VISCOSITY MEASUREMENT OF VISCOELASTIC INKS AT HIGH SHEAR RATES

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Abstract: Rotational rheometers equipped with a cone-and-plate or a narrow-gap concentric cylinder geometry are very useful for accurately determining rheological properties of newsinks. These instruments fail to measure high shear viscosity of highly viscoelastic commercial inks due to the occurrence of shear fracture. A recently developed axial viscometer is capable of measuring high shear viscosity of commercial inks. Its features are explored in this paper.

A wide variety of inks ranging from newsinks to waterless lithographic inks were studied. Experimental results show that the viscosity data obtained from the axial viscometer are complementary to the viscosity data obtained from a rotational rheometer. When plotting these viscosity data against shear rate or shear stress, a viscosity profile curve is produced. Cross equation is used to fit the viscosity profile data of the inks. Correlations of measured rheological parameters with ink performance on press are discussed.

BACKGROUND

A lithographic printing ink experiences, in a complicated way, a very wide range of shear rates that may span over ten decades. It must fulfill rheological requirements at various stages of printing that range from pigment sedimentation to the extremely high shear actions in the roller nips (Chou et al., 1990). Accurate viscosity measurements over such a wide range of shear rates are essential for correlating rheological properties of printing inks with press performance.

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Rheological behavior of lithographic inks is further complicated by the emulsified fountain solution (Chou and Fadner, 1986; Chou and Cher, 1989). The emulsified water particles may be deformed, break up into smaller droplets, or coalesce into larger droplets or free water phase, depending on the stability of emulsion and the shear conditions. Rheological behavior of emulsion inks is out of the scope of this paper and will not be studied.

Pigment sedimentation, ink levelling, and ink feed mechanism of an open fountain press are stress-controlled rheological phenomena and occur at very low shear rates (Chou et al., 1990). It has been shown that the creep technique is the most promising method for determining the viscosity of inks at this shear rate range (Chou, 1991). Low to medium shear rheological results of conventional and keyless newsinks determined by the flow technique were reported in a previous publication (Chou and Bain, 1988). Flow technique has proven very powerful for distinguishing rheological characteristics of keyless inks from conventional inks.

The internal structure of an ink is subjected to breakdown by the compression, shear, and extension actions in the roller nips for a very short moment. The ink is at rest most of the time on the press during which the internal structure may recover. The rates of structural breakdown and recovery must be balanced according to the press conditions. Poor transfer and hence ink starvation may occur if the viscosity of ink is too high and/or the structural recovery is too fast. Ink may spread over the halftone dots and result in excessive dot gain if its viscosity is too low and/or its structural recovery is too slow. Fast recovery of the internal structure may also produce mottled prints. A study of structural recovery of printing inks has been reported (Chou et al., 1990).

Measurements of high shear viscosity are important for characterizing flow behavior of inks in the roller nips. The purpose of this paper is to evaluate an axial viscometer and a cone-and-plate rotational rheometer for measuring high shear viscosity of printing inks, especially of highly viscoelastic inks.

EXPERIMENTAL SECTION

Printing Inks

A wide variety of lithographic inks ranging from newsinks to waterless lithographic inks were selected in this study. They were received from American and Japanese sources. Table I lists the suppliers, ink types and colors. Also listed in Table I are the measured rheological parameters of these inks.

Carri-Med Rheometry

A Carri-Med controlled-stress rheometer with a cone-and-plate measuring geometry was used in this study to determine the viscosity of inks at very low to medium shear rates. The cone diameter was 2 centimeters and the cone angle was 0.5 degree. The maximum shear stress of the measuring system used in this study is about 48,000 dynes/cm^2. The maximum shear rate is about 5,200 sec^{-1}.

Low shear viscosity was determined by the creep technique (Chou, 1991). A constant shear stress was instantaneously applied to the sample. The shear strain was recorded as a function of time, resulting in a creep curve. The slope of the linear portion of the creep curve is the shear rate, from which the viscosity can be calculated.

Medium shear viscosity was determined by the flow method (Chou and Bain, 1988). The shear stress was logarithmically incremented in 200 steps from a minimal value to the maximum stress of the system. The corresponding shear rates were recorded. The minimal stress was so determined that the viscosity data obtained from creep and flow measurements had an overlap.

Duke Viscometry

Falling rod viscometers, such as Laray viscometer, have been widely used in the ink industry for determining high shear viscosity of heavy paste inks. The rod is made to slide through the collar by its own weight. The ink carried by the rod passes through a very narrow orifice between rod and collar. The time for the rod to fall a given distance, usually ten centimeters, is recorded. The falling time can be converted into shear rate. Shear stress is calculated from the total weight of rod and added weights. So, falling rod viscometers are actually a controlled-stress instrument.

A computer-controlled, newly developed axial viscometer, Duke viscometer, was used in this study. This instrument is a reverse of the falling rod viscometer, though. Their basic principles are the same. The rod of Duke viscometer is locked to a load cell in the bottom. The collar is made to move at constant speeds by a closed-loop servo-motor. So, the Duke viscometer is a controlled-rate instrument.

The diameter of rod is 1.2 centimeter and the gap between collar and rod is 40 micrometers. The measuring system is encased in a temperature controlled enclosure. Temperature can be regulated to within ±0.1 °C. The maximum shear stress of the Duke viscometer used in this study is about 2,000,000 dynes/cm^2 and the maximum shear rate is approximately 10,000 sec^{-1}.

The shear rate was programmed to increment logarithmically from 2.5 to 5000 sec^{-1} in 30 steps. All the rheological measurements were made at 25°C.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Lithographic printing inks have to fulfill rheological requirements at each stage of the printing process (Chou et al., 1990). The best graphical presentation of rheological behavior of inks over such a wide range of shear rate is the viscosity profile curve, in which the viscosity is plotted against shear rate or shear stress on a log-log scale.

Viscosity Profile Curves of Newsinks

Figure 1 shows the viscosity profile curves of the magenta newsink from supplier D. The low shear viscosity data were obtained from the creep measurements and the medium-to-high shear viscosity data were obtained from the flow measurements. Both measurements were made on the Carri-Med rheometer. The data from creep and flow measurements overlap each other. The resulting viscosity profile curve consists of a first-Newtonian, a shear thinning, and a second-Newtonian regions. All of the newsinks studied in this experiment exhibited similar viscosity profile curves.

A number of equations derived to describe the viscosity profile curve could be found in the literature (Barnes et al., 1989). The Cross equation is the simplest one and is selected in this paper to fit experimental data.

$$\frac{\eta - \eta_\infty}{\eta_\circ - \eta_\infty} = \frac{1}{1 + (k\dot{\gamma})^m} \qquad (1)$$

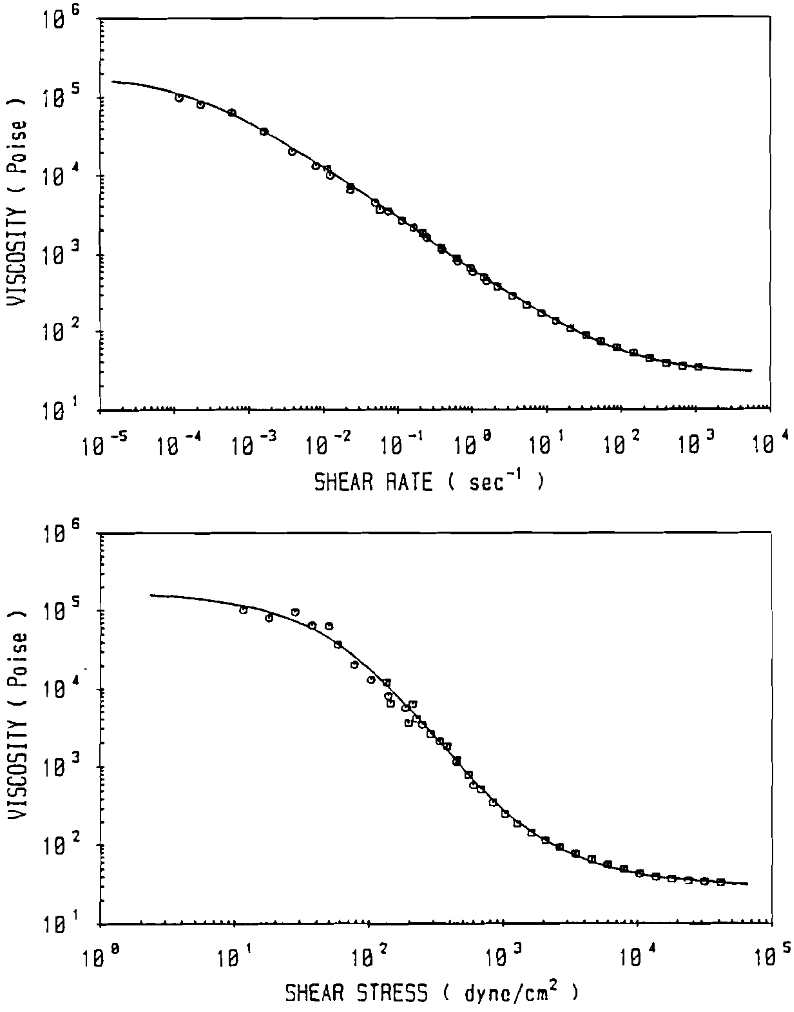


Figure 1. Viscosity profile curves of the magenta newsink from supplier D. Low shear viscosity data (○) were obtained from the creep method and medium-to-high shear data (□) from the flow method.

where η is the viscosity at any shear rate, η_∞ the infinite-shear-rate viscosity in the second-Newtonian region, and η_0 the zero-shear-rate viscosity in the first-Newtonian region. The infinite-shear-rate viscosity is equivalent to the plastic viscosity commonly used in the ink industry. The constant m is the slope of viscosity profile curve in the shear thinning region and hence is termed as power-law or shear thinning index. The constant k is a time constant characterizing the structural breakdown of fluid. The larger the constant k, the lower is the shear rate at which the internal structure begins to break down (Cross, 1965). Figure 1 shows that the theoretical curve calculated by the Cross equation fits the experimental data very well. It makes no difference if the viscosity is plotted against shear rate or shear stress. The calculated rheological parameters of newsinks are summarized in Table I.

Characteristics of Viscoelastic Fluids

Figure 2 shows the viscosity profile curve of the sheetfed yellow ink from supplier B. The viscosity decreases suddenly at shear rates above 20 sec^{-1} instead of levelling off to the second-Newtonian region. The abrupt decrease in viscosity is more pronounced when the viscosity is plotted against shear stress. All the commercial inks studied in this experiment exhibited a similar behavior. Close examination of the sample during measurement revealed that a portion of ink crept out of the measuring gap when the shear rate exceeded a certain value. This phenomenon is generally termed as shear fracture and can be ascribed to the nature of viscoelastic fluids.

Two most well known rheological phenomena of viscoelastic fluids are rod-climbing and die swell (Barnes, 1989), as shown in Figures 3a and 4a, respectively. When a rotating rod is dipped into a vessel containing a Newtonian fluid, the fluid moves towards the rim of the vessel due to the centrifugal force, and thus produce a vortex. A viscoelastic fluid will, instead, climb up the rotating rod. This rod-climbing effect is usually referred to as the Weissenberg effect.

The Weissenberg effect may be viewed as a result of the normal stresses. The polymeric materials such as resins or additives are present in the ink vehicle as random coils at rest. When the fluid is forced to flow, the polymer molecules are stretched along the streamline of flow. Counter forces, or normal stresses in the rheological terminology, are produced to resist the stretching. The counter stress in the direction of flow is the largest and acts like a hoop stress around the rod (Figure 3b). This stress causes the fluid to strangle the rod and hence climb up it.

Die swell phenomenon is also a result of the normal stress. When a viscoelastic fluid is extruded from a die, the polymer molecules are stretched in the die. Once they emerge from the

Table I. Rheological properties of a wide variety of lithographic printing inks.

Supplier	Ink Type	Color	η_∞	η_0	k	m
A	Waterless	Black	371.63	14910	3.11	0.636
		Cyan	392.89	128773	53.58	0.664
		Magenta	408.05	437167	82.30	0.762
		Yellow	408.43	274553	51.29	0.789
B	Waterless					
	Hard	Black	609.97	362979	95.76	0.756
	Medium	Black	541.57	532974	99.66	0.767
	Soft	Black	392.14	179136	98.63	0.687
	Sheetfed	Black	264.89	18172	63.02	0.597
		Cyan	343.36	72873	45.27	0.683
		Magenta	243.08	8818	8.52	0.470
		Yellow	202.02	42668	659.76	0.473
	Heatset	Black	173.65	38711	10.67	0.772
		Cyan	212.56	34386	10.40	0.772
		Magenta	141.78	26437	10.73	0.636
		Yellow	153.56	59869	21.97	0.761
C	Newsink	Cyan	31.33	71011	681.35	0.701
		Magenta	32.38	39641	817.06	0.594
		Yellow	34.06	60139	325.91	0.745
D	Newsink	Cyan	20.78	674497	15742.15	0.722
		Magenta	27.80	213004	6139.54	0.673
		Yellow	28.89	181997	2097.54	0.746
E	Newsink	Black	20.40	72014	844.79	0.651

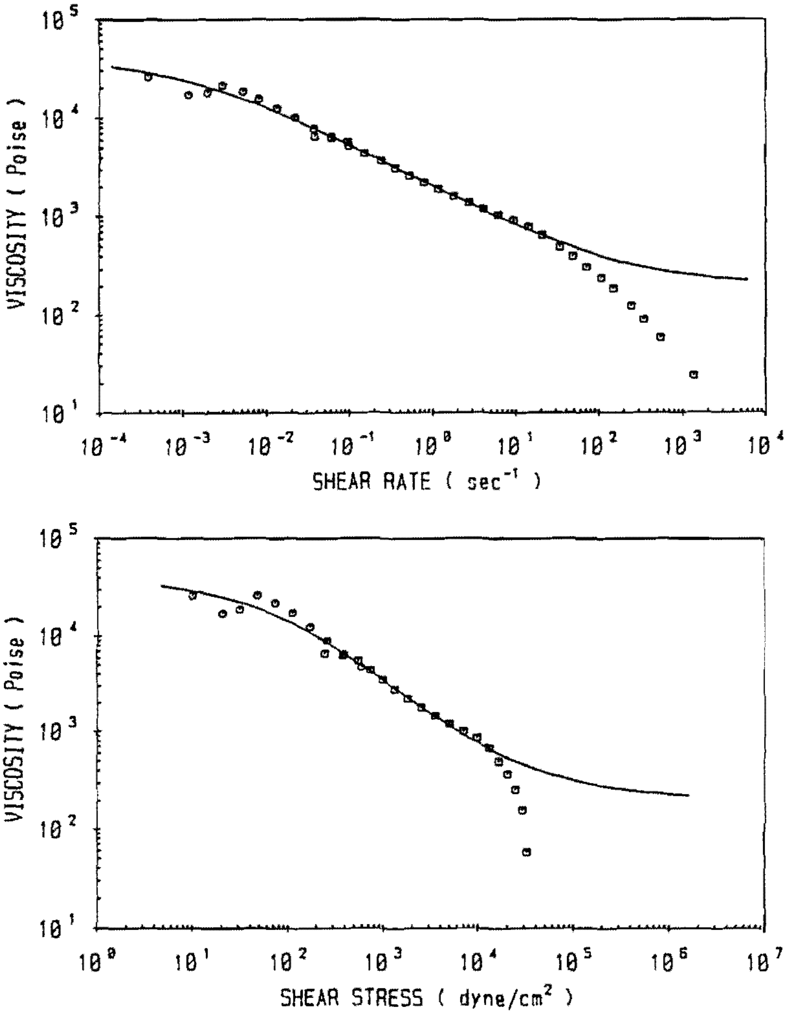


Figure 2. Viscosity profile curves of the sheetfed yellow ink from supplier B. Low shear viscosity data (○) were obtained from the creep method and medium shear data (□) from the flow method.

nozzle, the constraint is removed and the molecules are free to restore their random coil configuration (Figure 4b). This causes an expansion of fluid whose diameter can be many times greater than that of the hole.

The molecules of a Newtonian fluid are so small that they

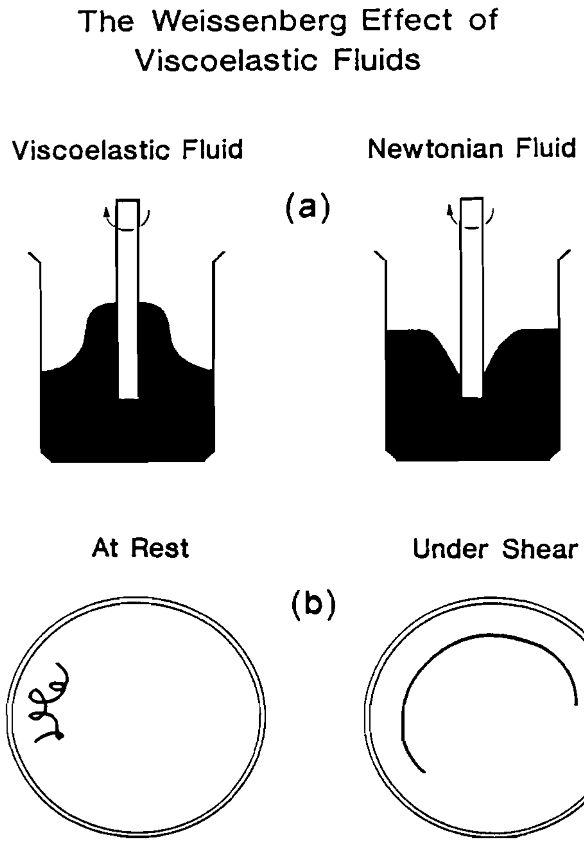


Figure 3. Schematic diagram showing (a) rod-climbing phenomenon of viscoelastic fluids and vortex formation of Newtonian fluids and (b) configuration of polymer molecule at rest and under shear.

are not deformed by the shear action. So, the normal stresses of Newtonian fluids are equal to the hydrostatic pressure which is isotropic. A W/O emulsion is a good example that helps visualize the anisotropic normal stresses typical of viscoelastic fluids. The water particle has a spherical shape at rest and becomes ellipsoidal in motion. The deformation is the largest in the direction of flow, while the deformations are nearly identical in the other two directions. According to the principle of thermodynamics, the deformation gives rise to the counter stresses that will restore the water particle to its original shape of sphere. The largest counter stress

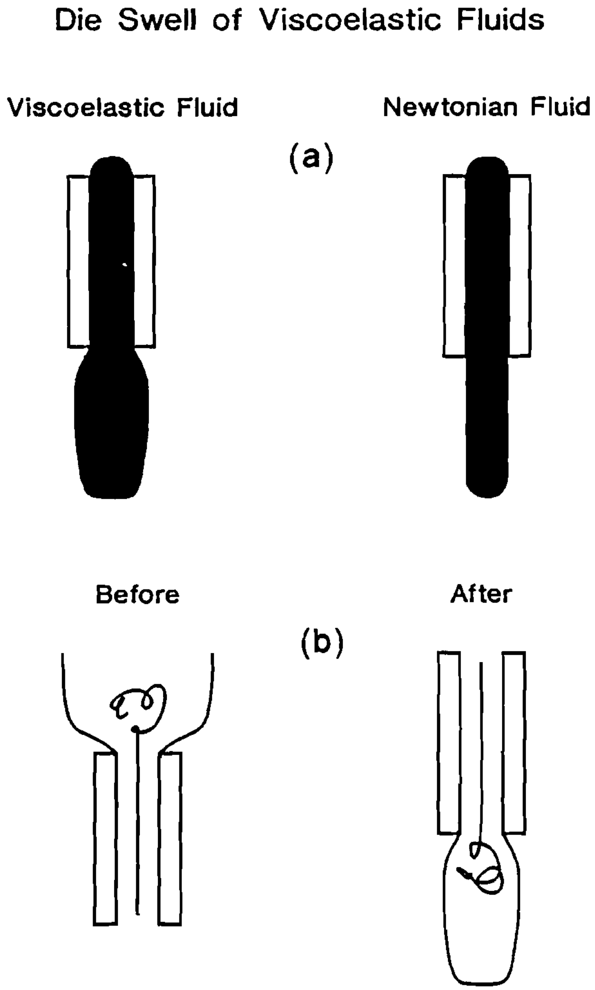


Figure 4. Schematic diagram showing (a) die swell phenomenon of viscoelastic fluids and (b) configuration of polymer molecule before and after emerging from the die nozzle.

is in the direction of flow. Therefore, the normal stresses of viscoelastic fluids are equal to the sum of these counter stresses and hydrostatic pressure. The normal stress in the direction of flow is usually represented by σ_{xx}. The normal stress in the direction of velocity gradient is represented by σ_{yy} and the remaining normal stress by σ_{zz}.

The first and second normal stress differences rather than the normal stresses themselves are reported in the literature. Because the contributions of hydrostatic pressure cancel each other, the normal stress differences are the net results of material's response to the shear action. That is, they are material's properties. The first and second normal stress differences are defined as

$$N_1\,(\dot{\gamma}) = \sigma_{xx} - \sigma_{yy} \tag{2}$$

$$N_2\,(\dot{\gamma}) = \sigma_{yy} - \sigma_{zz} \tag{3}$$

The first normal stress difference of viscoelastic fluids is usually much greater than the second normal stress difference, whereas both normal stress differences are equal to zero for Newtonian fluids. The rod-climbing and die swell phenomena result from the first normal stress difference.

Rotational Rheometry For Viscoelastic Fluids

Rotational rheometers equipped with a cone-and-plate or a narrow-gap concentric cylinder geometry are frequently used to accurately measure the viscosity of many fluids. They have proven very useful for low viscosity fluids such as newsinks but fail to produce meaningful data at high shear rates for highly viscoelastic fluids such as commercial inks. Figure 5 illustrates schematically the response of a viscoelastic fluid to the cone-and-plate and the concentric cylinder geometries. The deformation of polymeric materials and hence the first normal stress difference increases with increasing shear rate. As the shear rate exceeds a critical value, the fluid begins to crawl out of the measuring gap due to the Weissenberg effect. The higher the shear rate, the less is the ink volume left in the gap to resist flow. The consequence is a rapid reduction in the measured viscosity, as shown in Figure 2. So, cone-and-plate and concentric cylinder viscometers are not applicable to the high shear viscosity measurements of highly viscoelastic fluids.

Axial Rheometry For Viscoelastic Fluids

Axial viscometers are capable of making accurate viscosity measurements due to the very narrow gap between collar and rod. Figure 6 shows a schematic illustration of the axial viscometry. The fluid is continuously dragged into the

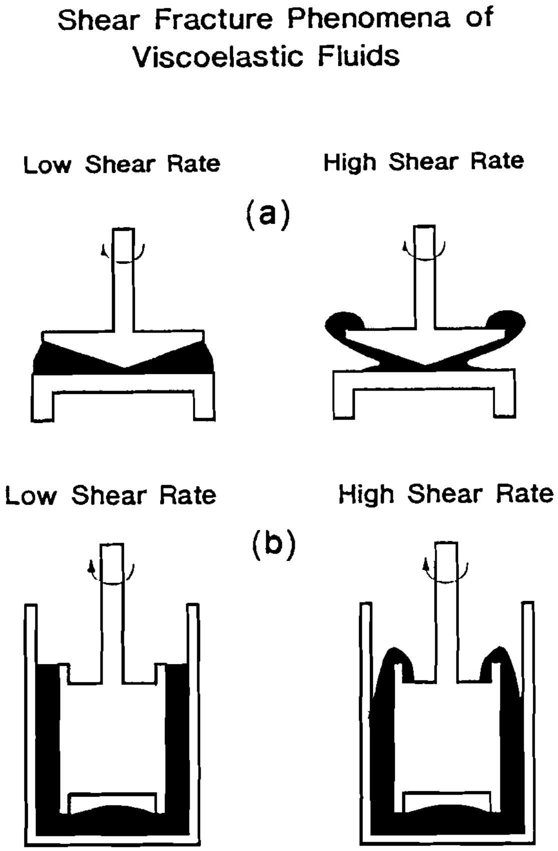


Figure 5. Schematic diagram showing the shear fracture phenomenon of viscoelastic fluids occurring at high shear rates for (a) cone-and-plate and (b) concentric cylinder rheometers.

orifice by the relative motion between rod and collar. Die swell may occur at high shear rates but will not influence the volume of fluid in the measuring gap. Consequently, axial viscometers are expected to produce accurate viscosity data at high shear rates due to the absence of shear fracture. Figure 7 demonstrates that the high shear viscosities obtained from the Duke viscometer supplement very well the low to medium shear viscosities obtained from the Carri-Med rheometer for the sheetfed yellow ink from supplier B.

Laray viscometer has been widely used in the ink industry.

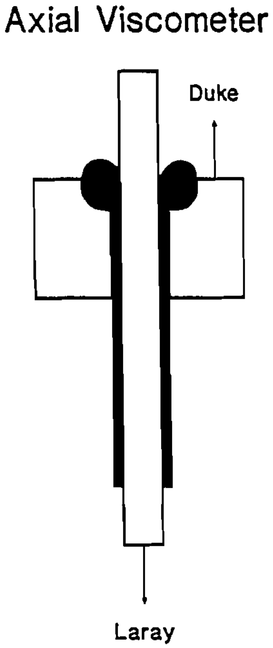


Figure 6. Schematic diagram showing the assembly of axial viscometers such as Laray and Duke viscometers.

Manual operation and lack of accurate temperature control are its major drawbacks. The shear rate calculated from the falling time may not be correct, because the shear rate is directly related to the speed of the falling rod. The falling time can be used to calculate shear rate only if the falling rod reaches the terminal speed, i.e. a constant speed, before the timing begins. It is, however, not easy to verify this required condition.

These difficulties has been mostly overcome by a recently developed, computer-controlled Duke viscometer. The collar position, shear stress, and temperature can be constantly monitored during the movement of the collar. Figure 8 shows the shear stress and collar position as a function of time for the sheetfed magenta ink from suppler B and the waterless black ink from suppler A. The linear relationship between collar position and time indicates that the collar is moving at a constant speed and the shear rate is given by the slope of this straight line. An acceleration period was sometimes observed at high shear rates. When this occurred, only that portion of data showing linear relationship between collar

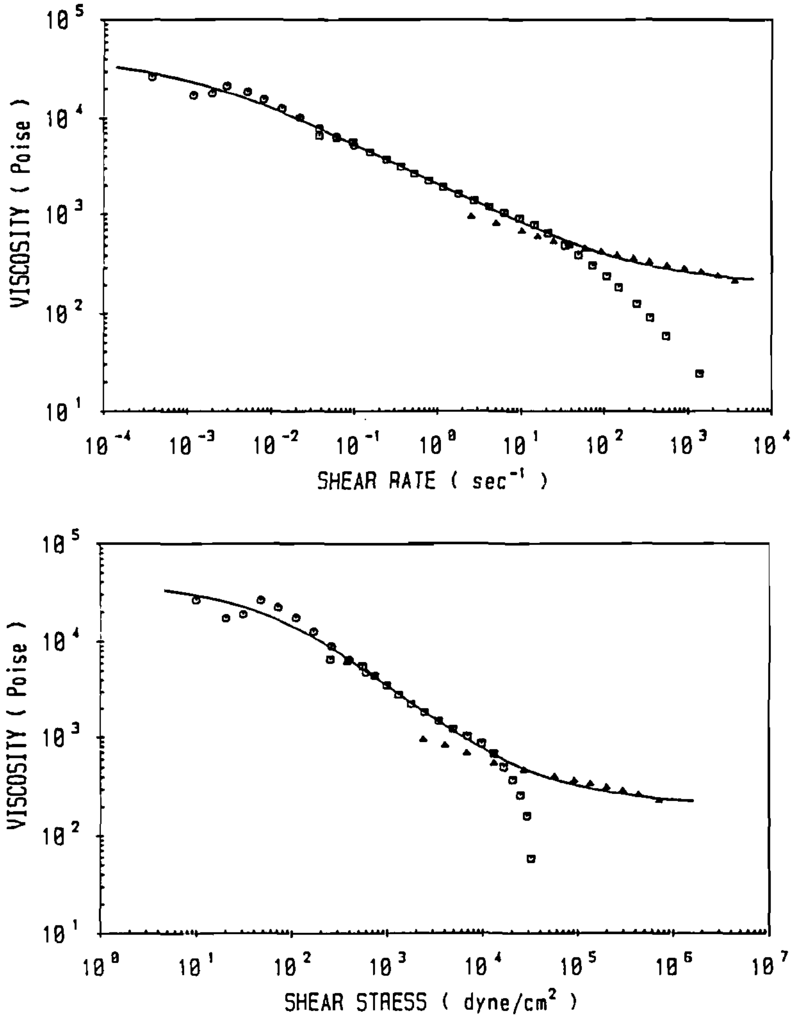
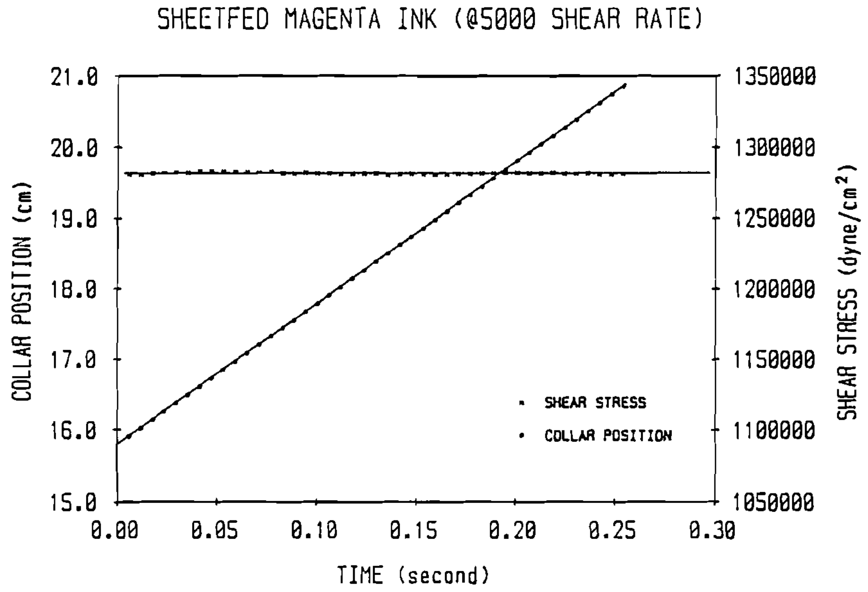


Figure 7. Viscosity profile curves of the sheetfed yellow ink from supplier B. Low-to-medium shear viscosity data are the same as Figure 2 and high shear data (△) were obtained from the Duke viscometer.

position and time was used in the calculation of shear rate and shear stress to assure high degree of accuracy.

The measured stresses scatter slightly around the average value represented by the horizontal line in the figure. This guarantees a high degree of precision in the measured stress



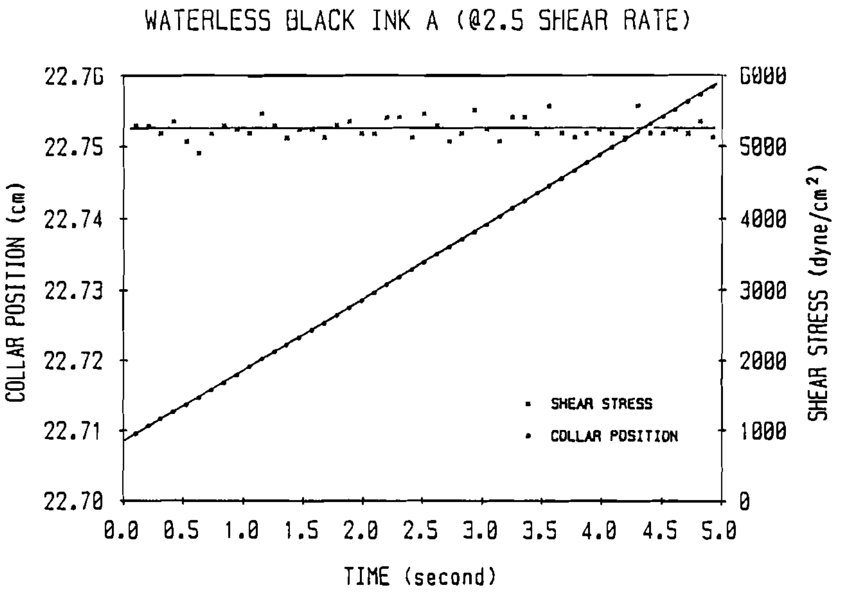


Figure 8. Collar position and shear stress as a function of time for the sheetfed magenta ink from supplier B and the waterless black ink from supplier A.

from the statistical viewpoint. The measurement is doubtful if the stresses exhibit certain patterns. In most cases, the standard variation of shear stress is less than 0.1% of the average value. These results indicate that the shear stress and shear rate measured by the Duke viscometer are very accurate. Any doubt about the measurement can be verified and false results can be eliminated.

Reproducibility of measurements is another major concern of the users. Figure 9 shows the experimental results of three duplicates for the sheetfed magenta ink from supplier B and the waterless black ink from supplier A. The data of three duplicates almost overlap each other, indicating good reproducibility of this instrument. This can be attributed to the fully automated instrument that does not need further operator's manipulation after the sample is loaded.

Heat generation during the viscosity measurement is always a problem to the Laray viscometer. The rate of heat generated by a unit volume of flowing fluid, Q, is given by

$$Q = \tau \dot{\gamma} \tag{4}$$

where τ is the shear stress and $\dot{\gamma}$ the shear rate. Eq. 4 indicates that the higher the shear rate, the more heat is generated. The viscosity of an ink decreases rapidly with increasing temperature. Their relationship can be represented by an Arrhenius-type equation (Barnes et al., 1989)

$$\eta = A e^{E_a / RT} \tag{5}$$

where T is the absolute temperature and R is the gas constant which is equal to 8.314 J/mol/°K. A is a constant and E_a is the activation energy of the fluid.

A thermostat or a constant temperature room is generally used with the Laray viscometer. None of them is sufficient to guarantee a high accuracy of the measurements (Laraignou, 1984). Laraignou (1984) also proposed a factor of 0.1 to correct the falling time for each degree Celsius change of temperature. It has been shown that E_a may be significantly different for fluids that have the same viscosity at one temperature (Chou, 1992). There is no universal constant for the viscosity correction to compensate for the temperature variation. Consequently, the control of temperature during measurement is extremely important.

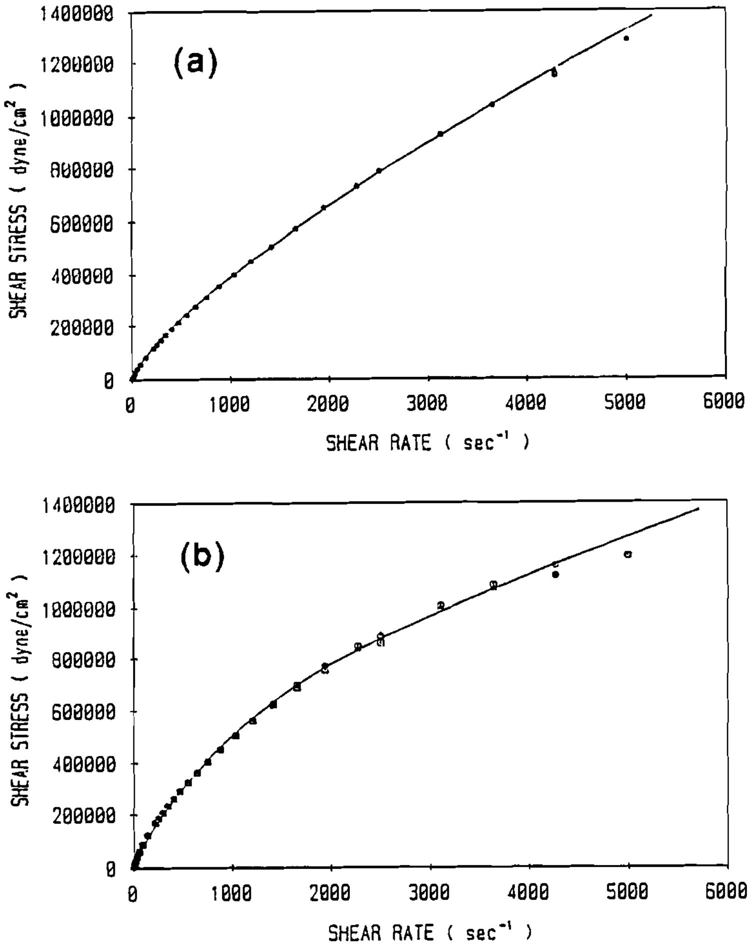


Figure 9. Viscosity data of (a) sheetfed magenta ink from supplier B and (b) waterless black ink from supplier A showing good reproducibility of the Duke viscometer.

A precision, fast response temperature probe is mounted in the sample reservoir of the collar of the Duke viscometer to enable the temperature of materials under test to be monitored during measurement. The temperature of the air circulating within the enclosure is automatically adjusted by the computer to compensate for any changes of sample temperature. The error bars in Figure 10 indicate the variation of temperature in each stroke. The temperature variation increases with shear rate because more frictional heat is generated at higher shear rates. However, the temperature could be maintained to within 0.1 °C during the movement of the collar in a stroke, even at the shear rate of 5000 sec^{-1}.

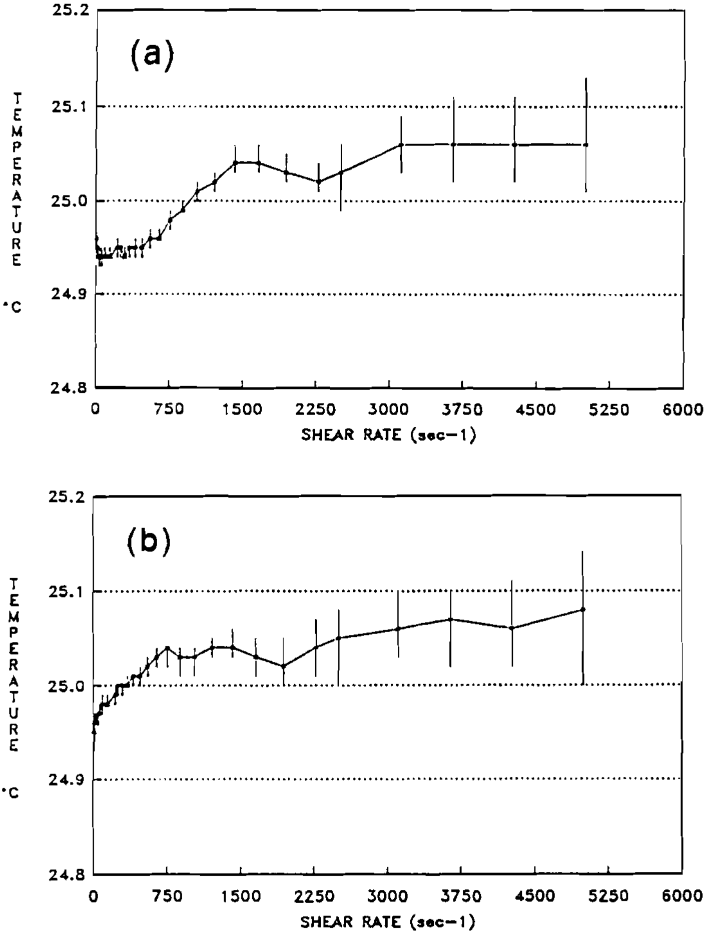


Figure 10. Temperature variation during viscosity measurements of (a) sheetfed magenta ink from supplier B and (b) waterless black ink from supplier A by the Duke viscometer.

Figure 10 also shows that the average temperature of each stroke increases with shear rate but is still kept to within 0.1 °C from the target temperature of 25 °C for a total of 30 strokes. It took less than one hour to complete 30 strokes. These results indicate that the Duke viscometer is very effective in maintaining a constant temperature during measurement.

The viscosity data of the waterless black ink from supplier A depart slightly downwards from the second-Newtonian region at high shear rates, as shown in Figure 11. This kind of behavior was often observed for very heavy inks. It is shown in Figure 10 that the average temperature of this ink varies from 25.04 to 25.08 °C. Such a subtle change in temperature should not cause a viscosity reduction as significant as that in Figure 11. It is very possible that the temperature of sample in the gap between rod and collar may be much higher than the temperature of sample in the reservoir. This localized temperature rise reduces dramatically the viscosity of fluid in the measuring gap. However, this needs to be verified in the future.

The viscosity data obtained from the Duke viscometer at shear rates below about 20 sec^{-1} are lower than those obtained from the Carri-Med rheometer for all the inks, as shown in Figures 7 and 11. This phenomenon can be ascribed to the partial destruction of ink structure during the conditional stroke which coats the rod with the test ink before the commencement of measurement. So, Duke viscometer should be used with caution to measure low shear viscosities. The resolution of shear stress of Duke viscometer is about 150 $dynes/cm^2$. That is, low shear viscosity measurements by Duke viscometer may not be accurate, especially for low viscosity fluids.

Correlation of Press Performance To Rheological Properties

The transition from the first-Newtonian region to the shear thinning region appears at about 10^{-5} sec^{-1} for the magenta newsink from supplier D (Figure 1) and at about 10^{-1} sec^{-1} for the waterless black ink from supplier A (Figure 11). These results indicate that the imposed deformation causing the internal structure of an ink to break down is much greater for the waterless ink than for the newsink. Table I data also show that the time constant k is much smaller for commercial inks than for newsinks. These data indicate that the internal structure of newsinks begins to break down at a deformation smaller than that of viscoelastic commercial inks. It can be concluded that the internal structure of newsinks is more likely a pigment network and the internal structure of commercial inks is more likely a colloidal network (Chou, 1991).

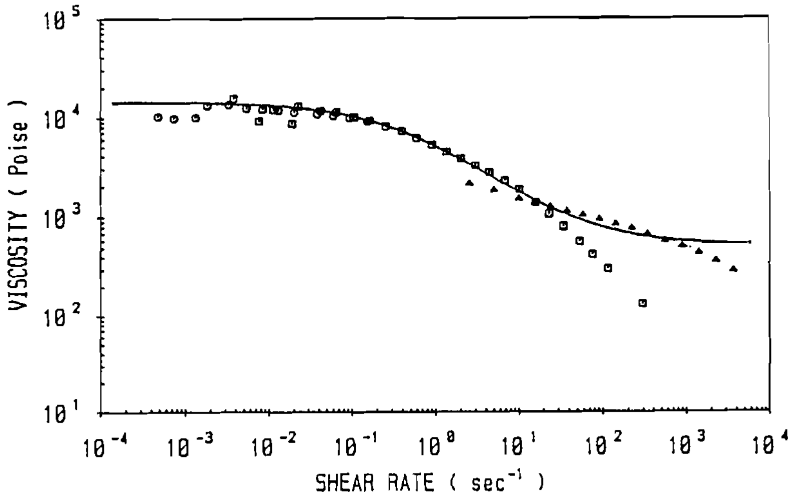


Figure 11. Viscosity profile of the waterless black ink from supplier A.

In general, the quality of prints produced by waterless inks is better than that produced by conventional lithographic inks. The minimum and standard line screens are respectively 175 and 300 at the National Printing and Packaging of Denver (Anon, 1990). Print quality of sheetfed inks is better than that of heatset inks. Newsinks produce the lowest quality. The print quality in terms of dot gain correlates very well with the plastic viscosities of these inks. The extremely high compression and shear actions in the roller nips tend to force the ink to spread over the halftone dots. The higher the plastic viscosity of the ink, the less lateral movement and hence the less dot gain it produces.

CONCLUDING REMARKS

Rotational rheometers equipped with a cone-and-plate or a narrow-gap concentric cylinder geometry are very useful for low-to-medium shear viscosity measurements for most fluids. They are, however, incapable of measuring high shear viscosity of highly viscoelastic commercial inks. Duke viscometer has proven capable of determining high shear viscosity of highly viscoelastic fluids. Yet, it may not be suitable for low shear viscosity measurements. These two types of instruments are actually complementary to each other. None of them can cover the entire shear rate range of interest to the printers.

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