Structural Recovery Of Printing Inks Studied By Steady Shear Rheometry

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ABSTRACT

Pseudoplasticity and thixotropy may be the most important rheological properties of printing inks. The viscosity of a printing ink decreases with increasing shear (shear thinning or pseudoplasticity) and with time under a given constant shear (thixotropy). To control these two properties properly, one needs to know what causes them in a microscopic sense.

Two experimental techniques used to study structural recovery of inks are presented. Results reported in this paper show that pseudoplastic structure recovers much faster than thixotropic structure. These two structures can be distinguished by the state of pigment particles present in the ink vehicle. The physical significance of pseudoplastic and thixotropic structures and their implications to press performance are discussed.

BACKGROUND

Printing is a process that applies an ink to a substrate, by means of a printing plate and a press, to form an image. The uniformity of ink film laid down on the surface of a substrate and the fidelity of halftone dot reproduction determine the quality of image reproduction. These two properties are closely related to ink rheology. Rheological study of printing inks helps us explain and predict flow behavior of inks at various stages of the printing process. It also relates flow behavior to the composition and structure of inks. To achieve high quality of image reproduction, an ink formulator must understand ink rheology so that he can design an ink with structure controlled according to the specific printing conditions.

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There are four major printing processes: letterpress, lithography, gravure, and flexography. Each of these methods can be classified further into many subsystems. The application method and the printing speed determine the flow characteristics required for the ink. Due to the wide variety of printing processes that run at various speeds, inks are normally custom made to suit a particular set of printing conditions.

Flexography and gravure involve ink transfer into and out of many tiny cells recessed respectively from the anilox roller and the printing plate surfaces. Inks for these two processes must have very low resistance to flow to ensure complete ink transfer. These inks are generally referred to as liquid or fluid inks.

In the letterpress and lithographic printing processes, inks are traditionally fed to the distribution rollers from an undershot open fountain. These processes require high viscosity inks to prevent seepage between the fountain roller and the metering blade when the press is not running. Accordingly, the inking train consists of a large number of distribution rollers that continuously work on the ink to ensure that a uniform film of ink is delivered to the plate. These inks are referred to as paste inks.

Because fountain solution complicates rheological behavior of lithographic inks (Chou and Fadner, 1985; Chou and Cher, 1989), this paper will focus on fresh inks only. Our current interest is to investigate the relation of ink structure to rheological properties of lithographic inks. Consequently, the observations and the basic principles expressed in this paper may be applied to the other printing processes.

Our previous results show that yield stress, shear thinning, thixotropy, and viscoelasticity are the important non-Newtonian rheological properties of printing inks (Chou and Bain, 1988). Shear thinning characterizes the viscosity reduction due to increasing shear. Thixotropy characterizes the viscosity reduction as a function of time. These two conceptually different properties were very confusing. For instance, the observed high degree of correlation between shear thinning and thixotropy indices implies that they are determined by the same internal structure. Their relationship has remained ambiguous. Uncertainty remains whether we can control these two properties independently. Their roles in the printing process has also been debatable.

These are the major issues to be addressed in this paper. First, the physical significance of non-Newtonian rheological properties of printing inks will be reviewed. Then, the flow behavior of printing inks at various stages of the printing process will be discussed.

NON-NEWTONIAN RHEOLOGICAL BEHAVIOR OF INKS

Printing inks are basically dispersions of solid pigment particles in a fluid vehicle. Pigment flocculation and/or colloidal aggregates created by thixotrope additives form a three-dimensional network in the ink (Patton, 1979). This structure, also known as internal structure, complicates the flow behavior of inks. However, if the internal structure is formed under control, the printing process will benefit from it because the ink must satisfy rheological requirements over a very wide range of shear conditions.

The presence of internal structure results in the following prominent non-Newtonian rheological properties: viscoelasticity, yield stress, shear thinning and thixotropy. The importance of viscoelastic properties of inks has been addressed (Douglas and Spaull, 1969; Rohn, 1987). We have not yet made meaningful viscoelastic measurements of inks and this property will not be discussed in this paper.

Yield Stress

Yield stress is the minimum stress needed to induce flow of fluid. It is ascribed to the internal structure that gives the ink a solid-like character. Inks behave like a solid substance if the applied stress is lower than the yield stress, under which condition viscosity is infinitely high. The internal structure collapses when the applied stress becomes greater than the yield stress and the ink starts to flow as a liquid.

The existence of yield stress has been challenged (Barnes and Walters, 1985). First of all, the yield stress can not be measured directly. It is obtained by extrapolating the shear stress versus shear rate flow curve to the stress axis or calculated by fitting some empirical equations to the experimental data. Our previous results (Chou and Bain, 1988) support the argument that the yield stress is an artifact. We found that yield stress decreased with increasing time scale of measurement. As shear rate or shear stress became smaller and smaller, the viscosity of an ink approached a plateau instead of an infinite value. This plateau, generally called zero-shear-rate viscosity, will be discussed later. A reported high yield stress is actually equivalent to high zero-shear-rate viscosity.

The concept of yield stress is, however, very useful for interpreting many phenomena. For example, high yield stress is desirable in an ink to prevent pigment settling during storage and to prevent ink seepage from an undershot open fountain. If the yield stress is too high, the ink will not level properly and may fail to feed the fountain roller in the ink fountain.

Shear Thinning And Thixotropy

The viscosity of most dispersions including printing inks tends to decrease with increasing shear and/or with time under a constant shear rate. The shear-dependent property is known as shear thinning and the time-dependent property is known as thixotropy. If a fluid exhibits only shear thinning behavior, its downcurve will superimpose the upcurve. That is, its viscosity is independent of time at any shear rate. These fluids are called pseudoplastic.

When the viscosity of a fluid decreases with time at a constant shear rate, this fluid is called thixotropic. Its downcurve falls below the upcurve, resulting in a hysteresis loop, also called a thixotropic loop. Unfortunately, a thixotropic fluid is also shear thinning. Confusion easily arises. To make distinctions between pseudoplastic and thixotropic fluids, one needs to know the forces involving in the flow of fluid. They are shear force (F_S), thermal force (F_T), and pigment/molecular interactions (F_M).

Shear force will induce pigment/molecule alignment into layer structure along streamline in the direction of forced flow. An aligned layer of pigment particles can easily slide over another layer without much resistance. Shear force will also break down the internal structure to release immobilized fluid. So, the viscosity of inks decreases with increasing shear force.

It is a common phenomenon that the viscosity of an ink decreases with increasing temperature as a result of the thermal force induced Brownian motion that weakens the strength of internal structure. On the other hand, Brownian motion tends to randomize pigment/molecule distribution. It resists the formation of layer structures and acts to increase an ink's resistance to flow.

Pigment/molecular interactions tend to create a three-dimensional internal structure. This internal structure immobilizes the vehicle and the resulting fluid becomes more resistant to flow. So, viscosity of an ink will increase with increasing strength of the internal structure.

Thixotropic and pseudoplastic fluids have been differentiated by the relative rates of structural breakdown and recovery (Schramm, 1981). When a thixotropic fluid is subjected to a shear force, it may take seconds or minutes to break down the internal structure and the viscosity of the fluid decreases asymptotically to an equilibrium value. As soon as the applied shear is removed, the disrupted structure starts to reform. It may take minutes, hours or even months to recover the internal structure completely and the viscosity eventually regain its original value. If the structure can recover as fast as it breaks down, within the time frame of measurement, the measured viscosity appears independent of time. This fluid is termed pseudoplastic. So, for pseudoplastic fluids pigment/molecular interactions are often neglected.

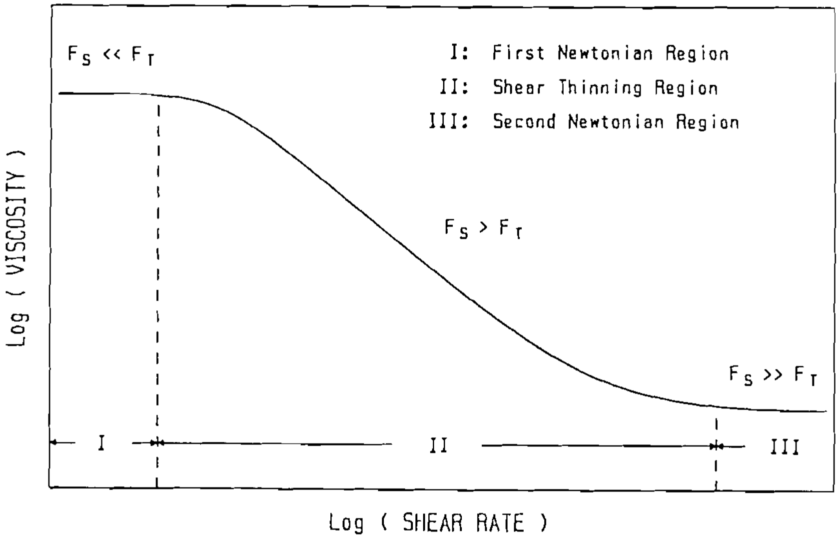


Figure 1. Viscosity profile curve of a pseudoplastic fluid which relates three distinct rheological regions to the controlling forces.

Figure 1 schematically illustrates the viscosity profile curve of a pseudoplastic fluid. Viscosity is conventionally plotted against shear rate on a log-log scale to allow illustrating a complete picture of flow behavior of fluids. At very low shear rates, the thermal force dominates over the shear force. The fluid behaves like a Newtonian liquid in the absence of shear induced pigment/molecular layering or orientation. Its viscosity is independent of shear rate. This shear rate range is called the first Newtonian region and the corresponding viscosity is the zero-shear-rate viscosity mentioned earlier.

At higher shear rates, the shear force becomes increasingly more important than the thermal force. Shear induced pigment/molecular orientation exceeds the randomizing effect of Brownian motion. As a result, the viscosity decreases dramatically with shear rate, and their relationship is often represented by a power law. This power law region is known as the shear thinning region.

At very high shear rates where the shear force becomes dominant, pigment particles align themselves into more or less perfect layer structures. The fluid again behaves like a Newtonian liquid but at a much lower viscosity value. This shear rate range is called the second Newtonian region and the corresponding shear-independent viscosity is termed infinite-shear-rate viscosity.

RHEOLOGICAL REQUIREMENTS OF PRINTING INKS

The first problem encountered after an ink is made is pigment sedimentation. Then, when introduced to a printing press, the ink has to fulfill rheological requirements of the various phases of the process: transport, distribution, and transfer (Voet, 1952). Levelling is an important process after the ink is laid down onto the substrate surface. These processes involve a very wide range of shear rates. A complete viscosity profile curve such as Figure 2 is essential to describe all of these phenomena.

Pigment Sedimentation

Due to the density difference between pigment and ink vehicle, pigment particles tend to settle down because of the force of gravity. The sedimentation process occurs at very low shear rates, 10^{-6} to 10^{-4} sec^{-1} (Barnes et al., 1989), which appear in the first Newtonian region. The three dimensional internal structure is very useful for preventing pigment settling. Terms such as yield stress and thixotropy are frequently associated with the absence of settling. It is more appropriate to state that a high zero-shear-rate viscosity is desirable for precluding pigment sedimentation.

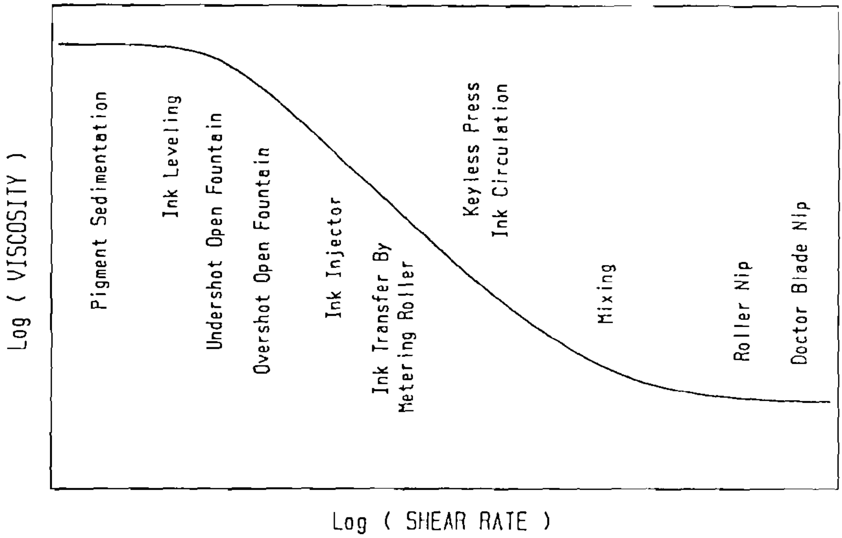


Figure 2. Viscosity profile curve showing rheological requirements of printing inks at various stages of the process.

Transport Phase

Transport relates to ink feed mechanisms. Inks are commonly fed to the distribution rollers either by undershot or overshot open fountain systems. Ink injectors are also widely used in the newspaper industry. In both open fountain systems, ink is fed to the fountain roller by its own weight, a process taking place in the shear rate range of 0.1 to 10 sec^{-1} (Barnes et al., 1989). Lithographic inks designed for the undershot open fountain have very high viscosity at low shear rates to prevent ink from dripping down to the floor through the gap between fountain roller and metering blade. However, if the low shear viscosity is too high, ink will not flow properly toward the fountain roller to replace ink carried away by the distribution system. It is therefore a tough task to control precisely the low shear viscosity of inks for the undershot fountain. This may be one of the reasons why the overshot fountain is popular in Europe.

The low shear viscosity of injector inks must be lower than that of open fountain inks. If not, the injector will not be able to pump sufficient ink out to the distribution ink drum. Shear rates for injection range from 1 to 100 sec^{-1} (Barnes et al., 1989).

The transport phase is much more complex for anilox offset printing or keyless lithography (Fadner and Bain, 1987). It involves removing and recirculating unused return ink, replenishing the ink into many tiny cells in the surface of the engraved metering roller, scraping off excess ink from the metering roller surface, and transferring some of the ink from the cells to the transfer roller. The return ink containing emulsified fountain solution is circulated back to the ink reservoir for mixing to maintain homogeneity of the mixture. Keyless inks in this phase experience a shear rate range nearly as wide as the entire printing process. Ink transfer by the metering roller is dictated by the low shear viscosity of keyless inks. The shear rate range is 1 to 10^3 for ink circulation, and 10 to 10^3 for mixing (Barnes et al., 1989). We estimated that the shear rate range in the doctor blade and metering roller nip is 10^5 to 10^7 sec^{-1}. Compared with inks for flexography and gravure processes, keyless inks should have low-to-medium shear viscosities as low as possible (Chou and Bain, 1988). Only then, will the ink properly fill up and transfer out of those tiny cells of the engraved metering roller. Low viscosity also assists ink recirculation and mixing.

Distribution Phase

The function of distribution system is to break down the internal structure of the ink, which facilitates formation of a uniform ink film on distribution roller surfaces. Inks are compressed, sheared, stretched, fractured, and split in each nip (Zettlemoyer and Myers, 1960), as they pass from one roller to another in the distribution system. Shear rates in the roller nips are of the order of 10^3 to 10^6 sec^{-1} (Mewis, 1980; Barnes et al., 1989), which appear in the second Newtonian region for most newsinks (Chou and Bain, 1988).

For a given printing speed if the ink viscosity is too high (Voet, 1952) or the ink is too short (Zettlemoyer and Myers, 1960), the ink will not follow the rollers properly, resulting in ink starvation and/or uneven distribution. The ink splits into filaments at the roller nip exit. If the ink is too long (Zettlemoyer and Myers, 1960) or is not elastic enough (Douglas and Spaull, 1969), misting will occur.

Transfer Phase

The ink is transferred first to the plate, then to the blanket, and finally to the printing substrate in the transfer phase. The shear conditions in these roller nips are similar to those in the distribution system. The tremendous compressive and shear forces in the roller nips will cause the ink to spread beyond the image halftone dots and result in dot enlargement. So, the infinite-shear-rate viscosity of inks should be as high as possible for quality halftone reproduction (Zettlemoyer and Myers, 1960). If the ink is too elastic (Douglas and Spaull, 1969) or the infinite-shear-rate viscosity is too high, picking will occur.

Levelling

In the moment after the ink is transferred to the substrate, the film is not smooth due to the presence of collapsed filaments and to the substrate surface roughness. Proper levelling will help prevent mottled solid prints. Levelling is governed primarily by surface tension (Patton, 1979) and the corresponding shear rate range is 10^{-2} to 10^{-1} (Barnes et al., 1989). The viscosity of inks should be as low as possible in this shear rate range to facilitate levelling.

EXPERIMENTAL APPROACH

Materials

Eight black lithographic newsinks used in this study were obtained from worldwide suppliers. Inks A, B, and C are American inks. Inks D and E are European inks. Inks F, G, and H are Japanese inks.

Rheometry For Studying Thixotropic Structure

Two methods commonly used for studying thixotropy of fluids are step change and loop tests (Mewis, 1980; Barnes, et al., 1989). We found that the step change test was more appropriate to the study of pseudoplastic structure than thixotropic structure.

The technique used in this experiment for studying thixotropic structure involves repeated loop tests, as illustrated schematically in Figure 3. A Carri-Med controlled-stress rheometer was used with a 4-centimeter, 1.5-degree cone and plate measuring system. The applied shear stress was incremented in 200 equal steps from zero to a maximum value of 4774 dyne/cm^2 in a period of 5 minutes. It was then decremented in the same way back to zero. The shear stress versus shear rate curve obtained from increasing shear stress is called upcurve. Similarly, the curve obtained from decreasing shear stress is called downcurve. For most inks, the two curves form a hysteresis or thixotropic loop.

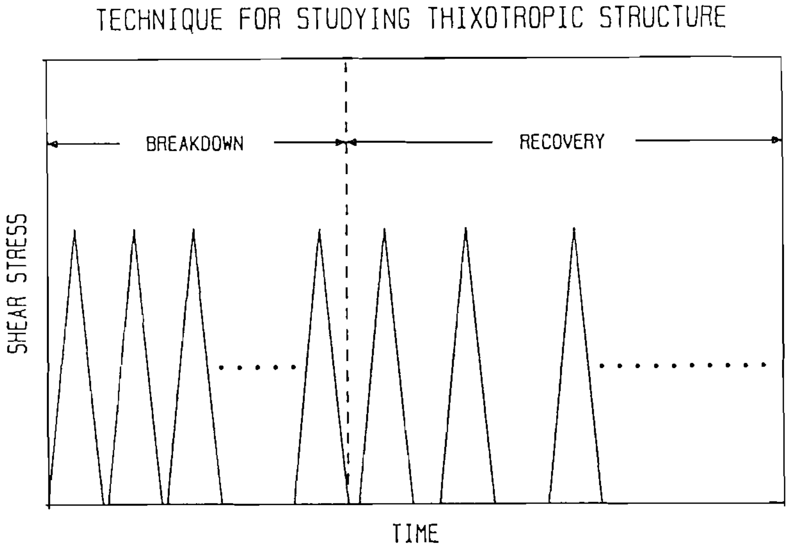


Figure 3. Schematic illustration of repeated loop tests for studying thixotropic structural breakdown and recovery.

The loop test was repeated twelve times in the thixotropic structural breakdown portion of the tests. A time span of one minute between two consecutive cycles was necessary for the computer to store experimental data. In the structural recovery study, the time duration between two consecutive cycles was gradually increased to as high as four hours. All measurements were made at 25° C.

In a separate control experiment, one pint of ink B was sheared vigorously with a high speed mixer to destroy its internal structure. Ink samples were periodically taken out of the container for flow measurements. This method simulates the conditions experienced by an ink after it is made.

Rheometry For Studying Pseudoplastic Structure

Figure 4 illustrates the step change technique used for studying pseudoplastic structure of inks. A high shear stress was applied to the sample in the structural breakdown phase until a steady state response was established. In the structural recovery phase, the applied shear stress should be decreased instantaneously to a low value and the resulting shear rate monitored with time. Due to the restrictions imposed by the current version of our software, the applied shear stress drops to zero for about five seconds before the low shear stress can be applied to the sample. Valuable information during the first few seconds is lost. It is impossible to analyze data quantitatively. Yet, it does not exclude qualitative analysis.

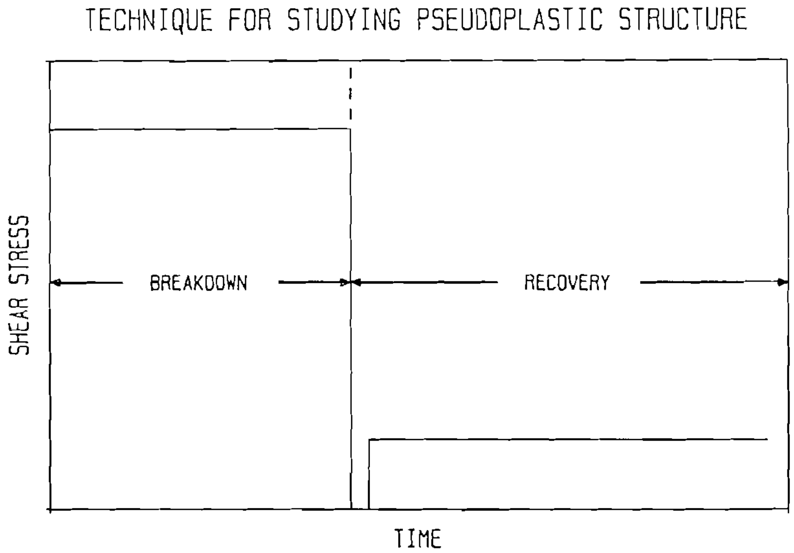


Figure 4. Schematic illustration of step change technique for studying pseudoplastic structure.

A 2-centimeter, 1.5-degree cone was used in this study. Three levels of applied shear stress were selected to result in steady shear rates of 50, 500, and 1000 sec^{-1}. The pseudoplastic structural recovery was determined at a shear rate of about 2 sec^{-1}.

Rheometry For Determining Plastic Viscosity

A 2-centimeter, 0.5-degree cone was used to determine plastic viscosities of inks. Each ink was first sheared to destroy its internal structure under a shear condition as high as the rheometer allows. The loop test commenced immediately after the steady state was reached. The resulting flow curve contained almost no thixotropic loop. At high shear rates flow curve became a straight line whose slope was taken as the plastic viscosity (Zettlemoyer and Myers, 1960).

EXPERIMENTAL RESULTS

In a previous publication (Chou and Bain, 1988), we have shown that dynamic yield stress, shear thinning index, and thixotropy index are very useful rheological parameters for characterizing printing inks. Figure 5 explains schematically the definitions of these rheological parameters for the benefit of discussion. The Herschel-Bulkley equation was used to fit the upcurve experimental data, from which dynamic yield stress and shear thinning index were calculated. Thixotropy index was calculated from the ratio of the loop area to the area underneath the upcurve. It corresponds to the fraction of total energy applied by the rheometer that is consumed in breaking down the internal structure.

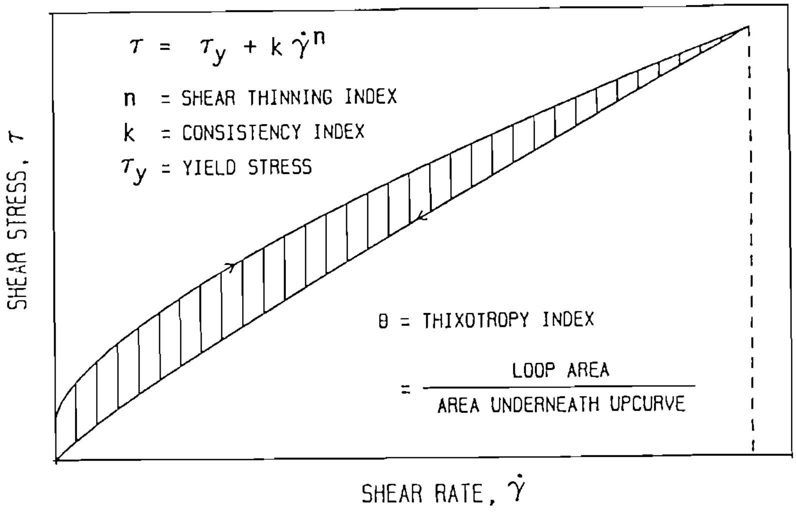


Figure 5. Schematic illustration explaining the definitions of rheological parameters useful for characterizing printing inks.

Table I summarizes rheological parameters of the eight inks. The dynamic yield stress (τ_y), shear thinning index (n), and thixotropy index (θ) were calculated from results of the first loop test, that is, the inks were not disturbed prior to the measurement. Plastic viscosities (η_p) are also listed in the table.

Table I. Rheological parameters of fresh, undisturbed inks.

Ink	η_p (poise)	τ_y (dyne/cm^2)	n	θ
A	18.15	240	0.613	0.122
B	21.77	633	0.866	0.098
C	6.47	68	0.803	0.082
D	35.50	0	0.557	0.185
E	---	0	0.801	0.084
F	11.12	0	0.588	0.150
G	9.64	335	0.651	0.182
H	35.59	0	0.506	0.235

Thixotropy Index Curve

Figure 6 shows the flow curves of ink B at several stages of thixotropic structure determination. The flow curve from the first loop test in Figure 6a displays a substantial hysteresis loop, indicating ink B is a thixotropic fluid. The loop area diminished rapidly with the number of test cycles, and was hardly changed after about two to three cycles. The loop area from the twelfth cycle almost disappeared except at low shear rates (Figure 6b). All the inks exhibited similar behavior in the structural breakdown measurements.

In the structural recovery measurement, the loop area at the low shear range increased rapidly (Figure 6c) and eventually became exaggerated (Figure 6d). The loop area extended further into the higher shear rate range with increasing rest time. The hump at low shear rates was also observed with ink A. The other inks showed a considerable growth of loop area at low shear rates but the low shear hump was lacking.

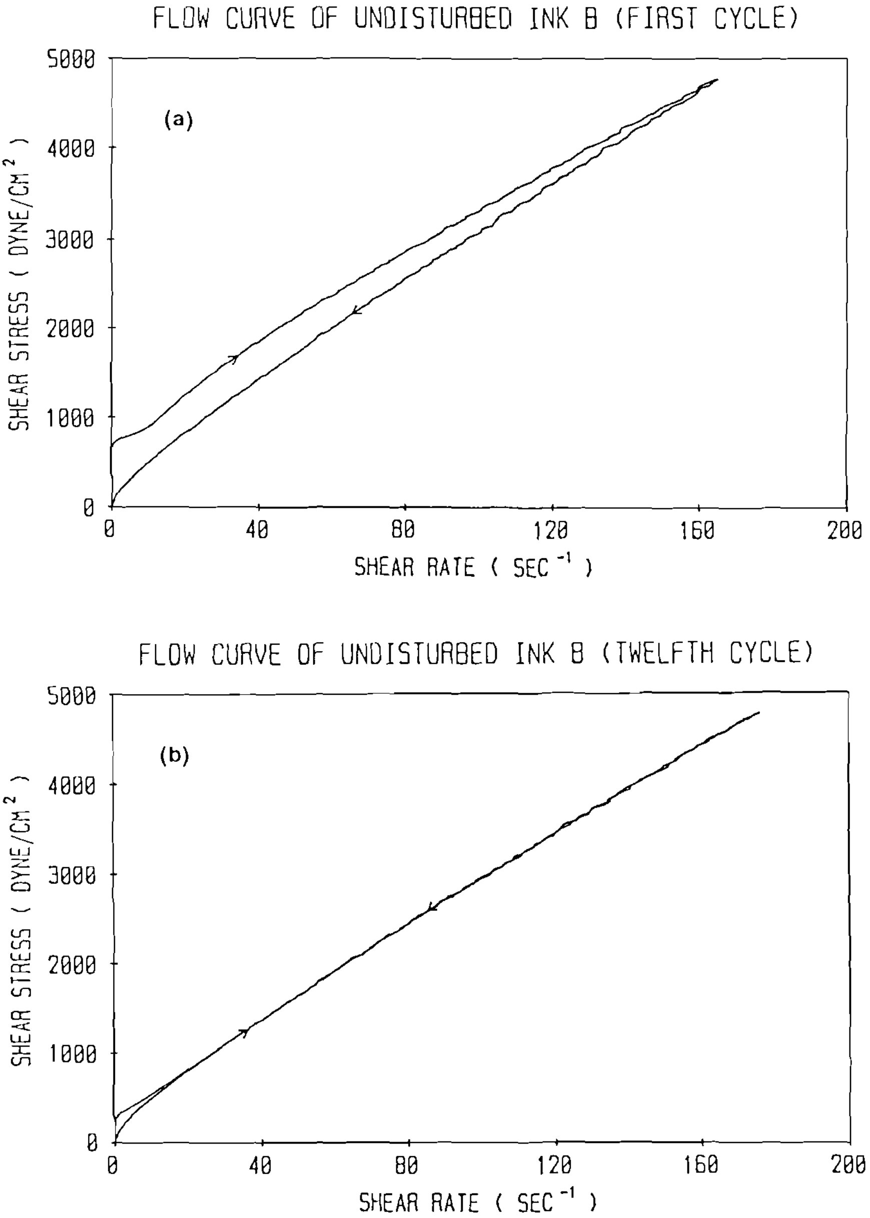
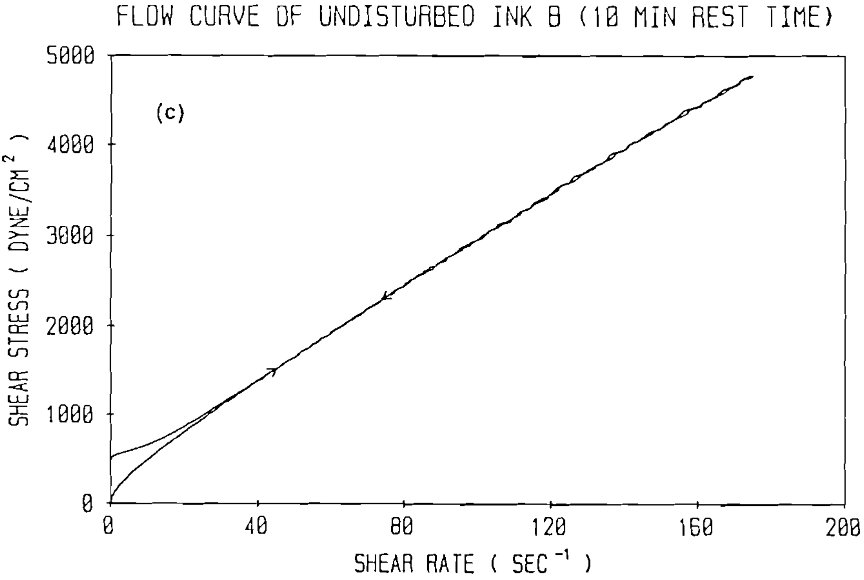


Figure 6. Flow curves of ink B obtained (a) from the first loop test; (b) from the twelfth loop test; (c) after a rest time of 10 minutes; and (d) after a rest time of 4 hours.



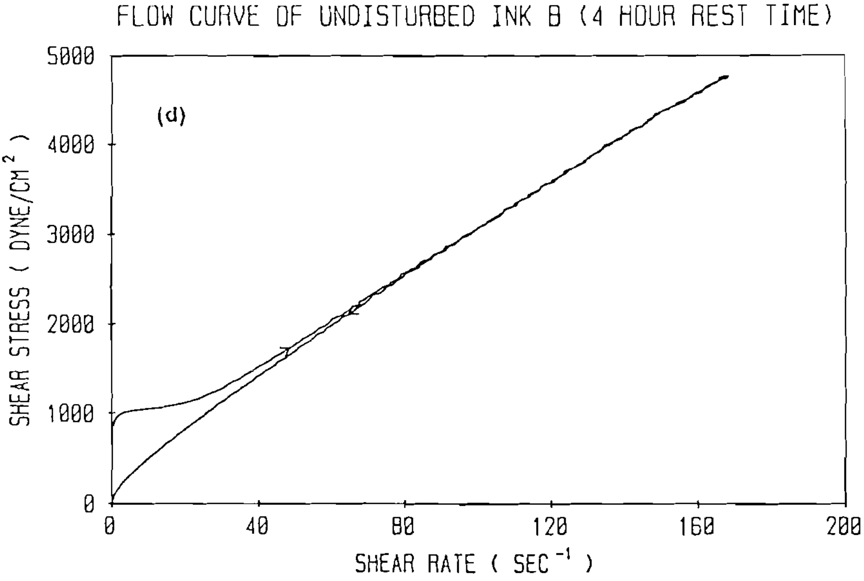


Figure 6. Continued.

Thixotropy index curves in Figure 7 show the combined plots of thixotropy index versus hysteresis cycle in the breakdown phase and versus rest time in the recovery phase. All the ink samples behaved similarly. In the structural breakdown phase, the thixotropy index decreased rapidly and levelled off within two to three cycles. In the structural recovery phase, the thixotropy index gradually increased to an asymptotic value but did not regain its original level even after a rest time of four hours.

The structural breakdown and recovery data can be fitted satisfactorily by exponential-type equations.

$$\text{Breakdown:} \quad \theta = \theta_{b,e} + (\theta_{b,i} - \theta_{b,e}) \exp(-N/\lambda_{b,\theta}) \tag{1}$$

$$\text{Recovery:} \quad \theta = \theta_{r,e} - (\theta_{r,e} - \theta_{r,i}) \exp(-t/\lambda_{r,\theta}) \tag{2}$$

where θ is the thixotropy index. N is the number of hysteresis loops. N is equal to zero for the first loop, and so on. The parameter t is the rest time and λ is a time constant associated with the rate of structural breakdown or recovery. The subscripts i and e stand respectively for initial and equilibration states, and b and r for breakdown and recovery. Table II lists the calculated equilibrium thixotropy indices and time constants.

Table II. Parameters characterizing thixotropy index curve of inks.

Ink	$\theta_{b,e}$	$\lambda_{b,\theta}$ (cycle)	$\theta_{r,e}$	$\lambda_{r,\theta}$ (min)
A	0.002	0.58	0.020	61.6
B	0.002	0.41	0.038	72.6
C	0.001	0.60	0.009	62.3
D	0.018	0.69	0.048	63.6
E	0.008	0.50	0.020	79.6
F	0.020	0.49	0.034	54.8
G	0.010	0.63	0.039	45.0
H	0.026	0.76	0.082	70.0

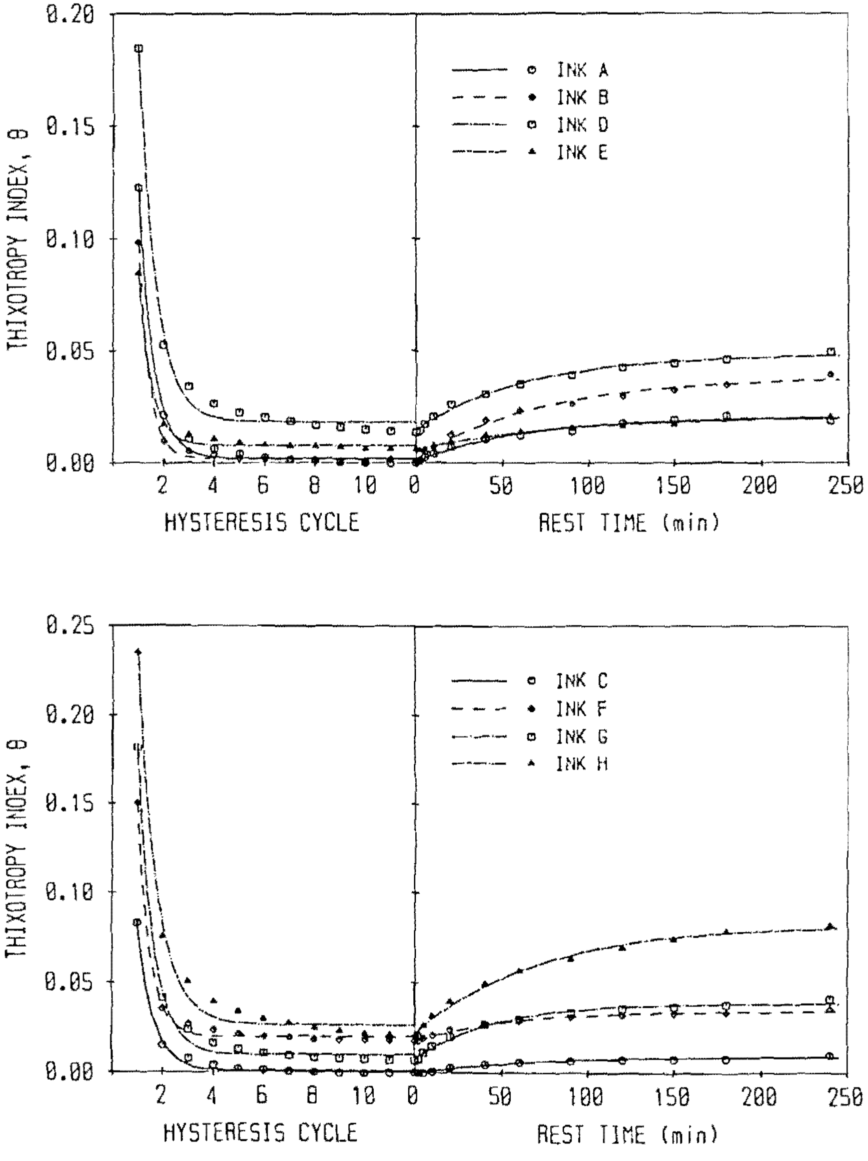


Figure 7. Thixotropy index curves characterizing thixotropic structural breakdown and recovery behavior of printing inks.

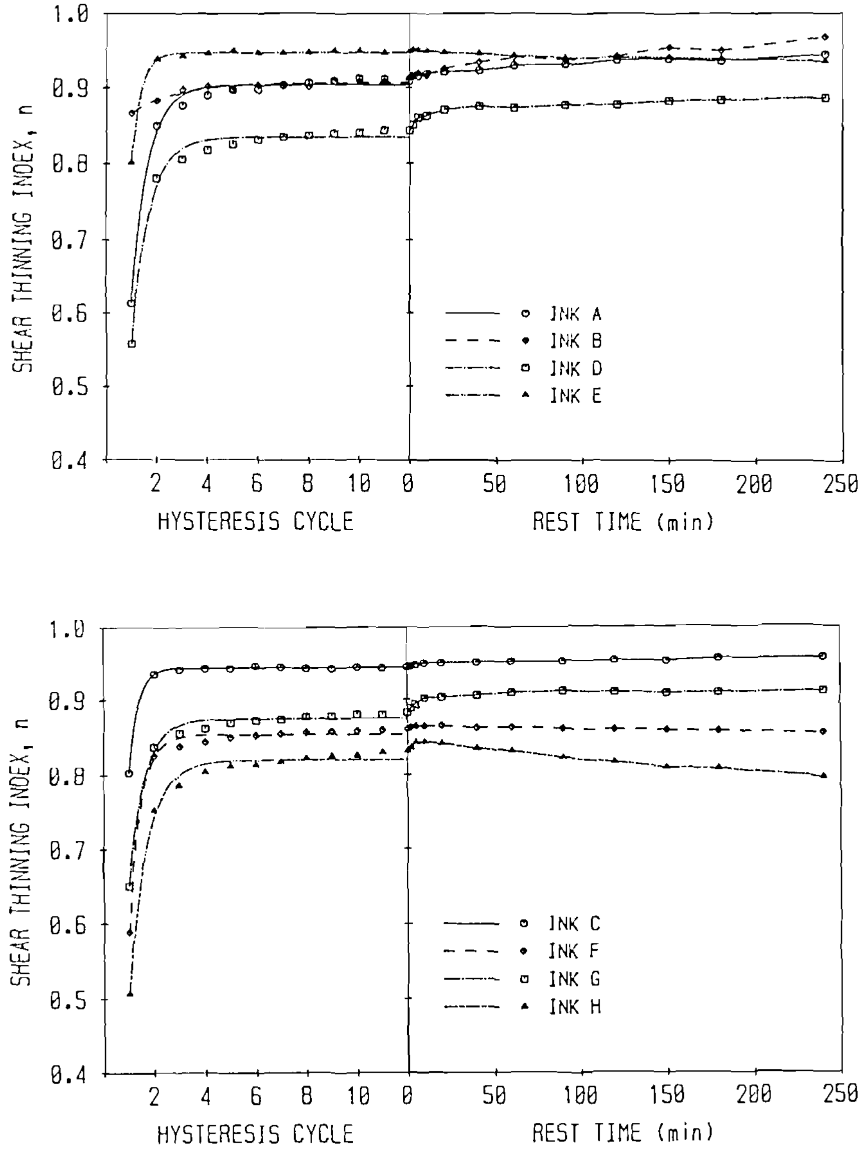


Figure 8. Shear Thinning index curves characterizing thixotropic structural breakdown and recovery behavior of printing inks.

Shear Thinning Index Curve

The calculated shear thinning indices of inks A and B in the structural recovery phase are greater than 1 because of the considerable humps at low shear rates. These shear thinning indices imply that inks A and B became rheopectic or shear thickening when the internal structure was reformed. However, close examination of flow curves in Figures 6c and 6d shows that the slope of either curve decreases with shear rate at any point beyond the hump region. This indicates that inks A and B are indeed shear thinning. So, the hump portion of flow curves were not included in the calculation of shear thinning indices of inks A and B.

Figure 8 shows the shear thinning index curves in a way similar to the thixotropy index curves. In the structural breakdown phase, the shear thinning index increased rapidly and approached a plateau within two to three cycles, like a mirror image of the thixotropy index curve.

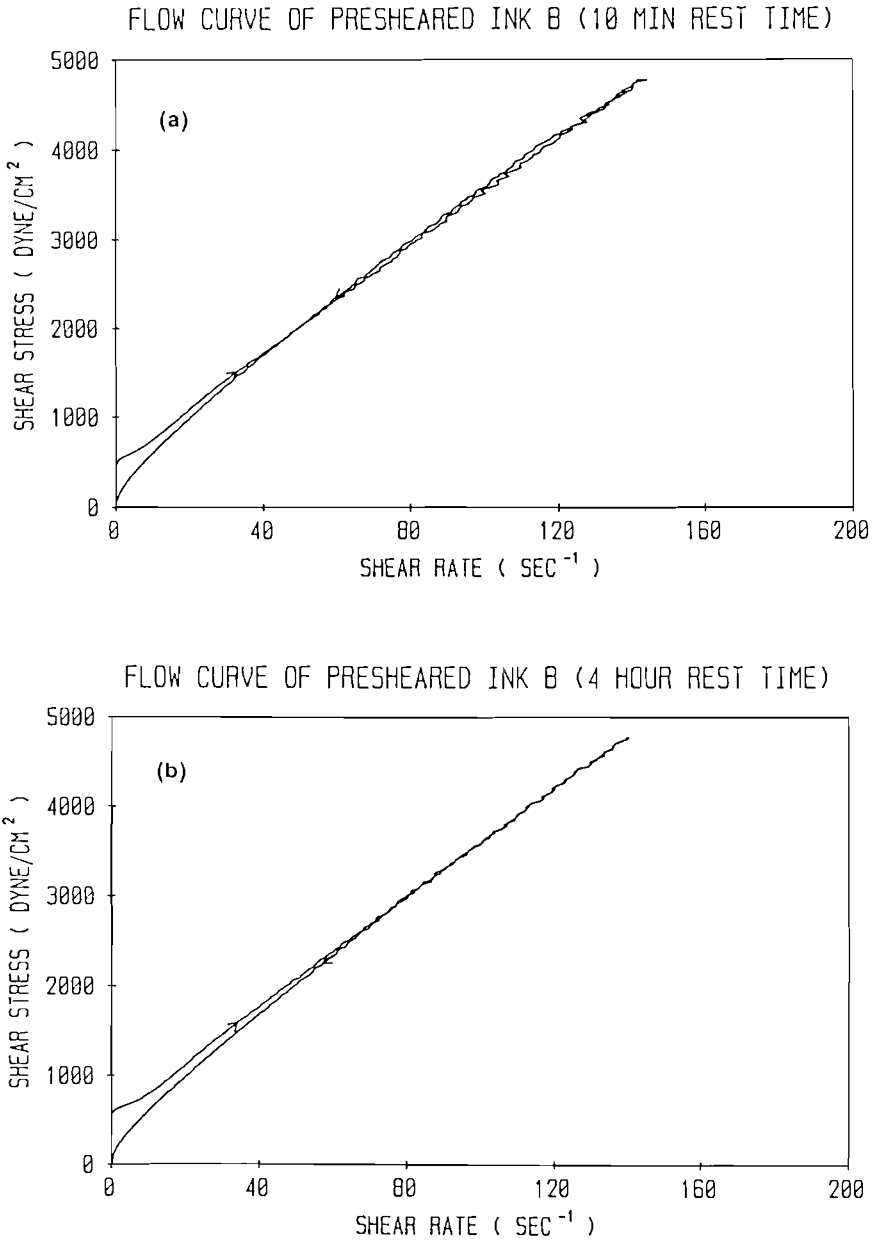
The shear thinning index data of the structural breakdown portion can be fitted by an equation similar to Equation (2).

$$\text{Breakdown:} \quad n = n_{b,e} - (n_{b,e} - n_{b,i}) \exp(-N/\lambda_{b,n}) \tag{3}$$

where n is the shear thinning index. The other notations are the same as those mentioned before. The calculated equilibrium shear thinning indices and time constants for the structural breakdown are summarized in Table III.

Table III. Parameters characterizing shear thinning index curve of inks in structural breakdown phase.

Ink	$n_{b,e}$	$\lambda_{b,n}$ (cycle)
A	0.903	0.64
B	0.907	1.80
C	0.943	0.36
D	0.835	0.69
E	0.947	0.37
F	0.854	0.46
G	0.875	0.60
H	0.820	0.72


FLOW CURVE OF PRESHEARED INK B (10 MIN REST TIME)

FLOW CURVE OF PRESHEARED INK B (4 HOUR REST TIME)

Figure 9. Flow curves of presheared ink B obtained after a rest time of (a) 10 minutes and (b) 4 hours.

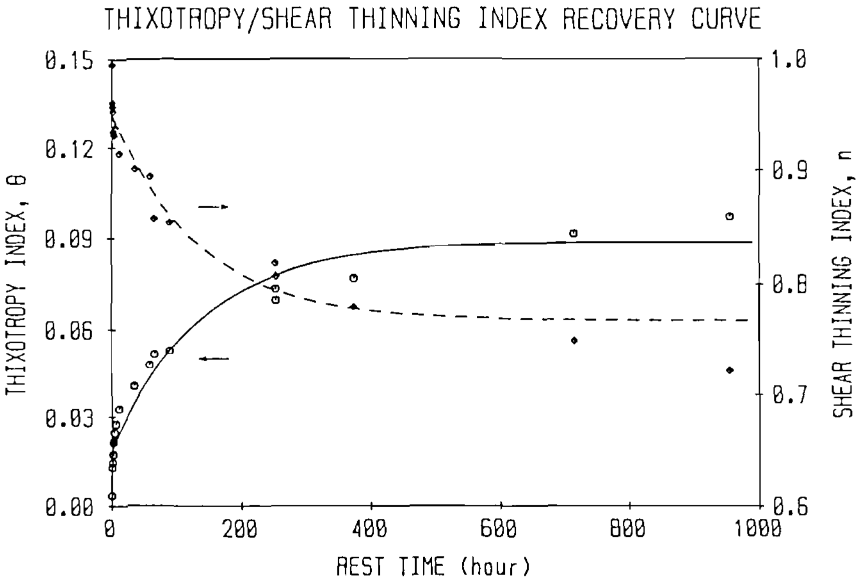


Figure 10. Thixotropy index and shear thinning index curves characterizing structural recovery behavior of presheared ink B.

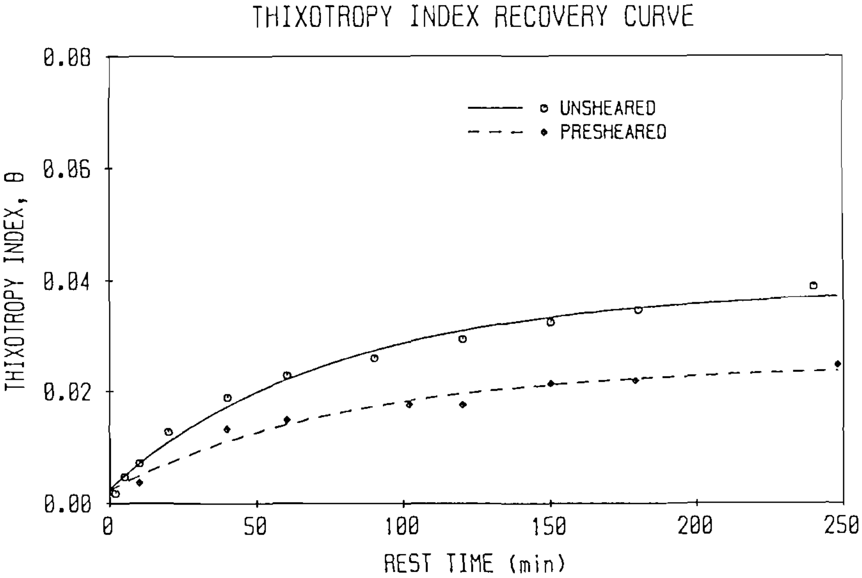


Figure 11. Thixotropy index curves of ink B that was intact or thoroughly agitated prior to the thixotropic structural measurements.

Contrary to our expectation, the shear thinning index in the structural recovery study continued to increase to a maximum value. It then either remained at that level or started to decline.

Results From Control Experiment

Figures 9a and 9b show the flow curves of ink B obtained 10 minutes and 4 hours after the ink was vigorously sheared with a high speed mixer. These curves at low shear rates behaved more like the undisturbed ink (Figure 6a), compared with the flow curves in Figures 6c and 6d. The low shear hump did not show up.

The thixotropy index and shear thinning index recovery curves of the control experiment are shown in Figure 10. The thixotropy index increased exponentially with rest time to a plateau and the data could readily be fitted by Equation (2). The shear thinning index was found to decrease exponentially with rest time according to the following equation.

$$\text{Recovery:} \quad n = n_{r,e} + (n_{r,i} - n_{r,e}) \exp(-t/\lambda_{r,n}) \qquad (4)$$

Table IV summarizes the calculated equilibrium thixotropy and shear thinning indices and the time constants that characterize the rate of structural recovery.

Figure 11 compares the thixotropy index curves of ink B, retrieved from Figures 7 and 10, for rest times not more than four hours. The two curves differ significantly and both approach asymptotes after four hours of rest. When this portion of data from the control experiment is analyzed, the calculated time constant and equilibrium thixotropy index are much smaller. These values are also listed in Table IV for comparison.

Table IV. Parameters characterizing thixotropic structural recovery of ink B obtained from the control experiment of varying rest time range.

Rest Time Range (hour)	$n_{r,e}$	$\lambda_{r,n}$ hour	$\theta_{r,e}$	$\lambda_{r,\theta}$ hour
955	0.767	133.5	0.089	135.0
4			0.025	1.4

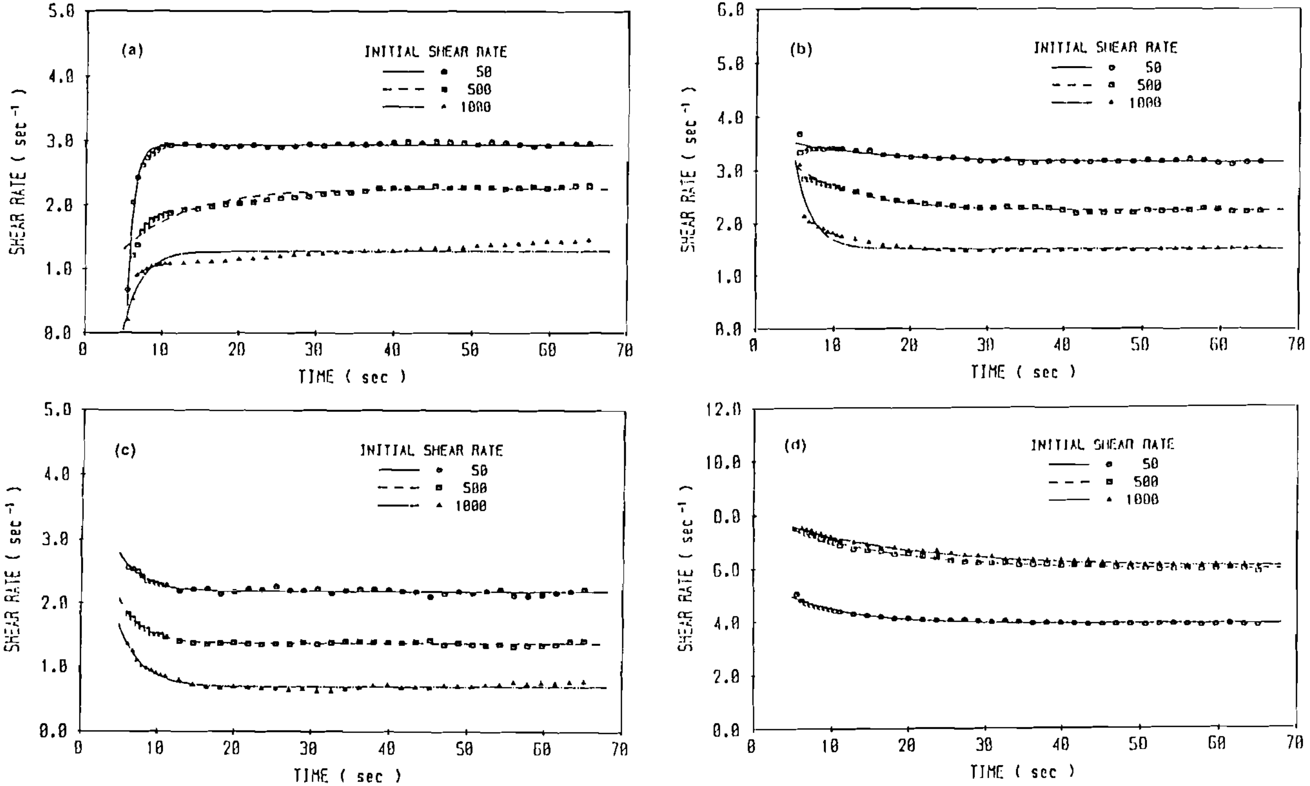


Figure 12. Pseudoplastic structural recovery curves of inks A to H.

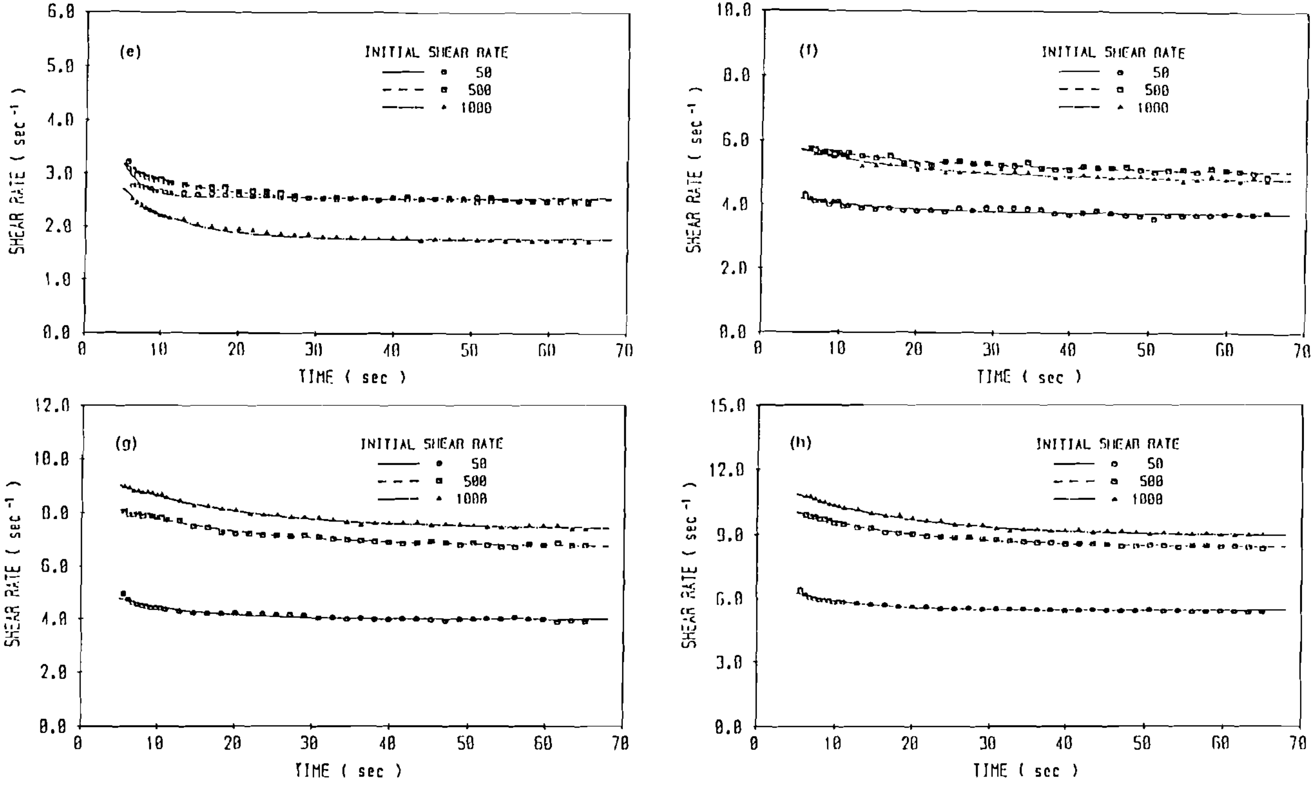


Figure 12. Continued.

Pseudoplastic Structural Recovery Curve

Figures 12a to 12h show the pseudoplastic structural recovery curves of inks A to H, respectively. Except ink A, the resulting shear rate dropped rapidly and levelled off in about 10 to 20 seconds. Rates of pseudoplastic structural recovery appeared more or less independent of the preshear conditions for all the inks studied.

Ink A differed from the other inks in that the resulting shear rate dropped to zero as soon as the applied shear stress was removed. When a low level stress was subsequently applied to the ink sample, the shear rate increased rapidly to a plateau, also in about 10 to 20 seconds. These curves resemble the structural breakdown curves.

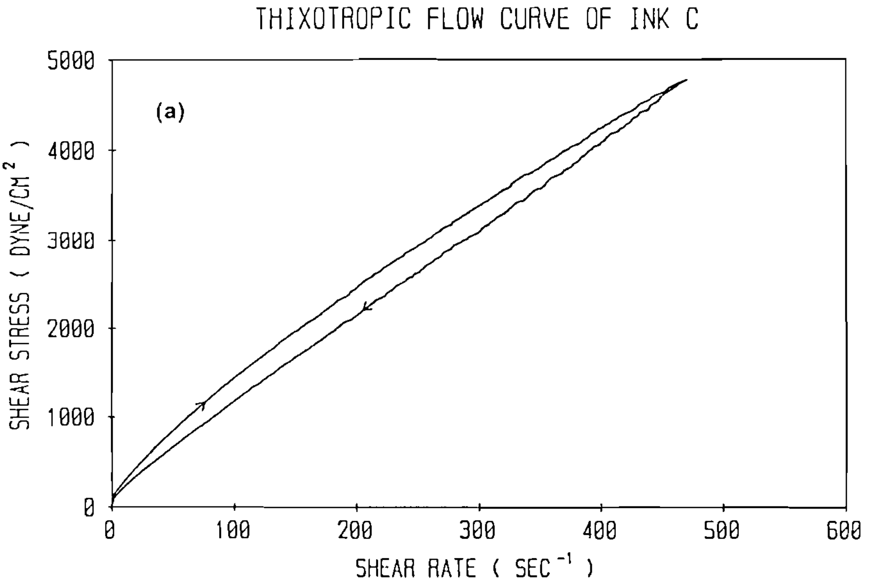
DISCUSSION

Thixotropic Versus Pseudoplastic Flow

Whenever the viscosity of a fluid is independent of time for any given shear rate, the fluid is said pseudoplastic. The viscosity of a thixotropic fluid will decrease with time under a set of constant shear conditions. In other words, if the structure of a fluid can break down and reform instantly within the time frame of measurement, it is a pseudoplastic fluid. When the structure requires a finite time to recover, the fluid is thixotropic. Consequently, a fluid cannot exhibit both thixotropic and pseudoplastic behavior under identical shearing conditions.

Figure 13a shows a flow curve of ink C. The upcurve and downcurve form a distinct hysteresis loop, and ink C is a thixotropic fluid. Figure 13b shows another flow curve of the same ink, in which the downcurve superimposes the upcurve and ink C is said to be pseudoplastic. These flow curves were obtained under identical experimental conditions, and ink C exhibited both thixotropic and pseudoplastic behavior. How did ink C in Figure 13a differ from that in Figure 13b? The two flow curves were obtained respectively from the first and the ninth loop tests of the thixotropic structural breakdown measurements. The internal structure of ink C was progressively disintegrated and completely destroyed after eight test cycles (Figure 7).

When the internal structure of an ink is completely destroyed under high shear conditions, pigment will behave like individual particles. As soon as the applied shear is



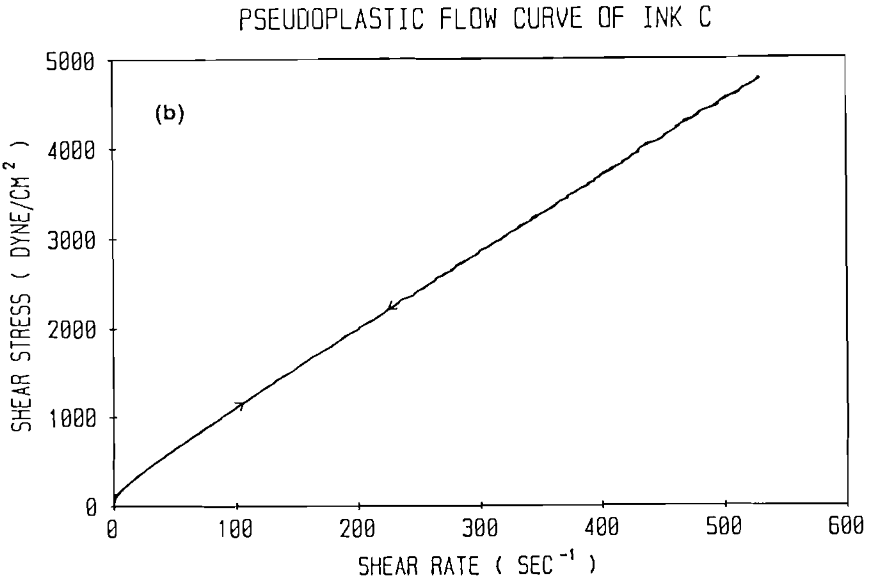


Figure 13. Flow curves of ink C showing thixotropic as well as pseudoplastic flow behavior.

reduced or removed, they will diffuse in the ink vehicle and collide one another due to the Brownian motion. This random particle movement disturbs the orderly flow pattern produced previously under high shear conditions and hence the viscosity increases almost instantly. Meanwhile, particle-particle collisions may also lead to the formation of associated particles, the building blocks of internal structure. It is a common knowledge of chemical kinetics that only a very small fraction of particle collisions will actually result in the associated state. Accordingly, it will take a while for the associated pigment particles to grow into a three dimensional internal structure. Instantaneous recovery of internal structure is thus impossible. The internal structure will gradually reform in an extended period of time if the ink is allowed to rest.

It is our tentative conclusion, based on the results of Figure 13 and the foregoing speculations, that the presence of internal structure may be a better criterion for distinguishing thixotropic fluids from pseudoplastic fluids. Thixotropic structure is characterized by the association of pigment particles to form of a three dimensional network, that is, thixotropic structure is the same as internal structure. Pseudoplastic structure is characterized by pigment particles which are present in the ink vehicle as randomly distributed individual identities. Recovery of thixotropic structure is a very slow process, while pseudoplastic structure recovers almost instantly.

Thixotropic Structure

Close examination of Figure 7 and Table II data show that American inks completely lost their thixotropy at the equilibrium state of the structural breakdown measurement. Their $\theta_{b,e}$ values are nearly zero. Conversely, Japanese inks still possessed considerable thixotropy; $\theta_{b,e}$ values range from 0.010 to 0.026. European inks whose $\theta_{b,e}$ values are 0.008 and 0.018 appeared in a range between American and Japanese inks. This difference can be ascribed to varying ink formulation philosophy in these different parts of the world. We have a suspicion that the thixotropic structure in American inks are produced by pigment flocculation and in Japanese inks by colloidal aggregation. In any case, our results indicate that there is a distribution of structural linkage strengths. Accordingly, the extent of structural linkage destruction is dependent upon the shear force being applied.

Flow curves in Figures 6c, 6d, 9a, and 9b demonstrate that the reformation of thixotropic structure is detected first at the low shear range and gradually extends into higher shear rates. These results imply that Brownian motion induced pigment particle collisions create loosely associated particles which slowly rearrange themselves into a stronger network.

The time constants characterizing structural recovery of ink B, Tables II and IV, indicate that the thixotropic structural recovery rate from the repeated loop tests is about two orders of magnitude faster than that from the control experiment. This discrepancy can be attributed to two reasons. First, loosely associated particles are expected to form a continuous network filling the small gap of the cone and plate system much more easily than that of the one-pint container. This is also evidenced by the results in Figure 11. The rapid growth of thixotropic structure in the small dimension of the cone and plate gap also accounts for the appearance of exaggerated humps at low shear rates (Figures 6c and 6d), which are practically nonexistent in flow curves of the control experiment (Figure 9).

Size of experimental data is the second attribute to the discrepancy. Table IV shows that the time constant and the equilibrium thixotropy index calculated from the first four hour thixotropy index curve are much smaller than those from the 955 hour curve. Obviously, data from a four hour experiment are insufficient to characterize a recovery phenomenon that spans hundreds hours. Similarly, the equilibrium thixotropy indices in Table II are several times smaller than their original values in Table I. These results support our previous speculation that thixotropic structural recovery is a very slow process. It may take hundreds hours for the destructed thixotropic structure of an ink to regain its original state.

The formation of loosely associated particles in the initial stage of structural recovery process causes the hysteresis loop area to grow at low shear rates. This is particularly noticeable when the sample was allowed to recover in the small gap of the cone and plate system, which resulted in an increased shear thinning index calculated according to the Herschel-Bulkley equation. So, the shear thinning index curves rise initially in the structural recovery phase of repeated loop tests (Figure 8). As soon as this loose structure rearranged into a stronger one that could balance the low shear effect, the shear thinning index began to decline. When the recovering sample is not limited to a very small volume such as in the control experiment, the shear thinning index, as is expected, decreases with increasing rest time (Figure 10).

Correlation Between Thixotropy And Shear Thinning Indices

Our previous results (Chou and Bain, 1988) showed a high degree of linear correlation between thixotropy and shear thinning indices, which was independent of ink types. More data have been collected since then. They are plotted in Figure 14. A high correlation between the two parameters still exists, but it departs from linear with decreasing shear thinning index. There is no real fluid whose shear thinning index is equal to zero. Consequently, the maximum measurable thixotropy index is expected to be less than the hypothesized value of 0.5. The nonlinear dashed-curve relationship shown in Figure 14 is more likely the real one.

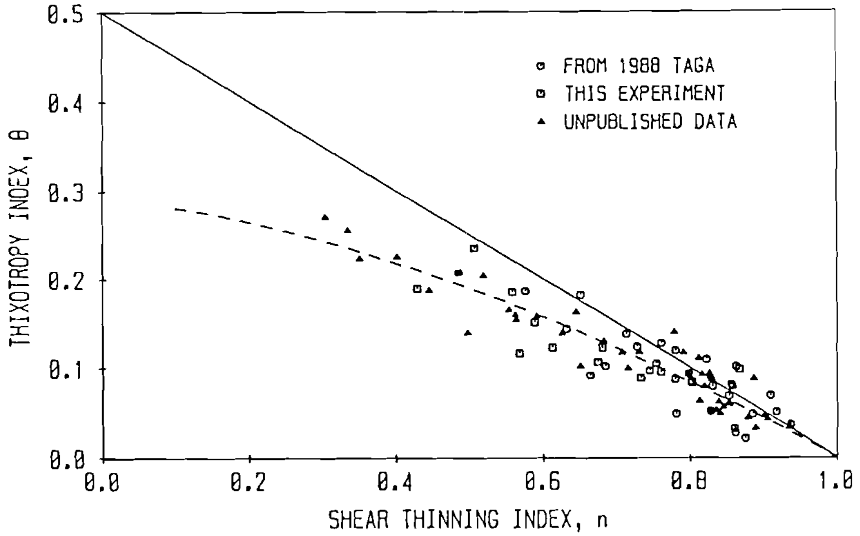


Figure 14. Correlation between thixotropy index and shear thinning index.

The nearly mirror image relationships between shear thinning index curves and thixotropy index curves in the structural breakdown experiments, Figures 7 and 8, as well as in the structural recovery experiments, Figure 10, also imply that these two parameters are determined by the same internal structure factors.

Pseudoplastic Structure

Figure 12 shows that for all the inks studied the steady state shear rates were accomplished almost instantaneously after the applied shear stress was reduced. This rapid recovery is a characteristic of the pseudoplastic structure discussed previously. The step change technique may have been misused by many researchers to determine thixotropy because thixotropic structural recovery is such a slow process. This step change technique involves changing the shear stress instead of the time; it is more appropriate for determining shear-dependent properties than time-dependent properties.

Variation in preshear conditions did not affect the time needed to establish steady state (Figure 12). However, the equilibrium shear rates varied even though the applied low shear stress remained the same in each set of measurements. For American inks the resulting equilibrium shear rate was higher if preshear conditions were less severe. A reversed trend was observed with Japanese inks. It seems that the effect of preshear on the equilibrium shear rate is related to the internal structure type. Further investigation is needed to reveal this effect.

It was proposed in an early section that diffusion of pigment particles in the vehicle due to Brownian motion is the mechanism of pseudoplastic structural recovery. A relationship between pseudoplastic structural recovery rate and plastic viscosity is then expected. Results of Figure 12 and data in Table I do not exhibit any direct relationship. It appears that some factors other than the thermal force induced Brownian motion may by involved in the recovery of pseudoplastic structure. These forces which we do not know yet are distinctively large for ink A that causes the overshooting response.

Forces Governing Rheological Behavior Of Printing Inks

Printing inks are thixotropic in nature. Their response to shear varies with the immediate past history of the inks. To describe rheological behavior of inks, a viscosity profile zone, Figure 15, is needed in place of a viscosity profile curve, Figure 1. The upper bound of this viscosity profile zone contains full information about ink's internal structure and the lower bound represents the state of ink whose internal structure has been completely broken down. Depending on the shear history, the viscosity of an ink can be any value within the zone bounded by the two curves.

Both the upper and the lower bounds exhibit the three rheological regions similar to those in Figure 1, that is, the first Newtonian, shear thinning, and second Newtonian regions. Similar arguments used in Figure 1 for explaining the physical significance of the three regions for any pseudoplastic fluid are applicable to the thixotropic inks. The upper bound is controlled by the shear force, thermal force, and pigment/molecular interactions. The lower bound is controlled by the shear force, thermal force, and a force yet unknown to us $(F_?)$.

The thixotropic structure controls the transition between the upper and the lower bounds and determines both shear thinning and thixotropy properties of an intact ink. The pseudoplastic structure controls the transition of rheological states along the lower bound and determines the shear thinning property of a thoroughly worked ink.

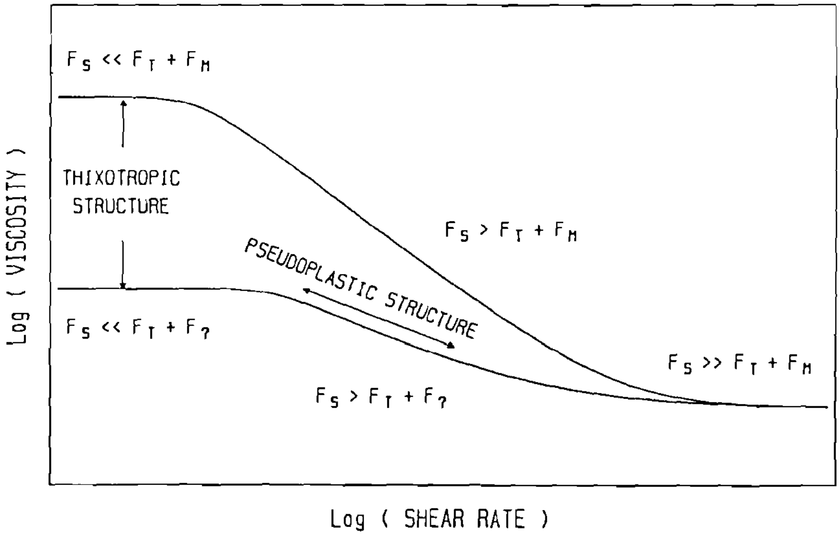


Figure 15. Viscosity profile zone typical of printing inks and its relations to the controlling forces and structures.

IMPLICATIONS TO PRESS PERFORMANCE

An ink has to pass through a large number of distribution roller nips before it reaches the printing plate, and in each roller nip it is subjected to extremely high shear conditions. Consequently, the internal structure is nearly or completely destroyed before the ink reaches the plate. The implication is that the lower bound of viscosity profile zone in Figure 15 best represents the rheological behavior of printing inks on the press because of the extremely slow recovery of internal structure.

Thixotropy may be overestimated by the ink industry. For example, dot gain and levelling may have nothing to do with thixotropy. Dot gain is more likely controlled by the high shear viscosity and elasticity properties. Our statement relating dot gain to thixotropy (Chou and Bain, 1988) may need revision. Levelling is related to the zero-shear-rate viscosity determined by the pseudoplastic structure of inks. This relieves ink formulators of making a compromise between low shear viscosities separately needed for both levelling and pigment sedimentation.

Thixotropy is important to the pigment sedimentation without doubt. It is also an important property of inks for the undershot open fountain. Those inks are generally designed to be very thixotropic and have very high viscosity at low shear rates. As a result, they will not flow properly under their own weight and tend to back away from the fountain roller. An ink agitator is essential to partially break down internal structure and keeps the ink flowing properly towards the fountain roller. Once the press stops, rapidly recovering pseudoplastic structure significantly increases the viscosity, disallowing continued flow of ink. The slowly reforming internal structure further increases the viscosity. Both factors stop ink flow and prevent ink seepage from the gap between fountain roller and metering blade.

In the newspaper industry, ink is generally pumped from a central storage tank through a very long pipe to the printing press. Inks which are too thixotropic are not desirable. They may not flow at all at the startup in the morning, especially on cold days. The internal structure gradually rebuilds during the overnight shutdown and the ink becomes too viscous to flow the next morning.

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