SHEAR STABILITY OF FOUNTAIN SOLUTION EMULSIFIED IN LITHOGRAPHIC INKS

Shem M. Chou* and Thomas A. Fadner*

Abstract: The rheology of lithographic printing inks containing emulsified fountain solutions was studied with a stress-controlled rheometer using a cone-and-plate sensor system. An unusually rapid increase in the rate of shear was observed as the applied shear stress approached a critical value. This abnormal behavior is believed to be associated with the formation of a water layer within the bulk ink. At this critical value, the shear stress being applied to the system acts on the water layer instead of acting on the homogeneous emulsion-ink mass, resulting in the observed rapid increase of shear rate. This hypothesis is consistent with the appearance of water droplets on both the cone and plate ink films.

The critical shear stress value and the shape of shear stress versus shear rate curve of emulsion inks varied with water content and with temperature; these also varied with fountain solution and ink composition. Rheological measurements of this kind provide a useful technique for studying the shear stability of fountain solution emulsified in lithographic ink. Implications of these emulsion ink shear stability factors are discussed relative to press performance.

INTRODUCTION

It is generally known that press performance is determined largely by the rheology of the ink. However, predictions based on the rheology of a fresh ink are generally not highly successful because lithographic printing requires a second component, fountain solution, which confounds predictions of press performance. Others have attempted to use water-pickup properties of an ink as a predictor of press performance (Surland, 1980 and MacPhee, 1979). A recent study made at Flint Ink Corpora-

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tion of the Surland water pickup method indicated that this method might not be reliable for predicting press performance (Koniecki et al, 1985).

Efforts to predict lithographic ink performance by studying the rheology of the emulsion ink at various fountain solution contents were also reported recently (Bassemir, 1981 and Bassemir and Shubert, 1985). These authors used a Laray viscometer to measure high shear apparent viscosity (at 2500 sec^{-1}) and low shear yield stress (at 2.5 sec^{-1}) of inks as a function of water content. Their experimental results, reported as shortness ratios, correlated reasonably well with press performance. Flow behavior of emulsion inks under a wider range of shear conditions appeared important in our R&D program. Accordingly, we have studied the rheology of lithographic inks containing various amounts of fountain solution using a rather sophisticated, highly accurate, stress-controlled cone-and-plate rheometer.

EXPERIMENTAL

Materials

Two newsinks and two fountain solutions were used in this study. Inks A and B were supplied by two major ink manufacturers. The inks differed in their rheological properties but also differed in laboratory-measured water-pickup properties with the two fountain solutions. Fountain solution C, a neutral solution, and fountain solution D, an alkaline solution, were also obtained from two different suppliers. Both fountain solutions were prepared at 1.5 ounce per gallon of deionized water. Emulsification rate curves of the four fountain solution/ink combinations were obtained with a Duke emulsification test procedure.

Preparation Of Emulsion Inks

About 150 grams of fresh ink were weighed into a container. Mixing was carried out with a Talboys Stirrer rotating at 750 rpm by gradually adding the predetermined amount of fountain solution to the ink. During mixing, the container was moved up and down and sideways relative to the blades to help optimize the mixing process. Each sample was mixed for approximately 15 minutes. The container was then tightly sealed with a lid.

Rheological Measurements

A Carri-Med programmable stress-controlled rheometer with a 2 cm/1.5° cone was used to determine the rheology of the fresh and emulsion inks. The shear stress was programmed to increased linearly from nil to 47.75 Kdyne/cm^2 over a test period of five minutes. The temperature was controlled within 0.1°C by the cool-water circulator and the heating element that are built into the bottom plate. To operate the rheometer, a thin ink film is smoothly applied to the bottom plate. The plate is then raised to the preset operating position with ink between the plate and the cone. The ink sample is left undisturbed for about two minutes to ensure equilibrium with the plate temperature. The automatic stress controlled program is then initiated with no further operator manipulations.

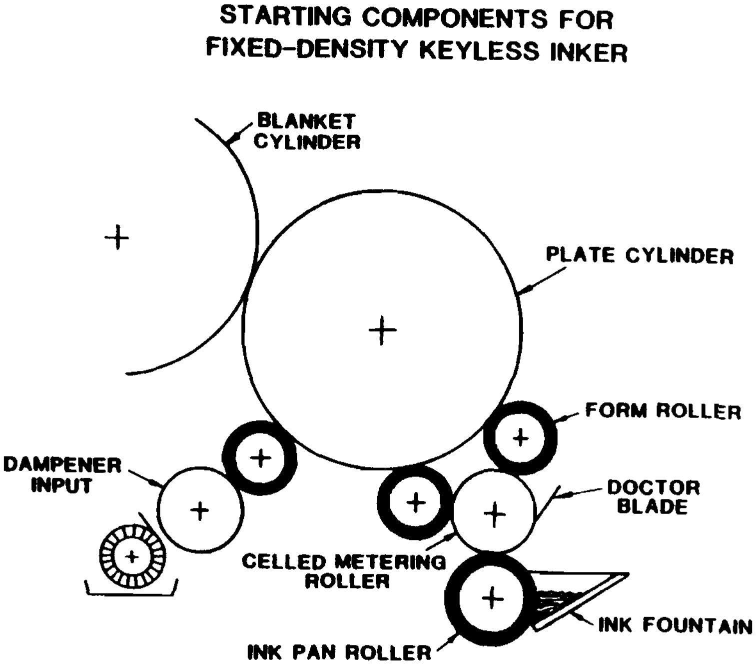


FIGURE 1. The schematic diagram of our keyless inking laboratory press. The ink circulating system is omitted for simplicity.

Test Press

A keyless inking laboratory press with direct-to-plate spiral dampening was used. The configuration is diagramed schematically in Figure 1. The celled-anilox-metering roller was fitted at 30° angle with a reverse angle doctor blade of 0.008 inch spring steel. The typical newspage pattern shown in Appendix I was used as the test format. The unit was run at 20,000 impressions per hour (20 KIPH). The dampener setting was maintained throughout the tests at the just-above-scum condition.

In this keyless system, ink is continuously and rapidly circulated with a pump to ensure uniformity since water continuously enters the inker. Ink samples were removed from the circulating line during press runs for subsequent water content determination. Water contents of the inks were determined with a Dean-Starke xylene co-distillation procedure. Water content values by this procedure have been shown in our laboratories to be accurate within ± 0.5% (Fadner and Doyle, 1985).

RESULTS AND OBSERVATIONS

Characteristics Of Fresh Inks

The shear stress versus shear rate curves of fresh inks A and B at 25°C are shown in Figure 2. Values characterizing the flow behavior of the two inks are summarized in Table I. These were derived from the flow curves using the empirical Herschel-Bulkley equation (Whorlow, 1980):

$$\tau = \tau_y + k\dot{\gamma}^n \qquad (1)$$

where τ is the applied shear stress, τ_y the dynamic yield value, $\dot{\gamma}$ the resultant shear rate, and k and n are constants. The index n characterizes the shear dependence of a fluid; for example, $n < 1$ represents a shear thinning flow, $n > 1$ a shear thickening flow, and $n = 1$ a Bingham body. Both inks A and B have a value of n less than one, indicating that they are shear thinning fluids, a fact typical of printing inks. Ink A exhibits a slightly greater shear thinning behavior than ink B. The latter ink behaves almost like a Bingham body, that is, the flow curve is almost linear.

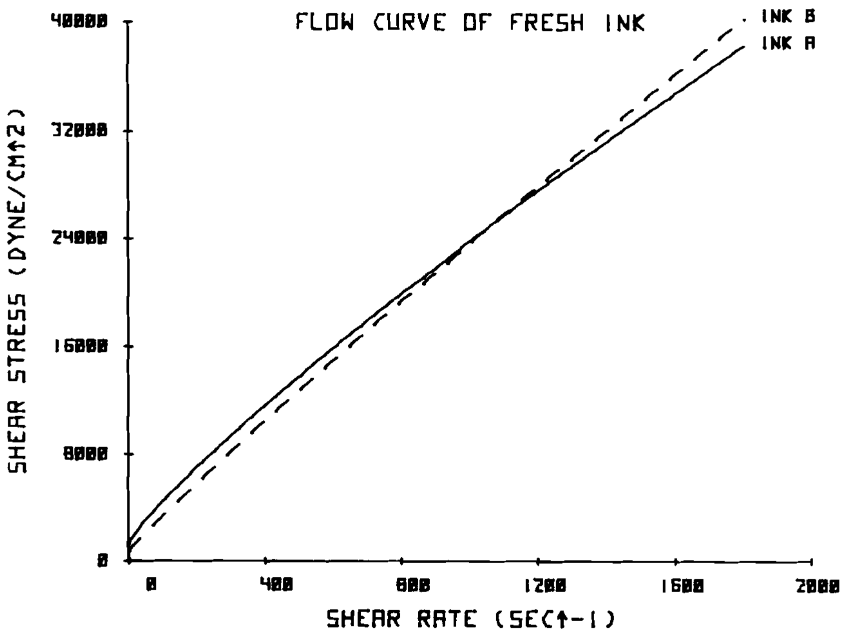


FIGURE 2. Flow curves of fresh inks at 25°C.

Shortness ratio was determined as the ratio of the apparent yield value to the plastic viscosity as proposed by Zettlmoyer and Myers (1960). The plastic viscosity is obtained as the slope of the flow curve at high shear rates where the curve tends to be linear; the apparent yield value is obtained by extrapolating this linear portion back to the shear-stress axis. These values are also summarized in Table I. Ink A has a much greater value of shortness ratio than ink B.

TABLE I. FLOW PROPERTIES OF FRESH INKS.

Flow Property	Ink A	Ink B
Dynamic Yield Value (Kdyne/cm^2)	1.21	0.66
Shear Thinning Index, n	0.84	0.93
Apparent Yield Value (Kdyne/cm^2)	4.25	1.76
Plastic Viscosity (Poise)	19.2	21.7
Shortness Ratio (Sec^{-1})	221	81

The water-pickup curves of the two inks with fountain solutions C and D in Figure 3 show: (1) ink A picked up significantly greater amounts of both fountain solutions than ink B; (2) the amount of fountain solution C emulsified in both inks was less than that of fountain solution D; and (3) neither combination tended to reach a saturated state within ten minutes.

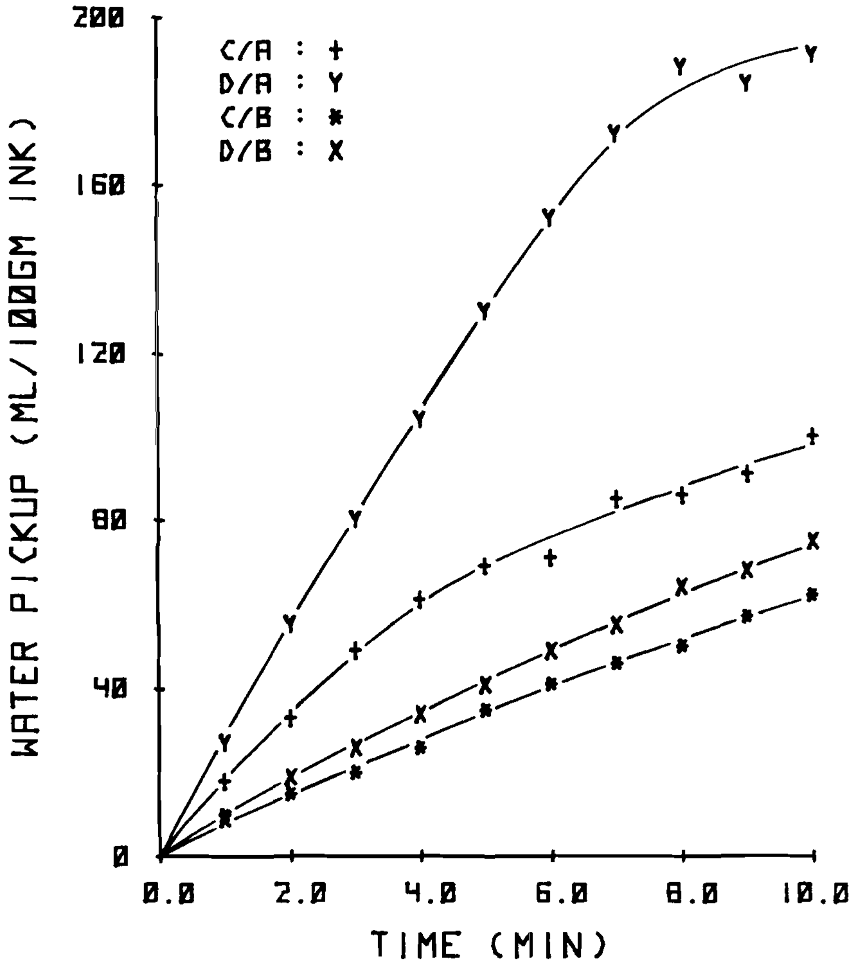


FIGURE 3. Duke emulsification curves of inks A and B with fountain solutions C and D.

Shear Stability Of Emulsion Inks

The large number of fountain solution, ink, and temperature combinations in this rheological study allowed establishing the following empirical equation to describe the rheological behavior of emulsion inks:

$$\tau = \tau_c - \alpha \exp(-\beta\dot{\gamma}) \qquad (2)$$

where τ_c is the critical shear stress value at which bulk phase separation is evident under conditions of our experiments, and α and β are constants. At zero shear rate, the right-hand-side of Equation (2) reduces to $(\tau_c - \alpha)$, which is equivalent to the yield value of the emulsion ink. The constant β characterizes the shape of the flow curve; the higher its value, the lower is the shear-rate value at which the shear stress reaches the critical value. Figure 4 demonstrates that the curves drawn according to Equation (2) have excellent fit with experimental data over a wide range of conditions. The conditions and values of both τ_c and β are summarized in Table II.

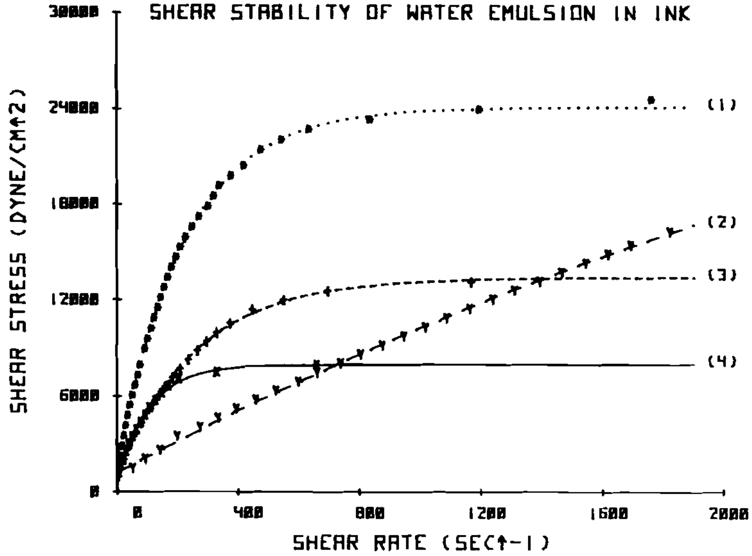


FIGURE 4. Typical flow curves of the emulsion inks. Conditions of temperature and composition are summarized in Table II.

TABLE II. CHARACTERISTIC PARAMETERS FOR EMULSION INKS SHOWN IN FIGURE 4.

Curve	1	2	3	4
Water/Ink	C/B	D/A	C/A	D/B
Temp(°C)	15	45	35	25
Water Content (%)	20	20	40	45
τ_c (Kdyne/cm^2)	24.1	42.3	13.4	8.0
β	4.49×10^{-3}	0.25×10^{-3}	3.83×10^{-3}	9.08×10^{-3}

Viscosity is defined as the slope of the shear stress versus shear rate flow curve. Consequently, the viscosity of emulsion inks at any shear rate can be derived from Equation (2) and is given by:

$$\eta = d\tau/d\dot{\gamma} = \alpha\beta\exp(-\beta\dot{\gamma}) \qquad (3)$$

where η is the viscosity of an emulsion ink. As shear stress approaches the critical value, $(d\tau/d\dot{\gamma})$ becomes zero, and the limiting viscosity according to Equation (3) is zero. This zero value is close to the 0.01 Poise viscosity of water, which is effectively zero compared with typical lithographic newsinks at 20 to 40 Poises.

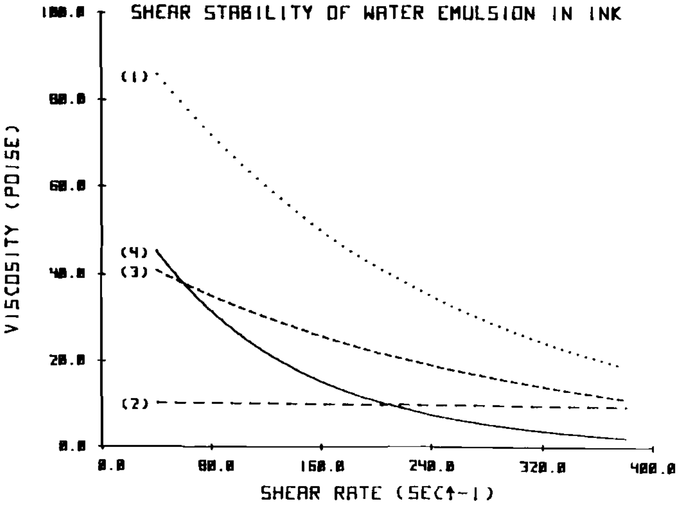


FIGURE 5. Shear dependence of viscosity for the Figure 4 emulsion inks.

Figure 5 shows viscosity, obtained from Equation (3), as a function of shear rate for the same emulsion inks as in Figure 4. These curves illustrate that the shape of the viscosity versus shear rate curves is also characterized by the constant β, that is, as the shear rate is increased, the viscosity of an emulsion ink having a larger value of β decreases more rapidly.

Effect Of Water Content

Table III summarizes the values of τ_c and β for the four fountain solution/ink combinations. The corresponding flow curves are shown in Figure 6. The critical shear stress decreased with increasing water content, whereas the constant β increased with increasing water content. The corresponding shear dependence of viscosity is illustrated in Figure 7 as a function of water content, demonstrating that the viscosity curve of emulsion inks drops more rapidly at higher water contents.

TABLE III. CHARACTERISTIC PARAMETERS FOR EMULSION INKS AT THREE WATER CONTENTS

Water/Ink	Flow Property	Water Content 20%	 30%	 40%
D/A	τ_c (dyne/cm^2)	3.38×10^4	2.58×10^4	1.80×10^4
	β	1.34×10^{-3}	2.56×10^{-3}	6.25×10^{-3}
C/A	τ_c (dyne/cm^2)	2.14×10^4	1.66×10^4	1.25×10^4
	β	1.98×10^{-3}	3.83×10^{-3}	7.55×10^{-3}
D/B	τ_c (dyne/cm^2)	1.95×10^4	1.62×10^4	1.10×10^4
	β	2.39×10^{-3}	3.63×10^{-3}	6.39×10^{-3}
C/B	τ_c (dyne/cm^2)	1.93×10^4	1.22×10^4	0.77×10^4
	β	2.21×10^{-3}	4.91×10^{-3}	9.49×10^{-3}

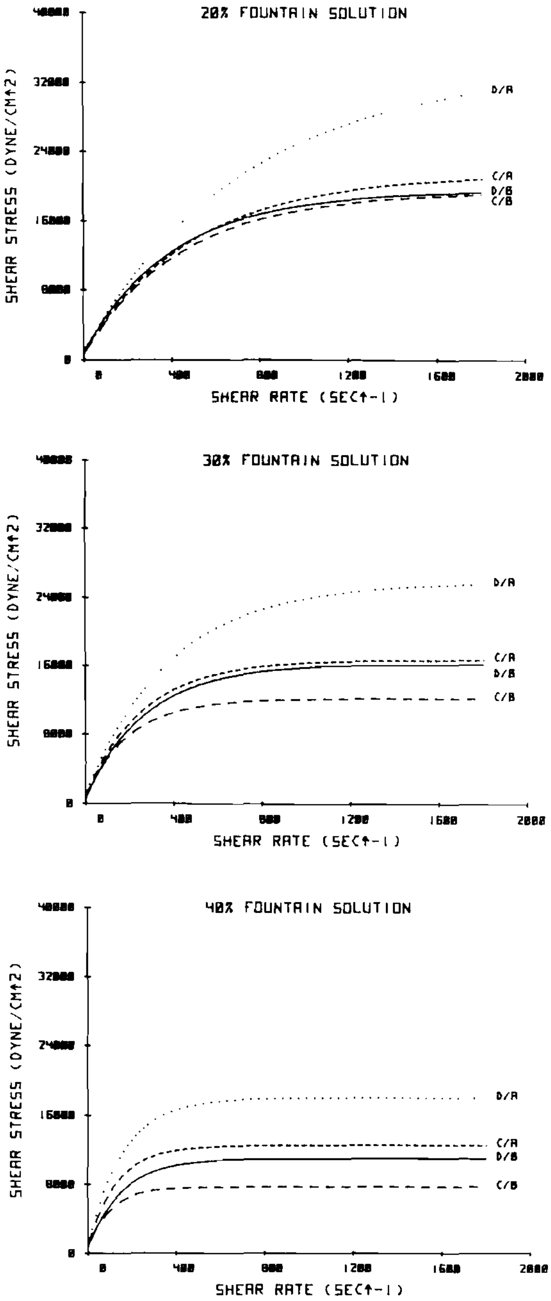


FIGURE 6. Flow curves of emulsion inks at various fountain solution contents.

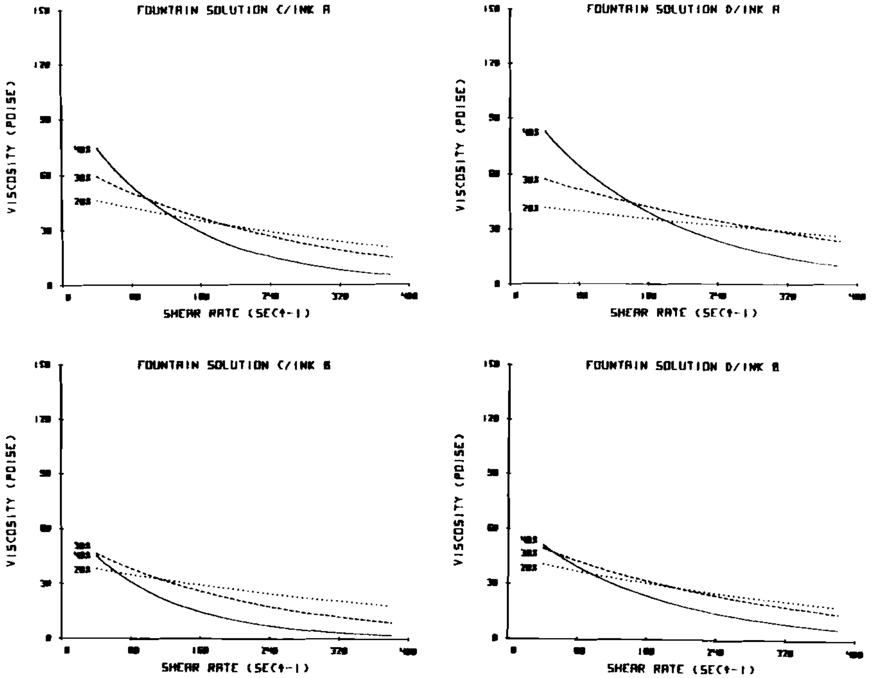


FIGURE 7. Shear dependence of viscosity for emulsion inks at various fountain solution contents.

The viscosities at a typical low shear rate value of 40 sec^{-1} are plotted in Figure 8 against water content of these emulsion inks. This low-shear viscosity increased with increasing water content in all cases, except the fountain solution C/ink B set, which decreased slightly at the highest water content studied.

Effect Of Temperature

The effect of temperature on the shear stability of emulsion inks was determined at 30% water content. The experimental results graphed in Figures 9 to 12 show: (1) the viscosity at low shear rates invariably decreases with increasing temperature, a common phenomenon for all fluids; (2) at low temperatures, the viscosity-decrease is more pronounced as shear rate is increased; (3) at higher temperatures, the viscosity of emulsion inks is not highly affected by the rate of shear; and (4) the temperature dependence of flow curves is different for each set and is greater for fountain solution D/ink A set.

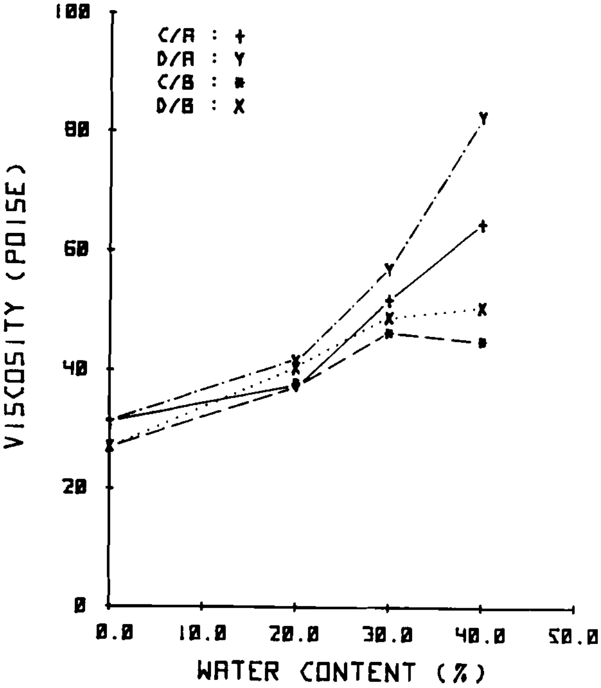


FIGURE 8. Effect of water content on the viscosity of emulsion inks at shear rate of 40 sec^{-1}.

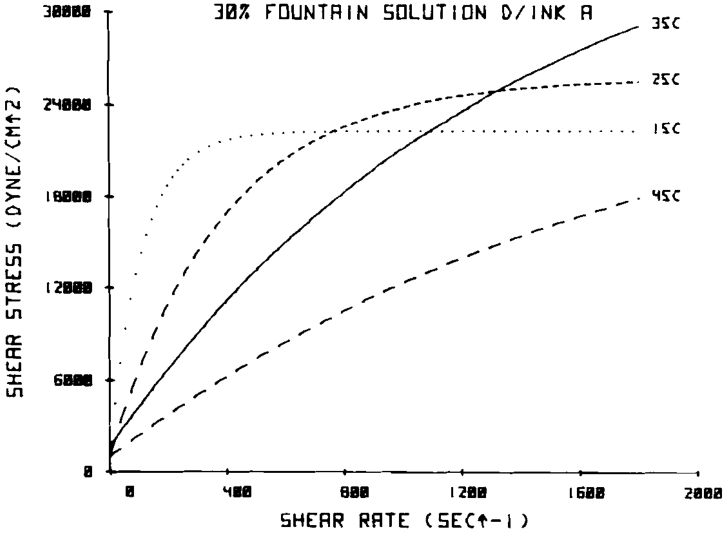
Effect Of Aging

Rheological measurements were carried out at 25°C for ink A containing several concentrations of fountain solution C immediately after mixing and three months later. Flow curves in Figure 13 show that the emulsion inks became more stable after storage in the laboratory environment. A higher shear stress is, therefore, required to destabilize these emulsion inks.

Effect Of Added Emulsifier

The addition of emulsion stabilizing agent to an emulsion ink does in fact have a significant stabilizing effect as shown in Figure 14. The shear stability of ink

A containing 45% fountain solution C was considerably increased with successive additions of Glycomul SOC (Glyco Inc.).



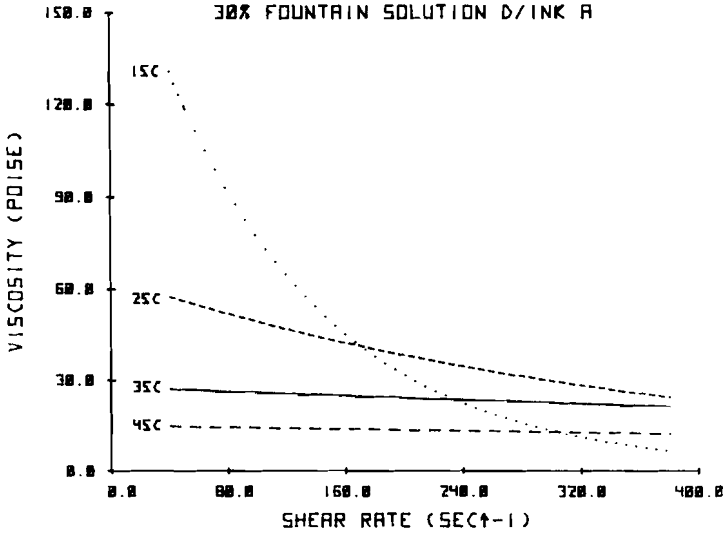


FIGURE 9. Flow behavior of ink A containing 30% fountain solution D at various temperatures.

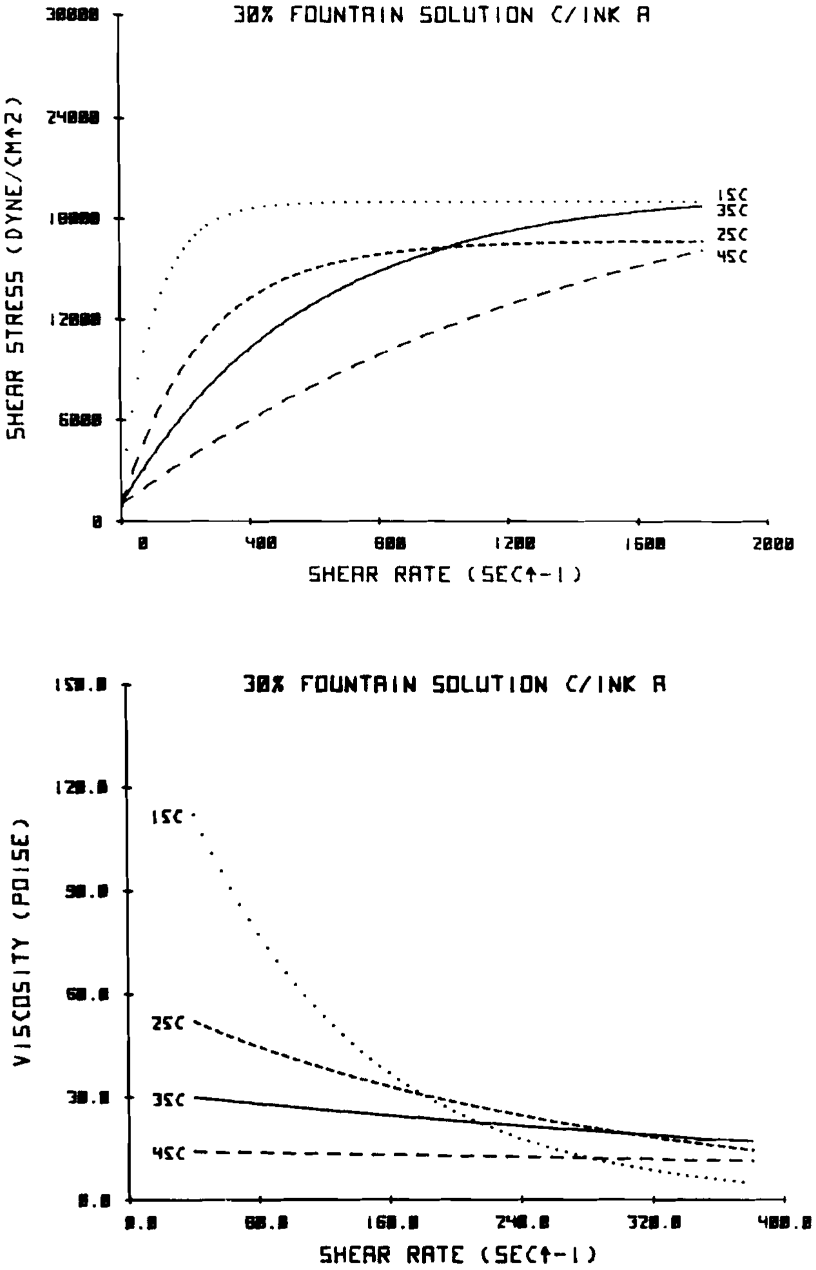
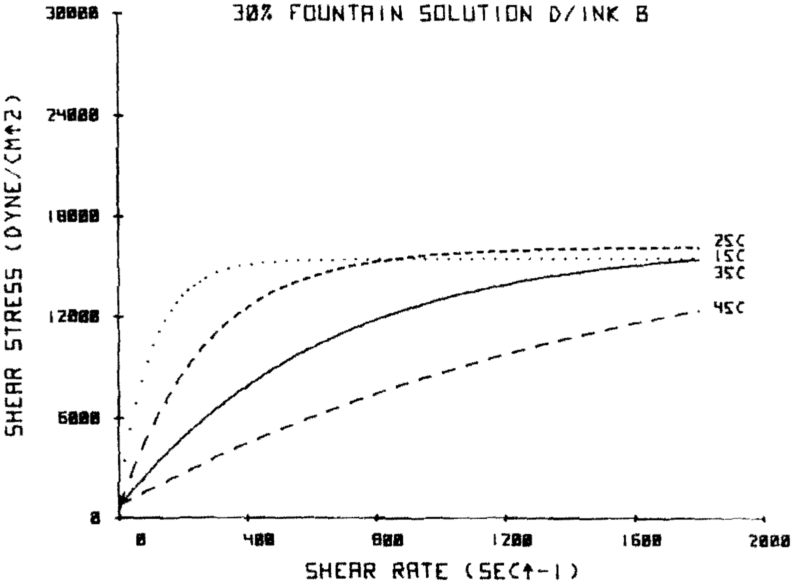


FIGURE 10. Flow behavior of ink A containing 30% fountain solution C at various temperatures.



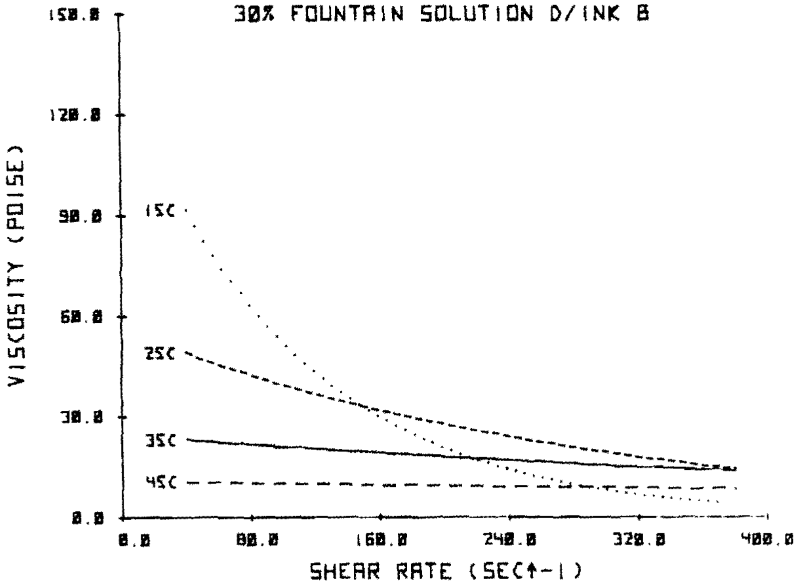


FIGURE 11. Flow behavior of ink B containing 30% fountain solution D at various temperatures.

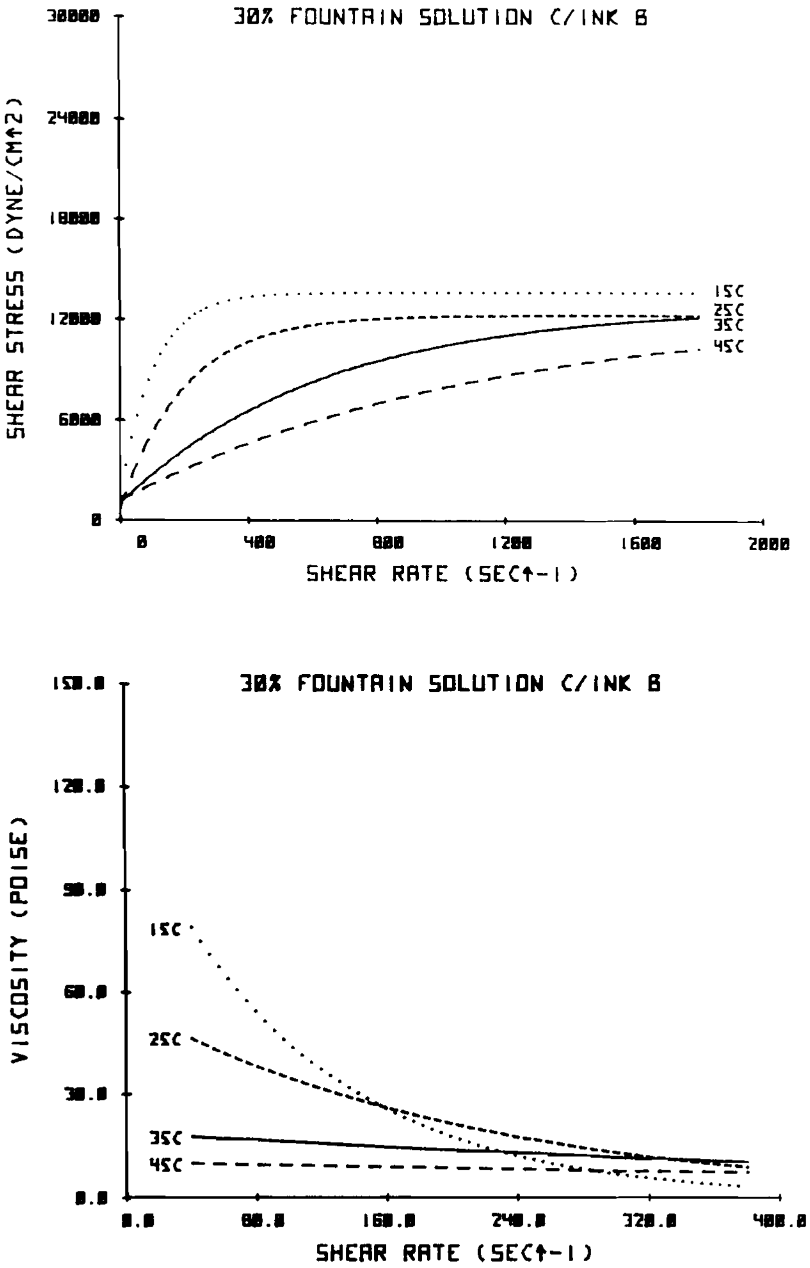


FIGURE 12. Flow behavior of ink B containing 30% fountain solution C at various temperatures.

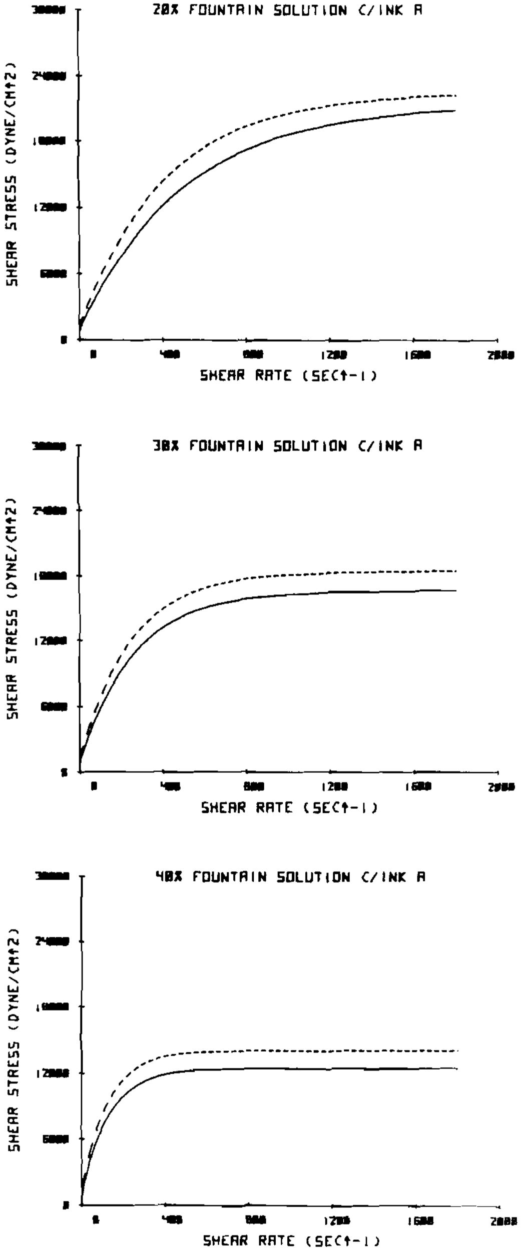


FIGURE 13. Effect of aging on the shear stability of emulsion inks. Solid curves were obtained immediately after mixing and dotted curves three months later.

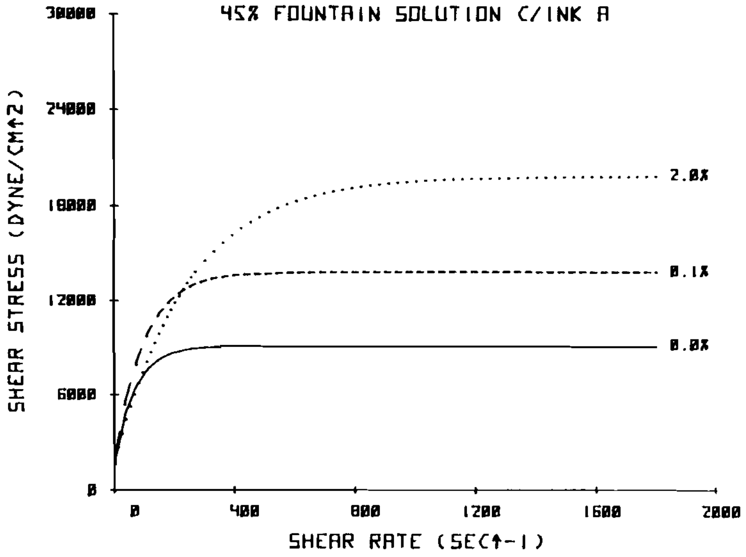


FIGURE 14. Effect of added emulsifier on the shear stability of an emulsion ink.

Press Performance

Severe blanket linting and the corresponding lint marks on the printed image were observed for ink A with fountain solution D and for ink B with fountain solution C.

Very slight linting was observed on the blanket for both ink A/fountain solution C and ink B/fountain solution D sets. The printed image was smooth and exhibited sharp halftones. Our test engineer had already concluded during the printing tests that ink A should be used with fountain solution C and ink B with fountain solution D.

Figure 15 shows the water contents of inks removed from the ink circulating line during press tests. The amount of fountain solution C in ink B increased nearly linearly with the time of printing and showed no evidence of leveling off during 28,000 impression test. In fact, considerable free water was also observed in the ink pan during and immediately after press test of ink B with fountain solution C. Water contents of the other three sets fell within a small band-width and tended to reach a saturated value, after about 24,000 impressions, of approximately 20 to 25%.

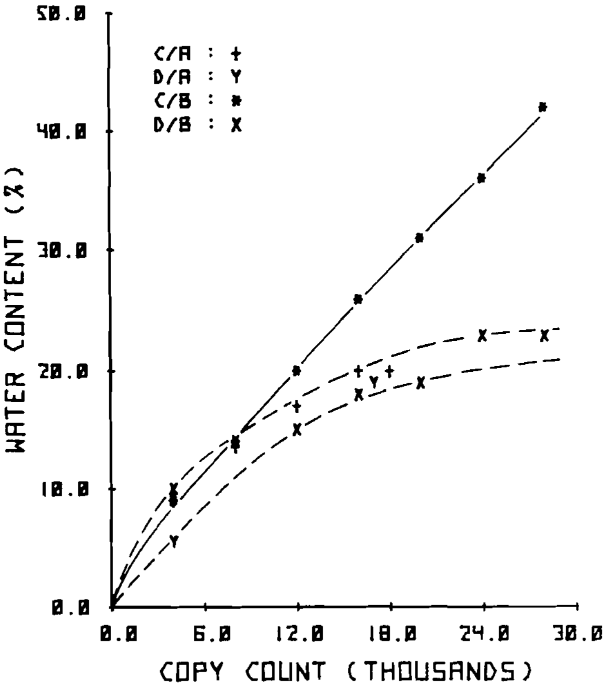


FIGURE 15 Accumulation of fountain solution in the ink during press runs.

DISCUSSION

Our results show that the low-shear viscosity of emulsion inks generally increases with increasing water content (Figure 8). And, the increase in viscosity is greater for the more stable emulsions. These factors are in general accord with practical observations and with principles of colloid science, as briefly discussed in the following paragraphs.

Shear-Rate Dependence Of Rheological Properties

At low rates of shear, the energy imparted to an emulsion ink by the rotating cone is probably not sufficient to induce significant coalescence of emulsified fountain solution. Under this condition, the emulsion ink acts as a more-or-less homogeneous dispersion of pigment and water particles, resulting in rather high values of low-shear viscosity, 35 to 82 Poise compared with fresh ink viscosities of 27 and 31 Poise, as shown in Figure 8.

It appears that as the rate of shear is gradually increased, more and more of the emulsified fountain solution coalesces into water droplets. Accordingly, an increasing proportion of the applied stress acts on the incipient water phases instead of acting on the relatively-viscous homogeneous emulsion-ink mass. Ultimately, at the critical-shear-stress value, the system responds as if the rheometer is acting only upon a very fluid water phase having virtually no resistance to the applied stress. Since all lithographic inks pick up fountain solution on press and since excess free water at the printing plate can interfere with ink transfer, it appeared to us that emulsion ink stability, as defined here, may be a critical lithographic printing parameter.

Emulsion ink viscosity decreases differently as a function of increasing shear rate depending upon the fountain solution used and its content in the ink. This result supports the ink industry's experience that fresh ink rheology without consideration of fountain solution interaction may not correlate well with press performance of that ink.

Relationships With Press Performance

Water contents of the two inks, measured at the recirculating ink pan line, increased with copy count (Figure 15), a natural result of water-containing ink being returned continuously to the ink pan in keyless inking systems (Figure 1). The water contents of the fountain solution C/ink B set are generally higher than those of the other three sets, with no indication of the ink becoming saturated with water. During and immediately after the fountain solution C/ink B press test, a considerable amount of free fountain solution was observed on ink surfaces in the pan. This observation is consistent with its poor laboratory-measured water-pickup capability (Figure 3). When an ink cannot rapidly assimilate and stabilize the excess water that always appears at the printing plate, the excess water cannot leave the press as part of the ink and must accumulate somewhere or else evaporate. This view is also consistent with the results of our rheology investigation. High rates of shear, for instance, in the doctor blade/anilox-metering-roller nip, should cause rapid coalescence of emulsified water from the least stable emulsion ink, namely fountain solution C/ink B. And, the observed result was bulk phase separation for this ink set. Conversely, it appears that the other three more-stable emulsion inks can pass through this high shear-rate nip, retaining the excess water that had been picked up, eventually printing it out onto the paper as part of the emulsion ink. Similar considerations are expected to apply, at differing shear-rate values, to other inking or printing nips.

As press speed is increased, the shear rate at the blade nip will increase. Accordingly, the next fountain solution/ink combination to fail is expected to be fountain solution D/ink B. It has a critical-shear-stress value just above that for the fountain solution C/ink B (Figure 6). Unfortunately, a faster press was not available.

According to predictions from Surland's laboratory water-pickup curves, none of the fountain solution/ink combinations used in this study should perform well on press; saturation in water content was not reached within the ten-minute time frame of the test. In fact, we obtained good print quality using fountain solution C/ink A and using fountain solution D/ink B. No problems were encountered when printing with these two ink sets.

Bassemir and Shubert (1985) later commented on such anomalies and concluded that when the emulsification rate curve appears contradictory with press results (such as here), rheological measurements of the emulsion ink at various fountain solution contents should be made. We agree. Doing so will allow making significantly better correlations with press performance.

Temperature Dependence

The temperature dependences of the emulsion ink stability and viscosity are illustrated in Figures 9 to 12. The shear stress of emulsion inks increases with shear rate significantly more rapidly at the lower temperatures of our 15° to 45°C experimental range. This infers that the emulsified water is least stable at the lowest temperature. In fact, we observed the appearance of considerable amount of free water from fountain solution C/ink B sample after overnight storage in a cool place. And, it appears that at the highest temperature studied, the emulsion inks are so stable that they respond over the entire shear-stress range like stable systems of dispersed particles; slightly shear-thinning, similar to fresh ink when no water is present, and exhibiting no indication of phase separation. At this stage in our research program, we are not certain why emulsion inks are more stable at the higher temperatures.

Other Implications

As a general rule in colloid science, more emulsion-stabilizing agent is coincident with smaller emulsion particles and higher emulsion stability; a greater force field is required to cause coalescence of the emulsified liquid particles. This general view is consistent with the results shown in Figure 14. Emulsion inks, like other colloids, become more stable (have a higher critical-shear-stress value) with increasing amounts of emulsion-stabilizing agent. This result infers that the addition of emulsion-stabilizing agent to the least-stable fountain solution C/ink B set may improve its performance.

Greater stability may not necessarily correspond with better overall press performance. The most stable emulsion ink is the fountain solution D/ink A set. An emulsion ink of this type has a high operating viscosity. Mills (1967) has shown that tack is a monotonic function of viscosity. Accordingly, emulsified water that is too stable may lead to high emulsion-ink tack and, therefore, the severe linting we observed in the press test.

It is not unusual that small-scale mixing of one fluid into another with high speed devices is often overdone. Over-emulsification of fountain solution into an ink is expected to form a pseudo-stable system of smaller emulsion particles than would be formed under less-forceful mixing conditions. In the over-mixed case, the amount of emulsion-stabilizing components may be insufficient to fully cover and stabilize the larger-than-expected interfacial surface area. Typically, the small, pseudo-stable particles will subsequently merge into larger particles, slowly if allowed to stand, or more rapidly if agitated under modest shearing conditions. Eventually, an equilibrium particle size is established corresponding to the inherent capability of the stabilizing components. The result is a more-stable-emulsion ink after standing, for instance, in the laboratory environment. This effect was observed for the three-month storage results shown in Figure 13.

It is interesting to note that the critical-shear-stresses of the four fountain solution/ink combinations rank exactly the same as their laboratory-measured water-pickup capabilities (Figures 6 and 3); higher critical-shear-stress values are coincident with higher water-pickup values. This infers that both these properties depend on the same set of physico-chemical characteristics of the ink and of the fountain solution. Our work indicates that these are probably also related to the rheological properties of the fresh inks, a factor of common knowledge among ink formulators. The data in Table I show that ink A has a higher yield value, smaller shear-thinning index, and greater shortness ratio than ink B. This combination of properties corresponds to a stronger internal structure for ink A. Reference to Figure 6 will verify that critical-shear-stress values for emulsion ink A are greater at all water contents than for emulsion ink B. Restated, ink A is more stable than ink B regardless of which fountain solution is used. Perhaps, the stronger internal structure is responsible for the greater water pickup capacity and for the higher stability of ink A as an emulsion ink. Further investigation is necessary to substantiate this relationship.

CONCLUSIONS

Cone-and-plate stress-controlled rheometry allows simple and rapid characterization of emulsion ink properties and provides insights that were previously unavailable to the industry. Accordingly, a number of practically useful and technically interesting factors were encountered during this work:

1. Rheological properties of emulsion inks can be readily and easily measured using a programmable stress-controlled, rheometer.

2. Viscosities of emulsion inks are generally much higher at low shear rates than those of the fresh inks but the emulsion inks are also more highly shear-thinning. Consequently, at high shear rate printing conditions, emulsion inks flow more readily than the fresh inks.

3. Emulsion ink stability increases with increase in temperature; above 40°C rheological behavior again approximates that of fresh ink and the influence of water in the ink is not seen.

4. The critical-shear-stress, at which bulk phase separation occurs, appears to be a meaningful emulsion ink parameter.
5. Critical-shear-stress values appear to correlate with laboratory-measured water-pickup values; the most stable emulsion inks are those that pick up water most readily.
6. Emulsion ink stability may correlate with degree of internal structure of the fresh ink. This may or may not conflict with the fact that emulsion inks are more stable at high temperature where the internal structure is presumably weaker.

ACKNOWLEDGMENTS

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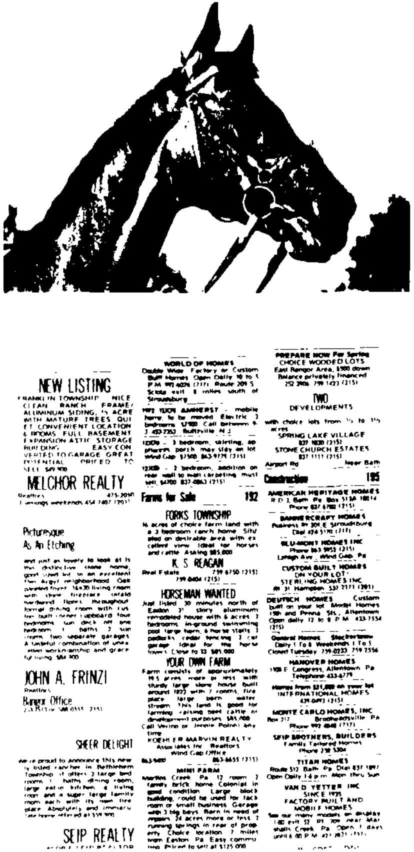
APPENDIX I
TYPICAL NEWSPAPER PATTERN



NEW LISTING

MELCHOR REALTY

Picturesque
As An Etching

JOHN A. FRINZI

SHEER DELIGHT

SEIP REALTY

WORLD OF HOMES

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YOUR OWN FARM

KOEHLER MARVIN REALTY

MINI FARM

PREPARE NOW For Spring
CHOICE WOODED LOTS

TWO
DEVELOPMENTS

SPRING LAKE VILLAGE

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AMERICAN HERITAGE HOMES

CUSTOM BUILT HOMES
ON YOUR LOT
STERLING HOMES INC

DEUTSCH HOMES

HANOVER HOMES

INTERNATIONAL HOMES

MONTE CARLO HOMES, INC

SEIP BROTHERS, BUILDERS

TITAN HOMES

VAN D. YETTER INC
SINCE 1935
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IN STEWARTSVILLE AREA

REAL ESTATE FOR SALE

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