FURTHER INVESTIGATION INTO THE EFFECT OF DAMPENING SOLUTION HARDNESS ON OFFSET LITHOGRAPHY

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Abstract : the literature often mentions the hardness of water in dampening solutions as a possible source of problems (in terms of "water pick-up", ink transfer and deposits).

A paper we presented at TAGA' 97 showed that the damping water hardness had a clear effect on both the viscosity of emulsions and the contrast of printed sheets. Such results encouraged us to further investigate some rheological properties of emulsions obtained at different levels of hardness, as well as emulsification measurements, and related physico-chemical properties.

The experiments, carried out in the laboratory and on a sheetfed press, involved model inks (cyan, magenta and black) and fountain solutions of different hardnesses. Intermediate levels of hardness (70 to 200 ppm as $CaCO_3$) enhanced the elastic character of the cyan emulsion and improved the tone value increase on press. An increasing hardness affected the efficiency of a non ionic surfactant (ethylene oxide-propylene oxide copolymer). The dampening solutions of higher hardnesses tended to emulsify more in the inks, not only during laboratory experiments, but also during printing tests.

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Introduction

Dampening solution hardness is often mentioned as a possible source of problems in offset lithography. However, few printers tackle this issue as long as they are not facing serious process troubles.

In a previous paper [Pineaux et al., 1997], the authors showed that dampening solution hardness could affect the viscosity of emulsions, as well as print quality.

These results encouraged us to investigate further the rheological and physico-chemical properties of emulsions obtained at various levels of hardness.

I. Background

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

An acidic dampening solution contains typically :

- an acid ;
- a buffer ;
- a desensitizer ;
- one or more surfactant(s) ;
- a corrosion inhibitor ;
- one or more biocide(s) ;
- additional specific ingredients that process conditions may require.

Commercial additives made up of these components are usually mixed with water at a 2 % dilution. The resulting dampening solution may also contain isopropanol or a substitute in order to improve wetting and emulsification.

Water, which represents 80 to 98 % of the dampening solution, may be "raw" (that is, coming out of the tap) or treated (i. e., filtered, softened or deionized).

Water "hardness" is defined as the total amount of calcium and magnesium ions present. A commonly used unit is the *ppm as* $CaCO_3$ (parts per million as calcium carbonate) which stands for the amount of calcium carbonate that, if it were dissolved in pure water, would lead to the same level of hardness as the calcium and magnesium ions actually present. This does not necessarily mean that the water sample in question holds *any* dissolved calcium carbonate.

Even if untreated raw water is often the main source of hardness in the dampening solution, hardness may also result from some ink components (pigments such as Lithol Rubine contain calcium ions). A third (and often main) source of hardness may be the paper coating, when the printing unit configuration (such as the contact dampening system) allows particles to come back into the fountain pan.

Known effects of variations in dampening solution hardness in offset lithography are of two types.

a. Short term effects

Changes in dampening solution hardness will affect :

- the rate of emulsification [NPIRI Task Force on Water Pickup, 1990] ;
- the pH value (in spite of the buffer) [MacPhee, 1988 ; Page, 1984 ; Walther, 1988]

b. Middle to long term effects

An increase in dampening solution hardness may induce various types of precipitations :

- soaps, e. g. by reaction between calcium or magnesium ions and fatty acids present in some inks [Burris, 1993 ; MacPhee, 1988] ;
- insoluble salts resulting in "roller glazing" [Burris, 1993 ; Schmitt, 1993], "plate blinding" [Bassemir & Bean, 1979], or simply disturbances in the dampening solution flow [Burris, 1993 ; Zanon & Charrier, 1990].

  Hardness may also modify the emulsion stability (defined as its resistance to coalescence) [Trauzeddel & Kempe, 1985].

When we carried out a first round of printing experiments using dampening solutions of various hardnesses, these tests revealed a significant improvement in printing contrast at intermediate levels of hardnesses (70 and 140 ppm as $CaCO_3$). This effect occurred only several minutes after adding the hardening agents to the dampening solution [Pineaux et al., 1997].

After having prepared emulsions of different hardnesses in a laboratory mixer and measured their viscosities on a controlled stress rheometer, we observed a significant drop in viscosity at the same levels of 70 and 140 ppm as $CaCO_3$ [*Ibid.*].

We did not own enough elements to correlate these two sets of results, but we assumed they could be linked. This is why we decided to look more closely into surface and rheological properties of emulsions produced with dampening solutions of varying hardness.

II. Experimental

In most cases, we chose to use the same ingredients (inks and dampening solution) in the laboratory and on press. This presented a double advantage :

- we could more easily compare (and possibly link) features observed during laboratory and press experiments ;

- the materials used in our tests, although simplified, remained representative of process materials. Therefore, specific phenomena observed during experiments could alert the printer working with similar conditions in his shop.

We worked on a sheetfed press and thus used corresponding model ingredients. *Hartmann Druckfarben* kindly manufactured and provided quick set inks and dampening additives.

The damping additive was made of :

- citric acid ;
- disodiumhydrogenophosphate (buffer) ;
- glycerol (desensitizer) ;
- ethylene oxide-propylene oxide copolymers (EOPO, non ionic surfactants) with HLB values of 3 and 29.

HLB stands for "Hydrophilic-Lipophilic Balance" and corresponds to the proportion between ethoxylate units (hydrophilic) and propoxylate units (lipophilic).

Inks (black, cyan and magenta) held :

- a pigment ;
- an alkyd resin ;
- a solvent.

For several specific experiments, we also used simpler compositions or slightly different ingredients.

The hardening agent was calcium carbonate because calcium ions are the most likely hardening species to be found in dampening solutions (regardless of their origin).

Thus, our dampening solutions contained deionized water, 2 % damping additive and calcium carbonate in various concentrations. Isopropanol made up for 5 % of the solution during printing tests.

We adjusted pH to 5.0 ± 0.05 **after** having added all the ingredients. Consequently, all solutions were working at the same pH.

II.1. Surface properties

We used a Wilhelmy plate tensiometer (*Dognon Abribat*) (respectively a maximum bubble pressure tensiometer - *Sensadyne 6,000* -) to measure static (respectively dynamic) surface tension of dampening solutions of different hardnesses.

II.2. Rheological properties

II.2.1. Viscosity measurements

We used a controlled stress rheometer with a cone-plate geometry (2 cm, 4°) and variable temperature (*Carri-Med CSL 500*), which enabled the plotting of flow curves (shear stress as a function of shear strain) by increasing stress from 0 to 1,000 Pa. No breaking of the emulsion ever occurred during these experiments.

II.2.2. Viscoelasticity measurements

A viscoelasticimeter (*Metravib*), working at frequencies going from 7.8 to 1,000 Hz, enabled us to calculate the elastic and viscous moduli of emulsions undergoing shear. The emulsion constituted a liquid ring (10 mm high and 0.5 mm thick) inside which oscillated a 5 mm diameter piston. The maximal oscillation amplitude was 20 µm.

II.3. Emulsification properties

II.3.1. Surland test

This test was designed to predict the behavior of process inks on press by checking their rate of emulsification under standard conditions in the laboratory. By following the procedure described by Surland [Surland, 1980], we did not manage to stabilize emulsification, even after 20 minutes. However, our model inks did perform well enough on press to be considered as satisfactory.

Consequently, we decided to adapt this test and plot only the first 6 values (i. e., the amount of dampening solution emulsified by the ink every minute during the first 6 minutes). We then drew the best matching linear function (amount of emulsified damping solution vs. time) at different levels of hardness (0, 70, 140, 200, and 350 ppm as $CaCO_3$).

The slope of these linear curves enabled us to compare emulsification rates (aver 6 minutes) among the studied hardnesses.

II.3.2. *Graphometronic* sensor

Thanks to the *FOGRA* Institute, we could carry out printing tests on a sheetfed press (*Heidelberg Speedmaster 74 F*) equipped with a *Graphometronic* sensor on its first unit.

This allowed us to know the emulsification conditions on the plate that corresponded to a given printing quality (measured in terms of contrast).

II.4. Printing tests

The purpose of these tests was to check previous results obtained at our school with the same inks [Pineaux & al., 1997] and to add the information on emulsification provided by the *Graphometronic* sensor.

We printed with the cyan and magenta inks (the sensor cannot measure the emulsion with a black ink) at hardnesses of 0, 140, 350, and 700 ppm as $CaCO_3$.

III. Results and discussion

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 helix 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. Droplets of dampening solution were added into the ink until the former reached 15% (in weight). The emulsification took 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]. The amount of emulsified dampening solution commonly reaches 15 % on press. This value also allowed a better reproducibility in our measurements (lower standard deviation).

Remarks :

- We also checked the influence of emulsification conditions on model systems (alkyd resin plus distilled water) by trying two other revolution speeds (2,000 and 5,000 rpm) and two other percentages of emulsified water (5 % and 10 %). The 10,000 rpm speed resulted in higher viscosities (measured at a 1,000 Pa shear stress) : we assume this raise in viscosity arose from a finer dispersion of droplets within the resin. Because the latter is preferable on a press, we confirmed our choice for a 10,000 rpm speed.
- However, it is important to note that using a mixer to create an emulsion "forces" the dampening solution into the ink (or resin). On a press, the same ink is present on the plate in the form of a thin film. Therefore, the ink may not emulsify the same amount of damping solution ; the behavior of the resulting emulsion may then differ from that observed in the lab.

III.1. Influence of hardness on surface tension

When the damping additive held a surfactant with an HLB value of 3, hardness had virtually no influence on either static or dynamic surface tension. However, using an HLB 29 surfactant had provided different emulsification behaviors during former experiments [IFRA, 1996].

This is why we checked the influence of hardness on a solution containing 2 % additive at two different HLB values : 3 (the one applied in our model additive) and 29. The results appear on figure 1.

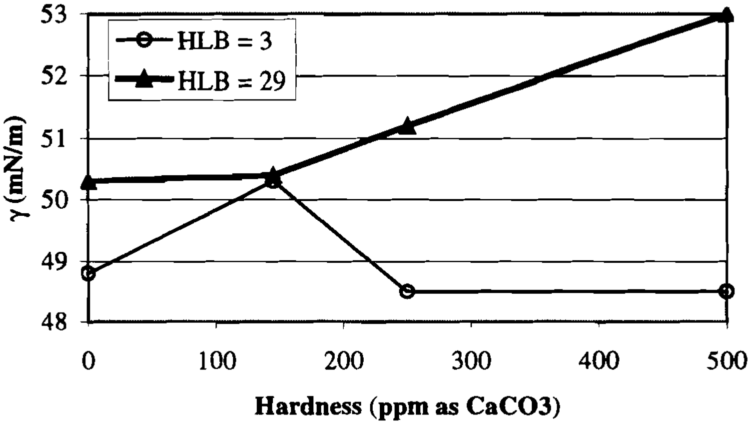

Fig. 1. Influence of hardness (calcium acetate) and HLB value of the surfactant on static surface tension.

The surface tension remained approximately constant for the HLB 3 additive, whereas it tended to increase with hardness for the HLB 29 additive. The observed shifts largely exceeded the standard deviation (which remained lower than 0.5 % of the average surface tension).

It is very likely that ethoxylate units and calcium ions form complexes that inhibit (at least in part) the surfactant ability to lower the surface tension. This shows that the choice of the HLB value for a non ionic surfactant is crucial :

- first because of its behavior under dynamic conditions (which depends on the more or less pronounced hydrophilic character of the molecule) ;
- secondly because of these possible interactions between ethoxylate units and hardening species.

III.2. Influence of hardness on the activation energy

As specified in our previous paper on the issue of dampening solution hardness [Pineaux & al., 1997], the Eyring-type relationship that expresses viscosity as a function of temperature is

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

with,

η : viscosity,

A : constant related to molecular oscillation frequency,

T : absolute temperature,

R : gas constant,

E_a : activation energy for viscous flow, viz. the energy needed for a particle in the liquid to translate.

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 is the case with our inks) [Blayo, 1994].

By plotting the viscosity logarithm (measured at 1,000 Pa shear stress) as a function of 1,000/T, we had access to this parameter and could check the effect of hardness on it.

Figure 2 shows this effect on black emulsions. It appears that the Eyring theory applies to all hardnesses tested. Table 1 gives the corresponding E_a values.

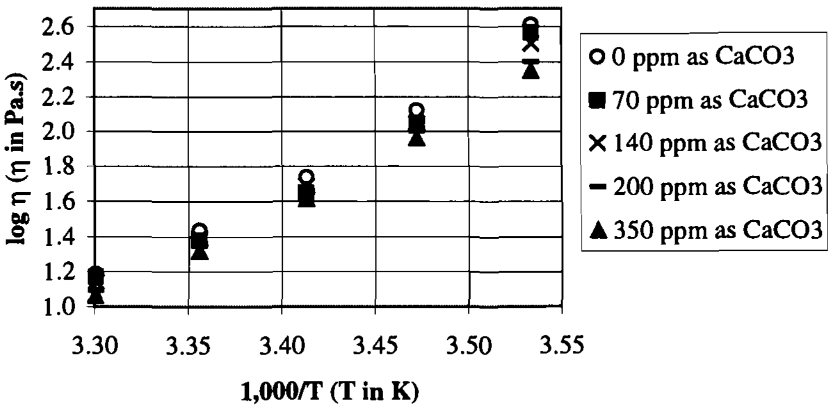

Fig.2. Influence of hardness on the activation energy. Black emulsions, calcium carbonate, HLB 3.

Hardness (ppm as $CaCO_3$)	0	70	140	200	350
Correlation coefficient of the linear regression	0.99	0.97	0.99	0.996	0.996
E_a (kJ/mol)	55.4	49.4	48.4	46.6	45.9

Table 1. Influence of hardness on the activation energy. Black emulsions, calcium carbonate, HLB 3.

This table shows that the activation energy decreased when the hardness increased. According to Angell [Angell, 1991], this would mean that calcium ions "fragilize" the emulsion, so that less energy is required to make it flow.

III.3. Influence of hardness on viscoelastic properties

Figures 3 and 4 display respectively the elastic and viscous moduli of cyan emulsions as a function of frequency and hardness.

Two intermediate levels of hardness, namely 70 and 200 ppm as $CaCO_3$, reached much higher G' values on both graphs than other levels.

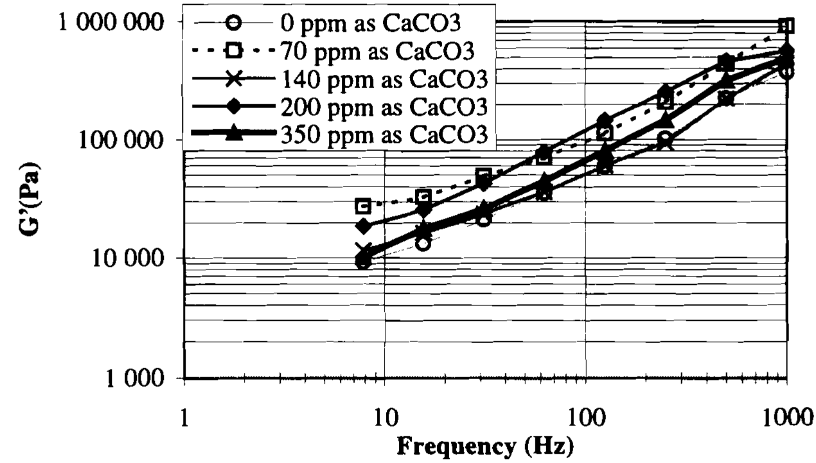

Fig 3. Elastic modulus of cyan emulsions of various hardnesses as a function of oscillation frequency at 25 °C. Calcium carbonate.

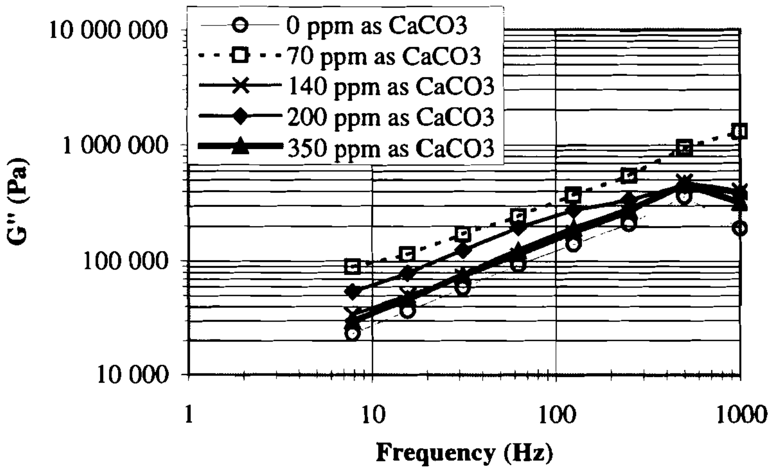

Fig 4. Viscous modulus of cyan emulsions of various hardnesses as a function of oscillation frequency at 25 °C. Calcium carbonate.

Interestingly, the same levels of hardness led to much lower tone value increases when the same ink was printed on paper (see figure 5). This graph refers to printing experiments carried out on a sheetfed press at our school [Pineaux & al., 1997].

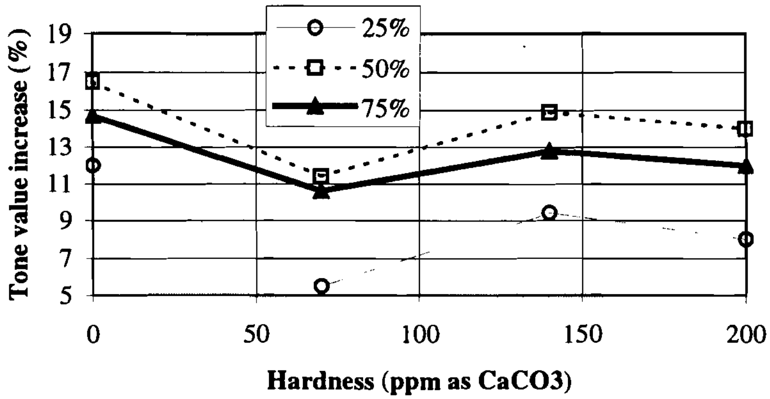

Fig 5. Tone value increase at 25 %, 50 % and 75 % dot coverage. HLB 3, cyan ink, calcium carbonate.

A more enhanced elastic character of the cyan emulsion could explain its better ability to lower tone value increase on press. Indeed, the printed dot would tend to keep its original shape more easily when the transferred emulsion has an elastic character.

If this were the case, we would have a direct correlation between a rheological property of an emulsion measured in the laboratory and its printed result on press.

III.4. Influence of hardness on emulsification

III.4.1. Surland test

Standard deviations varied between 4 and 7 % throughout the experiments conducted with the cyan, black and magenta inks. The shifts observed between extreme curves on figure 6 (dealing with the black ink) largely exceed this experimental error.

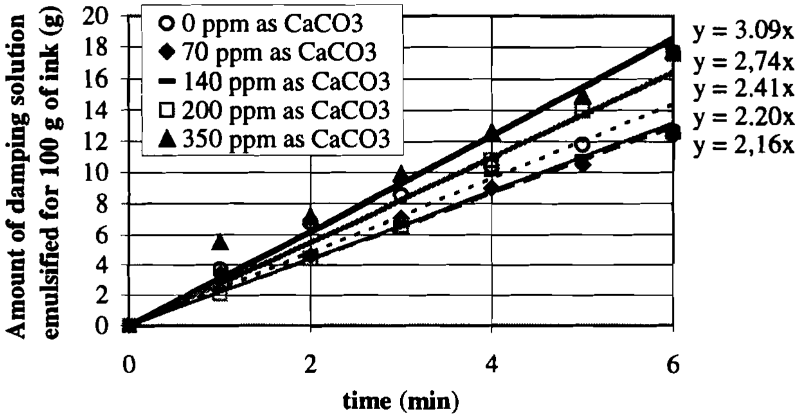

Fig. 6. "Rate of emulsification" of the black ink as a function of hardness. HLB 3, calcium carbonate

The slope related to 70 ppm as $CaCO_3$ is lower than that obtained at other hardnesses. This phenomenon was also true when testing cyan and magenta inks, and could be interpreted as a reduction in the rate of emulsification at 70 ppm as $CaCO_3$.

However, despite this peculiar behavior, the level of emulsification tended to increase with hardness. This result agrees with the literature stating that hard dampening solutions increase emulsification [MacPhee, 1988 ; Schmitt, 1993], but not with papers mentioning very soft water as increasing emulsification [NPIRI Task Force on Water Pickup, 1990 ; Fuchs, 1994].

III.4.2. *Graphometronic* sensor

The infrared sensors (sensitive to O-H moieties) provide 2 outputs : one related to the amount of dampening solution on the non-image areas of the plate, the other to the amount of dampening solution emulsified in the ink on the image areas of the plate. Figure 7 displays these two outputs, obtained while printing with the cyan and magenta inks.

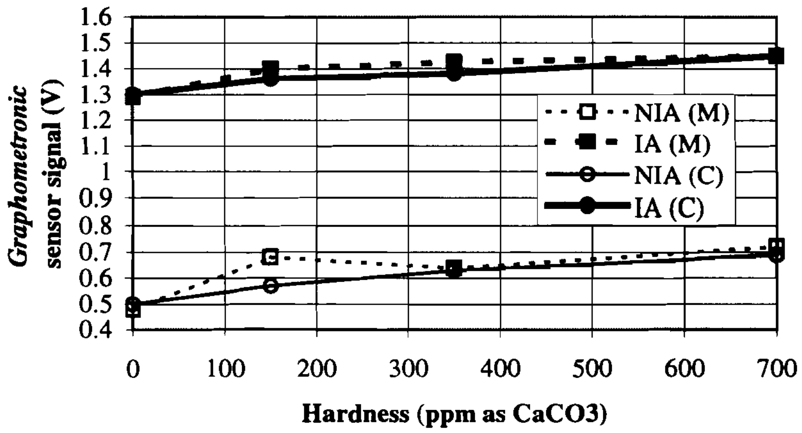

Fig. 7. Level of dampening solution measured on the non-image area (NIA) of the plate and emulsified in the ink, measured on the image area (IA) of the plate. Cyan (C) and magenta (M) inks, HLB 3, calcium carbonate.

These graphs show a general increase of the amount of dampening solution consumed during the process (either to clean the non-image area of the plate or to form an emulsion with the ink) when hardness was increased.

Again, we found no proof that soft waters increase the emulsification of damping solutions.

III.5. Influence of hardness on print quality

We define print quality in terms of print contrast in this paper.

Contrast K is defined here by :

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

with, D_s : solid ink density,

D_{50} : density measured on a 50% halftone.

During our tests on the sheetfed press at *FOGRA*, we managed to maintain solid ink densities, obtained with the cyan and magenta inks, respectively to 1.07 ± 0.01 and 1.18 ± 0.01. Therefore, measuring tone value increase was enough to characterize print quality, since contrast only depends on solid ink density and halftone density.

Tone value increase is defined as the difference between the dot coverage as measured on the printed document and as expected.

Figure 8 presents the tone value increases obtained at 40 % and 80 % dot coverage, on offset paper.

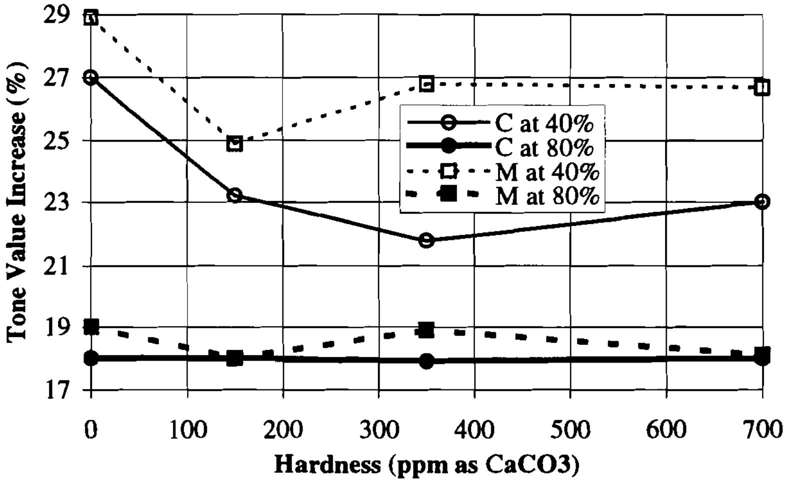

Fig. 8. Tone value increase (at 40 % and 80 % dot coverage) as a function of hardness. Cyan (C) and magenta (M) inks, HLB 3, calcium carbonate.

We notice two distinct features in these graphs :

- because of a clear tendency to fill in, tone value increase appears relatively constant at an 80 % dot coverage, whatever the dampening solution hardness ;
- as we had noticed in previous experiments [Pineaux & al., 1997], intermediate levels of hardness (140 and 250 ppm as $CaCO_3$) lead to a better rendering of the printed dot.

The relatively good results obtained at a 700 ppm as $CaCO_3$ hardness should not hide the high risks of precipitations and deposits that such a level of hardness may raise in the long run. One must not forget that our printing tests could only reveal short term effects.

Conclusion

This investigation confirmed the role played by dampening solution hardness in the emulsification process and in the behavior of quick set emulsions.

Even if some phenomena can be more easily connected to hardness on a macroscopic scale (especially as far as rheological properties are concerned), we still cannot interpret what actually takes place at a molecular level. Indeed, although we simplified our systems as much as we could, while keeping them operational, they remain too complex to understand all possible interactions among components.

Only a systematic microscopic approach on extremely simplified inks and damping solutions (made of one or two components at most) would possibly give a deeper insight on how hardness actually affects the emulsification process.

Nonetheless, these series of experiments have provided the important conclusion that by no means should the issue of damping solution hardness be overlooked. At a time when quality and consistency become more and more important, the printer must fully control the parameters affecting printing : hardness may vary, mainly from the water supply or the coating of paper, and knowing its range of variation is a good means to better master the lithographic process.

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