STUDY OF INK STRUCTURE BY CREEP TECHNIQUE

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Abstract: Creep is a very useful technique for studying the stress-controlled, ultra-low shear rate rheological phenomena such as pigment sedimentation, ink leveling, and ink feed mechanism by the open fountain presses. Some mechanical models commonly used to analogize the viscoelastic behavior of materials are reviewed. Creep method for determining viscous and elastic properties of viscoelastic inks is presented.

As a constant stress is applied to a viscoelastic fluid in the creep experiment, the deformation or shear strain shall initially increase rapidly with time and gradually approach asymptotically to a linear region. It was observed in this study that the creep curve of printing inks followed that normal pattern up to a certain shear strain and beyond which it departed upward from the steady, linear region and eventually approached another linear asymptote. This abnormal creep behavior is attributed to the progressive destruction of the internal structure of inks. It also provides a reasonable explanation to the thixotropic behavior of inks.

Some inks exhibit the abnormal creep behavior at relatively small strain. Other inks can tolerate much larger shear strain before the abnormality shows up. The discrepancy is ascribed to the difference in internal structure. The former group is characterized by a pigment network and the latter by a colloidal network.

BACKGROUND

It was mentioned in a previous publication that a printing ink has to fulfill rheological requirements over a very wide

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range of shear rates during printing (Chou et al., 1990). A plot of viscosity versus shear rate on a log-log scale, also known as the viscosity profile curve, is essential to describe all of those rheological processes. Figure 1 illustrates schematically a viscosity profile curve typical of printing inks and associated rheological phenomena.

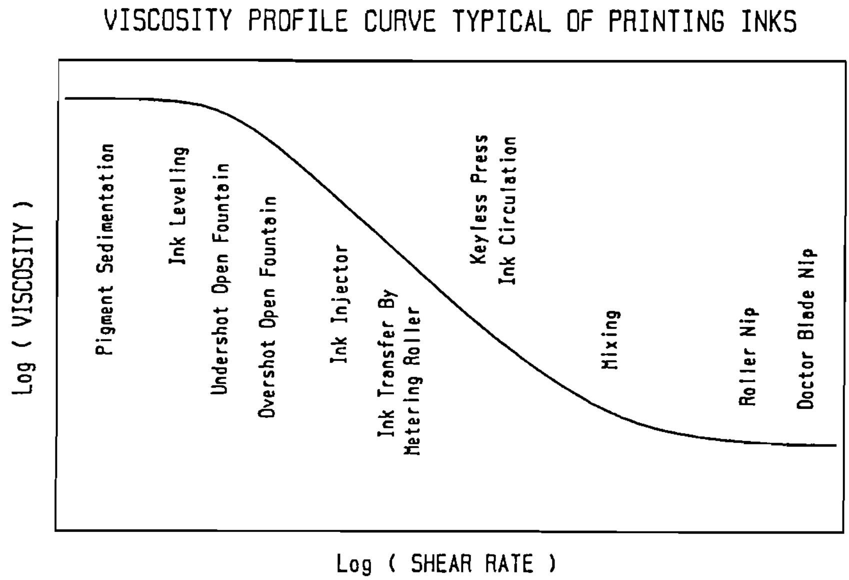

Figure 1. Viscosity profile curve showing rheological requirements of printing inks at various stages of the process. Reproduced from Chou et al. (1990).

In the newspaper industry, printing inks are frequently pumped from a central storage tank to the press. The ink is then extruded to the distribution ink drum by injectors according to the rate of ink consumption. In the anilox lithographic presses, ink is continuously circulated between the ink fountain and a reservoir to flush off the returned ink that contains dampening solution and to replenish the engraved cells of the metering roller with homogenized emulsion ink. The mixing process is generally controlled by the rotating speed of the mixer blade. The shear rates in the roller nip or in the doctor blade/metering roller nip are determined by printing speed. All of these processes are rate-controlled rheological phenomena and generally take place at relatively high shear rates. Rheological characteristics of printing inks in the medium to high shear rate range have been reported (Chou and Bain, 1988; Chou et al., 1990).

Pigment sedimentation proceeds under the influence of gravity due to the density difference between pigment and vehicle. Surface tension is the dominant driving force for ink leveling by minimizing the surface area of the printed ink film. In the open fountain presses, ink is fed to the fountain roller by the gravitational force. These processes are stress-controlled rheological phenomena and take place at relatively low shear rates. The creep technique available only to controlled-stress rheometers is able to simulate the shear conditions of these processes and is therefore an ideal method for studying these low shear rheological phenomena.

Two distinct structures were proposed for printing inks (Chou et al., 1990). The pseudoplastic structure results from the randomizing distribution of pigment particles in the vehicle due to Brownian motion. The randomly distributed pigment particles align themselves into a layer structure under the influence of an external force. Pigment particles instantaneously regain random distribution as soon as the applied force is removed. This structure accounts for the shear-dependent behavior of printing inks.

The thixotropic structure results from pigment flocculation or colloidal aggregates that form a three-dimensional internal structure in the ink (Patton, 1979). It is relatively easy to disrupt thixotropic structure. Its recovery is, however, a very slow process (Chou et al., 1990). This structure accounts for both shear- and time-dependent behavior of printing inks.

It was reported that Japanese and European inks had lower dynamic yield value and were more shear thinning and more thixotropic than American inks (Chou and Bain, 1988). These differences were attributed to the differences in press design, availability of the materials used to formulate inks, and in the print quality requirements. Those experimental results also infer that the thixotropic structure of Japanese and European inks may be dominated by the colloidal aggregates and American inks by the pigment flocculation. This paper will provide further evidence to this speculation.

EXPERIMENTAL SECTION

Three lithographic news inks designed for the open fountain presses were used in this study. One of them was from a Japanese source and the other two are American inks.

A Carri-Med controlled-stress rheometer with a cone and plate measuring system was used in this experiment for investigating low shear rheological behavior of printing inks. The cone diameter and angle were four centimeters and five degrees, respectively. Because rheological properties of printing inks are strongly dependent upon shear history, ink samples were loaded to the measuring system as carefully as possible to minimize any disturbance to them. The sample was then allowed to rest for at least one hour before the measurement was carried out.

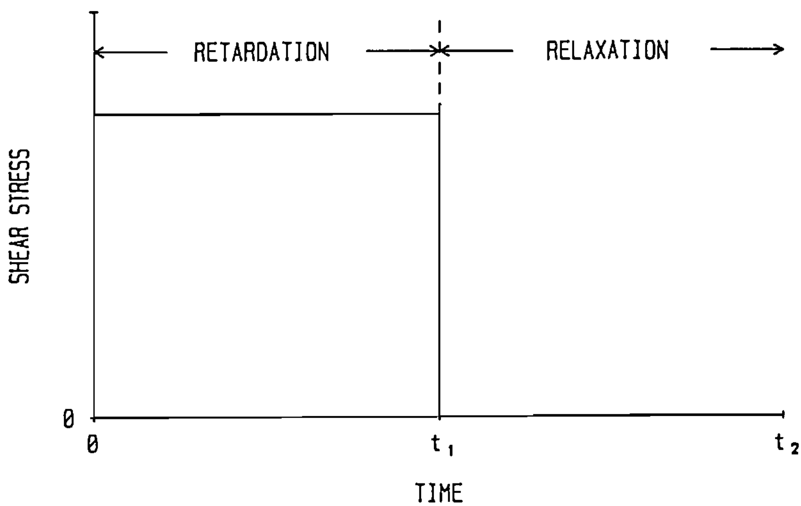

Figure 2. Creep technique for studying low shear rheological behavior of viscoelastic fluids.

In the creep measurement, a constant shear stress is applied instantaneously to the sample at time zero and removed instantaneously at time t_1, as shown in Figure 2. The experiment is completed at time t_2. The resulting angular displacement or shear strain is recorded as a function of time. In this report, the retardation duration was set to ten minutes and the relaxation period to five minutes.

MECHANICAL MODELS FOR VISCOELASTIC FLUIDS

Printing inks are viscoelastic fluids, that is, both viscous and elastic properties coexist. It would be very useful to use some mechanical models for interpreting the viscoelastic response of inks to an imposed shear force. It also allows us to develop some mathematical expressions to describe viscoelastic behavior of inks. Viscous and elastic properties can be obtained by fitting those equations to the experimental data.

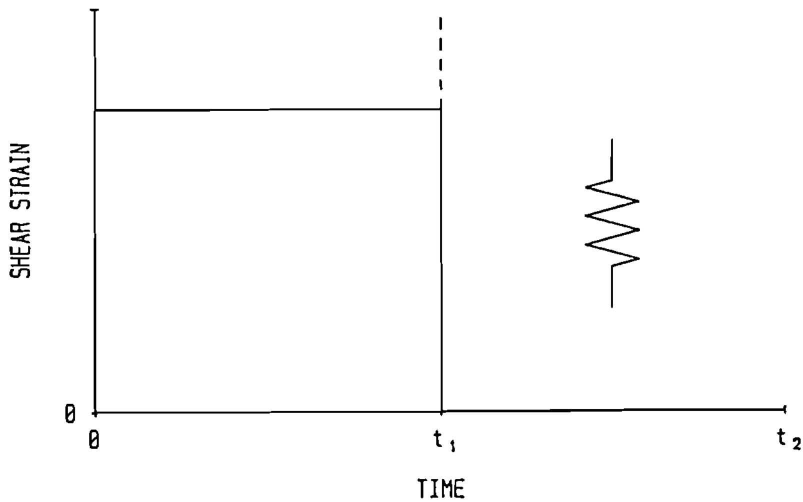

Figure 3. Schematic diagram showing creep behavior of a Hookean spring.

A spring is usually used to represent a Hookean elastic solid. When a force is applied to an elastic solid, its deformation is in phase with and proportional to the applied force, as shown in Figure 3. Their relationship is given by

$$\tau = G\gamma \tag{1}$$

where τ is the applied shear stress, G the shear modulus, and γ the deformation or shear strain. The work done by the applied force is converted into the potential energy of the spring and stored there. As soon as the applied force is removed, the stored energy is released that forces the spring to restore immediately to its original state. The net shear strain for this extension and retraction process is zero.

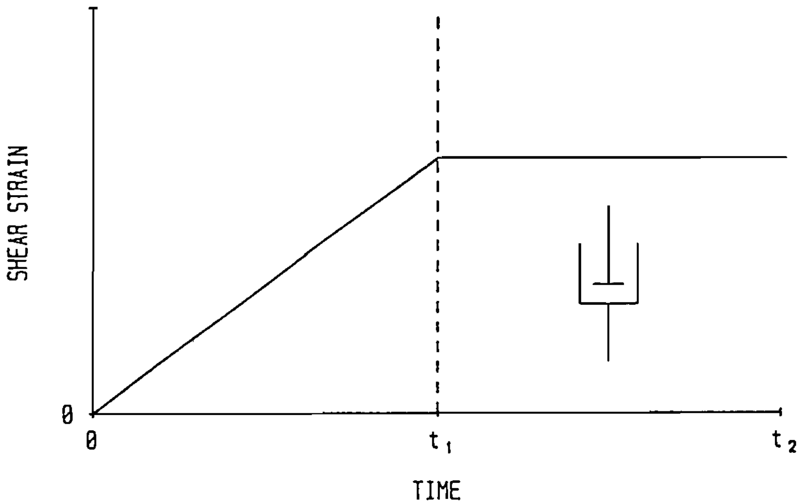

Figure 4. Schematic diagram showing creep behavior of a Newtonian dashpot.

A dashpot is usually used to represent a Newtonian viscous fluid. When a force is applied to a viscous fluid, it causes the fluid to flow steadily, as indicated by the linear relationship between shear strain and time in Figure 4. The resulting shear rate $\dot{\gamma}$ is given by the slope of that straight line. Shear stress is related to shear rate by the following equation.

$$\tau = \eta \dot{\gamma} \qquad (2)$$

where η is the viscosity. The work done by the applied force is completely dissipated as heat. So, as soon as the applied force is removed, the fluid is unable to recover at all, resulting in a permanent strain.

Various combinations of spring and dashpot have been used to model rheological behavior of viscoelastic fluids. Some commonly used models will be briefly reviewed here. Refer to Barnes et al. (1989) for details.

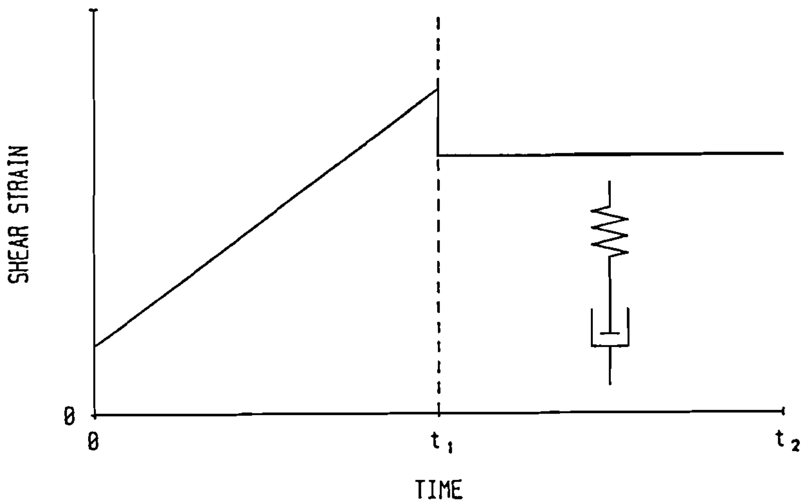

Figure 5. Schematic diagram showing creep behavior of a Maxwell-model fluid.

Maxwell Model

A Maxwell model consists of a spring and a dashpot connected in series and its creep curve is shown in Figure 5. The spring causes an instantaneous strain and the dashpot simultaneously results in a steady flow. The resulting creep curve does not resemble any experimental creep curve. In fact, the Maxwell model is generally used to analogize the stress relaxation behavior of viscoelastic fluids, which will not be discussed in this paper.

Kelvin Model

A Kelvin model, also known as a Voigt model, is a spring connected in parallel with a dashpot and its creep curve is shown in Figure 6. The response of the spring to the applied force is retarded by the dashpot. So, the deformation increases at a decreasing rate and eventually reaches an

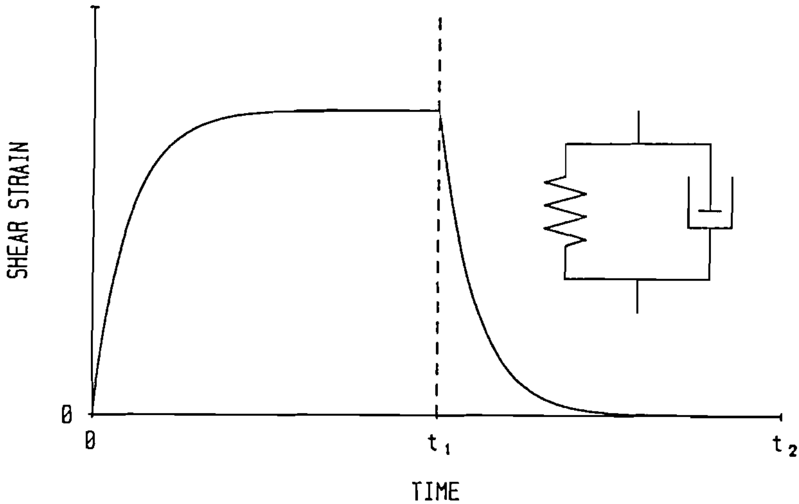

Figure 6. Schematic diagram showing creep behavior of a Kelvin-model fluid.

equilibrium value. The equilibrium strain or the retarded strain is determined by the shear modulus of the spring. The rate of growth of strain is determined by the viscosity of the dashpot and the shear modulus of the spring.

When the applied shear stress is removed, the spring tends to restore to its original state. Its response is delayed again by the dashpot, resulting in a relaxation curve that is a mirror image of the retardation curve. The net strain is zero, that is, the Kelvin model is able to regain its original state.

Jeffreys Model

A Jeffreys model consists of a Kelvin unit and a dashpot connected in series. Figure 7 shows its creep curve. The retardation curve increases at a reducing rate and finally approaches asymptotically a steady state. It is a superimposition of the curves in Figure 4 and 6. The slope of that asymptotic line is the shear rate, which is determined by the viscosity of the dashpot in series. Upon removal of the applied stress, the retarded strain is gradually recovered, leaving a residual strain resulting from the permanent deformation of the dashpot in series.

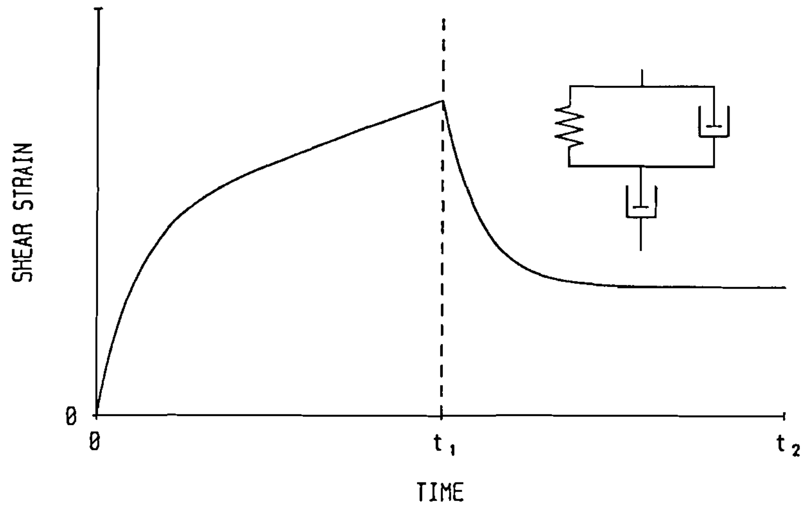

Figure 7. Schematic diagram showing creep behavior of a Jeffreys-model fluid.

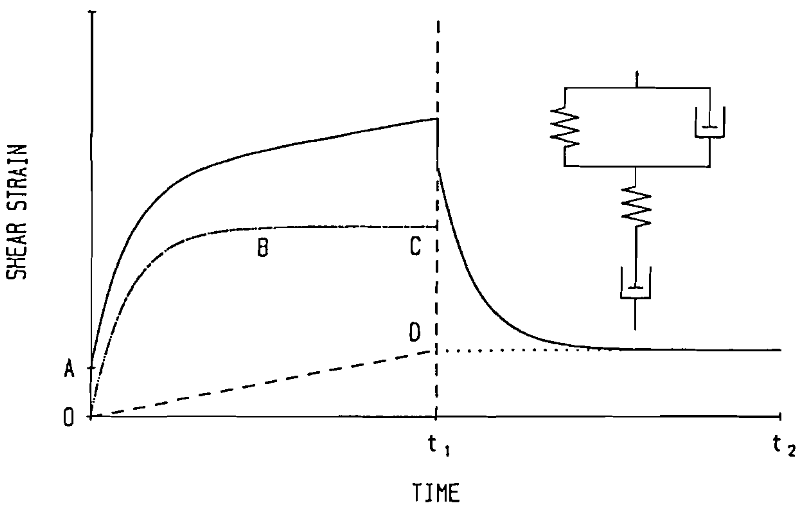

Figure 8. Schematic diagram showing creep behavior of a Burgers-model fluid.

Burgers Model

A Burgers model is a Kelvin unit connected in series with a Maxwell unit. Figure 8 illustrates the creep curve of a Burgers model and its composition. The instantaneous strain OA results from the spring of the Maxwell unit. The steady flow OD is caused by the dashpot of the Maxwell unit. The retarded strain OBC originates from the Kelvin unit. This retardation curve can be expressed mathematically by

$$\gamma = \gamma_o + \dot{\gamma}\, t + \gamma_1 [1 - \exp(-t/\lambda_1)] \tag{3}$$

and

$$G_o = \frac{\tau}{\gamma_o}, \qquad \eta_o = \frac{\tau}{\dot{\gamma}} \tag{4}$$

$$G_1 = \frac{\tau}{\gamma_1}, \qquad \eta_1 = \lambda_1 G_1 \tag{5}$$

where γ_o = the instantaneous strain.
G_o = the shear modulus of the spring of the Maxwell unit.
η_o = the viscosity of the dashpot of the Maxwell unit.
γ_1 = the retarded strain of the Kelvin unit.
G_1 = the shear modulus of the spring of the Kelvin unit.
η_1 = the viscosity of the dashpot of the Kelvin unit.
λ_1 = the retardation time which controls the growth rate of strain.

Fitting Eq. 3 to the experimental data enables us to calculate the parameters γ_o, $\dot{\gamma}$, γ_1, and λ_1, from which the viscous and elastic properties of the Maxwell and Kelvin units can be derived.

The instantaneous strain γ_o and the retarded strain γ_1 are recovered completely after the applied stress is removed, while the strain resulting from the steady flow is not recovered at all.

RESULTS AND DISCUSSION

It was observed that the creep measurement was not very reproducible no matter how carefully it was carried out. This is ascribed to the unavoidable disturbance imposed on the ink during sample loading. Chou and coworkers (1990) have shown that the destruction of thixotropic structure of printing inks is a fast process, while the rate of structural recovery is very slow. Consequently, the shear history of one ink sample may differ significantly from another. Poor reproducibility is therefore not unusual. This may affect the quantitative measurement of material properties but should not influence the qualitative analysis of the internal structure of printing inks.

Viscoelastic Properties of Printing Inks

Figure 9 shows the creep curves of an American yellow ink at three levels of applied shear stress. The dots represent the experimental data points, and the solid curve is drawn according to Eq. 3. These results indicate that the Burgers model is an excellent analogy for describing creep behavior of the yellow ink as long as the shear strain is limited to within about 0.02. Table I lists the viscous and elastic properties determined from the curve within the range of normal creep behavior.

Table I. Viscous and elastic properties of the American yellow ink.

τ	$\dot{\gamma}$	G_o	$\eta_o x10^5$	G_1	$\eta_1 x10^5$
20	$2.42x10^{-5}$	11054	8.28	5642	3.17
40	$7.57x10^{-5}$	19380	5.28	11218	1.72
80	$1.09x10^{-3}$	28235	0.73	12357	0.90

Similar observations were made with the American magenta ink (Figure 10) and the Japanese magenta ink (Figure 11). The critical shear strain is about 0.4 for the former and slightly greater than 2 for the latter. The measured viscous and elastic properties of the two inks are summarized in Table II and III.

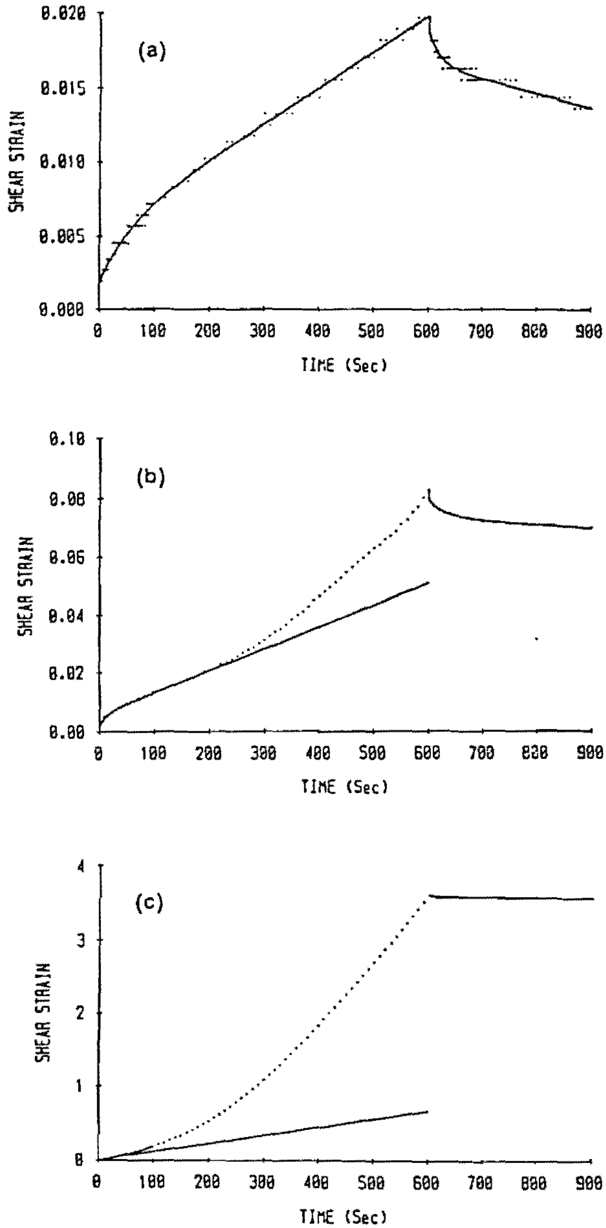

Figure 9. Creep curves of the American yellow ink. The applied shear stresses are (a) 20, (b) 40, and (c) 80 dyne/cm^2.

Table II. Viscous and elastic properties of the American magenta ink.

τ	$\dot{\gamma}$	G_o	$\eta_o x10^5$	G_1	$\eta_1 x10^4$
70	$3.83x10^{-5}$	4674	18.27	2364	5.42
370	$1.68x10^{-3}$	4309	2.20	3968	4.28
510	$1.13x10^{-2}$	3334	0.45	3322	1.62

Table III. Viscous and elastic properties of the Japanese magenta ink.

τ	$\dot{\gamma}$	G_o	$\eta_o x10^5$	G_1	$\eta_1 x10^4$
560	$2.21x10^{-3}$	3938	2.53	3184	5.75
800	$8.70x10^{-3}$	4068	0.92	3159	3.36
1000	$1.83x10^{-2}$	4655	0.55	3682	2.13

The current and unpublished results show that the Burgers model can be used to illustrate the viscoelastic behavior of most lithographic inks as long as the shear strain is smaller than the critical value. Some inks may need one or two additional Kelvin units connected in series with a Burgers unit to describe their creep behavior.

The data in Table I and II show that the creep technique allows the measurement of viscosity at a shear rate as low as 10^{-5} sec^{-1}. In fact, viscosity measurement can be made at even lower shear rates if the applied shear stress is reduced and meanwhile the test duration is extended. The data also show that the viscosities of both dashpots in the Burgers model decrease with increasing shear stress, while the trend for shear modulus is ambiguous. There is no attempt at the present stage to explain the physical significance of shear modulus data.

Figure 9 to 11 exhibit that as the shear strain becomes greater than a critical value, the creep curve departs upward from the linear, steady flow region and eventually approaches another asymptote. This abnormal creep behavior has never

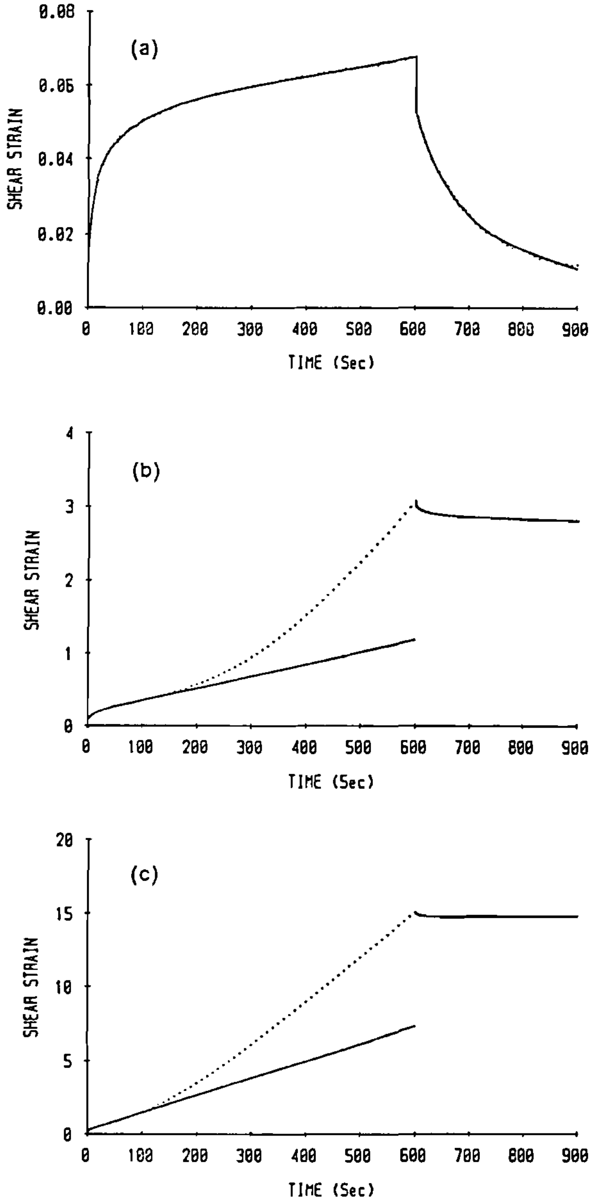

Figure 10. Creep curves of the American magenta ink. The applied shear stresses are (a) 70, (b) 370, and (c) 510 dyne/cm^2.

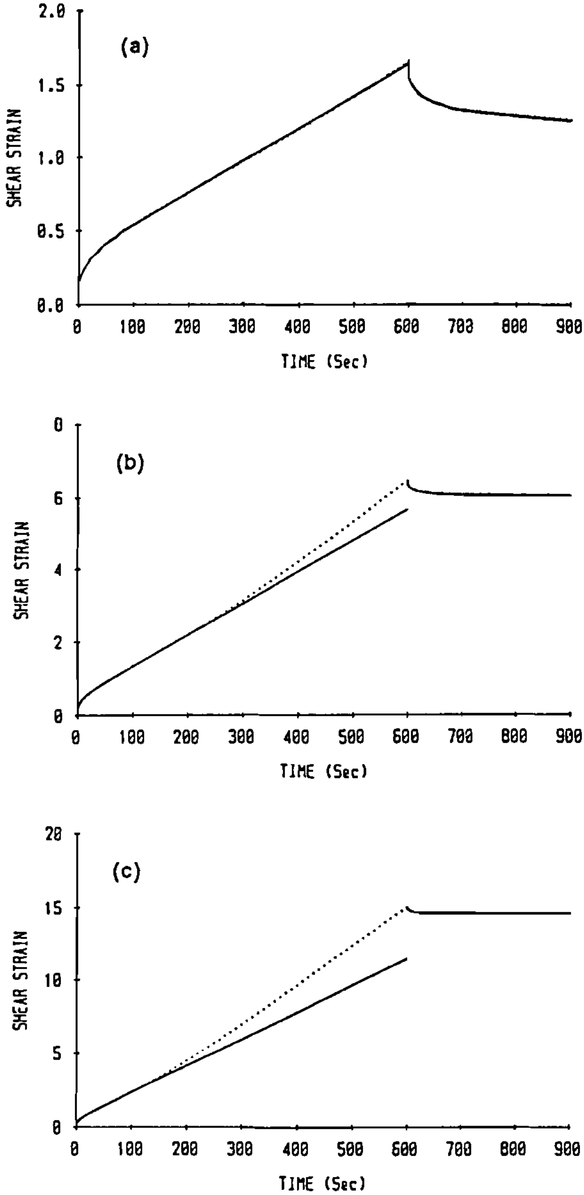

Figure 11. Creep curves of the Japanese magenta ink. The applied shear stresses are (a) 560, (b) 800, and (c) 1000 dyne/cm^2.

been reported in the literature before. It will be discussed later that this peculiar creep behavior arises from the structural variation in the course of creep measurement. It is less likely caused by the malfunction of instrument.

Peculiar Creep Behavior of Printing Inks

As previously mentioned, the thixotropic structure may result from pigment flocculation or colloidal aggregates that form a three-dimensional network in the ink. This internal structure may be continuous or discrete, depending on the formulation. It is present in the ink in a relaxed state at rest and is readily stretched upon the application of a shear stress. The consequence is an instantaneous strain. The fluid may flow if the internal structure is discrete or may not flow if it is continuous. Meanwhile, the applied shear stress tends to pull pigment particles apart. The stretching of structural linkages is, however, hindered by the flow of fluid around pigment particles. This accounts for the retarded strain.

The strengths of structural linkages are expected to follow a normal distribution, regardless of the nature of internal structure. When the strain exceeds the capacity of some weak linkages, these linkages start to break down and the viscosity decreases accordingly. The structural breakdown continues until the applied shear stress is unable to destroy any more structural linkages and the viscosity reaches an equilibrium value. This speculation explains the upward departure of creep curve which eventually approaches another linear region. It also provides a reasonable explanation to the time-dependent, thixotropic behavior of printing inks.

Internal Structures of Printing Inks

The critical shear strain beyond which abnormal creep behavior occurs can be related to the nature of internal structure. Pigment flocculation results from a poor dispersion of pigment particles in the vehicle. Pigment particles are not well protected by the dispersant or poorly wetted by the ink vehicle. They will attract each other due to van der Waals force and form a number of flocs. These flocs may grow into a continuous network. Because van der Waals force is a short range interaction, a relatively small deformation induced to the fluid is large enough to tear down the linkages between pigment particles. Consequently, the abnormal creep behavior takes place at relatively small shear strain. This behavior is illustrated schematically in Figure 12. The American yellow ink is a typical example.

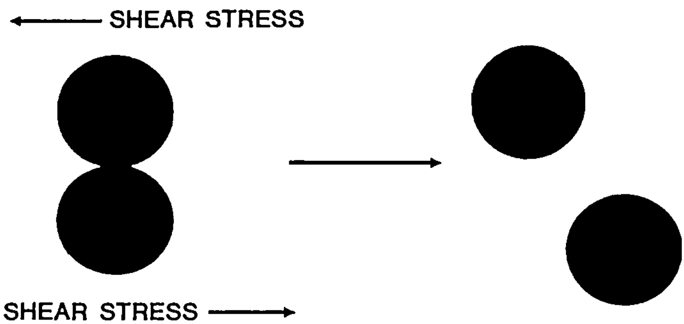

Figure 12. Schematic diagram showing the creep behavior of a pigment network.

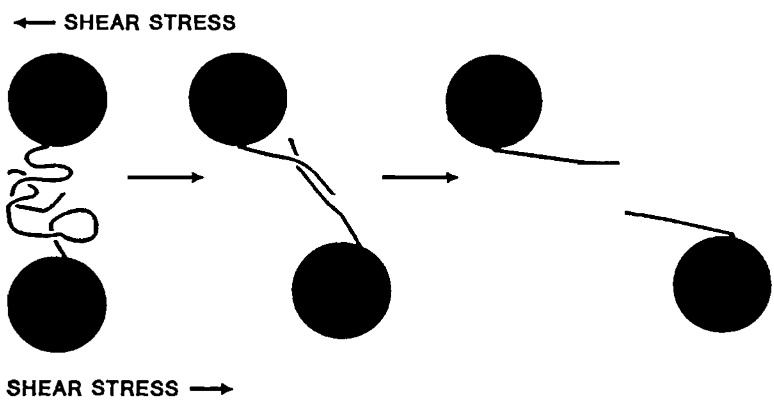

Figure 13. Schematic diagram showing the creep behavior of a colloidal network.

For a good dispersion, a number of dispersant or resin molecules are attached to each pigment particle. These molecules improve the wetting of pigment particles in the vehicle and may also provide a steric barrier (Hampton and MacMillan, 1985). The associated solvent layer or the steric barrier prevents pigment particles from close encounter and hence pigment particles are well dispersed and stabilized. A three-dimensional network can be created by the entanglement between those polymeric chains of dispersant or the entanglement of dispersant with resin and/or gellant molecules. This network is referred to as the colloidal structure (Patton, 1979). Those long flexible polymeric chains or molecules are present in a randomly coiled configuration in the vehicle. They are extensible upon the application of an external force. Chain disentanglement occurs when they are more or less fully stretched. Consequently, the abnormal creep behavior of a colloidal network takes place at a shear strain much larger than that of a pigment network. The critical shear strain is expected to increase with increasing molecular weight of dispersant and/or resin. Figure 13 illustrates schematically the creep behavior of a colloidal structure.

Both Japanese and American magenta inks may possess a colloidal structure because their critical shear strain values are at least one order of magnitude greater than that of the American yellow inks. The critical shear strain of the American magenta ink is less than that of the Japanese magenta ink. This infers that the molecular weight of resin in the former ink is lower than that in the latter.

An undisturbed ink may contain a continuous internal structure which is disintegrated during sample preparation for the creep measurement. Even if the ink sample is allowed to rest to rebuild the structure for an extended period before the measurement is carried out, some weak linkages may still be destroyed by the applied shear stress. This is probably the reason why the steady flow always exists. The number of structural linkages that will be destroyed increases with increasing shear stress. Consequently, the fluid's resistance to flow decreases as the applied shear stress increases. This is consistent with the viscosity data of η_0 and η_1 in Table I to III. Due to the progressive destruction of weak structural linkages in the retardation stage of creep measurement, the relaxation curve never becomes a mirror image of the retardation curve (Figure 9 to 11), as predicted by the theory.

FUTURE STUDY

Rheology is the most important, and probably least understood, physical property of printing inks that determines press performance. Researchers at Rockwell Graphic Systems made substantial efforts in the past to develop techniques for measuring rheological properties of inks and to correlate ink rheology with press performance (Chou and Bain, 1988; Chou, et al., 1990). Speculations relating rheological behavior of inks to internal structure sound logical but lack of solid supporting foundation. They originate from extensive experiments made on commercially available inks the ingredients of which are not known to the experimenters. It is essential in the future to study rheological behavior of some model inks with known ingredients to gain an insight into composition/rheology correlations.

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