

RHEOLOGICAL CHARACTERISTICS
KEYLESS VERSUS CONVENTIONAL LITHO NEWSINKS

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ABSTRACT

The rheological properties of keyless and conventional lithographic printing inks from U.S., European, and Japanese sources were characterized using a Carri-Med stress-controlled rheometer. The Herschel-Bulkley equation was used to fit the experimental data in the low to medium shear rate region, from which the shear thinning index, the consistency index, and the dynamic yield value were obtained. A plot of the shear thinning indices as a function of the consistency index shows a high degree of linear correlation and a distinct difference between keyless inks and conventional inks. A plot of the dynamic yield values as a function of the consistency index does not indicate any correlation between these parameters but does show that the dynamic yield value of a conventional ink is higher than that of a keyless ink with the same consistency index.

A thixotropy index is defined in this paper to characterize the thixotropy of various inks. A high degree of linear correlation between thixotropy indices and shear thinning indices was observed for all inks. This infers that these two parameters are controlled by the same internal structure of the ink, even though shear thinning is a shear-dependent property and thixotropy is a time-dependent property.

The physical significance of these rheological parameters are discussed. The rheological requirements for keyless inks are outlined in relation to on-press performance. The results indicate that a keyless ink should be more shear-rate dependent and have a much lower

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dynamic yield value than a conventional ink of the same consistency. A higher thixotropy is also desirable in a keyless ink. The major importance of these results is that, from a rheological perspective, keyless inks can be engineered from standardized, measurable parameters without the need for extensive and expensive on-press trial and error testing.

INTRODUCTION

The original process of lithographic printing invented by Senefelder was done from limestones that carried image information. A thin ink film of uniform thickness was applied to the pre-dampened limestone surface by a hand roller, and the ink transferred to the paper substrate had the same thickness everywhere on the image. This process was very slow, but simple. It was a keyless process.

In modern lithographic printing presses, the ink is continuously supplied to an image-carrying plate from an ink fountain through a relatively large number of rollers. If every unit area of printed image is to have the same ink-film thickness, the ink must be supplied in such a way that every unit width across the press receives ink at a rate corresponding to the product of the desired ink-film thickness and the area of printed image passing per unit time. This is accomplished with keys and speed controls on the ink fountain. Having zones across the press with different ink feed and consumption rates complicates the process of maintaining ink-water balance (Chou, et al., 1987), because dampeners generally do not have zone controls and thus the ratio of ink volume to fountain solution volume in any width is also image dependent.

Press operators then have the tasks of adjusting the ink keys to match the image-imposed demand for ink and of finding the dampener setting which gives the best overall ink-water balance. The growth in electronic press controls has been spurred by the magnitude of printed waste and productivity losses associated with manual execution of these tasks.

One of our major printing technology research programs is keyless lithography, which restores the simplicity of the original lithographic process while retaining the high productivity needed in today's environments. Our keyless technology adopts the celled metering roller from

flexography. The amount of ink available to the printing plate is controlled by the predetermined cell volume of the doctored metering roller, not by the image area. However, several new challenges arise from this process. In the keyless system, only a small fraction of the ink available to the plate is taken away by the paper, and the unused ink carries a significant amount of emulsified fountain solution back to the ink fountain to be reintroduced to the ink train. The press soon operates with an "emulsion" ink instead of a "dry" ink as in the conventional lithography (Fadner and Doyle, 1985). This requires that the metering roller be oleophilic and hydrophobic in addition to being wear resistant (Fadner and Bain, 1987).

Both ink and fountain solution inputs to the plate are more or less uniform across the plate in a keyless lithographic system. This suggests that the correct ink-water balance should be easier to achieve on a keyless press than on a conventional press. Our laboratory tests and our production experiences in the field have shown that this is the case. The dampener requires much less attention from the press operator, and the waste is minimal. However, early in the development program, printing failures were encountered due to the appearance of free water that interfered with ink transfer. The ink in the ink fountain of a keyless press may contain up to 30 percent emulsified water (Fadner and Doyle, 1985). High shear conditions existing in the roller nips and at the point of contact between the doctor blade and the metering roller tend to cause the ink to release water (Chou and Fadner, 1986), especially when the water content of the ink is high. Improving the water handling capability of the inks eliminated this source of ink transfer interference.

The optical density of the printed image on the paper substrate is determined by the quantity of the ink on the plate, which is in turn controlled by the amount of ink supplied by the metering roller. We observed that some inks printed darker than others, even though the same metering roller was used. It appears that the amount of ink that flows out of the cells of the metering roller is not controlled solely by the volume of the cells. Ink build up on the back side of the doctor blade was also observed with several inks. This build up caused ink slinging and spitting problems. These phenomena can be attributed to the rheological properties of the ink and

will be discussed in this paper.

EXPERIMENTAL PROCEDURE

Materials

Keyless ink samples, including process colors, were obtained from worldwide suppliers. These inks were tested on our keyless presses in the United States, Japan, and Norway. Three sets of conventional offset newsinks were obtained from different newspaper printing sites. For convenience, each ink was designated by an alphanumeric code (C1, C2,, K1, K2,). The letter K stands for keyless inks, and the letter C stands for conventional inks. The numbers were arbitrarily assigned to identify each ink by supplier and color.

Rheometry

A Carri-Med stress-controlled rheometer was used in this study to determine the rheological properties of each ink. This rheometer allows us to look at the behavior of inks over a range of shear rates covering about six decades. Ink viscosity at shear rates of less than 0.1 reciprocal seconds was measured using the creep method and a 4-centimeter, 1.5-degree cone. Ink viscosity at low to medium shear rates, up to a few hundred reciprocal seconds, was obtained using the flow method with a 4-centimeter, 1.5-degree cone. Ink viscosity at high shear rates, up to a few thousand reciprocal seconds, was obtained using the flow method with a 2-centimeter, 0.5-degree cone.

In the flow measurement, the applied torque was incremented in 200 equal steps from zero to a programmed maximum value and then decremented in the same way back to zero. A hysteresis loop thus resulted. The duration of applied torque in each step was equal to one two-hundredths of the programmed test time. The angular velocity of the rotating cone was continuously monitored with a tachometer. The velocity at the end of each step was recorded as the corresponding shear rate.

In the creep measurement, a constant torque was applied instantaneously to the sample at time zero, and the resultant angular displacement was sampled as a function of time with a proximity sensor. The duration of the applied torque in the creep measurement was taken to be

infinite as compared to that in the flow measurement. The shear rate was calculated from the slope of the linear portion of the creep curve. This method enabled us to extend the viscosity measurement of inks to very low shear rates.

All lithographic inks we have studied to date exhibit a viscoelastic property, and their flow behavior is strongly dependent upon the test conditions. Except as otherwise mentioned, all the measurements were made under identical conditions. The temperature was controlled at 25 ± 0.1 degrees Celsius, the test duration of upward and downward measurements in the flow method was set to five minutes, and the maximum shear stress was programmed at 4774.4 dynes per square centimeter.

A set of experiments was made by the flow method to reveal the effect of test time, which was varied from 0.5 to 40 minutes. The maximum shear stress was programmed at 2387.2 dynes per square centimeter. Once the sample started to flow, the program was terminated so that the sample was hardly disturbed and was ready for next measurement after a short relaxation period. Only the first few data points were recorded.

A common technique used to study the viscoelastic property of polymeric materials is carried out by applying a stress cycle repeatedly to the sample and monitoring the changes in the hysteresis loop. This technique was applied here to four ink samples. A hysteresis loop was made on each sample under standard conditions in the flow measurement. The next loop was initiated on the same sample immediately after the data from the previous run was stored on the floppy disk, which took less than one minute. This procedure was repeated four times. The results are reported as a function of the number of hysteresis loops.

RESULTS

We have found that in the high shear conditions inks behave more like one another than they do in the low to medium shear range. As we will discuss later in this paper, the rheological behavior of inks in the low to medium shear range is more important in the ink transfer from the metering roller than is the behavior in the high shear range. Consequently, the present study of ink rheology was concentrated in the low to medium range.

Evaluation of Rheological Parameters

Figure 1 shows the flow curves of two keyless black inks and an ink oil. These curves differ significantly. The up and down curves of the ink oil overlap one another, are linear, and pass through the origin. This type of fluid is referred to as a Newtonian fluid. The up and down curves of the two inks form hysteresis loops and have definite curvature. This type of ink is referred to as a non-Newtonian fluid. More specifically, the two inks are shear thinning, the slope of the flow curve decreases with increasing shear rate, and are thixotropic, the down curve locates below the up curve. Ink K2, from U.S. supplier B, has a yield value, which is the intercept of the up curve at the stress axis, while ink K16, from Japanese supplier A, does not. The yield value is the minimum stress needed to initiate the flow of the fluid.

The flow curve alone, such as those in Figure 1, only provides a qualitative comparison between inks. That is, ink K2 is less shear thinning and less thixotropic than ink K16, and it has a yield value. It is essential to quantitatively describe the flow behavior of non-Newtonian inks. Many equations have been reported in the literature to fit the experimental rheological data. They are derived from empirical or theoretical considerations. Some of them that are simple and widely used in non-Newtonian fluid mechanics are given here, along with the equation for a Newtonian fluid (Whorlow, 1980).

Newtonian Model $\tau = \eta_n \dot{\gamma}$ (1)

Bingham Model $\tau = \tau_d + \eta_p \dot{\gamma}$ (2)

Casson Model $\sqrt{\tau} = \sqrt{\tau_d} + \sqrt{k \dot{\gamma}}$ (3)

Power Law Model $\tau = k \dot{\gamma}^n$ (4)

Herschel-Bulkley Model $\tau = \tau_d + k \dot{\gamma}^n$ (5)

- where τ is the shear stress in the ink.
- τ_d is the dynamic yield value.
- $\dot{\gamma}$ is the rate of shear strain or shear rate in the ink.
- k is a parameter that is indicative of the consistency of the ink.
- n is the shear thinning index which is indicative of the degree of

η_n departure of the ink from Newtonian behavior ($n = 1$ for a Newtonian fluid).
 η_p is the viscosity of a Newtonian fluid.
 is the plastic viscosity of a Bingham fluid.

The consistency index, k' , has been defined by researchers in non-Newtonian fluid mechanics as follows (Rohsenow, 1964).

$$k' = k \left(\frac{3n + 1}{4n} \right)^n \quad (6)$$

The power law model has been very successfully applied to polymeric fluids. We have found that the Herschel-Bulkley model, which is a modification of the power law model, best fits the experimental data of all the inks we have studied, because most of these inks have a yield value. The rheological parameters reported in this paper are derived from the Herschel-Bulkley model.

It is impossible to measure a "true" yield value in a non-Newtonian fluid. Consequently, the yield value obtained from the best-fitting Herschel-Bulkley equation is called the "dynamic" yield value. The dynamic yield value varies with test conditions. In some cases, the calculated value is a small negative number and is reported as zero in this paper. Table I summarizes the initial yield values and their corresponding shear rates as a function of test time for ink K2. Data from the creep measurements are also included. The initial yield value is the minimum applied stress that induces a flow that can be detected by the instrument. The data in Table I indicate that the initial yield value, and presumably the dynamic yield value, increases with decreasing test duration at each applied stress. The results from creep measurements also show that a much lower applied stress can induce a measurable ink flow. A linear relationship was found between the viscosity and the corresponding shear rate on the first few data points when plotted on a log-log scale, as shown in Figure 2. The lines shown are more or less parallel and tend to shift to upper right hand of the plot with decreasing test time.

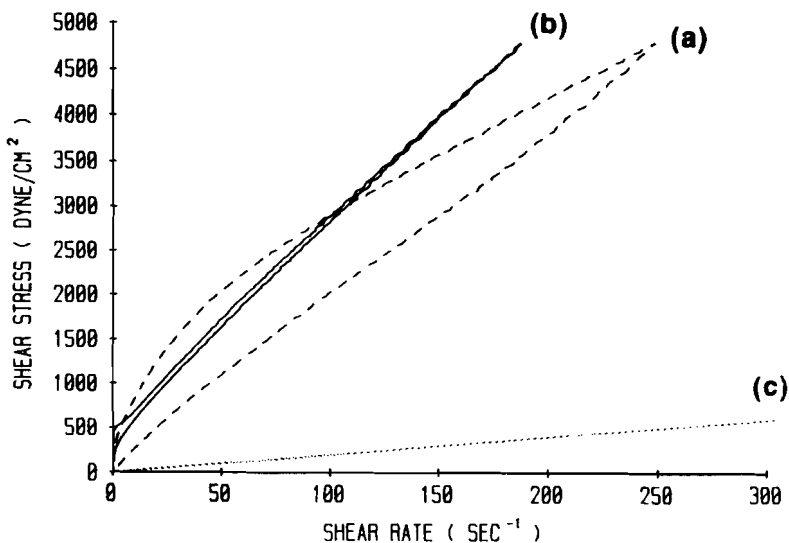


Figure 1. Flow curves of (a) a Japanese keyless black ink, K16; (b) an American keyless black ink, K2; and (c) an ink oil from Magie Bros. Oil Co.

TABLE I. INITIAL YIELD AND SHEAR RATE AS A FUNCTION OF TEST TIME FOR INK K2.

TEST TIME (MINUTE)	DURATION OF EACH STEP (SECOND)	INITIAL YIELD (DYNE/CM ²)	SHEAR RATE (SEC ⁻¹)
*	INFINITE	71.6	.0063
*	INFINITE	95.5	.0086
*	INFINITE	119.4	.0130
*	INFINITE	149.2	.0272
40	12	214.8	.0425
20	6	238.7	.0425
10	3	274.5	.0772
5	1.5	346.1	.1352
2	0.6	417.8	.1429
1	0.3	549.1	.4287
0.5	0.15	620.7	.2240

* Data from the creep measurements. Value given under the initial yield is the actual shear stress applied to the sample.

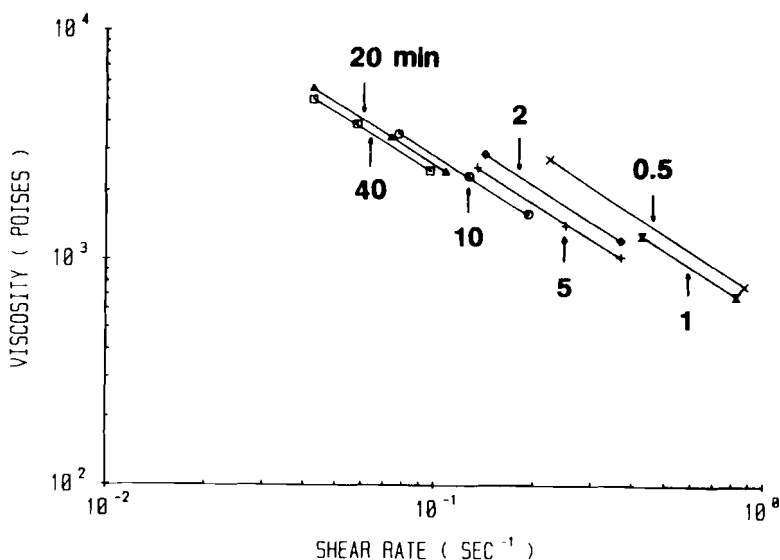


FIGURE 2. Viscosities of ink K2 as a function of shear rate and test time.

Many non-Newtonian fluids possess a time dependent property called thixotropy. When these fluids are sheared at a constant rate, the shear stress, and hence the viscosity, decreases with time until a steady state is reached. This occurs because the internal structure of the fluid is progressively destroyed by the shearing action and the fluid becomes less resistant to flow. Thixotropy accounts for the down curve in the flow measurement experiments being below the up curve. The loop area enclosed between the up and down curves is therefore indicative of the magnitude of thixotropy. Different inks cover different shear ranges under a given set of test conditions and make the comparison of this property ambiguous when based solely on the loop area. A better parameter is the thixotropy index, θ , defined here as the ratio of the loop area to the area underneath the up curve. The physical significance of the thixotropy index will be discussed later in this paper.

Correlations between Rheological Parameters

The dynamic yield value, the shear thinning index, the consistency index, and the thixotropy index for conventional and keyless inks are summarized in Tables II and III, respectively. A plot of the shear thinning indices as a function of the consistency index shows a

TABLE II. RHEOLOGICAL PARAMETERS OF CONVENTIONAL INKS.

INK		τ_d (DYNE/CM ²)	n	θ	k'
U.S. SOURCES					
BLACK	A, C1	813	.828	.051	128
	B, C2	567	.781	.048	99
CYAN	A, C3	430	.936	.036	59
	B, C4	518	.754	.104	131
	C, C5	621	.855	.081	107
MAGENTA	A, C6	250	.780	.087	160
	B, C7	811	.664	.091	380
	C, C8	331	.780	.119	130
YELLOW	A, C9	497	.822	.109	136
	B, C10	823	.713	.137	239
	C, C11	291	.745	.096	194

TABLE III. RHEOLOGICAL PARAMETERS OF KEYLESS INKS.

INK		τ_d (DYNE/CM ²)	n	θ	k'
U.S. SOURCES					
BLACK	A, K1	355	.861	.027	32
	B, K2	388	.874	.021	48
	C, K4	276	.860	.032	37
CYAN	A, K4	209	.761	.127	121
	B, K5	199	.857	.079	56
	C, K6	71	.830	.079	88
MAGENTA	A, K7	0	.632	.143	274
	B, K8	157	.728	.123	126
	C, K9	79	.884	.048	70
YELLOW	A, K10	187	.798	.093	76
	B, K11	225	.852	.068	48
	C, K12	190	.916	.050	64
EUROPEAN SOURCES					
BLACK	A, K13	48	.685	.101	248
	B, K14	353	.908	.069	33
	B, K15	75	.862	.101	62
JAPANESE SOURCES					
BLACK	A, K16	0	.485	.207	370
	B, K17	0	.576	.186	263

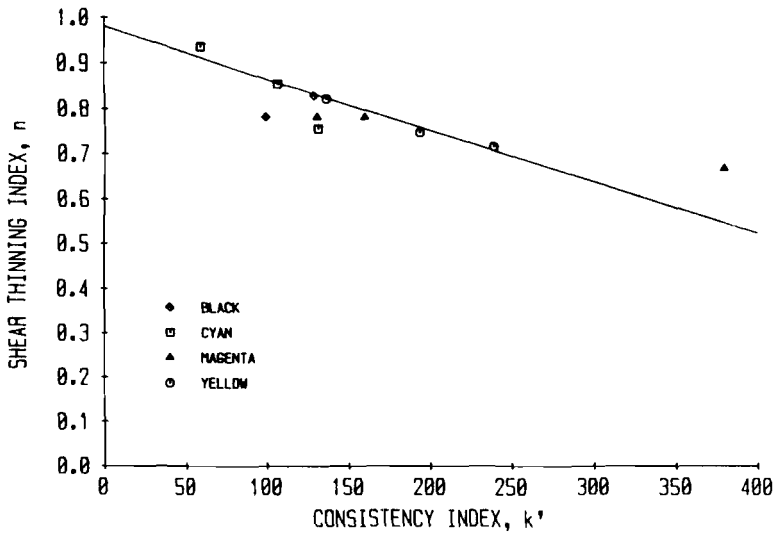


Figure 3. Shear thinning indices of conventional inks as a function of the consistency index.

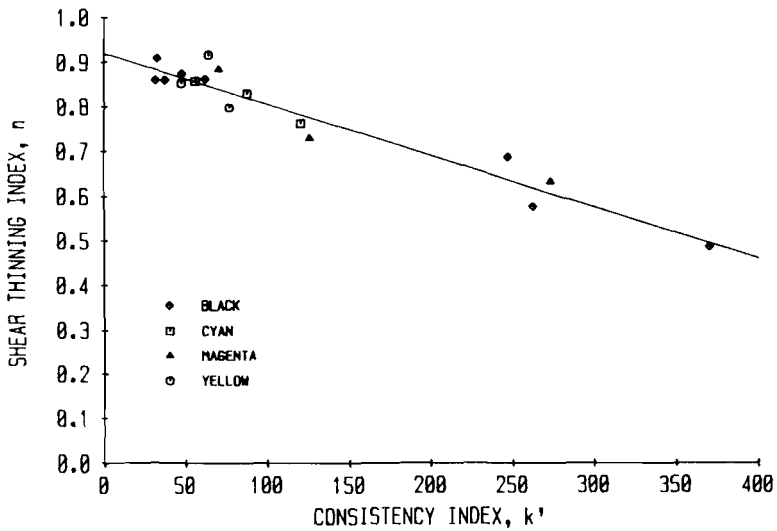


Figure 4. Shear thinning indices of keyless inks as a function of the consistency index.

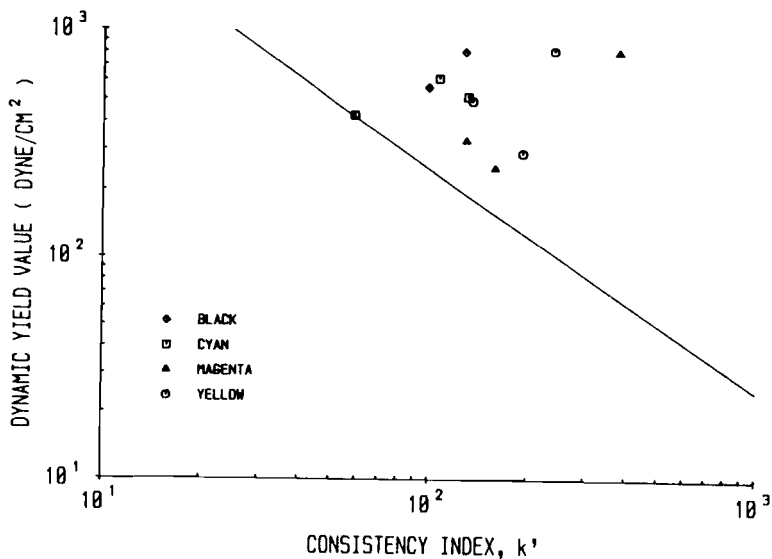


Figure 5. Correlation between the dynamic yield value and the consistency index for conventional inks.

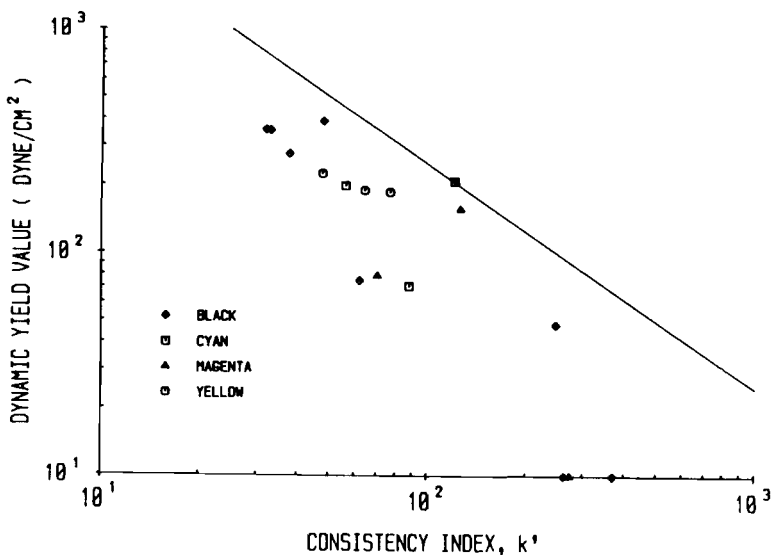


Figure 6. Correlation between the dynamic yield value and the consistency index for keyless inks.

high degree of linear correlation and a distinct difference between keyless inks and conventional inks, as shown in Figure 3 and Figure 4. The correlation is indicative of the fact that all inks are the result of a process which adds structure producing materials to a Newtonian vehicle. The higher values of n found in conventional inks have implications on thixotropic behavior as discussed below.

A plot of the dynamic yield values as a function of the consistency index does not reveal any correlation, but there is again a clear difference between the convention and keyless inks. At any given consistency index, the keyless inks always exhibit a lower dynamic yield value than the conventional inks, Figure 5 and Figure 6.

A plot of the thixotropy indices as a function of the shear thinning index shows a high degree of linear correlation, but no distinction between keyless and conventional inks, Figure 7. The data fit a line that bounds the extremes of thixotropic behavior wherein a more shear thinning ink has a larger thixotropy index, the theoretical maximum value of θ being 0.5 at $n = 0$, and the minimum value of θ being 0 at $n = 1.0$, the Newtonian fluid.

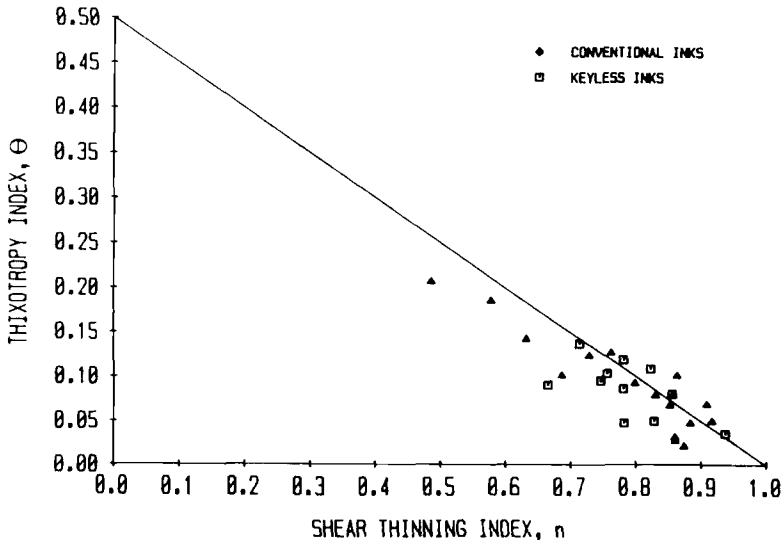


Figure 7. Correlation between the thixotropy index and the shear thinning index for conventional and keyless inks.

Viscosity Profile

The viscosity is generally plotted as a function of the shear rate on a log-log scale to provide a complete picture of the flow behavior. Figure 8 shows the viscosity profiles of six inks. These profiles all tend to reach asymptotes in the very low shear region and in the very high shear region. Thus, in all cases, a shear thinning region locates between these two plateau regions. The low shear region is generally referred to as the first Newtonian region and the high shear region as the second Newtonian region. The corresponding viscosities are called the zero-shear-rate viscosity and the infinite-shear-rate viscosity. The dynamic yield value of an ink increases rapidly with increasing zero-shear-rate viscosity. Figure 8 reveals significant differences between inks in this regard. The infinite-shear-rate viscosities are, on the other hand, of the same order of magnitude for all the inks in Figure 8.

The viscosity profiles of three keyless inks, K2, K7, and K16 are compared on the same scale in Figure 9. Two of them, K7 and K16, have no dynamic yield value, and their viscosities tends to decrease more slowly than the ink with a dynamic yield value, K2. The results contradict the prediction made upon the shear thinning indices. Ink K2 has a larger shear thinning index and is supposed to be less shear thinning. The contradiction will be discussed later in this paper.

TABLE IV*. EFFECT OF TEMPERATURE ON LOOP AREA AND THIXOTROPY INDEX

INK	TEMPERATURE (°C)	LOOP AREA (DYNE/CM ² /SEC x 10 ⁵)	θ
K2	15	0.06	0.029
	25	0.11	0.022
	35	0.17	0.016
	45	0.32	0.016
K16	15	0.88	0.312
	25	1.61	0.210
	35	2.77	0.149
	45	4.26	0.122

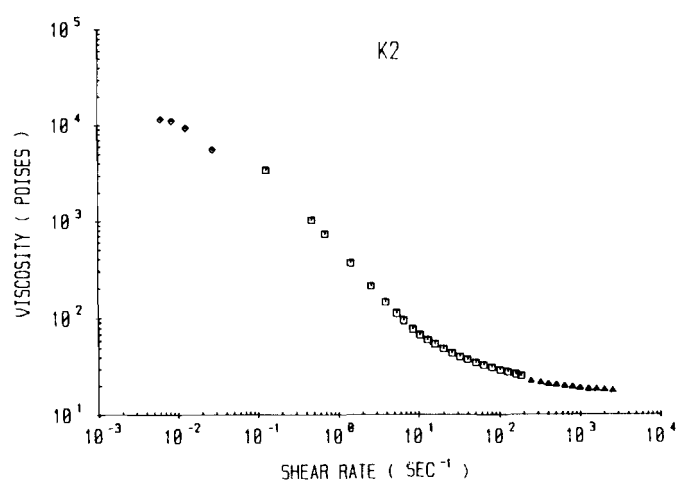
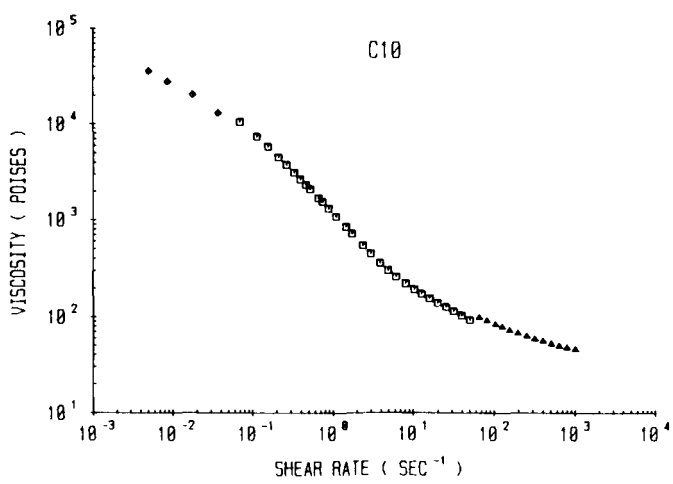
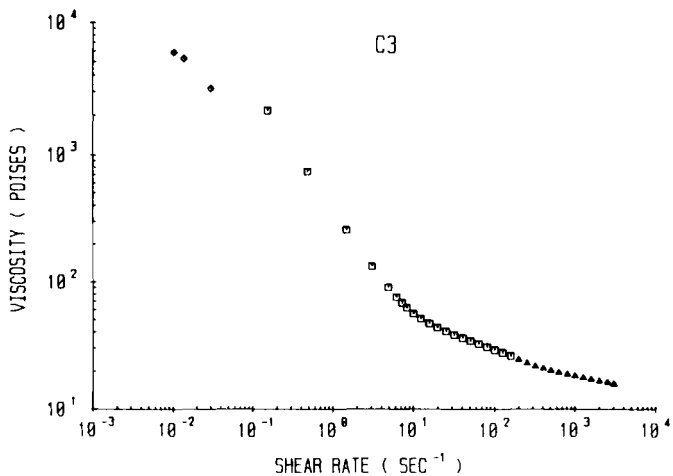
TABLE V*. EFFECT OF MECHANICAL SHEAR ON LOOP AREA AND THIXOTROPY INDEX

INK	LOOP NUMBER	LOOP AREA (DYNE/CM ² /SEC x 10 ⁵)	θ
K2	1	0.11	0.022
	2	0	0
	3	0	0
	4	0	0
K16	1	1.61	0.210
	2	0.26	0.035
	3	0.17	0.022
	4	0.14	0.017
K14	1	0.42	0.069
	2	0.09	0.015
	3	0.06	0.010
	4	0.04	0.007
K15	1	0.42	0.101
	2	0.10	0.025
	3	0.07	0.017
	4	0.05	0.013

* The data of inks K2 and K16 in Table IV and V were obtained several months after the data reported in Tables II and III.

Effects of Temperature and Mechanical Shear

Figure 10 shows the flow curves of ink K16 at four temperatures. The flow curve shifts toward the right with increasing temperature. This is a common phenomenon, in which a fluid becomes less resistant to flow at higher temperatures. Table IV lists the area of hysteresis loops and the thixotropy indices of inks K2 and K16 at different temperatures. The loop areas increase with temperature for both inks, whereas the thixotropy indices decrease with temperature. Figure 11 compares the rheological parameters of the two inks as a function of temperature. They dynamic yield values, the consistency indices, and the thixotropy indices all decrease with temperature; and the shear thinning indices increase with temperature.



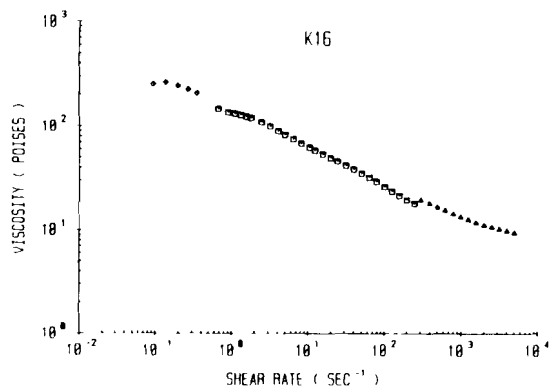
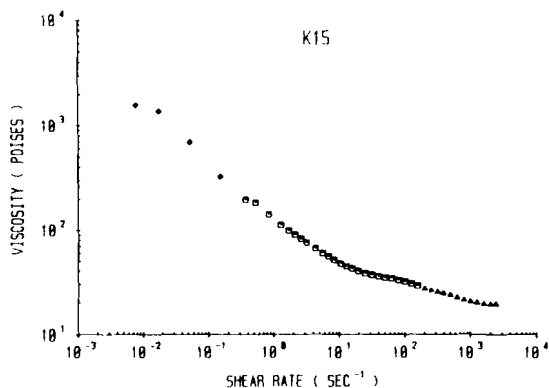
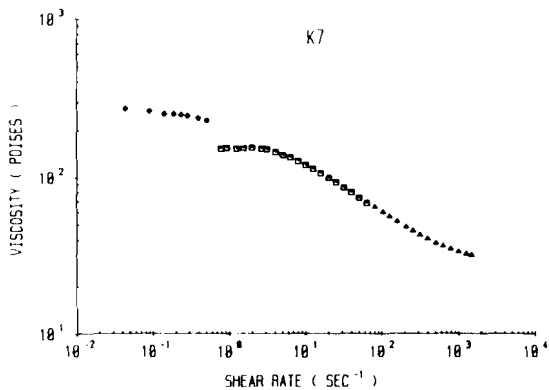


Figure 8. Viscosity profiles of inks C3, C10, K2, K7, K15, and K16. \diamond represents data from the creep measurements; \square from the flow measurements at low-medium shear rates; and \triangle from the flow measurements at high shear rates.

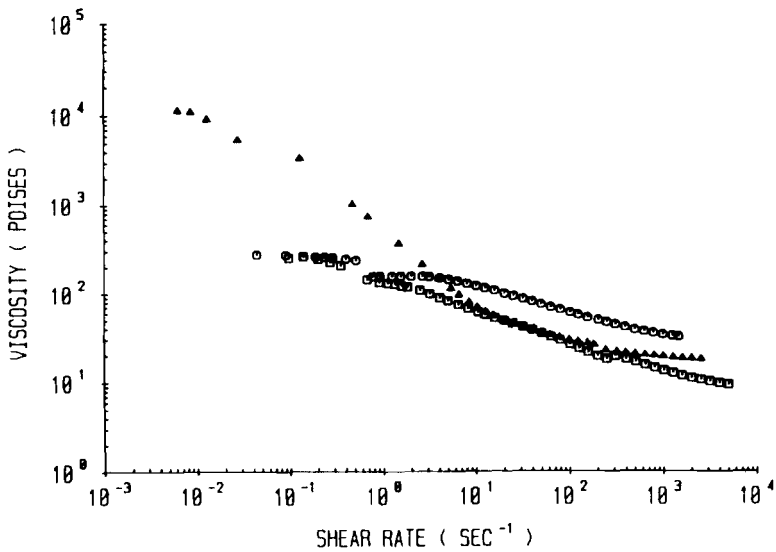


Figure 9. Comparison of viscosity profiles of inks K2 (Δ), K7 (\circ), and K16 (\square).

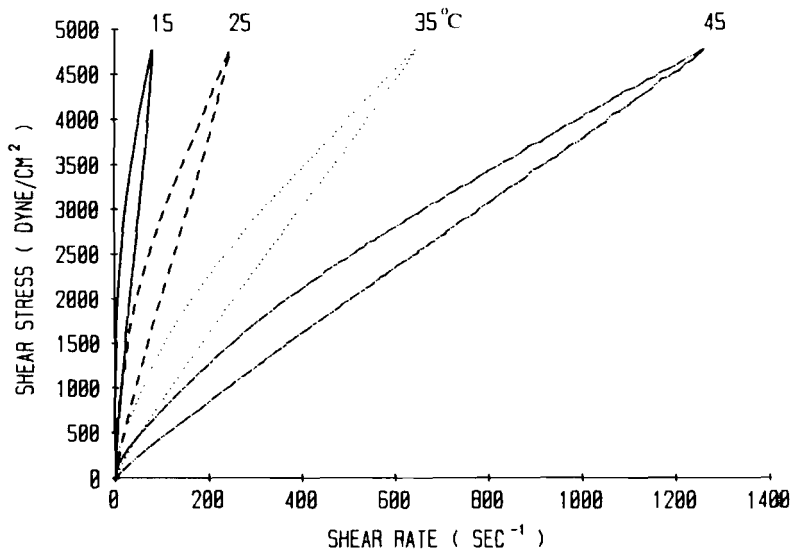


Figure 10. Flow curves of ink K16 at four temperatures.

The results from repeated shear cycles are summarized in Table V and Figures 12 and 13. The trend is similar to that observed by varying temperature. The only qualitative difference is that the loop area decreases with the number of hysteresis cycles.

These data made it clear that the rheological properties of non-Newtonian fluids are strongly dependent upon the test conditions and shear history of the sample. The measurements upon which the following discussions are based were made under identical test conditions. The ink sample was very carefully introduced to the measuring system and left undisturbed for at least five minutes before the start of the measurement to minimize disturbance to the sample.

DISCUSSION

Dynamic Yield Value

The existence of a "true" yield value in a non-Newtonian fluid has long been a matter of debate. Walters (1987) has pointed out that the yield value is merely an artifact caused by the measurement process. It is a matter of how patient an operator is and of what technique is used in the measurement. The data in Table I show that the yield value determined by the flow method decreases with increasing test time and that a much lower stress can induce a measurable flow when the creep method is used. The viscosity also decreases with increasing test time (Figure 2). This behavior is typical for viscoelastic materials such as lithographic inks.

Inks tend to behave more like elastic fluids as the time scale of measurement is shorter and thus become more resistant to flow. If a fluid possesses a "true" yield value, its viscosity will approach infinity at very low shear rates. This is not the case with inks, as is shown in Figure 8. All the inks tend to reach a constant viscosity at very low shear rates and behave like Newtonian fluids. The zero-shear-rate viscosity is about 300 poises for inks K7 and K16 which exhibit no dynamic yield value. As the dynamic yield value becomes measurable in the other inks, the zero-shear-rate viscosity increases.

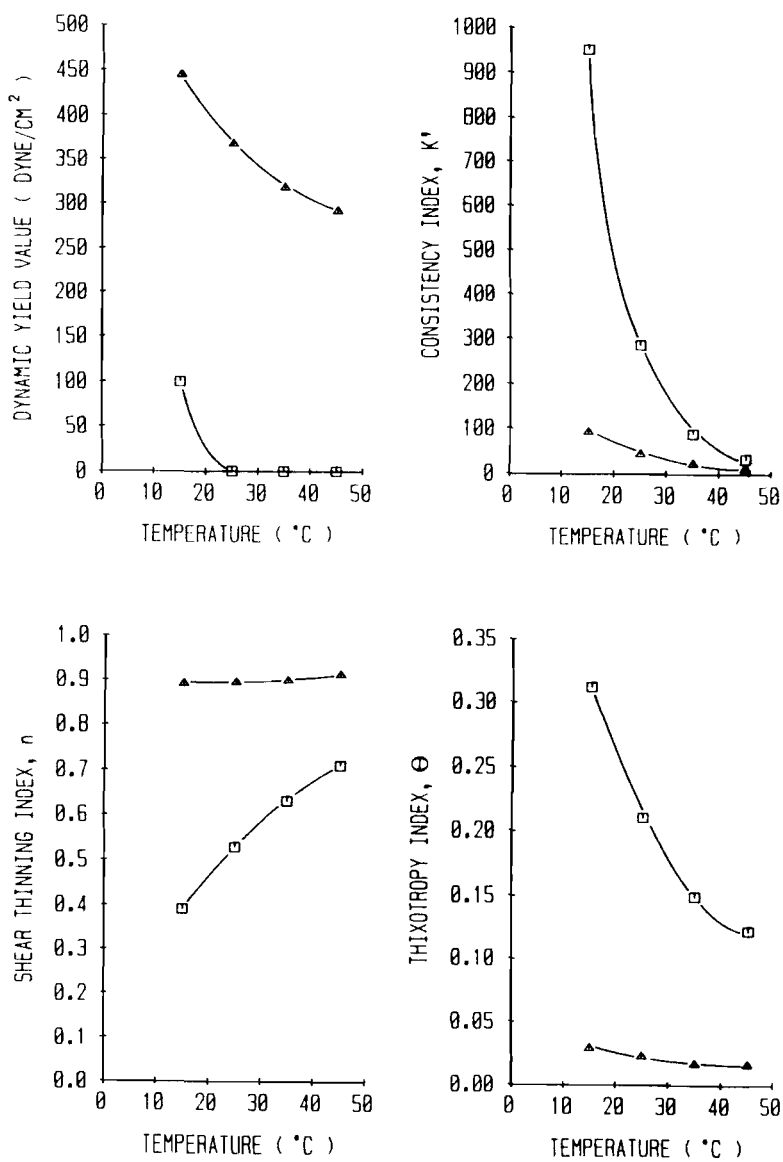


Figure 11. Variation of rheological properties of inks K2 (Δ) and K16 (\square) with temperature.

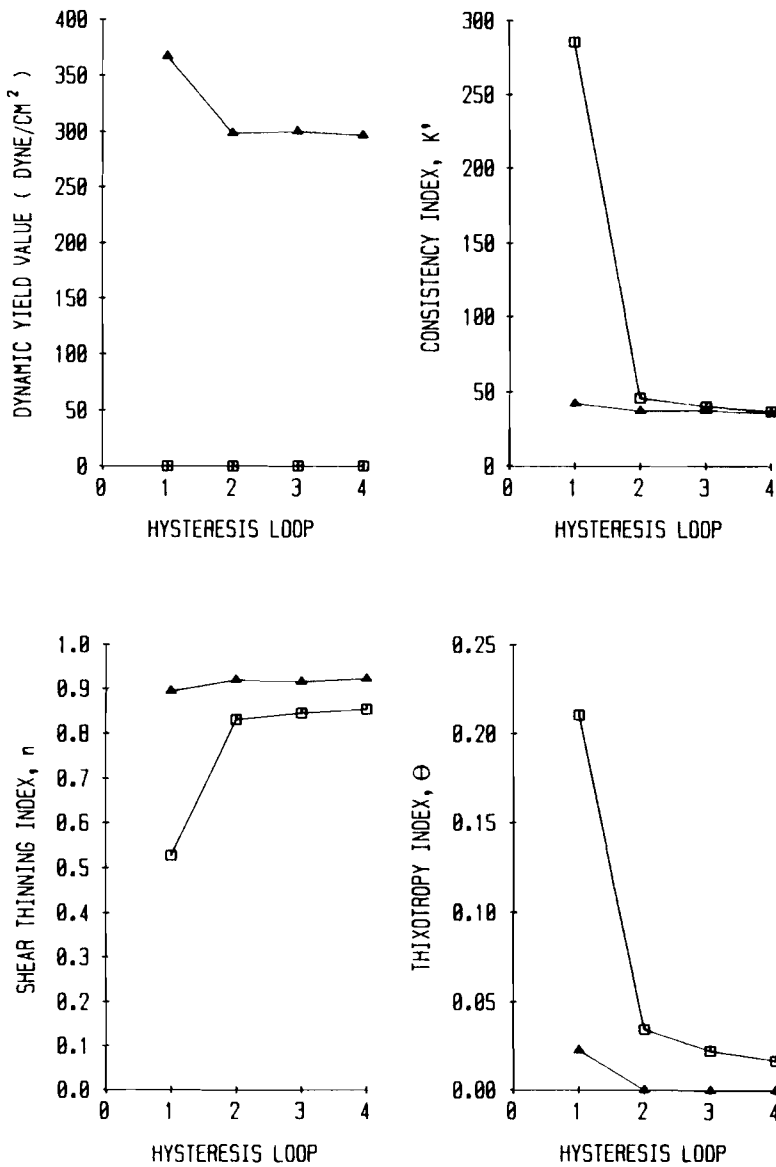


Figure 12. Changes in rheological properties of inks K2 (Δ) and K16 (\square) as a function of hysteresis cycle.

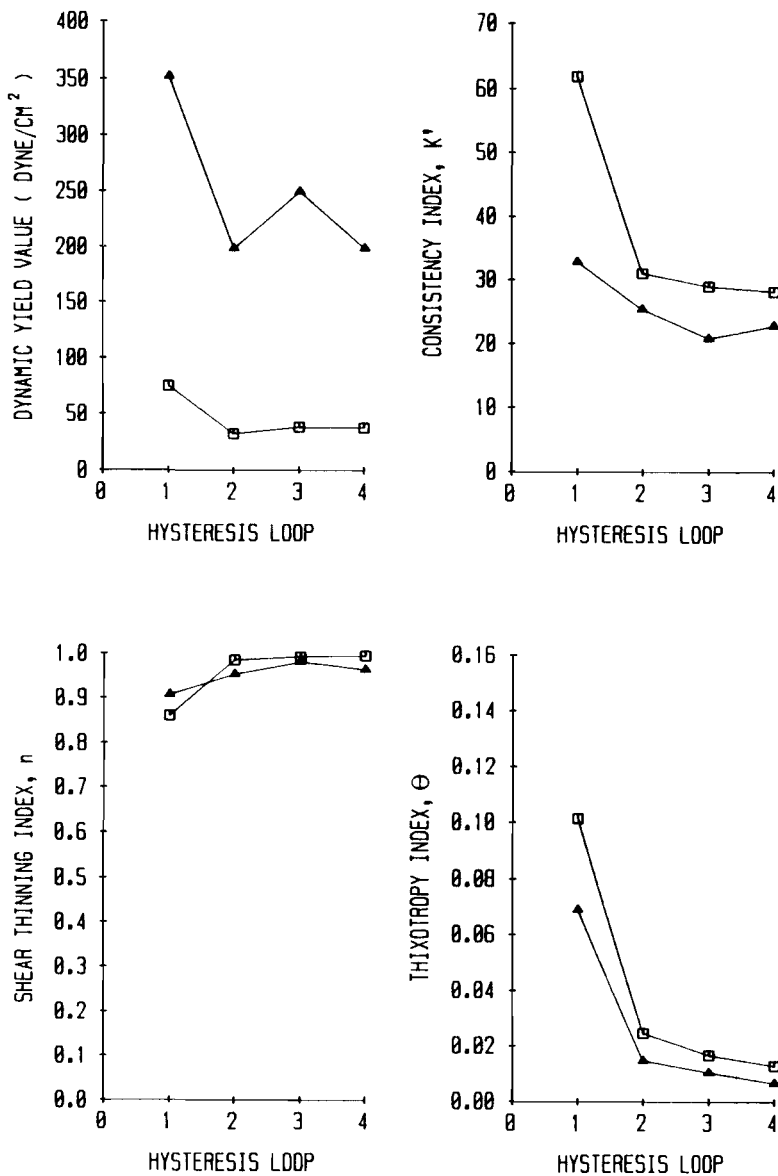


Figure 13. Changes in rheological properties of inks K14 (Δ) and K15 (\square) as a function of hysteresis cycle.

Shear Thinning Index and Viscosity

The shear thinning index is a measure of how rapidly the viscosity of a fluid decreases with increasing shear rate. The lower the shear thinning index, the greater the reduction in viscosity for a given change in shear rate. In other words, the fluid is more shear thinning. Figure 9 shows that the viscosity of ink K16 decreases more rapidly in the shear thinning region than the viscosity of ink K7. This is consistent with their shear thinning indices, as seen in Table III. Neither of these two inks have a finite dynamic yield value. Confusing results are obtained with inks that do have a finite dynamic yield value. Ink K2 has a higher shear thinning index and is therefore expected to be less shear thinning than the other two inks. Its viscosity, however, decreases more rapidly than does the viscosity of the other two inks. This discrepancy can be attributed to the appearance of the dynamic yield value and the definition of viscosity. The viscosity reported in this paper is defined as the ratio of shear stress to shear rate (Bird et al., 1987), which is the slope of the line that connects a point on the flow curve with the origin. It is sometimes called the apparent viscosity and is given as follows with the Herschel-Bulkley equation incorporated.

$$\eta_a = \tau / \dot{\gamma} = \tau_d / \dot{\gamma} + k \dot{\gamma}^{n-1} \quad (9)$$

where η_a is the apparent viscosity.

Some researchers (Bird, et al., 1987) calculated the shear thinning index from the slope of the line that characterizes the region of most rapid decrease of the apparent viscosity in the viscosity profile. By carefully examining the viscosity profiles in Figure 8, the shear thinning region is seen to occur at shear rates less than 10 sec^{-1} for inks that have a significant dynamic yield value, while it is seen to occur at much higher shear rates and extend over a wider shear-rate range for inks without dynamic yield values. In both bases, the shear thinning index is calculated from a portion of, rather than the entire, flow curve.

Other researchers (Schramm, 1985) have defined another viscosity term, which they called the true viscosity, as the slope to the flow curve at any given shear rate. It

is given by

$$\eta_t = d\tau/d\dot{\gamma} = nk \dot{\gamma}^{n-1}$$

where η_t is the true viscosity. The shear thinning index is calculated in this case by fitting the Herschel-Bulkley equation to the entire flow curve. It characterizes the changes in the slope of the flow curve, that is, changes in the true viscosity. The shear thinning indices reported in this paper were obtained by this method.

Table VI compares the shear thinning indices calculated by both methods for inks in Figure 8. Both methods give similar shear thinning indices for inks without dynamic yield values, but the results differ significantly for inks with definite dynamic yield values. The calculation of the shear thinning index using the viscosity profile tends to over emphasize the very low-shear-rate region when the ink has a dynamic yield value. The calculation of the shear thinning index based on fitting the Herschel-Bulkley equation to the entire flow curve obviously neglects the very low-shear-rate region.

In many cases, the apparent viscosity tends to explain the physical significance of rheological behavior of fluids better than the true viscosity. Figure 14 shows the apparent and true viscosity curves as functions of shear rate on a linear scale for both up and down curves of ink K16. The apparent viscosity of the down curve is less than that of the up curve at any shear rate, while the true viscosity of the down curve is greater than that of the up curve at high shear rates. The results from the true viscosity curves seem unrealistic. The resistance to flow of a thixotropic fluid should be lower in the down curve than in the up curve, because the internal structure of the fluid is progressively destroyed during the upward measurement and is unable to recover completely during the downward measurement. It is also expected that low-shear-rate viscosity should be higher for fluids with dynamic yield values, because a greater stress is required to induce flow. This is consistent with the results shown in Figure 8.

The flow curve of a Bingham fluid is shown schematically in Figure 15 with the corresponding apparent

and true viscosity curves. According to Eq. 2, the Bingham fluid is characterized by a single viscosity (the plastic viscosity), and its shear thinning index is equal to 1. In this case the true viscosity is a better way to describe its rheological behavior than the apparent viscosity. The apparent viscosity decreases with shear rate, and the shear thinning index is not equal to 1 when calculated from the viscosity profile.

TABLE VI. SHEAR THINNING INDICES CALCULATED FROM TRUE AND APPARENT VISCOSITY.

INK	FROM TRUE VISCOSITY	FROM APPARENT VISCOSITY
C3	.936	.102
C10	.713	.180
K2	.874	.089
K15	.862	.529
K7	.632	.689
K16	.485	.579

In summary, neither technique is sufficient to fully characterize the shear thinning behavior of non-Newtonian fluids. The confusion comes primarily from the appearance of the dynamic yield value. This does not invalidate the conclusions drawn from the work described in this paper. We are currently seeking a better model that will enable us to describe the rheological behavior of printing inks in a more straightforward way.

Thixotropy Index and Internal Structure

The thixotropy of a non-Newtonian fluid is generally explained by the presence of some internal structure. For printing inks, the interactions of pigments through the ink vehicle or the flocculated pigments may contribute to the formation of internal structure. This structure also accounts for the shear thinning behavior of inks. At very low shear rates, the deformation of the fluid is so small that the internal structure is hardly affected by the shearing action, and the fluid behaves as if it had no internal structure. The result is the first Newtonian region. At moderate shear rates, the internal structure is partially destroyed and simultaneously reforms as the

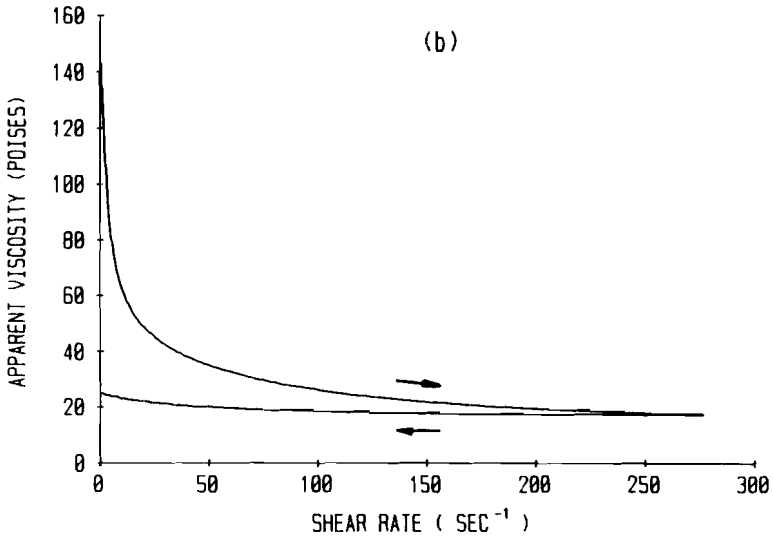
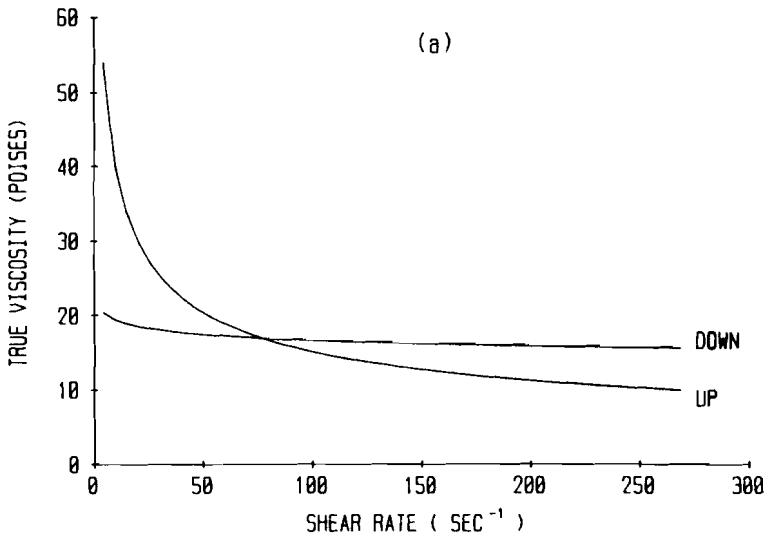


Figure 14. Viscosities of ink K16 as a function of shear rate: (a) true viscosity and (b) apparent viscosity.

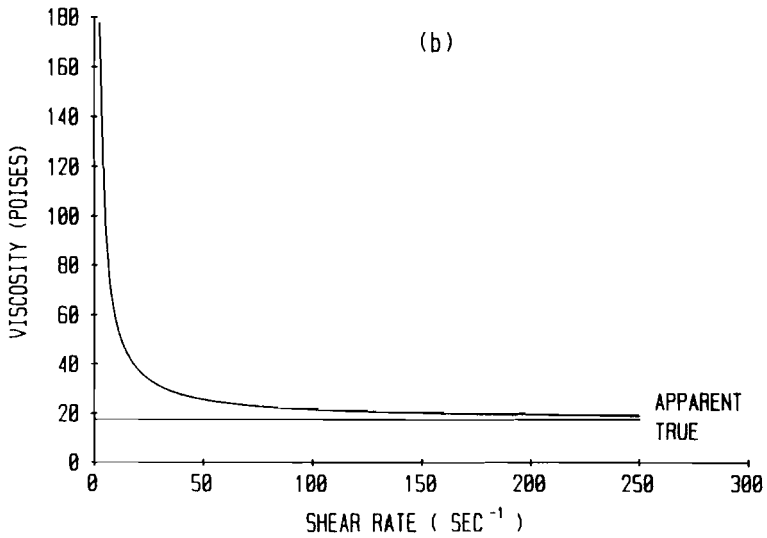
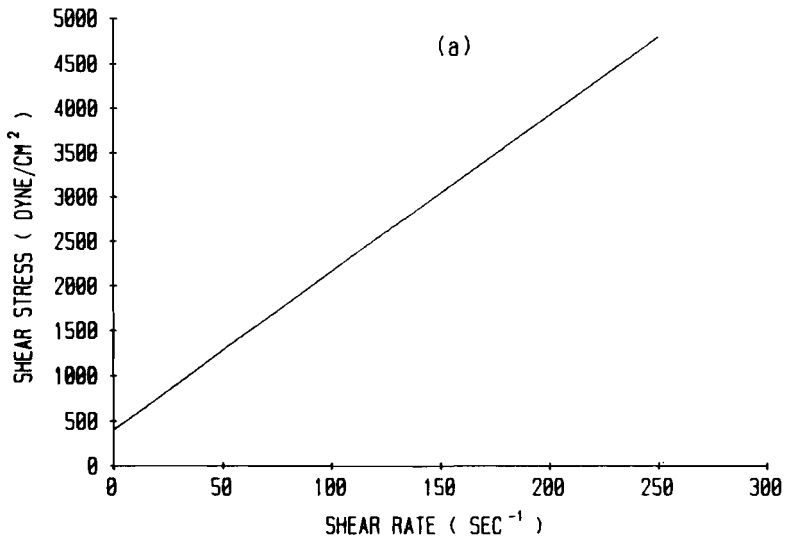


Figure 15. Rheological behavior of a Bingham fluid: (a) flow curve; (b) true and apparent viscosities as a function of shear rate.

shear rate is reduced, probably via a diffusion-controlled process. If the structure can reform instantaneously, the down curve will overlap the up curve. Fluids of this type are generally called pseudoplastics. They are shear thinning but not thixotropic. If the rate of structural recovery is slower than the destruction rate, the down curve appears below the up curve resulting in a hysteresis loop. Fluids of this type are thixotropic. When the shear rates are so high that the internal structure is completely destroyed, the fluid again behaves like a Newtonian fluid. The viscosity becomes independent of shear rate. This is the second Newtonian region.

The area under the flow curve, as in Figure 1, has the dimensions of ergs per cubic centimeter per second. It is a measure of the rate of energy deposited in a unit volume of flowing fluid. When the test times of upward and downward measurements are the same, this area becomes equivalent to the energy that is consumed to partially destroy the internal structure and is therefore indicative of the magnitude of thixotropy. Table IV illustrates that the loop area increases with temperature. This is unrealistic. The increasing thermal motion of molecules at high temperatures tends to weaken the internal structure of the fluid, and a reduction in the thixotropy is expected. The discrepancy is caused by the fact that the flow curves cover different shear ranges for different fluids and/or under different test conditions. Thus, there is no common boundary condition. However, when the flow curves in Figure 10 are plotted on a relative scale such that the initial and end points of flow curves coincide, the loop area then decreases with increasing temperature. A thixotropy index is accordingly defined as the ratio of the loop area to the area underneath the up curve. It is the fraction of total energy used in destroying the internal structure. Table IV shows that the thixotropy index does decrease with increasing temperature. Both the loop area and the thixotropy index decrease with the number of hysteresis cycles as expected (Table V).

Figures 11 and 12 indicate that changes in the rheological properties are affected less by temperature than by the number of hysteresis cycles. This is attributed to the smaller deformation of the internal structure caused by thermal fluctuation than by mechanical shear. The increase in the shear thinning indices in both cases confirms that the internal structure in the fluid is

also responsible for the shear thinning behavior.

The linear relationship between the thixotropy index and the shear thinning index (Figure 7) provides further evidence that these two properties are determined by the same internal structure. There is no internal structure in Newtonian fluids, and the thixotropy index is equal to zero. This accounts for the line in Figure 7 intercepting the shear thinning index axis at $n = 1.0$. The other extreme can be represented by a nonexistent, "super structured" fluid. A minimum stress is required to induce the flow, that is, the fluid has a yield value. Once this yield stress is reached, the super structure disappears and there is no resistance to flow at all. The up curve is parallel to the shear rate axis, and the shear thinning index is equal to zero. The fluid behaves like a Newtonian fluid in the downward measurement. The thixotropy index of this fluid is equal to 0.5. It is the intercept at the thixotropy index axis. When the shear thinning indices are calculated from the viscosity profiles, as seen in Table VI, the data points of inks with definite dynamic yield values deviate significantly away from this linear relationship. This indicates that the shear thinning index calculated on the basis of fitting the Herschel-Bulkley equation to the entire flow curve is a better parameter for characterizing the internal structure of fluids.

Correlation with Press Performance

The major configurational difference between a keyless and a conventional press is the presence of an engraved metering roller and a reverse-angle doctor blade to control the quantity of ink supplied to the printing plate. Ideally, the amount of ink delivered to the plate in a keyless press should be the same regardless of the nature of the ink. We found that low-yield-value inks printed darker, but transferred more consistently than high-yield-value inks, inferring that a greater amount of ink is being transferred out of the cells of the metering roller when the low-yield-value inks are used. The duration of the doctor blade induced shearing action is very short. The ink is at rest for most of the time, which allows the internal structure to recover to a certain extent. This indicates that the actual viscosity profile of the ink in the cells is more likely to resemble that shown in Figure 8. The area under the viscosity profile has the dimensions of ergs per cubic centimeter.

It is a measure of the energy deposited in a unit volume of flowing fluid, that is, a measure of fluid's resistance to flow. Figure 8 shows that the area under the viscosity profile is much greater for inks with high yield values than inks without yield values. Figure 9 shows that for inks without yield values, the area under the viscosity profile is greater for less shear thinning inks. These results indicate that inks with high yield values and high shear thinning indices are more likely to resist flowing out of the cells than inks with low yield values and low shear thinning indices. They form the basis of our belief that a keyless ink should be more shear thinning (Figures 3 and 4) and have a lower yield value (Figures 5 and 6) than a conventional ink of the same consistency.

Another phenomenon encountered with the keyless press is the build up of ink on the back side of the doctor blade, resulting in sporadic sling and spotting on the printed copies. This behavior is associated with the viscoelastic properties of inks. The ink passing through a doctor blade-metering roller nip tends to expand in the direction perpendicular to the flow direction. This is a common phenomenon in the polymer extrusion industry. The expansion of the ink combined with the angular momentum imparted to the ink by the doctor blade induces the deposition of ink on the back side of the doctor blade. Once on the doctor blade, the ink is relieved of shearing action, and its viscosity increases. If the yield value of the ink is low, gravitational forces will cause the deposited ink to flow down the blade and be carried out by the metering roller. For inks with high yield values, the gravitational forces are not large enough to cause continuous flow, so the ink accumulates until its volume is so large that it breaks away in large drop-like volumes that cannot be evened out in the downstream nips of the inker. Inks K14 and K15 are from the same supplier. Ink K14 exhibited unacceptable buildup. Ink K15 is a modified formulation with a reduced dynamic yield value that eliminated the problem.

Based on our experience to date, we have observed that Japanese and European inks are more likely to have the rheological properties desirable for keyless lithography than are the inks generally available in the United States. The Japanese inks are characterized by a low shear thinning index, no dynamic yield value, and a high thixotropy index as compared to U.S. inks (Table III). The European inks have small, but measurable, dynamic yield

values, slightly higher shear thinning indices than the Japanese inks, and less thixotropy. We attributed these general differences to the differences in the evolution of offset newspaper press design, availability of the materials used to formulate inks, and the print quality requirements that exist in these different parts of the world.

In Japan a major attribute of print quality is the fidelity of the Kanji (Chinese-based) characters. Excess "dot gain" will cause loss of definition in the details of these characters. When this occurs a greater amount of information is lost than would be the case when there is equal gain in an alphabetic character. We believe that the materials used in Japanese inks inherently result in the lack of yield value, but that dot gain control has to be provided by formulating these inks with high true viscosities in the low-shear-rate condition that exists after the ink has left the printing nip and is on the paper. This prevents subsequent spreading of the ink. To avoid excessive viscosity at the higher shear rates that occur in the ink train, these inks must be more shear thinning, so they exhibit greater thixotropy.

In Europe, offset newspaper presses are frequently designed with overshot ink fountains, whereas the typical U.S. offset newspaper press has either an undershot fountain or an ink injector system. The undershot fountain requires an ink with a higher low-shear-rate viscosity to prevent seepage between the fountain roller and the metering blade when the press is not running. The overshot fountain requires an ink with a lower low-shear-rate viscosity and a higher shear thinning property to facilitate maintenance of a uniform ink level around the slow turning fountain roller. Thus, many European inks have traditionally been formulated with these properties which implies a lower dynamic yield value than U.S. inks and a slightly lower shear thinning index, so they exhibit slightly greater thixotropy.

CONCLUDING REMARKS

It should be realized that a successful lithographic printing is determined by many factors. Though ink rheology is important, it does not provide all answers for optimal ink formulation. The major purpose of this paper is to provide the industry with the information about rheological requirements for keyless inks. The results

indicate that a keyless ink should be more shear-rate dependent and have a lower dynamic yield value than a conventional ink of the same consistency. A higher thixotropy is also desirable in a keyless ink. The major importance of these results is that, from a rheological perspective, keyless inks can be engineered from standardized, measurable parameters without the need for extensive and expensive on-press trial and error testing.

It is well known that the rheological properties of inks are changed during printing by the emulsified fountain solution, and the change should be minimal for good lithographic inks (Bassemir and Shubert, 1985). The results reported here were obtained from fresh inks. We are now investigating the effect of emulsified fountain solution on the rheological properties of lithographic inks.

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