emulsions at 200 PPM as CaCO3 as a function of temperature

A calculation of the activation energies gives values of about 45 kJ.mol^{-1} for the black emulsion, and about 55 kJ.mol^{-1} for the magenta and cyan emulsions.

Such values are in concordance with those usually obtained for inks (taking the emulsification into account) [Blayo, 1994].

,3.1.2. Influence of water hardness on viscosity

Figures 6 to 8 display viscosity as a function of water hardness, at three temperatures, and for each ink.

Remark : these results are the same as the ones presented in figures 2 to 4, but plotted in another way

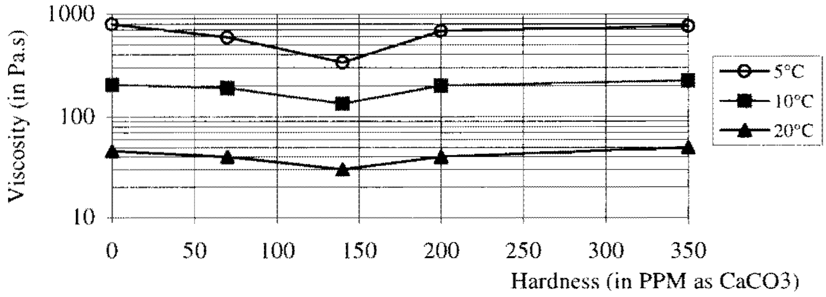

Fig. 6. Viscosity of black emulsions as a function of water hardness and temperature

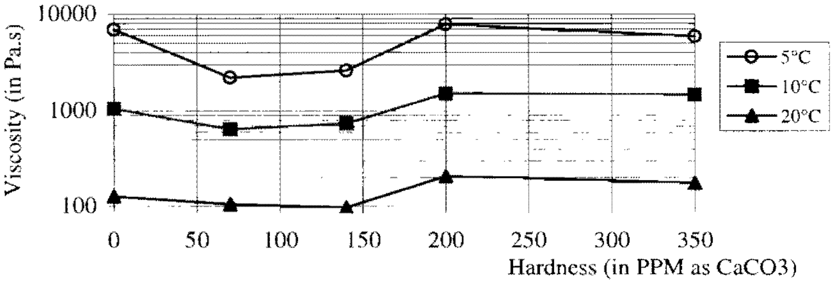

Fig. 7. Viscosity of magenta emulsions as a function of water hardness and temperature

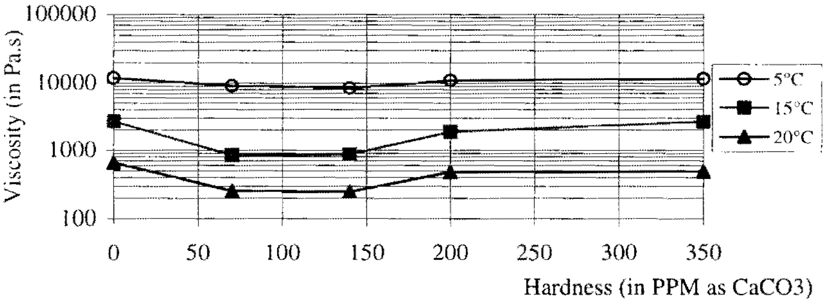

Fig. 8. Viscosity of cyan emulsions as a function of water hardness and temperature

For each ink, there was a clear drop in viscosity at intermediate levels of hardness (70 and 140 PPM as $CaCO_3$). Except for the cyan ink, this drop was all the more significant, the lower the temperature.

This behavior was particularly marked at "low" temperature (5°C to 20°C). However, it characterizes a general change in particle interactions (and possibly in structure, thus in fragility). We can therefore expect a specific behavior of emulsions made with intermediate levels of hardness (70 and 140 PPM as $CaCO_3$) on a printing press.

3.2. Contrast as a function of hardness

For each experiment , viz. with each ink and each hardness, we printed 1,200 documents after the okay sheet. We then measured densities of solids and halftones (25, 50, and 75% dot coverage) on a minimum of 12 consecutive printed sheets taken from the last twenty.

From these measurements, we calculated contrast at 75% dot coverage, using the following definition:

$$\mathbf{K = 100*(D_s - D_{75})/D_s}$$

with,

D_s : solid ink density,
D_{75} : density measured on a 75% halftone.

The following table sums up printing conditions :

Water hardness (PPM as $CaCO_3$)	**Dampening solution conductivity (µS/cm)**	**Ink**	**Dampening level (%)**	**T in the dampening pan (°C)**	**T on the 1st ink form roller (°C)**
0	1050	**Black**	40	6	23.1
		Magenta	40	6	21.4
		Cyan	40	7	21.8
70	880	**Black**	40	5	23
		Magenta	40	6	21.9
		Cyan	40	5	22.3
140	910	**Black**	40	5.5	23.5
		Magenta	45	6	23.5
		Cyan	40	5	23.8
200	1050	**Black**	40	7	23.1
		Magenta	50	6	22
		Cyan	40	6	23.2
350	1150	**Black**	40	5	23
		Magenta	45	5	22
		Cyan	40	5	21.5

It is interesting to notice that the dampening solution conductivity decreases when water hardness is 70 PPM as $CaCO_3$. This probably means that calcium ions react with one or more ingredient(s) from the dampening additive (e.g., the buffer). But when hardness keeps on increasing, conductivity rises again.

Remark : Measurements obtained with the 350 PPM as $CaCO_3$ hardness gave aberrant results (very low dot tone value increase and very high contrasts). We have no explanation for this behavior so far. Work is in progress to check this phenomenon

Figure 9 displays the resulting contrast values as a function of water hardness.

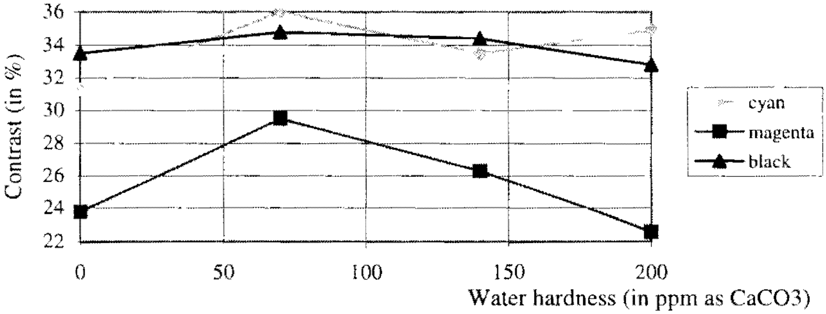

Fig. 9. Contrast after 1,200 impressions as a function of water hardness

These results show that, simply by changing the hardness of our dampening solution, we significantly affected print quality as measured by contrast. Just as it happened with the tests carried out at *Le Dauphiné Libéré*, we obtained a maximum contrast at an intermediate level of hardness, namely 70 PPM as $CaCO_3$ (the maximum contrast had been reached at 140 PPM as $CaCO_3$ during tests at *Le Dauphiné Libéré*). Except for cyan, contrast at 140 PPM as $CaCO_3$ was also higher than contrast at 0 or 200 PPM as $CaCO_3$.

Except for the black ink, for which solid ink density was set higher, relative differences in contrast were in the range of 10%, and even exceeded 20%. This is far beyond the standard deviations, which never exceeded 4%, the highest ones being obtained with the magenta ink.

Naturally, one may be tempted to link this change in contrast to the change in viscosity also observed at these two intermediate levels of hardness. We will remain careful with quick conclusions, but this latter set of experiments definitely shows that water hardness does affect print quality, at least when using model ingredients.

Conclusion

The experiments reported support the idea that water hardness does affect the behavior of a dampening solution, not only in the extreme hardnesses, but also in the intermediate values.

The change in viscosity of the ink-dampening solution mixtures undergoes characteristic slopes : when increasing the hardness of the water from 0 to 350 PPM as $CaCO_3$, it appears that, at intermediate levels of hardness (70 to 140 PPM as $CaCO_3$), the viscosity of emulsions is reduced. This effect becomes enhanced at lower temperatures.

At these intermediate levels of hardness, the print contrast also increases significantly, meaning that the print quality for the inks studied improves.

We assume that these macroscopic differences have a microscopic origin, probably at a molecular level. However, interpreting such behaviors would require deeper research. Indeed, the multiplicity of ingredients, even in model inks and dampening solutions, makes possible physico-chemical reactions quite numerous.

We are planning further investigations into rheological properties (flow and oscillation curves), as well as tests on a press during which we would print and record emulsification simultaneously. We will also consider interfacial and electrokinetic phenomena.

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