Lithographic Emulsion Rheology at Low and High Shear Rates

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The rheology of emulsions of water in varnish and water in complete lithographic ink was measured at shear rates covering the range 10^{-2} s^{-1} – 10^4 s^{-1} and compared with the behaviour of unemulsified samples. The low shear measurements were made with a conventional rotational rheometer. High shear measurements were made using a 'Multipass' capillary apparatus. The presence of water droplets always increases emulsion viscosity at low shear, and the effect is in many cases well predicted by the Batchelor equation. At high shear rates measured emulsion viscosities are usually lower than for the unemulsified ink. The reasons for this behaviour are discussed, and where appropriate evidence for microstructural change is presented. Inks for which there is a large change in viscosity upon emulsification tend to be more difficult to print and are susceptible to loss in density as the water feed is increased.

Introduction

Lithographic printing is a complex process and there are many variables that can affect the printed result. One of the most important, as discussed by Krishnan (1999), is the manner in which the rheological properties of the ink are modified by the incorporation of water. The amount of water emulsified during normal operation of a press is about 10-15%, although this figure may rise significantly when certain types of lithographic problem occur, and the shear rate experienced by the emulsion between the rollers of a press is about 5,000 s^{-1}. (Claypole et al, 1996). The aim of this paper is to report measurements of water/heatset ink

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emulsion rheology made on a novel capillary instrument, and to use optical observations of water-in-varnish emulsions under shear to gain an insight into the mechanisms influencing emulsion rheology as the shear rate increases.

Measurement of emulsion rheology at low shear rates is relatively straightforward, using either cone and plate or concentric cylinder geometry. However, for viscoelastic samples, these techniques are reliable only up to shear rates of a few hundred reciprocal seconds. Above this limit edge fracture effects can become significant (Hutton, 1963). A number of authors (e.g. Durand et al, 1993, Cartwright, 1966) report an increase in the viscosity at low shear rates as the volume fraction of water increases.

Higher shear rates are possible using a falling bar method such as the automated Laray described by Chou et al (1993). However the sample is open to evaporation, and there remains the uncertainty that large (perhaps coalesced) water droplets might bridge the gap between the rod and the collar or at least form a lubricating film on one of the metal surfaces.

A novel capillary instrument, known as the Multipass Rheometer (MPR), has been developed by the University of Cambridge (Mackley et al, 1994). This equipment offers a number of advantages, and has been used, together with low shear rotational measurements, to build up a comprehensive picture of emulsion rheology at both low and high shear rates. This has been done first for simple water-in-varnish emulsions, and thereafter for emulsions of finished inks.

Materials

The samples tested are all either heatset inks that have been commercially supplied, or varnishes used in their manufacture. The advantage of testing component varnishes is that the development of low shear structure due to pigment interactions is avoided, so the underlying trends can more easily be studied. Furthermore, changes in microstructure can more readily be optically observed. Varnish A is a rosin modified phenolic resin solution of good solubilty. Varnish B is similar but uses highly structured resins of limited solubility in the diluent. Emulsions were made by stirring 100 g of an ink/water or varnish/water blend for two periods of 30 seconds on a Dispermat stirrer at 4000 rpm with a 4 cm diameter sawtooth blade. All emulsions were made with distilled water. Control samples without water were stirred in the same way. All tests were made at 30°C except those on the alkyd which was tested at 20°C.

Experimental

The high shear rheology was measured on a Multipass Rheometer (MPR), a capillary instrument developed at the University of Cambridge, (Mackley et al, 1994, and shown schematically in Figure 1). Two pistons operate in tandem, and

are used to drive the fluid sample through a small capillary insert. This instrument is well suited to the measurement of ink emulsions for the following reasons:

1. Choice of an appropriate capillary permits measurement of the viscosity over a wide range of shear rates, typically covering the range 10^1-10^5 s^{-1}. This is more than adequate to cover the range experienced on a press.
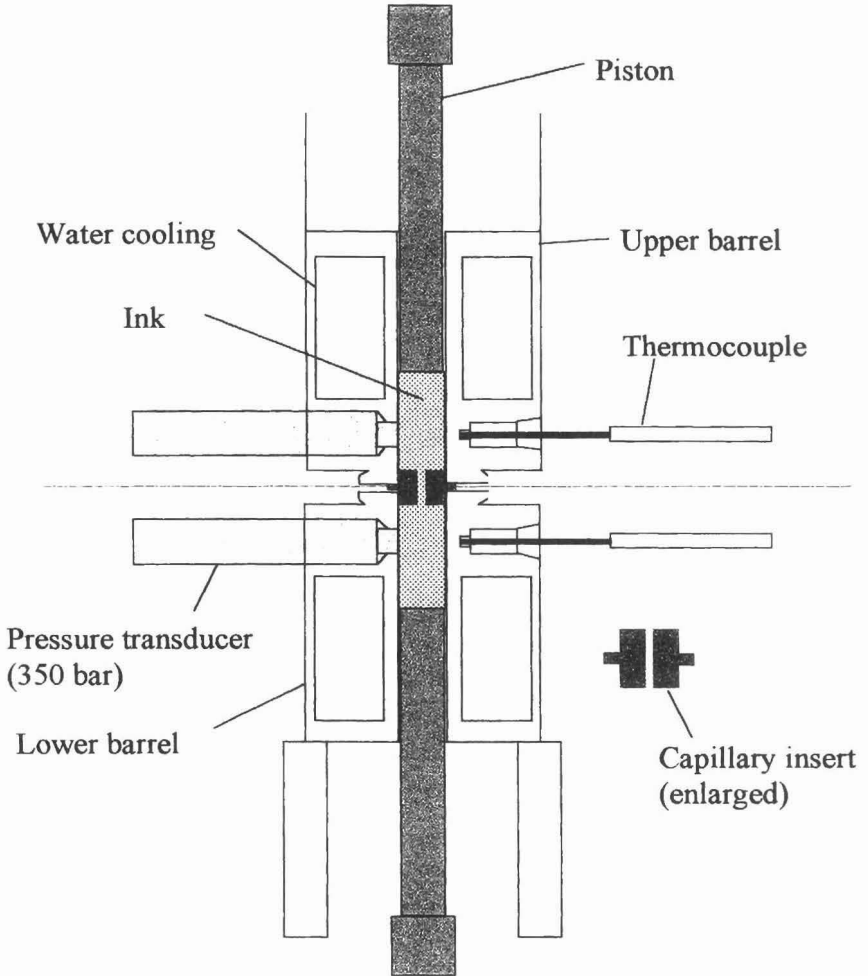

Figure 1 The Multipass Rheometer

2. Possible surface slip/lubrication effects can be minimised by using a screw thread instead of a straight walled capillary.

3. Experiments can be conducted at elevated pressure by forcing the pistons together. This is particularly useful as a technique for eliminating air bubbles.

4. There is no risk of evaporation.

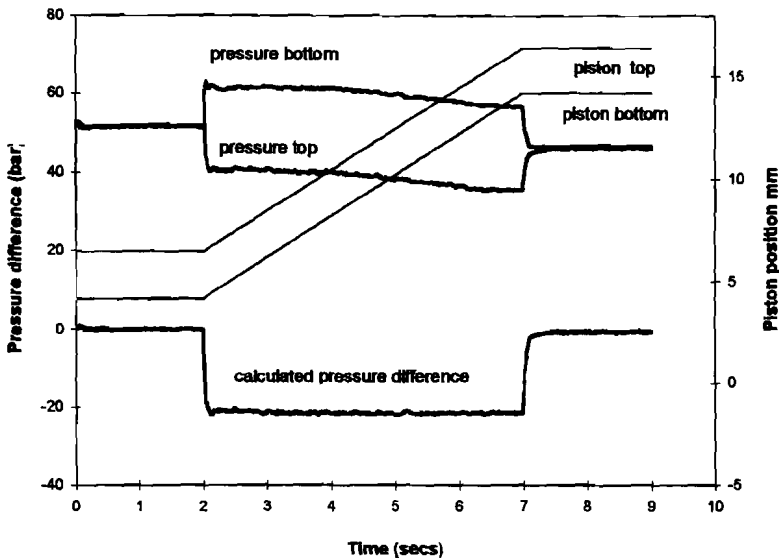5. Global temperature is well controlled by the water circulation system.

Figure 2 Single pass experiment, piston movement and pressure changes.

The result of a typical experiment is shown in Figure 2. The system has been pressurised to 50 bar, and the pistons moved in tandem to force the sample through a 1.1 mm diameter 28 mm long capillary. Pressure transducers are mounted in both barrels so that the pressure difference across the capillary can readily be calculated. The measured pressure difference quickly achieves a constant value following a short initial instability which arises mainly because each piston takes a short time to achieve constant speed. An estimate of the viscosity is obtained from the following expression,

$$\eta = \frac{\Delta \mathrm{P} r^4}{8LR^2 V_p}$$

where ΔP is the measured pressure difference across a capillary of length L and radius r, R is the radius of the barrel, and V_p is the piston velocity. A number of assumptions are implicit in such a calculation: notably (a) that entrance effects are negligible compared with the shear flow along the length of the capillary, (b) that the velocity profile is parabolic so that the shear rate at the wall is the same as it would be for Newtonian flow, and (c) that shear heating effects do not cause a significant reduction in the measured pressure drops. The methods by which these can be taken into account are described elsewhere (Thompson at al, 2000). The principal interest of the current paper is to report the effect of water on the rheology, and it is assumed that the errors associated with the aforementioned parameters are not significantly altered as a result of the changes in rheology induced by the water.

A flow curve can be built up by repeating the single pass experiment at piston speeds typically between 0.1 mm/s and 20 mm/s. For a 1 mm diameter capillary this will give shear rates in the range 10^2-2×10^4 s^{-1}. The capillaries used for the experiments described were as follows: alkyd, 1.1/1.4 mm diameter 10 mm long screw thread; varnishes, 1.1/1.4 mm diameter 71 mm long screw thread; inks, 1 mm diameter 59 mm long smooth bore capillary. The use of long capillaries allows the generation of measurable pressures at lower shear rates.

Rheology at shear rates below about 100 s^{-1} is more accurately measured on a rotational device. A Bohlin CS50 rheometer with concentric cylinder (C14) geometry has been used for the work described in this paper. Measurements are reliable only to shear rates of about 200 s^{-1}. Thereafter viscoelastic effects reduce the amount of material effectively being sheared in the gap. (Chou, 1992). Alternatively, cone and plate geometry may be used, but this was found in practice to give less consistent results, as well as suffering from a similar elastic effect known as edge fracture (Hutton, 1963).

Observations of microstructure under shear were made using the Linkam shear cell described by Bower et al (1999). The sample is placed between two quartz discs, one of which is rotated to generate the desired rate of shear. This optical stage is mounted on a standard Olympus microscope, and the images recorded with a high speed video (Kodak Motion Corder).

Results

Emulsions of water in alkyd resin

The simplest systems studied were emulsions of water in alkyd resin. The results at low shear are shown in Figure 3. Tested without water the resin is Newtonian throughout the range over which the data is reliable (above about 200 s^{-1} expulsion effects become important). The experimentally observed initial decrease in viscosity for small additions of water is attributed to a solution effect

– the resin will take about 0.5% water before the onset of turbidity. For volume fractions of water within the range 0.5% - 10% an emulsion forms of water droplets within the resin and a Newtonian plateau exists, the viscosity of which increases with increasing water content. At higher concentrations of water there is a further increase in viscosity, and a floc structure develops, which is partially broken down at a shear rate of 1 s^{-1}. (Figure 4).
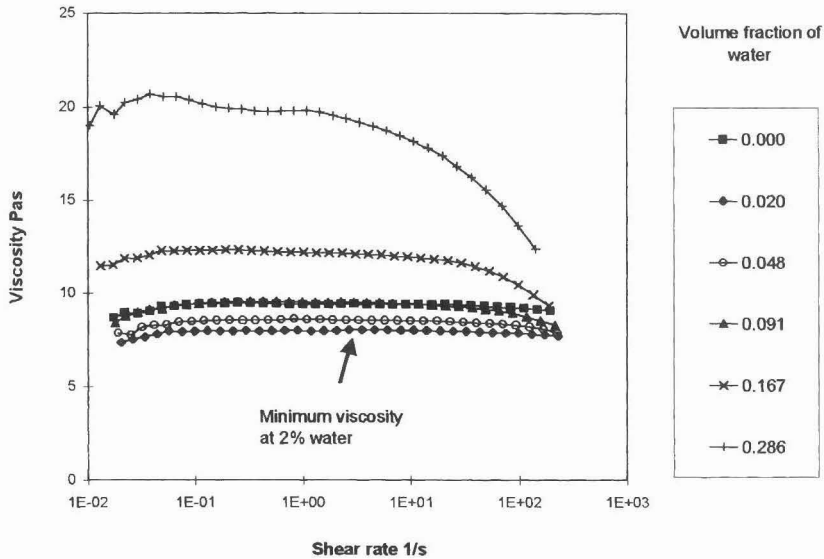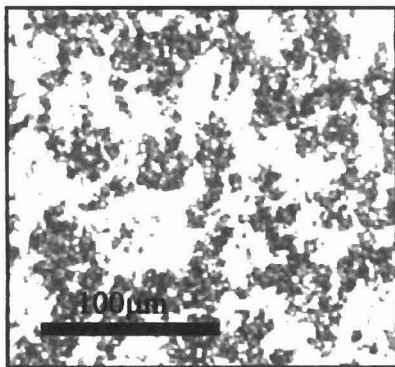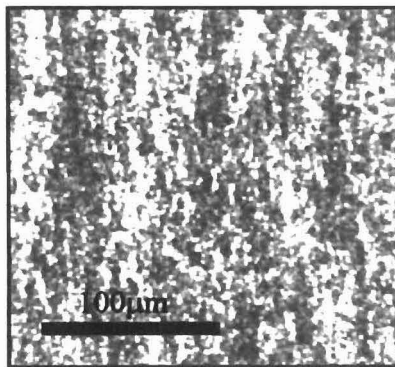

Figure 3 Low shear data for water in alkyd emulsions

At rest

Subject to a shear of 1 s^{-1}

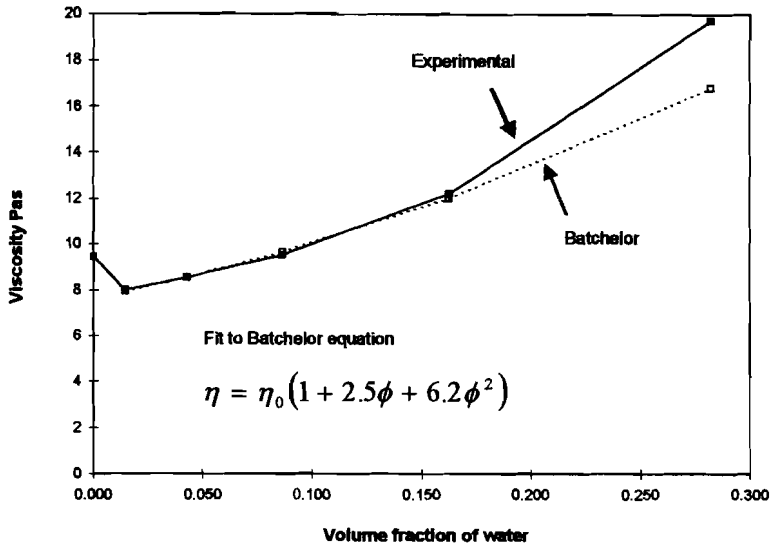Figure 4 Microstructure of emulsion droplets at $\phi = 0.167$

Figure 5 Fit of the low shear rate alkyd emulsion viscosities to the Batchelor equation using the data of Figure 4 at 0.1 s^{-1}

Figure 5 demonstrates that the data within the Newtonian plateau region are consistent with the model of suspension mechanics developed by Batchelor (1977). This is an extension of the well known Einstein model for hard spheres, where the $6.2\phi^2$ term takes into account the effect that each droplet has on its near neighbours. Implicit in this is the assumption that the droplets do not distort at low shear rates – an assumption that is confirmed by direct observation of droplets on the Linkam apparatus (Figure 6). The droplets shown in Figure 6 are larger than those used for the rheological experiments by a factor of 10. Distortion of these large droplets commences at a shear rate of about 10 s^{-1}, and it is therefore expected that a shear rate of about 100 s^{-1} will be necessary to distort the droplets of the finer emulsions used in the MPR and for the rotational rheology.

The results from the Multipass Rheometer for the same water in alkyd emulsions are shown in Figure 7. At all shear rates the viscosity of the 2% emulsion is less than that of the dry material by about 15%. This is again attributed to a solution effect. At the low shear end on the MPR data there is an increase in viscosity for high volume fractions of water, as seen on the rotational rheometer. However, there is a crossover at a shear rate of about $2,500 \text{ s}^{-1}$, and at and higher shear rates emulsion viscosity is not increasing but decreasing as the volume fraction
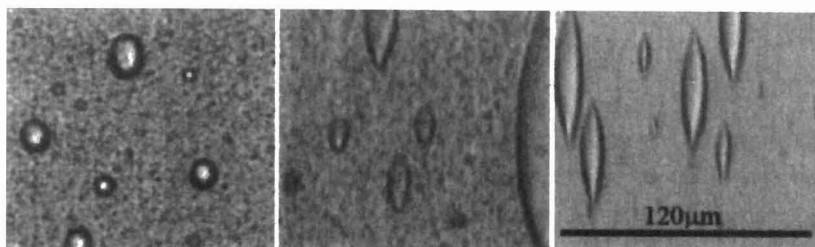
10s⁻¹   30s⁻¹   100s⁻¹

Figure 6 Droplet distortions of water in alkyd at various shear rates. The droplets shown are larger by a factor of 10 than the droplets in the emulsions used for the rheology.
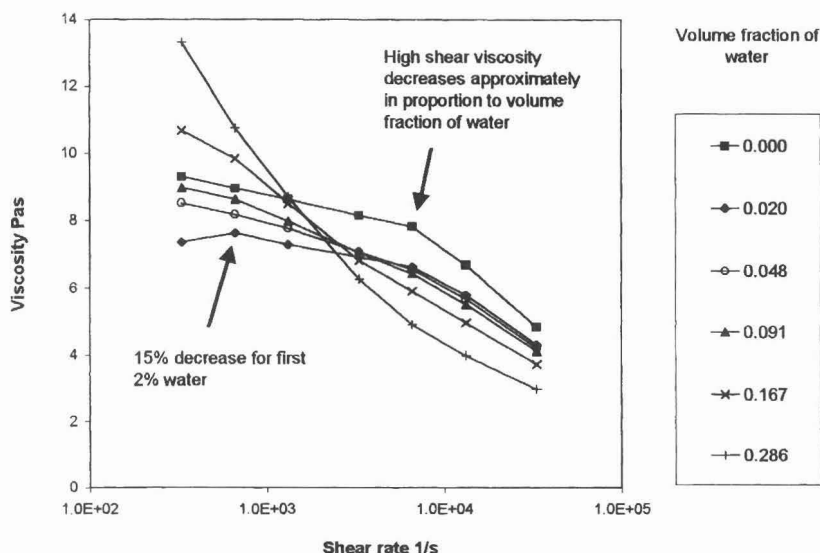

Figure 7 High shear rheology of water in alkyd emulsions

of water increases. The extent of the viscosity reduction is approximately in proportion to the volume fraction of water.

The degree of droplet distortion at the crossover shear rate can be estimated by considering the capillary number (Ca), which is the ratio of stresses which distort the droplet to those which tend to restore it to the spherical configuration (Rallison, 1984):

$$Ca = \frac{\eta \dot{\gamma} r}{\sigma}$$

η is the viscosity of the continuous phase, $\dot{\gamma}$ is the shear rate, r is the radius of the drop and σ is the interfacial tension. Small but discernible distortions are expected to occur from Ca≈0.05, with large distortions occurring when Ca>1.

An estimate of droplet radius (r ≈ 0.75 μm) was obtained from laser diffraction measurements. An estimate of the interfacial tension (5.5 mN/m) was made from droplet retraction experiments following the method of Guido et al (1999). Combined with the measured saturated viscosity of 7.65 Pas, this gives a capillary number of 2.6 at crossover (2500 s^{-1}). Considerable droplet deformation is therefore expected.
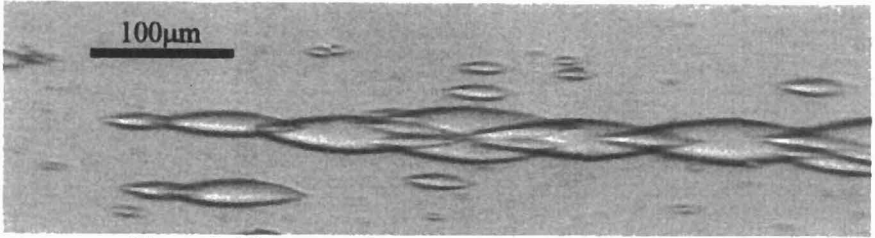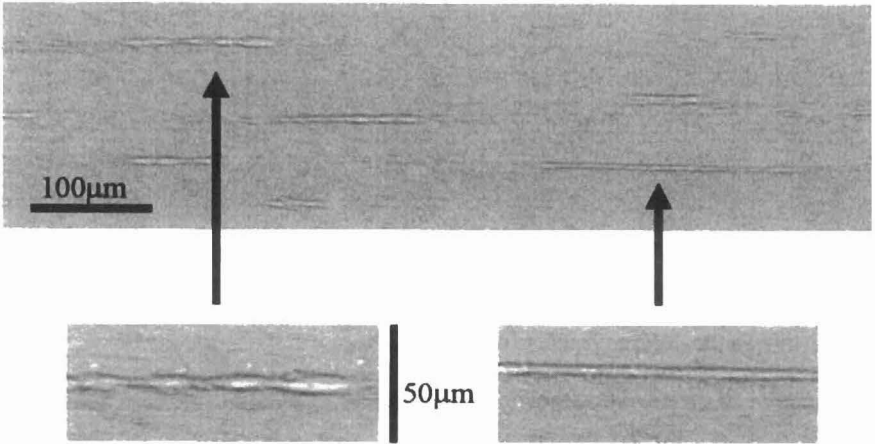

Figure 8 Alignment of water in alkyd droplets under shear

Figure 9 Coalescence of water in alkyd droplets under steady shear
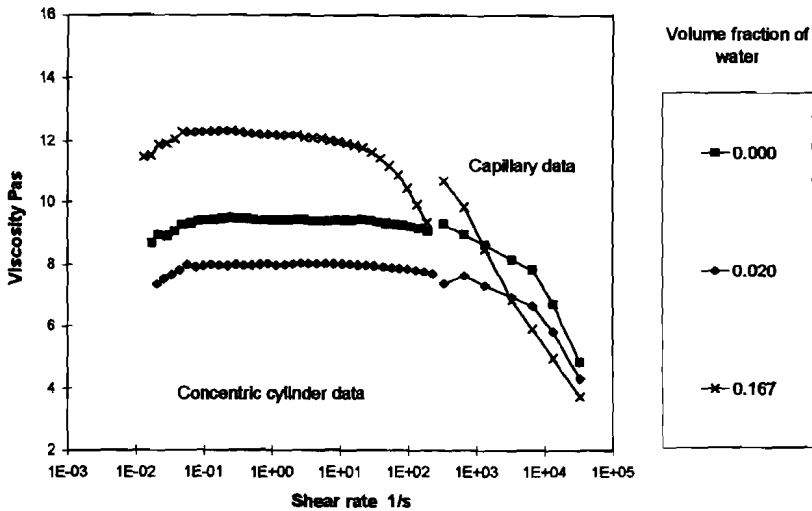(10% water, 30 s^{-1}).

Figure 10 Compilation of low and high shear data for selected water in alkyd emulsions.

The mechanisms giving rise to this rheology are complex. Coalescence of droplets into long filaments has been observed on the Linkam apparatus, and is illustrated in Figure 9. Under steady shear on the Linkam (parallel plate geometry) the droplets have a tendency to align as shown in Figure 8. This alignment can lead to coalescence into long filaments of water as shown in Figure 9. The extent to which this coalescence mechanism occurs in the MPR capillary is not known. (Observation of fluids under shear is possible on the MPR by replacing the capillary with a glass walled slit, but the droplets are too small and move too fast to allow good visualisation). The Bohlin and MPR data are compared in Figure 10. There is good continuity of the data at $\phi=0$ and $\phi=0.020$, but there is a mismatch at $\phi=0.167$. Chou et al (1989) have pointed out that in a concentric cylinder system droplets will tend to collect at the outer wall. In addition the same material is repeatedly sheared on a rotational device, so a greater degree of coalescence might be expected on the Bohlin than on the MPR for the same shear rate. The mismatch in our data is consistent with this explanation.

Water in varnish emulsions

The data for two ink varnishes is presented in Figures 11 and 12. Varnish A is formulated so that the resins are highly soluble in the solvent system. Varnish B contains resins which are only marginally soluble.

Differences in emulsion microstructure are difficult to observe on the Dispermat emulsions, since all the droplets are very fine. The inset images show water in varnish emulsions made under conditions of gentle stirring and demonstrate that the microstructure developed is very different. The emulsions used for rheological evaluation were made in the normal way.

Varnish A is significantly shear thinning even in the absence of water. Apart from this the behaviour is very similar to that of the alkyd resin. Plateau viscosities at $0.1\ s^{-1}$ decrease for small additions of water but thereafter fit the Batchelor model with viscosities which increase at high water content Once again the degree of shear thinning is greater for large volume fractions of water. These trends continue in the MPR data, and whilst the data presented are at relatively low shear rates (for direct comparison with varnish B), further experiments have shown that 'crossover' does occur if the shear rate is increased sufficiently.

Varnish B is also shear thinning in the absence of water. However the form of shear thinning is different: particularly there is a much higher viscosity at very low shear rates, reducing rapidly over the range $0.01 - 1\ s^{-1}$. The reduction in viscosity for small additions of water is still present but the data does not fit the Batchelor model. 'Crossover ' occurs at a shear rate of about $100\ s^{-1}$, and at higher shear rates there is a significant reduction in viscosity with increasing volume fraction.

The viscosity and interfacial tension for the two varnishes were as follows:

	Viscosity at 1000 s^{-1} Pas	Interfacial tension mN/m
Varnish A	13	4
Varnish B	20	2

If the droplet sizes are assumed equal, then the capillary number for varnish B will be about three times greater for the same shear rate. Unfortunately the true droplet sizes are not known because the resin precipitates under the large dilution required for laser diffraction.

Water in heatset ink emulsions

Figures 13 and 14 show the rheology of emulsions of two heatset inks, a cyan and a magenta. The cyan performed well on press. The magenta was susceptible
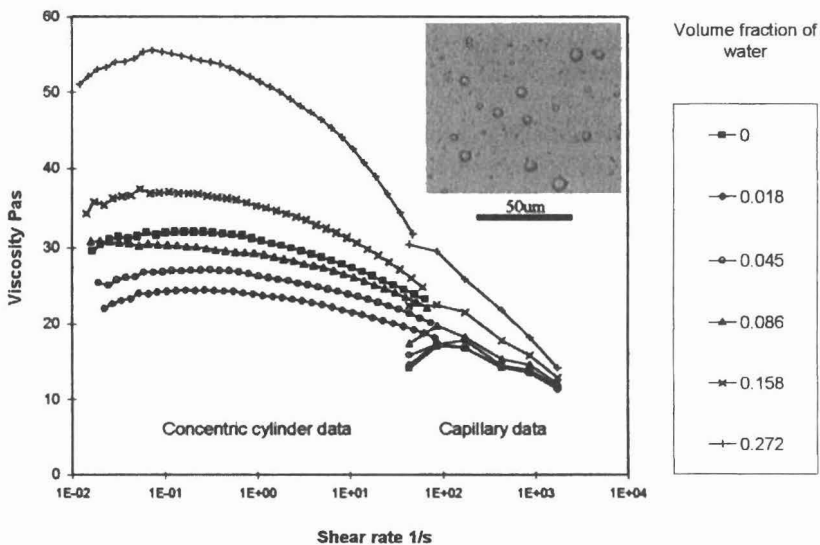
Figure 11 Rheology of emulsions of water in varnish A. Inset shows microstructure of a coarse emulsion made at 10% water content
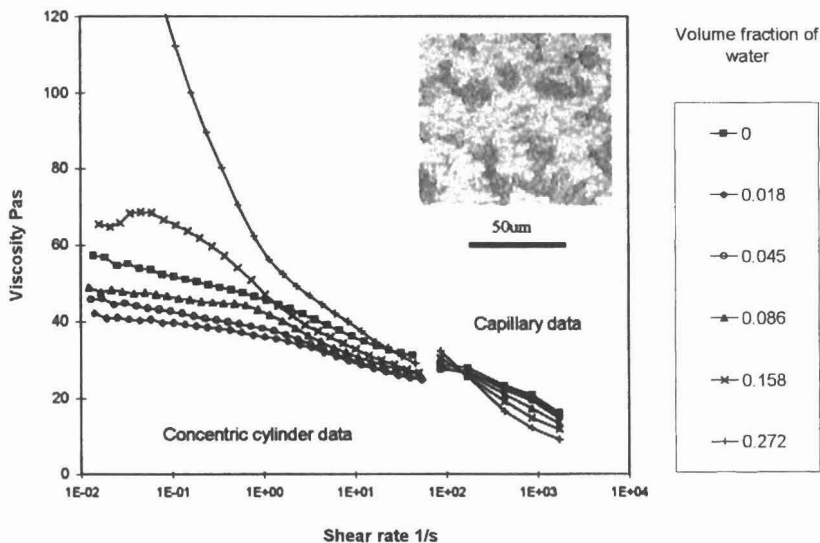

Figure 12 Rheology of emulsions of water in varnish B. Inset shows microstructure of a coarse emulsion made at 10% water content

to loss of colour density when the water feed was increased, and press adjustment was difficult because the colour density took some time to settle to a stable value following adjustment of either the water or ink feed to the press.

The rheology of the cyan emulsions follows some of the trends seen for the varnishes. In the absence of water the ink is shear thinning, to a viscosity of about 5Pas at the shear rates found on the press. The addition of 2% water causes a small decrease in viscosity at all shear rates. Larger additions of water cause an increase in viscosity at low shear rates. At high shear rates the viscosity is changed very little by the presence of the water, with the exception of the 40% water result which we attribute to partial separation of the emulsion. The form of shear thinning is different from that seen with most of the unpigmented systems.

The rheology of the magenta emulsions is considerably different. At low shear rates there is no decrease in viscosity for small amounts of water – in fact the 2% water sample had the highest viscosity – a result which was found to be repeatable. The viscosity at press shear rate is similar to that found for the cyan, but is very dependant upon the water content, decreasing through the range 6.5 – 4.1 Pas as the volume fraction of water increases. Moreover, the onset of the 'crossover' effect is at very low shear rates, about 50 s^{-1}.

Conclusions

The rheology of water in ink emulsions can be interpreted with reference to the following parameters:

1. Most of the component varnishes used are shear thinning, and follow a power law at high shear rates (n typically 0.7-0.8). There is often a Newtonian plateau at low shear rates.

2. The addition of a small amount of water (<0.5%) to most varnishes causes a reduction in viscosity of typically 10-15%. This is consistent with a solution effect. The addition of more than 0.5% water gives rise to optically observable droplets.

3. An increase in water content above the saturated solution threshold causes a viscosity enhancement at low shear rates which for some varnishes follows the Batchelor model. This is consistent with the presence of undistorted droplets.

4. Flocculation of water droplets sometimes occurs and contributes to a low shear viscosity which is higher than that expected from the Batchelor equation. When this is the case there is no longer a Newtonian plateau.
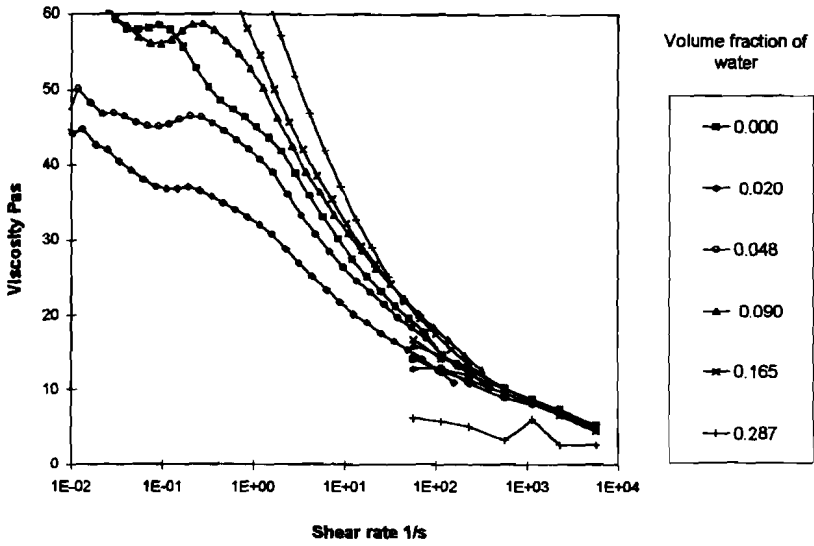
Figure 13 Rheology of emulsions of water in cyan heatset ink
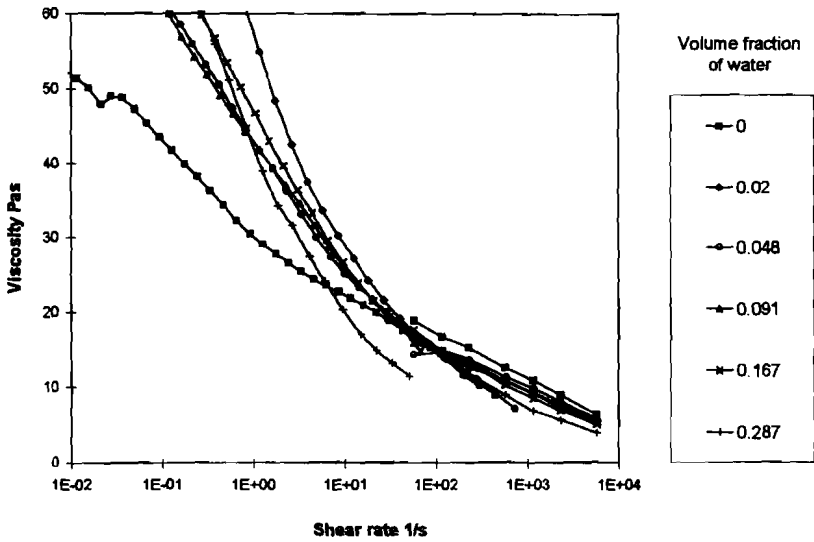

Figure 14 Rheology of emulsions of water in magenta heatset ink

5. Moderate shear will cause deformation of the droplets so that the viscosity enhancement by hydrodynamic disturbance is less than predicted by the Batchelor equation (but still positive).

6. Moderate shear can also cause droplet alignment leading to coalescence. There is reason to suspect that the extent of coalescence is both geometry and time dependant.

7. Emulsion viscosities at very high shear rates are often less than the viscosity of the unemulsified material. For the emulsions of water in alkyd resin, the shear rate at 'crossover' corresponded to a capillary number of 2.6, which is consistent with considerable distortion of the droplets.

8. Non –Newtonian effects due to the pigment may obscure measurement of some of the aforementioned factors in the complete ink, particularly at low shear rates. At high shear rates emulsions of pigmented systems exhibit crossover in a similar manner to that seen for the varnishes.

9. The crossover behaviour is not fully understood and is the subject of further work in our laboratory. A combination of the following mechanisms may contribute:

> Partial coalescence to form layers of water within the ink
> Partial wall slip
> Modification of matrix rheology provoked by the addition of water
> Rotation of water within the droplets

The information relating emulsion rheology to press performance is limited, but it seems to us that it would be an advantage to have a viscosity that is independent of water content at the shear rate relevant to the press on which the ink will be printed. This will give the best chance of maintaining consistent transfer as the water content of the emulsion changes, particularly during the start up period.

Acknowledgements

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