

Effect of additives on the physico-chemical interactions between ink, water and plate

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Abstract

In the context of the search for isopropanol substitutes, new methods of characterization were developed in order to investigate the role of additives on the physico-chemical interactions between *Ink, Fountain Solution and Plate* in lithographic printing. Ultrasound and shear dynamic measurements proved very useful to measure the average droplet size and the water/vehicle interfacial tension. The influence of the molar mass of non volatile additives and of their molecular structure on the droplet size was also studied.

In the context of the characterization of the water/plate interfaces, the use of a high speed camera coupled with image analysis was applied to the quantitative assessment of the dynamic spreading of the fountain solution on the non-image areas. The first results obtained pointed to the directions to be followed in subsequent more detailed studies.

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Introduction

The replacement of isopropyl alcohol by non-volatile additives in the offset printing process is a topic of great interest because of environmental restrictions. The use of non-volatile additives in the fountain solution produces drastic changes in the physico-chemical interactions between ink, fountain solution and plate. In order to acquire a better knowledge of the action of these additives, we developed new experimental methods which are useful in the context of the characterization of some important parameters governing the process. It was decided to concentrate on two basic systems, namely, (i) the water/ink emulsions and (ii) the dynamic spreading of water on the plate.

In her literature survey, Fetzko (1986, 1988) underlined that the properties of the emulsion strongly influence the ink transfer on the press and also the print quality. The radius of the water droplets and the interfacial tension between the fountain solution and the ink are two parameters of primary importance in this process.

Several techniques have been used for the determination of the size of the water droplets. Chambers (1994) carried out measurements using a time-size mapping system on samples in which the viscous ink vehicle had been diluted with xylene, and gave size distribution curves ranging from a few micrometers to several tens of micrometers. Optical microscopy can provide information about the droplet size without the need to dilute the vehicle and in this way values around a few micrometers have been reported by Rosenberg (1985) and Braun (1985), but of course this technique does not detect submicron droplets. The only published method to characterize these fine emulsions is scanning electron microscopy which has been applied to cryofractured systems by Bassemir (1992).

Likewise, various techniques have been used to determine the interfacial tension between an aqueous solution and a highly viscous ink. The most suitable method appears to be the determination of the dimension of a pendant drop of the fountain solution suspended at the end of a tube plunged into an ink vehicle as described by Andersen (1958). Other classical methods call upon the use of the Wilhelmy plate or the Du Nouy ring are reported by Laroignou (1963), Bitter (1956) and Karttunen (1978), but require the dilution of the ink with a non-polar organic solvent. The values of the interfacial tension are then obtained by extrapolation to zero dilution. This procedure leaves some doubts about the reliability of the values obtained because of the quantitative aspect related to a correct extrapolation and the qualitative problem related to the real change in the polarity of the interface associated with the dilution. The same uncertainty apply to the results obtained by the spinning drop method which also requires a dilution procedure as used by Karttunen (1985).

An alternative approach to the estimation of the interfacial tension consists in carrying out calculations based on the geometrical mean as described by

Owens (1969) and Kaelble (1971) or by the harmonic mean method as described by Wu (1982), but the validity of the procedure related to the calculation of the non-dispersive contribution to this parameter has been questioned by Fowkes (1990) and Ström (1984). Moreover, these calculations require the values of dispersive and non-dispersive contributions to the surface free energy of the ink as obtained from diluted samples and thus the recurrence of the problems just evoked. These unsolved questions prompted us to develop a novel approach to probe water-in-ink emulsions in order to determine the average droplet size and the interfacial tension *in situ* and without dilution. We therefore developed for that purpose an ultrasonic technique based on the measurements of the sound attenuation in the emulsion. Several theoretical and experimental investigations have shown that the ultrasonic attenuation is related to the radius of the droplets in a concentrated emulsion as shown by Harker (1988) and Lloyd (1967). Moreover, shear dynamic measurements have provided a way to determine the ratio between the interfacial tension and the radius of the droplets in an emulsion. The use of Palierne's theoretical treatment (1990) allows such determination through a relationship between the relaxation time of the dispersed droplets under shear and the ratio γ/R .

The first part of this section resumes our results obtained in order to test the two combined techniques on a model water/alkyd resin emulsion (Aurenty, 1995 a) whereas the second part describes the effect of the introduction of non-volatile additives such as glycols and macroglycols in water.

In the context of the fountain solution/plate (non-image area) interactions, the dynamic spreading of the aqueous phase on the high energy surface (aluminium oxide) is of primary importance for an efficient wetting during this fast process. In fact, new interfaces are created on a press within time scales which go from a few milliseconds to a few tenths of a second depending on the press configuration. For that reason, it was decided to carry out some experiments on the dynamic aspect of wetting. Lelah (1981), Marmur (1981) and Pesach (1987) investigated the spreading kinetics of drops on glass and split mica surfaces. Their experiments showed interesting effects related to temperature, humidity, viscosity, surface tension, pH, etc ... The mechanism of spreading of surfactant solutions was interpreted in terms of the primary film approach. The wetting kinetics of binary liquid mixtures was studied and related to the Marangoni effect.

In order to test the spreading dynamic behavior of different solutions on the aluminium oxide surfaces, an experimental device was constructed. The contact angle of the liquids versus time was followed with a high speed video camera (up to 200 images/s) connected to a video card and coupled with image analysis programme.

1. Characterization of the fountain solution/ink emulsions

The first part of the work was devoted to test the validity of the ultrasound and shear dynamic measurements applied to the determination of R and γ in concentrated emulsions.

1.1. Water/Alkyd resin emulsions

1.1.1. Experimental

1.1.1.1. The ultrasonic technique

The ultrasonic attenuation of an emulsion of spherical droplets can be expressed as the sum of three terms :

$$\alpha = \alpha_1(1 - \phi) + \alpha_2\phi + \delta\alpha$$

where ϕ is the volume fraction of the dispersed phase, α_1 and α_2 are the intrinsic attenuation of the continuous and dispersed phases respectively, and $\delta\alpha$ is an "excess attenuation" in the emulsion corresponding to scattering mechanisms of the ultrasonic wave at the interface between the continuous matrix and the suspended droplets. The parameter $\delta\alpha$ depends on the physical properties of the 2 components such as density, sound velocity, specific heat, thermal conductivity, thermal expansion coefficient, shear viscosity; on the volume fraction of the droplets, the ultrasonic frequency and the droplet average radius R . The velocity and attenuation measurements were performed in a typical broad band spike transmission cell designed in our laboratory and shown in figure 1. The FFT analysis of the reception signal was carried out scanning in the frequency range 600 kHz to 2.5 MHz. Once the cell geometry and the signal analysis parameters were fixed, the relative error corresponding to the reproducibility of measurements was found to be about ± 0.1 %.

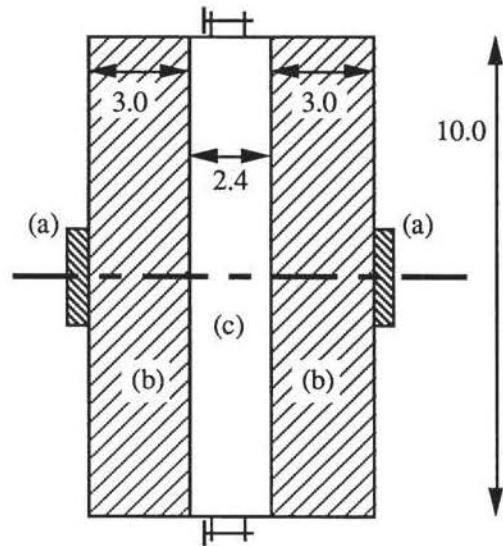


Fig. 1 : Schematic representation of the ultrasonic cell. (a) : piezoelectric elements; (b) : brass buffer rods; (c) : measurement cell. All dimensions are given in cm.

1.1.1.2. Shear dynamic measurements

Shear dynamic measurements have been previously carried out by Graebling (1993) and Aurenty (1994) on different types of emulsion (23, 24). The general trends observed on that kind of blend are an increase of the elastic modulus at the low frequencies and comparatively long relaxation times. These features have been rationalized theoretically by Paliarne (1990) and related to the value of the ratio γ/R of the emulsion. In fact, in a shear experiment the droplets are subjected to deformation of their spherical shape. The parameter γ/R can be considered as an elastic stress which acts on the deformed droplets to restore their original shape.

Taking into account a monodisperse distribution of droplets, the resulting complex shear modulus of the emulsion is therefore obtained as a function of the morphology and dynamic properties of the biphasic system, viz. the volume fraction of the inclusions, the interfacial tension, the droplet size and the complex shear modulus of each phase.

The effect of the presence of water droplets in the continuous phase is shown in Fig. 2. Because of a non-zero interfacial tension, the elasticity of the emulsion was greatly enhanced at low frequency. In that domain, the G' curve flattened progressively because of the relaxation of the water droplets discussed earlier. The corresponding relaxation time fell within

the early portion of our domain of measurements, viz. at about 20 Hz. After the fit of the experimental data and the calculation with Palierne's equation (1990), the values of γ/R could be deduced.

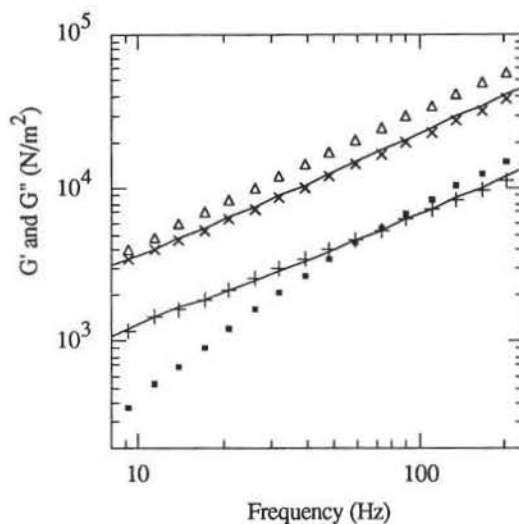


Fig. 2 : Elastic and viscous moduli versus frequency, of the pure alkyd (G' (\bullet) and G'' (Δ)) and of a 20 % water/alkyd resin emulsion (experimental data : G' ($+$) and G'' (\times); best fits according to Palierne's model : solid lines.

1.1.2. Earlier Results

The main results of a preliminary study to be published (Aurenty, 1995 a) are summarized for the sake of clarity. The results obtained with ultrasound and shear dynamic measurements on a 20 % water/alkyd resin emulsion are given in fig. 3 and 4. The alkyd resin used came from the polycondensation of a polyol, isophthalic acid and a vegetable fatty acid and had a molar mass of 3470 and a viscosity at 21 °C of 160 Pa.s in the newtonian region. The aging of the emulsion was followed for 35 days in order to test the sensitivity of our experimental techniques. The increase of the average droplet radius from 1.9 to 2.6 μm within that aging time was detected by ultrasound, whereas a constant value of about 8.5 mN/m was obtained for the interfacial tension at each aging time (table I). The very good correlation between the size determined by ultrasound and that measured by optical microscopy was taken as good validation of our experimental techniques. The value of the interfacial tension as obtained by shear dynamic measurements was found to be slightly smaller than that determined by Laroignou's procedure (1963) and much smaller than

calculated according to Owens-Wendt's equation. This disagreement was interpreted in terms of the migration into the water phase of a small fraction of monomers and oligomers present in the resin, namely the polyol and its first generation condensation products with isophthalic acid which are water-soluble. The occurrence of such migration was proved experimentally and was deemed responsible for the decrease in the surface tension of water and therefore for the decrease in the interfacial tension between water and alkyd resin.

Aging time	13 days	26 days	35 days
R (μm)	1.9	2.3	2.6
γ/R (N)	4390	3720	3230
γ (mN/m)	8.3	8.6	8.4

Table I: evolution of R and γ of the water/alkyd resin emulsion with aging as determined by ultrasound and shear dynamic measurements.

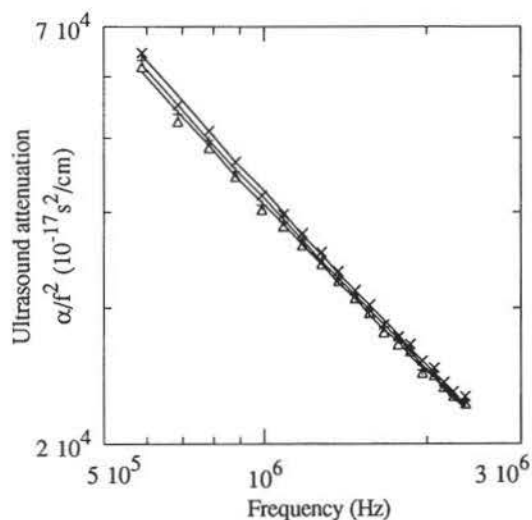


Fig. 3 : Ultrasound attenuation of the emulsion as a function of frequency. Effect of aging (Experimental data : after 13 days (x), after 26 days (+), after 35 days (Δ); best fits according to Fokumoto's model (1992) : solid lines).

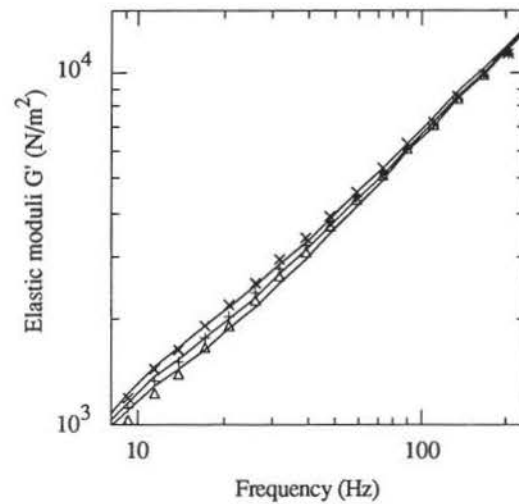


Fig. 4 : Elastic modulus of the emulsions versus frequency. Effect of aging time (Experimental data : after 13 days (x), after 26 days (+), after 35 days (Δ); best fits according to Palierne's model : solid lines).

It can be concluded that the first part of our investigation proved that the new experimental techniques developed for the "in-situ" characterization of a water/alkyd resin emulsion are very useful in the context of the determination of R and γ . We therefore decided to apply the same techniques to the effect of the addition of non-volatile additives, such as glycols and macroglycols to water.

1.2. Water+glycols and macroglycols/alkyd resin emulsions.

1.2.1. Materials

A preliminary qualitative study with optical microscopy in our laboratory showed that the molar mass of different poly(ethylene oxide) glycols (PEO) put into water had a strong influence on the size of the droplets (Aurenty, 1995 b). A decrease in the size of the droplets was observed when increasing the molar mass, indicating that PEOs with a sufficient molar mass could play an important role at the interface between water and alkyd resin. This feature was rationalized by the fact that PEO

is very soluble in water and only partly soluble in the alkyd resin. In such conditions, a stabilization of the emulsion could be envisaged as follows : some PEO chains share their length between the two media by multiple crossing of the interface and thus produce a decrease in the interfacial tension.

Unfortunately however the limitation of optical microscopy in terms of minimum detectable size (around 1 μm) made it impossible to detect any difference for PEOs of molar mass higher than 400. A more powerful approach was needed and it was decided to investigate the role of the molar mass of PEO additives from ethylene glycol to PEO 100000 with the ultrasound technique which can characterize emulsions with droplet sizes between 50 nm and 5 μm .

A second conclusion of this preliminary study was that the addition to the alkyd matrix of poly(propylene oxide) glycol (PPO) 4000, which is insoluble in water within our temperature range, produced a drastic increase in the size of the droplets. This observation clearly showed that the relative solubility of a given additive in the two liquid phases plays a fundamental role on the resulting properties of the emulsion reflected here by the variation of the average droplet size. In order to gain a deeper insight in this aspect, we carried out an investigation on the effect of PEO-PPO triblock-copolymers of different compositions on the droplet size.

The concentration of the different additives in water was kept constant at 4 % w/w. In order to cover a large range of molar masses, high purity ethylene glycol (EG), triethylene glycol (TEG), and PEOs of molar masses 400, 1500, 4000, 10000, 35000 and 100000, respectively, were used. Concerning the PEO-PPO copolymers, 4 Pluronic samples from BASF were tested. Their general structure was :



with $m \approx 30$ and $n \approx 2, 5, 13$ and 80 , respectively. The PEO fraction in these macromolecules was then 10, 20, 40 and 80%, respectively.

The alkyd resin used as the matrix of the emulsion was the same as described in 1.1. but the emulsification procedure was changed as follows: the alkyd resin was mixed for 3 minutes in a dispermat CV at 10000 rpm with a 40 mm diameter stirrer in order to attain the doughnut effect. The aqueous solutions were then added dropwise to the alkyd resin and the two liquids were homogenised for 4 minutes at 10000 r.p.m., then manually for 1 minute and finally for 4 more minutes at 10000 r.p.m. Each emulsion has an aqueous volume fraction of 15 %. During the emulsification, a temperature rose to about 70 °C was observed. All the measurements were carried out seven days after emulsification so that the air bubbles had been completely removed.

1.2.2. Results and discussion

1.2.2.1. Ultrasound measurements

Ultrasound measurements were carried out at 30 °C in the experimental cell described above. The attenuation data concerning the emulsions containing PEO of different molar masses and PEO-PPO copolymers were compared with values calculated from Schröder's model (27) which takes into account the contribution of the viscoelastic properties of the matrix to the ultrasound attenuation of the emulsion. The best fit between the experimental data and the theoretical model gave the corresponding values of the droplet's radius R as shown in figs. 5 and 6

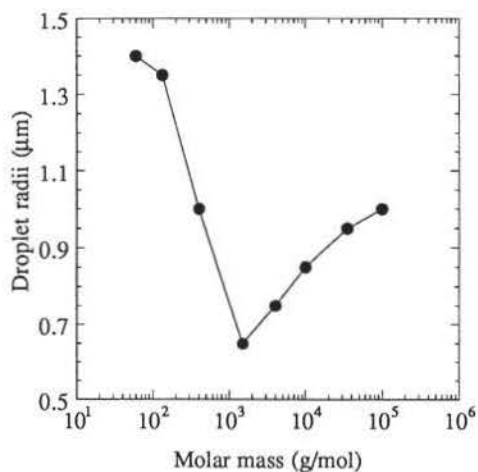


Fig. 5 : Effect of the molar mass of PEO additives on the size of the droplets as determined by ultrasound and using Schröder's model (1991).

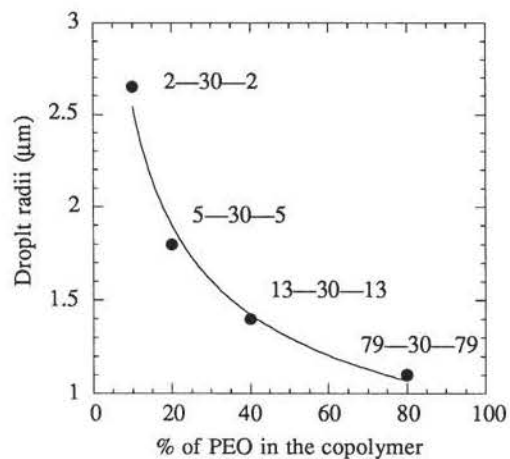


Fig. 6 : Effect of the fraction of PEO in the PEO-PPO copolymers on the size of the droplets in the emulsion as determined by ultrasound with Schröder's model (1991).

The surface tension of the aqueous solutions dispersed in our emulsions were measured with the maximum bubble pressure method using a Sensadyne PC 6000 at 1 bubble/s. The results are given in table II.

Additive	Surface Tension (mN/m)	Additive	Surface Tension (mN/m)
EG	70.5	PEO 35000	61.5
TEG	65.4	PEO 100000	63
PEO 400	65	2-30-2	32.1
PEO 1500	62.6	5-30-5	34.1
PEO 4000	62	13-30-13	35.7
PEO 10000	62.3	79-30-79	42.5

Table II : surface tension of the aqueous solutions (4 % additive in water) as measured by the maximum bubble pressure method.

Fig. 5 shows an interesting trend, viz. a dramatic decrease of the droplet size when going from EG to PEO 1500 followed by a more moderate increase of the droplet's size from PEO 1500 to 100000.

As for the surface tension measurements, it can be concluded that the surface activity of PEO at the *air/water interface* was rather low. A rapid decrease of about 10 mN/m and a subsequent stabilization around 62 mN/m was observed with increasing chain length.

A comparison of the droplet sizes obtained with PEO macroglycols ($R \leq 1 \mu\text{m}$), i.e. excluding EG and TEG which have no macromolecular character, with the droplet size obtained in the same emulsification conditions for pure water ($R = 1.25 \mu\text{m}$), suggests that PEO has an interesting surface activity in the case of our emulsions which allows a better dispersion of the water droplets. This interfacial activity seems more efficient than the surface activity of PEO at the air/water interface discussed above. The origin of this stabilization could be due to a lowering of the interfacial tension induced by the special interfacial configuration of PEO discussed earlier which obviously does not apply to small homologous molecules (EG, TEG) incapable of multiple boundary crossings.

The stabilization of the emulsion showed a maximum efficiency for a PEO with a molar mass of 1500. This fact has not yet been rationalised.

Concerning the results obtained with the 4 triblock PEO-PPO copolymers, the first observation was that the droplet size obtained with that series of additives was higher than that obtained for pure water ($R = 1.25 \mu\text{m}$) except for the 79-30-79 copolymer. The presence of a non hydrophylic PPO inner block seems to produce the same effect as that observed in our preliminary study where the introduction of PPO 4000 in the alkyd resin resulted in an important increase in the size of the droplets. The fact that the solubility of the copolymer in water increases as the PEO block length increases, could be the key parameter controlling the droplet size in the emulsions. In fact, the migration of a small amount of the additive from the aqueous phase to the alkyd matrix can reduce considerably its viscosity and thus promote a more efficient coalescence of the droplets after emulsification.

Apart from this general tendency to destabilization induced by the PPO moieties, there is also a more specific role of the relative proportion of PEO/PPO on the droplet size as shown in fig. 6. The rapid decrease in R when the PEO chain length increases indicates once again that these hydrophilic structures have a relative stabilizing effect on the emulsions. As in the case of pure PEO, this effect is more pronounced for shorter chains than for longer ones. Thus for example, the size of the droplets fell from $2.65 \mu\text{m}$ for the 2-30-2 copolymer to $1.8 \mu\text{m}$ for the 5-30-5 copolymer whereas the size decrease between the 13-30-13 and the 79-30-79 copolymers was only of $0.3 \mu\text{m}$.

Once more, the aqueous solution surface tension measurements are not related to the phenomenology of emulsification, as shown in table II. In fact, the surface activity of the copolymers at the air/water interface decreased with increasing PEO chain length, whereas at the water/alkyd resin interface, the stabilization of the emulsion was enhanced.

1.2.2.2. Shear dynamic measurements

Shear dynamic measurements were performed on the same emulsions. The relaxation of the droplets was observed at different frequency ranges, but unfortunately it was impossible to fit the experimental data with Palierne's model. Searching for the causes of such an anomaly, we discovered that slipping occurred between the wall and the probes in the case of the emulsions containing the additive. The measurements were carried out with different gap widths and gave non superposable curves because of slippage which rendered the quantitative determination of γ/R impossible. This effect was more pronounced for the coarser emulsions obtained with the addition of the copolymers 2-30-2, 5-30-5 and 13-30-13, than for the finer one's. A visual evidence for that effect was observed on the wall of the beaker containing the coarser emulsions : the wall behaved as if it had been lubricated.

2. Interactions between fountain solution and plate

The spreading of the fountain solution of the non-image area of the plate is a highly dynamic process which controls the printing quality. To our knowledge, the effect of the additives on the spreading rate of the fountain solution on the aluminium oxide surface has not been the object of any previous publication. It was therefore decided to build an experimental device that could follow the spreading kinetics of liquid drops on solid surfaces by recording the contact angle versus time.

2.1. The experimental system (fig. 7)

A high speed video camera (Pulnix TM6701-AN) which takes 60 images per second in the standard configuration (520 x 520 pixels) was adapted to capture 200 images/s in the configuration of 100 x 320 pixels. This rectangular configuration is better suited to our needs because the shape of the spreading drop evolves longitudinally. Furthermore, the higher acquisition frequency obtained in such conditions is particularly useful in our context. The camera was connected to a VPM video card which was programmed to record the images in real time. The card was able to stock about 3 Mo which represent about 140 images in the 200 Hz configuration. The acquisition frequency had to be defined before each measurement.

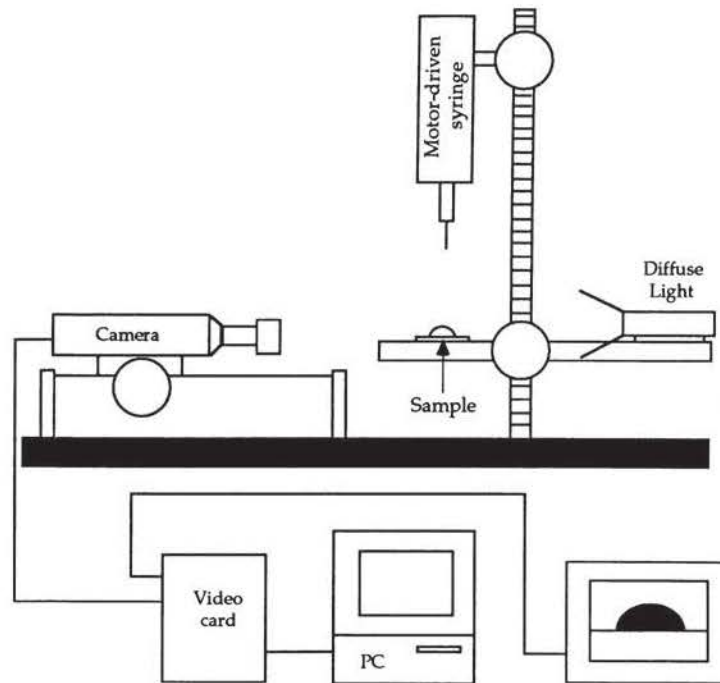


Fig. 7 : schematic representation of the experimental system.

The offset plate was glued to a metallic plate which could be oriented in all directions in order to reach perfect orizontality. In order to follow in an optimum fashion the moving triple points at the edges of the drop, the camera axis formed a slight angle with respect to the plate surface. First of all the contact line between the solid and the liquid has to be defined in the image analysis program by a straight-line placed exactly at equal distance between the top of the syringe and its reflected image on the plate. An automatic threshold which could be manually set was then applied to the image. Drops of 5 to 10 μl , depending on the surface tension of the liquids, were slowly generated at the flat top of the needle with a motor-driven system pushing the piston. The set-up was illuminated from above with a diffuse neon light powered by a high frequency ballast which transformed the 50 Hz line into a 30 KHz in order to obtain the same luminosity for all images during the acquisition at 200 images/second. The drop was released from the needle in such a way that it touched the surface immediately after being detached. The capture of the images began when the drop intercepted the reference contact-line described above. A minimum of 10 pixels of the straight-line

had to be intercepted in order to start the acquisition. In the experiments described below, the contact-angle evolution of the drops on the aluminium oxide surface was recorded only for the first 500 milliseconds.

For each image, the program analysed the contour of the drop and determined the drop height h and its diameter D . The standard equation

$$\tan \frac{\theta}{2} = \frac{2h}{D}$$

was applied in order to determine the contact angle θ . After each experiment, the file containing all θ values was stored on a PC 486 connected to the video card.

In the same condition of illumination and threshold, θ values were reproducible within $\pm 1^\circ$.

2.2. Materials

The plate samples were kindly provided by Polychrome and were taken from the production line before the interlayer and coating processes. The aluminium surface was grained electrolytically. 3.25 g/m^2 of aluminium oxide were measured on the surface and the roughness parameter R_a was found to be $0.57 \text{ }\mu\text{m}$.

Experiments were carried out with pure water and 2 isopropanol solutions in water.

2.3. Results and discussion

The results obtained with the three solutions are reported in fig. 8.

The first observation was that after some oscillations the contact angle of pure water on the aluminium oxide surface reached a stable value of about 15° . This result suggested that the non-image area was certainly contaminated by hydrophobic impurities which inhibited the spreading of pure water because otherwise its high surface energy would have induced an immediate total wetting ($\theta = 0$). This classical problem underlined the necessity of developing an adequate cleaning procedure for our surfaces.

The addition of 10 % of isopropanol to water produced total spreading of the liquid on the solid, whereas a drastic increase of the isopropanol concentration to 50 % improved only marginally the spreading efficiency. The parameters which will be studied shortly are the surface tension and the viscosity of the liquids which seem to act in opposite ways.

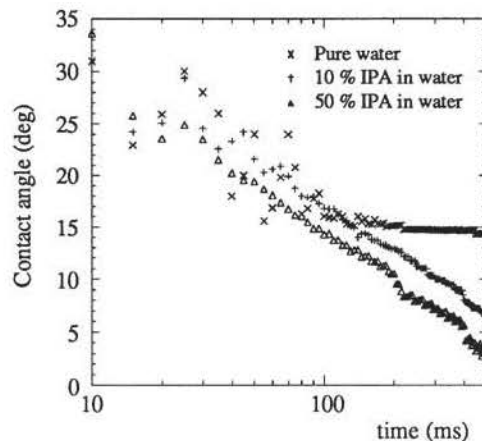


Fig. 8 : Wetting kinetics of pure water, 10 % isopropanol in water and 50 % isopropanol in water on the non-image area of the plate.

Conclusion

The "in-situ" characterization of emulsions was made possible by the use of the ultrasound technique which provided encouraging results concerning the determination of the aqueous droplet size. The variation of this parameter as a function of the structure and the molar mass of various glycols and macroglycols was rationalised in terms of their hydrophilic vs hydrophobic character and their consequent partition between the phases and their positioning at the interface. Unfortunately, the encouraging results obtained with the water/alkyd resin emulsion concerning the "in-situ" determination of the interfacial tension through shear dynamic measurements could not be confirmed for the moment when the additives were added, because of a slipping effects between the sample and the wall of the measuring cell. For the second part of our investigation dealing with the water/plate interactions, an experimental device was constructed in our laboratory and the first wetting kinetics obtained. The phenomenology observed in the first fraction of a second is meaningful and incites us to pursue our research in this direction. In that context, different studies concerning the cleaning procedure of the surface, the role of the humidity of the plate and the effect of surface active agents are in progress. Other parameters such as pH and viscosity of the solutions will also be tackled.

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Literature cited

- Andersen, P.W.
1958 *Int. Bull. Printing & Allied Trades*, vol. 6, pp. 109.
- Aurenty, P., Le Nest, J.F., Gandini, A.
1994 *TAGA Proceedings*, pp. 339.
- Aurenty, P., Schröder, A., Gandini, A.
1995 a *Langmuir*, in press.
- Aurenty, P., Lasfargue, C., Gandini, A.
1995 b *Grenoble TAGA Student Chapter*, vol.1, pp. 24.
- Bassemir, R.W.
1992 *TAGA Proceedings*, pp. 365.
- Bitter, J.H.
1956 *Int. Bull. Printing & Allied Trades*, vol.1, pp. 24.
- Braun, F.
1985 *American Ink Maker*, vol. 2, pp.26.
- Chambers, D.
1994 Ph.D. Thesis, London University.
- Fetzko, J.M.
1986, 1988 *A literature survey*, Lehigh University, National Printing Ink Research Institute, Inc. : New York..
- Fowkes, F.M., Riddle, F.L., Pastore, W.E., Weber, A.A.
1990 *Colloids and Surfaces*, vol. 43, pp. 367.
- Fukumoto, Y., Yzuyama, T.
1992 *Phys. Rev. A* , vol. 46, pp. 4905.
- Graebing, D., Muller, R., Paliarne, J.F.
1993 *Macromolecules*, vol. 26, pp.320.
- Harker, A.H., Temple, J.A.G.
1988 *J. Phys. D: Appl. Phys.*, vol. 21, pp. 1576.
- Kaelble, D.K.
1971 *Physical Chemistry of Adhesion*, Wiley : New York.
- Karttunen, S., Lindquist, U.
1978 *Graphic Arts in Finland*, vol. 2, pp. 4.

- Karttunen, A., Virtanen, J., Lindquist, U.
 1985 *Proceedings of the 18th IARIGAI Conference*; Banks :
 London, pp 241.
- Laraignou, R.
 1963 *Proceedings of the 7th IARIGAI Conference*; Banks :
 London, pp. 411.
- Lelah, M.D., Marmur, A.
 1981 *J. colloid Interface Sci.*, vol. 82, pp. 518.
- Lloyd, P., Berry, M.V.,
 1967 *Proc. Phys. Soc.*, vol. 91, pp. 678.
- Marmur, A., Lelah, M.D.
 1981 *Chem. Eng. Commun.*, vol. 13, pp. 133.
- Owens, D.K., Wendt, R.C.
 1969 *J. Appl. Polym. Sci.*, vol. 13, pp. 1741.
- Palierne, J.F.
 1990 *Rheol. Acta*, vol. 29, pp. 204.
- Pesach, D., Marmur, A.
 1987 *Langmuir*, vol. 3, pp. 519.
- Rosenberg, A.
 1985 *Proceedings of the 18th IARIGAI Conference*; Banks :
 London, pp. 264.
- Schröder, A.
 1991 Ph.D. Thesis, Strasbourg University
- Ström, G., Vanderhoff, J.W.
 1984 *Proceedings of the 17th IARIGAI Conference*; Banks :
 London, pp 229.
- Wu, S.
 1982 *Polymer Interface and Adhesion*, Dekker : New York.