CHARACTERIZATION AND CONTROL OF LITHOGRAPHIC INK EMULSIONS

R. R. Durand, Jr. and O. Wasilewski*

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Abstract

Recently, increased emphasis has been placed on characterization of the rheology of lithographic ink emulsions in addition to the neat ink. A new test method is described for assessing emulsion rheology using a portable parallel plate viscometer. The flow behavior of ink emulsions at various shear rates is compared to the neat ink. Applications are described with regard to the characterization and formulation of web offset newspaper inks. The effects of volume fraction of aqueous phase, ink composition, fountain solution, and temperature are described.

Introduction

It has been recognized for some time that the rheology of lithographic emulsions is important to press performance. Although not quantitatively distinguished in the early days of modern lithography, the desire has always been to

*Sun Chemical Corporation, Carlstadt, New Jersey

insure uniform printing via ink rheology which does not change with water uptake [Grunder (1936); Ellis (1940); Bulloff (1974)]. The recent developments of rheological instrumentation have led to increased efforts to characterize inks and their emulsions [Bassemir and Schubert (1985); Bassemir and Krishnan (1988, 1990); Chou and Cler (1989); Chou and Fadner (1990); D. Iyengar (1990); Wasilewski (1991)]. These studies have emphasized the utility and needs for examination of ink emulsions in greater detail.

As many printing problems have their roots in the ink/water interactions, the emulsion behavior is a critical parameter for laboratory characterization. In our laboratory, we have taken advantage of the recent introduction of inexpensive parallel plate viscometers for characterizing ink and emulsion rheology. A comparison of flow of inks and emulsions over a range of shear rates is possible with this equipment. In addition, the routine formulation of products which have preferred emulsion rheology can be accomplished. The new approach can also become a valuable part of quality control.

Experimental Section

The test methods utilize the following equipment and materials:

Bohlin Instruments V-88 Viscometer

Temperature Bath (30.0 ± 0.1 °C)

Laboratory Mixer (Paddle Blade)

Distilled Water or Press Ready Fountain Solution

The Bohlin viscometer is a portable cone/plate or parallel plate instrument which is suitable for measuring the flow behavior of a variety of letterpress and offset inks. The conditions which are optimal for the consistency of lithographic newspaper ink products were established for the parallel plate arrangement.

For a plate of 15mm diameter with a gap of 0.33mm between plates, a shear rate regime of 0-2100 s^{-1} can be obtained. It is important to note that these conditions were established to be compatible with typical newspaper ink rheology. As the viscometer is computer controlled, time delays and measurements were established to insure stable, reproducible measurement, unencumbered by temperature and thixotropic equilibria.

Initially, the neat ink is used to measure a shear stress vs. shear rate curve (i.e. flow curve) at 30°C. Then, an emulsion is prepared from either water or fountain solution. Typical levels of aqueous solution are 10-15%; however, in some cases, it may be desirable to examine this variable over a wider range. The emulsion is mixed for 5 minutes after all water has been added. The emulsion is then run on the parallel plate unit at the same setting as the neat ink. The flow curves are then compared. In addition to the volume fraction of aqueous phase and chemistry of the fountain solution, temperature is another important variable for examining inks and their emulsions.

Results

Several examples will be examined to illustrate the utility and sensitivity of the technique to characterizing emulsion rheology. Figures 1-1 and 1-2 contrast extremely different behavior possible when emulsions are compared to the neat ink. Figure 1-1 shows how an emulsion of 15% distilled water (B) behaved relative to the neat ink (A). The emulsion flow deviates strongly from the neat ink flow. The emulsion is more resistant to flow and is, in fact, more viscous and short relative to the neat ink. Under these circumstances, the formulation was found to lack flexible lithographic performance on press.

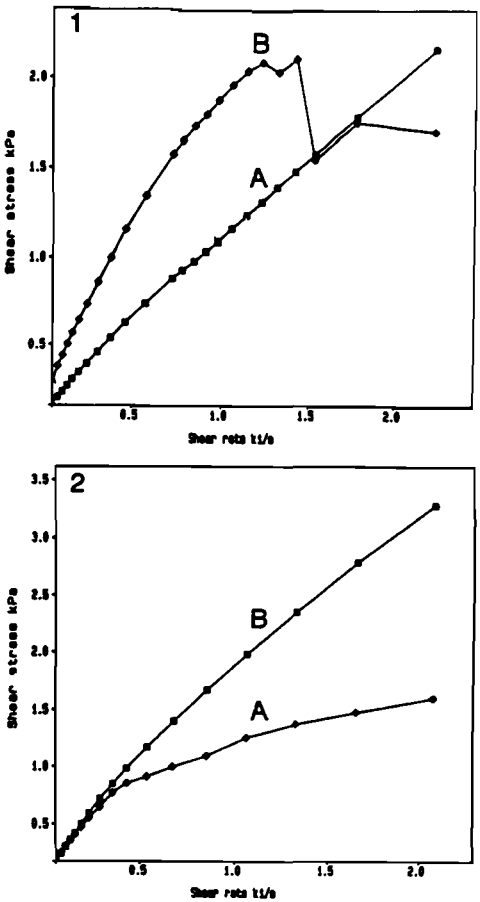


Figure 1. Typical comparison of neat ink and emulsified ink flow curves.

1 - Poor emulsion rheology

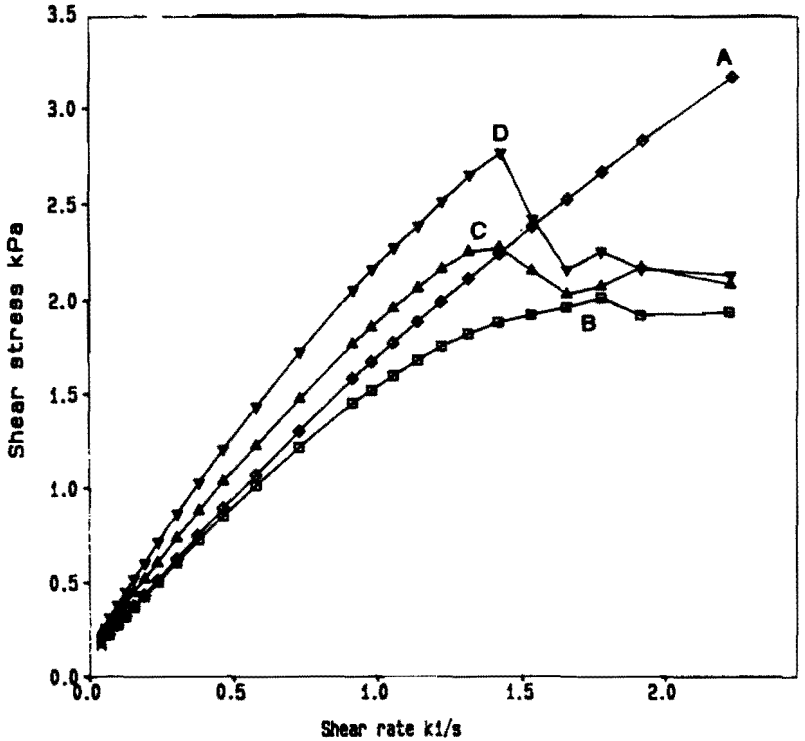
2 - Good emulsion rheology

Figure 1-2 represents a formulation similar to 1-1, but formulated to achieve better emulsion rheology. Notice in the low shear region, there is very similar flow for emulsified and neat ink. In fact, before the emulsion breaks, the viscosity may be lower for emulsified ink. This ink formulation did indeed perform much better than the ink in Figure 1-1 under similar press conditions. The behavior observed here was not significantly altered by the use of fountain solution for the test, but as noted below, it can be an important variable to examine.

Effect of Fountain Solution

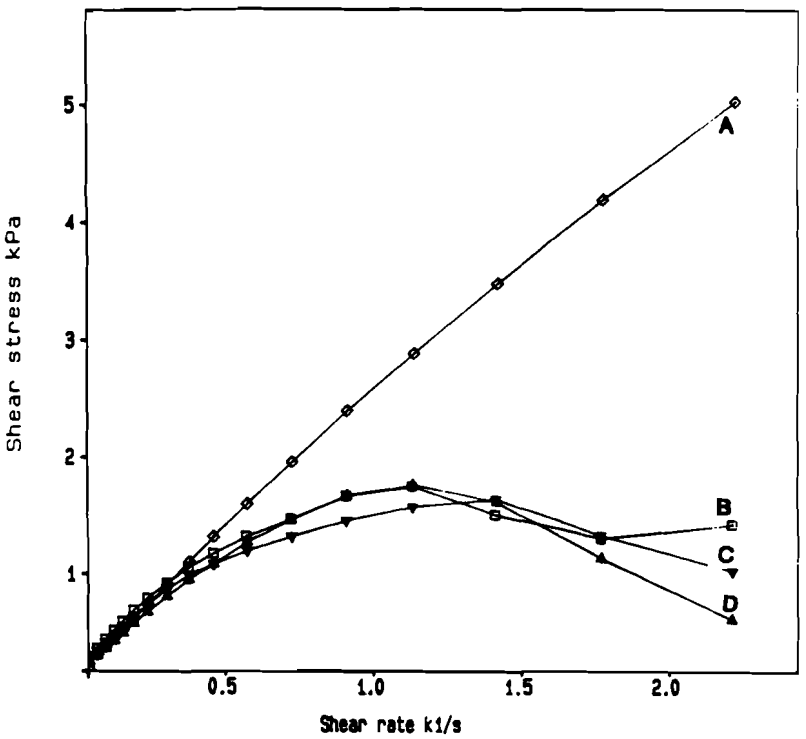
The sensitivity of an ink emulsion to changes in fountain solution is demonstrated in Figure 2. The particular ink examined was run by newspaper printers in three different neutral fountain solutions. Examination of the flow curves shows that the emulsions respond distinctly. It was noted that fountain solution #1 performed best whereas fountain solutions #2 and #3 were subject to random lithographic problems such as mottled print. An analytical investigation of the fountain solutions found that three different surfactant systems were in use. This result emphasized the origins of the compatibility problem often found between fountain solution and ink chemistry.

Figure 3 shows the behavior of a black ink formulated to maintain emulsion rheology which is more independent of fountain solution chemistry. This represents what may be an ideal situation for establishing more flexible ink performance on press. It also demonstrates that distilled water can be effectively used to characterize such an ink in the initial stages of formulation, with the actual fountain solution examined as the final assessment for improving emulsion rheology.



A - NEAT INK
B - 10% EMULSION W/ FOUNTAIN SOLUTION 1
C - 10% EMULSION W/ FOUNTAIN SOLUTION 2
D - 10% EMULSION W/ FOUNTAIN SOLUTION 3

Figure 2. Flow curve comparison of neat ink (A) and three different neutral fountain solutions emulsified at 10%.



A - NEAT INK
B - 15% EMULSION W/NEUTRAL FOUNTAIN SOLUTION
C - 15% EMULSION W/DISTILLED WATER
D - 15% EMULSION W/ALKALINE FOUNTAIN SOLUTION

Figure 3. Product reformulated to minimize sensitivity toward fountain solutions.

The results described in Figure 3 were derived from the adjustment of additives used in the formulation. The ink formulator becomes more aware of the chemical interactions between additives when attempting to improve emulsion stability. This fact is particularly important when considering that raw materials in use are rapidly changing due to product performance demands as well as environmental and economic constraints. It will be extremely important to understand how to maintain ink performance during such transitions. In addition, as noted below, it may be possible to improve material and ink performance by deliberate changes in chemistry.

Effect of Fillers on Emulsion Stability

An examination was made of how filler chemistry could be utilized to affect emulsion rheology. Typical extenders used in newspaper inks may be kaolin clays, calcium carbonate, talc, and silica. Often the kaolin clays are treated to render them more hydrophobic and thus improving their dispersibility in oil based systems. The effect of these clays on emulsion properties has not been reported. The example below emphasizes that they can, in fact, be significant contributors to interfacial chemistry.

Figure 4 shows the flow behavior of a single black formulation in which equal volumes of extender clays of two types were examined separately. The neat ink flow curves (4-1A, 4-2A) were nearly the same; however, the 15% emulsions with distilled water showed sensitivity to the clay filler present. The standard hydrophobic clay behavior (4-1) was improved when an anionic surfactant was adsorbed to the clay (4-2). The rheology of the emulsions for clay treated with an anionic surfactant more closely mimicked the neat ink.

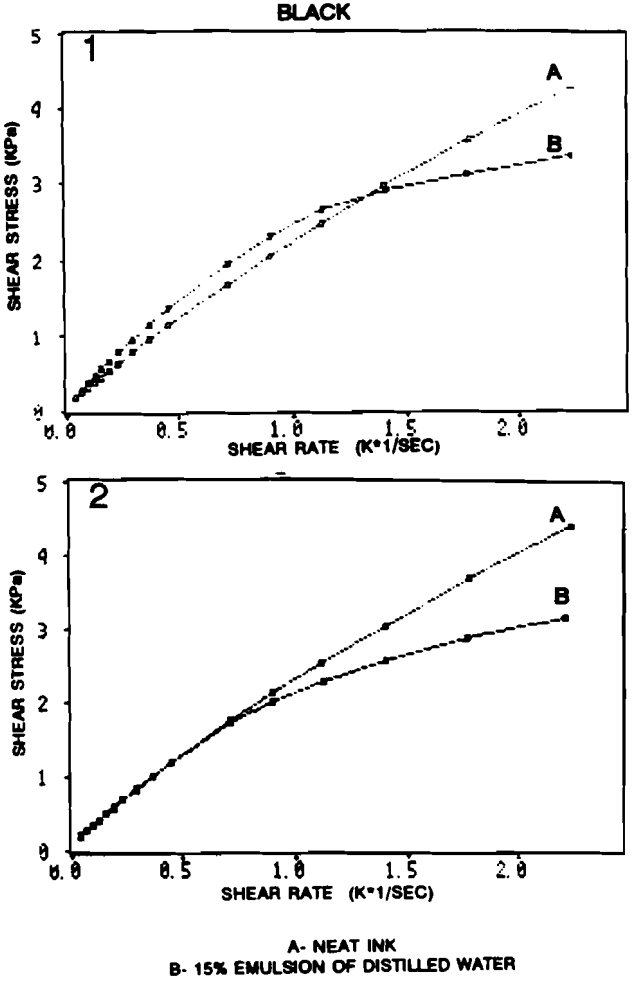


Figure 4. Flow curve comparison of black inks and emulsions.

1) Standard hydrophobic clay treatment

2) Same base clay treated with an anionic surfactant

Figure 5 shows a yellow ink formulation which represents a comparison of the standard hydrophobic treatment on two different clay source materials. There is, in fact, a dramatic impact on emulsion rheology even though the neat inks are identical. The behavior noted here is indicative of the sensitivity of the emulsions to filler chemistry.

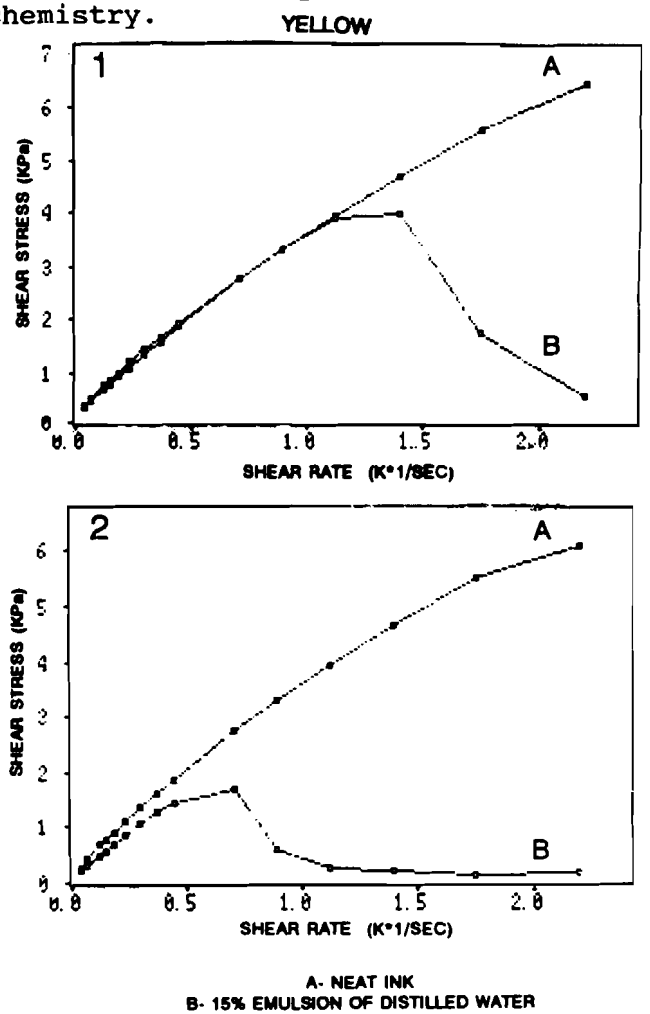


Figure 5. Flow curve comparison of yellow inks and emulsions.

1) Standard hydrophobic clay treatment
2) Same treatment on different clay source

Figure 6 shows a more subtle difference in emulsion behavior when the different clay sources (with the same treatment) were examined in a black ink formulation. The differences are not large, but real. This result is important in that the differences observed could be easily overlooked in a black formulation, but are dramatic in a yellow ink.

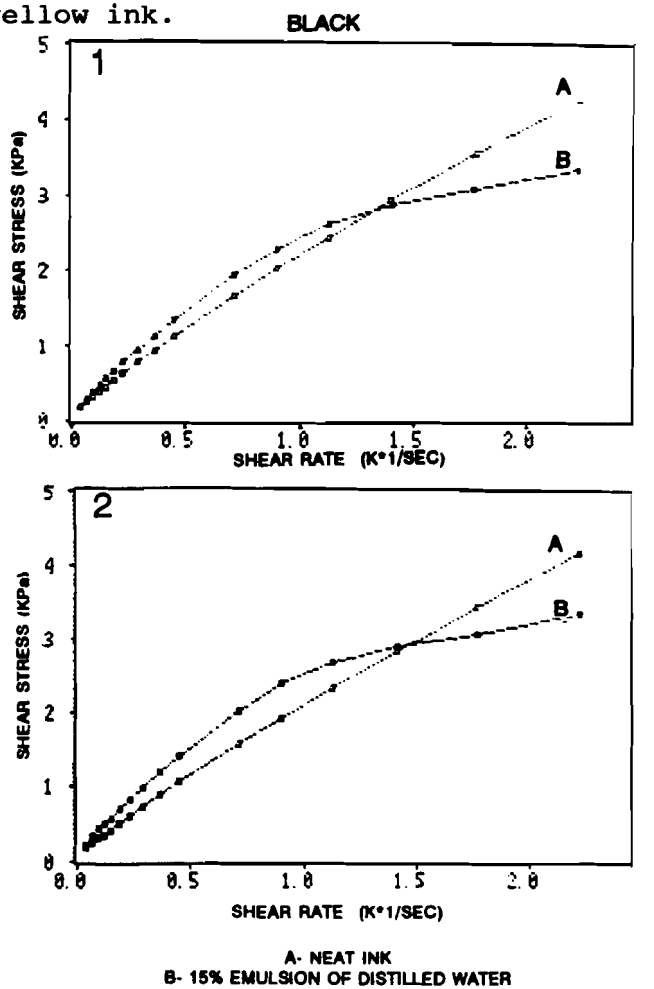


Figure 6. Flow curve comparison of black inks and emulsions.

1) Standard hydrophobic clay treatment
2) Same treatment on different clay source

The physical chemistry of the pigment surface must be playing a role in the observed emulsion behavior. This technique shows distinctions in ink chemistry which are not manifested in any other traditional ink properties (i.e. viscosity, tack, etc.).

Other Variables

As noted in the experimental section, there are additional variables available for testing. Temperature is obviously one which can be important to assessing the stability of emulsions. As the flow of neat ink is also sensitive to temperature, a comparison of behavior of emulsion and neat ink should be carried out at the same temperature.

A second variable which can be useful is the amount of emulsified fountain solution in an ink. This type of comparison can be important to discerning the sensitivity of the ratio of surface active agents in water or oil phases to the observed emulsion rheology. There are also printing configurations (such as keyless inking) which may require adequate flow for higher amounts of emulsified phase.

Discussion

It is our experience that the better performing lithographic newspaper inks show proper emulsion rheology. This has been observed many times for inks sampled throughout the marketplace. There is certainly still an important caveat to consider in that no single laboratory measurement will guarantee optimal press performance. This approach does provide us with a facile means to emphasize the emulsion behavior. It is a thermodynamic approach and certainly does not encompass the kinetic aspects of emulsion formation and breakdown.

It is important to note that the underlying physical chemistry which controls the behavior of water-in-oil emulsions is responsible to the observations made here. The contributions of

phase equilibria, interfacial tension, and microrheology need to be probed in detail. The present instrumentation does not provide this level of detail. It is the subject of future work in our laboratory.

Conclusion

A new test method for comparing emulsion rheology to neat ink has been developed using parallel plate viscometry. There are four important benefits to be obtained from this approach:

1. The ability to easily characterize ink/emulsion rheology under a variety of conditions (i.e. fountain solutions, temperature, volume fraction of aqueous phase).

2. Directs the formulation of lithographic inks with improved emulsion rheology.

3. Improves the understanding of the effects of an ink's composition on emulsion properties and, consequently, press performance.

4. May be suitable for quality control of inks to insure proper interfacial chemistry exists for lithographic emulsion.

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