Thixotropic Behavior of Gel-Like Systems

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Synopsis

The changes of shear stress with time under constant shear rate and temperature of several pigmented acrylic polymer gels were examined. This behavior, known as thixotropy, was interpreted based on a model which separates the stress into two regions. Region I covers the growth of the stress up to the yield point, represented by a peak stress, F_0. Region II covers the decay of the stress from the peak to the point it attains an asymptotic value, F_∞. The material in region I is assumed to be elastic and in region II is represented by a dynamic equilibrium between structure A, which is non-Newtonian and structure B, which is Newtonian. The transitions between A and B represent structure degradation and structure recovery. The concentrations of A and B are solved explicitly. The total shear stress is then evaluated following a theory proposed by Ree and Eyring and is shown to give relationship between shear stress–shear rate–shearing time in good qualitative agreement with experimental observations. The ratio $(F_0 - F_\infty)/F_\infty$, defined as the coefficient of thixotropy, is sensitive to the fundamental physical chemical parameters of the system and is easy to measure. It is shown to be useful in the characterization of thixotropic materials such as gels. Methods for evaluating the elastic modulus and yield stress of the material in the gel state are also illustrated.

INTRODUCTION

Thixotropy is a well-known phenomenon in colloidal systems, especially gels. The term thixotropy, however, has also frequently been confused with the phenomenon where viscosity decreases with increasing shear rate in steady-state flow, which should be described as "shear thinning" or "pseudoplasticity." Although shear thinning and thixotropy do usually occur together, a system is called thixotropic only when the decrease of rheological property, say, viscosity occurs with a distinct *time* dependence under the action of *constant shear rate* and temperature (see Fig. 1 for illustration). Upon removal of the shear, the rheological property recovers, with time, toward its initial value.

Quantitative determination of thixotropy has long been a problem because these materials are highly sensitive to their rheological history and to the conditions of shear. Various attempts in the past for such measurements have resulted with only limited success. One of the best-known methods[1] which measures the "hysteresis loop" was sound in theory but, unfortunately, was complicated with experimental difficulties. Another method[2] which measures the resistance to a thin cross pin moving along a
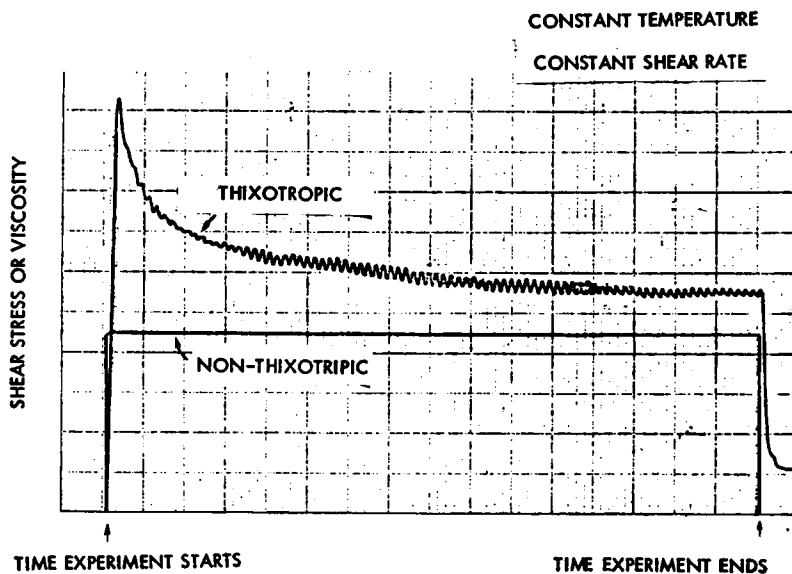
Fig. 1. Thixotropy—the decrease of shear stress with time of shear under constant shear rate and temperature.

helical path inside a material is debatable both in theory and in practice, since the flow encountered is not viscometric and the instrumental variables involved are not well defined.   Most of the early work in the related areas has been elegantly reviewed by Bauer and Collins.[3]

Thixotropy has been recognized as an important parameter in many industrial processes.   For example, the manufacturing, processing, application, and the final performance of paints are generally shear dependent and time dependent.   Understandably, the coating industry has maintained a high level of interest in characterizing and controlling thixotropy.[4,5]

This report describes some theoretical considerations leading to a method capable of allowing more accurate and convenient measurements of thixotropy.   The method has been found useful in the rheological characterization of many surface-coating systems and is believed to be of interest in the characterization of gels in general.

THEORETICAL

General

We shall assume that a thixotropic gel contains, initially, network structure which can be treated as an elastic body.   Under small external stresses, the system undergoes elastic deformation (region I, Fig. 2).   When the external stress applied exceeds the yield stress, the system starts to flow (region II, Fig. 2).   The flow characteristics are complex, dependent upon the magnitude as well as the duration of the shear as observed in steady-
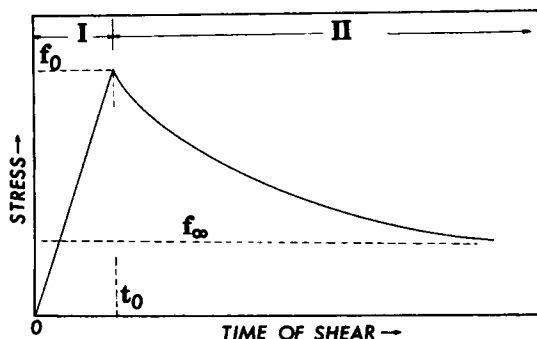
Fig. 2. Analysis of thixotropic behavior under steady-state shear.

state shear experiments. We shall further assume that the system at steady-state flow can be represented by a dynamic equilibrium between two types of rheological structure, designated by A and B. The rheological behavior of A is non-Newtonian,

$$F_A = F(\dot{\gamma}) \tag{1}$$

where F_A is the shear stress associated with structure A and $\dot{\gamma}$ is the rate of shear. The rheological behavior of B is simply Newtonian, namely,

$$F_B = \eta\dot{\gamma} \tag{2}$$

where F_B is the shear stress associated with structure B and η is the viscosity. The total shear stress of the system, at region II, will be written as

$$F = F_A + F_B \tag{3}$$

which will be considered in greater detail in this paper.

The equilibrium between A and B can be schematically expressed by the chemical reaction

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

where k_f and k_b are the reaction rate constants of the forward and backward processes, respectively, at zero shear rate. The forward direction represents the process of structure degradation, whereas the backward direction represents structure recovery. Most gelling colloidal systems have k_b larger than k_f since, under zero shear rate, the system tends to become gelled, or highly structured. Under large applied shear rate, thixotropic degradation is predominant.

Based on the generalized theory of viscosity proposed by Eyring and co-workers,[6] the flow of fluids can be considered as the passage of a molecule or a flow unit from one equilibrium position to another separated by an energy barrier. In a thixotropic system, such as one involving molecular entanglement and disentanglement, the process from A to B is promoted by an elastic energy stored up on the flow unit which can be formally repre-

sented by a Maxwell body.[7]   The elastic energy stored up during the relaxation time w is given by

$$w = C\dot{\gamma}^2$$

where C is related to the spring constant and relaxation time.   The rate of degradation can be expressed as

$$X_A k_f \exp(w/2kT).$$

The rate of recovery, likewise, can be expressed as

$$X_B k_b \exp(-w/2kT)$$

where X_A and X_B are the respective concentrations, expressed in mole fractions, k is the Boltzmann constant, and T is the absolute temperature.   It should be mentioned that k_f and likewise k_b can be expressed by an equation well known in rate processes:

$$k_f = \frac{kT}{h} \frac{G\ddagger}{G} \exp(-\epsilon_0/kT)$$

where h is the Planck constant; $G\ddagger$ and G are the partition functions of the transition and the initial state, respectively; and ϵ_0 is the excitational energy.

The Concentrations of the Structural Units

The net rate of change, expressed by $-dX_A/dt$, is

$$- \frac{dX_A}{dt} = X_A k_f \exp(w/2kT) - X_B k_b \exp(-w/2kT). \tag{4}$$

Thus, one can solve this differential equation for an explicit expression of X_A as a function of time.   Since $X_A + X_B = 1$, one obtains, with the initial condition $X_A = 1$ and $X_B = 0$,

$$X_A = \frac{k_b e^{-x}}{k_f e^x + k_b e^{-x}} + \frac{k_f e^x}{k_f e^x + k_b e^{-x}} e^{-(k_f e^x + k_b e^{-x})t} \tag{5}$$

where $x = w/2kT$.   This equation shows how X_A and likewise X_B change with the time of shearing under constant temperature and constant shear rate.   This is schematically shown in Figure 3.

Note that at $t = \infty$,

$$X_A = \frac{k_b e^{-x}}{k_f e^x + k_b e^{-x}}$$

$$X_B = \frac{k_f e^x}{k_f e^x + k_b e^{-x}}. \tag{6}$$

The actual concentrations at steady state at $t = \infty$ is determined by x, which is a function of C, a material constant of the system and of $\dot{\gamma}$ and T,
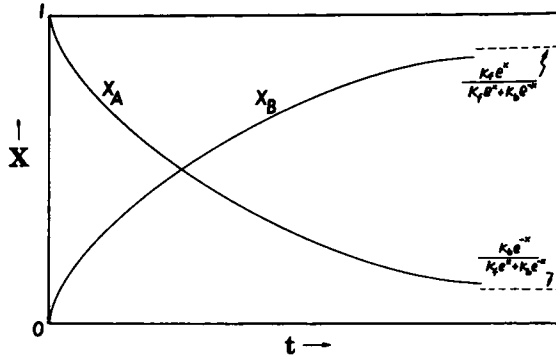
Fig. 3. Change of concentrations of different structures with time of shear.

which are experimental variables. At low shear rate, x approaches zero and the steady-state concentrations are

$$X_A = \frac{k_b}{k_f + k_b}$$

$$X_B = \frac{k_f}{k_f + k_b}$$

(7a)

since $k_b > k_f$, $X_A > X_B$. This is analogous to the condition at rest. On the other hand, at high shear rate such that x approaches infinity,

$$X_A \to 0, \; X_B \to 1.$$

(7b)

All the structures represented by A are transformed to structure B.

The Change of Shear Stress With Time

We now proceed to calculate the total shear stress on the basis of the theory of Ree and Eyring[8] who treated a non-Newtonian system as consisting of n groups of flow units each of which has a relaxation time β_n and a geometric dimension α_n; each group occupies a fractional area on the shear surface which, as a first approximation, can be taken as the fractional molar concentration X_n. For such a system, they conclude that

$$F = \sum_n X_n f_n$$

(8)

and

$$f_n = \frac{\text{Sinh}^{-1} \beta_n \dot{\gamma}}{\alpha_n}$$

(9)

For the thixotropic model described here which involves two groups of flow units, namely, A and B, with B being Newtonian,

$$F = \frac{\beta_B}{\alpha_B} X_B \dot{\gamma} + \frac{\text{Sinh}^{-1}\beta_A \dot{\gamma}}{\alpha_A} X_A.$$

(10)

Substituting X_A and X_B as obtained above into eq. (10), it follows that

$$F = F_\infty + (F_0 - F_\infty) \cdot e^{-mt} \tag{11}$$

where

$$m = k_f e^x + k_b e^{-x} \tag{11a}$$

$$F_\infty = L_B + \left(L_A \frac{\text{Sinh}^{-1} \beta_A \dot{\gamma}}{\beta_A \dot{\gamma}} - L_B \right) (\dot{\gamma}) \left(\frac{k_b e^{-x}}{m} \right) \tag{11b}$$

$$F_0 - F_\infty = \left(L_A \frac{\text{Sinh}^{-1} \beta_A \dot{\gamma}}{\beta_A \dot{\gamma}} - L_B \right) (\dot{\gamma}) \left(\frac{k_f e^x}{m} \right) \tag{11c}$$

with $L_n = \beta_n/\alpha_n$ which can be shown to be the viscosity of group n at zero shear rate. This equation describes the process of thixotropic degradation and shows how the total shear stress varies with time, a function which can be measured accurately. Clearly, there are two types of factors involved in the shear stress: (a) rheological properties such as ϵ_0, k_f, k_b, L_A, and L_B, and (b) experimental conditions such as T, $\dot{\gamma}$, and t. Thus, by measuring the shear stress under chosen experimental conditions, the fundamental rheological parameters of a thixotropic system can be evaluated.

An attempt has been made to evaluate eq. (11) numerically by assigning to each molecular parameter a number based on theoretical estimates. A three-dimensional model showing the relationships F–$\dot{\gamma}$–t can be obtained. The model can be expressed two-dimensionally as shown in Figures 4a–4d. The ordinate in these figures is the shear rate $\dot{\gamma}$, in sec^{-1}, and the abscissa is the time of shear t, in minutes. Shear stresses are represented by letters A to Z and by (......) and (,,,,,,) whose limits of magnitude, in dynes/cm^2, are tabulated as shown in each figure. The lines of same letters represent lines of equal stress. The change of stress as a function of time of shearing is shown in each figure by horizontal lines representing constant shear rate. At both very high and very low shear rates, the variation of stress with time is much smaller than that at intermediate shear rates.

Other parameters being equal, a comparison of the figures shows that thixotropic behavior increases with increasing L_A and with increasing k_b (Figs. 4a and 4b, 4c and 4d, respectively) and decreases with decreasing k_b/k_f (Figs. 4b and 4c). Whereas these figures represent extreme conditions of certain theoretical conditions and are thus difficult to reproduce experimentally, the effects these figures represented are in good qualitative agreement with experimental observations.
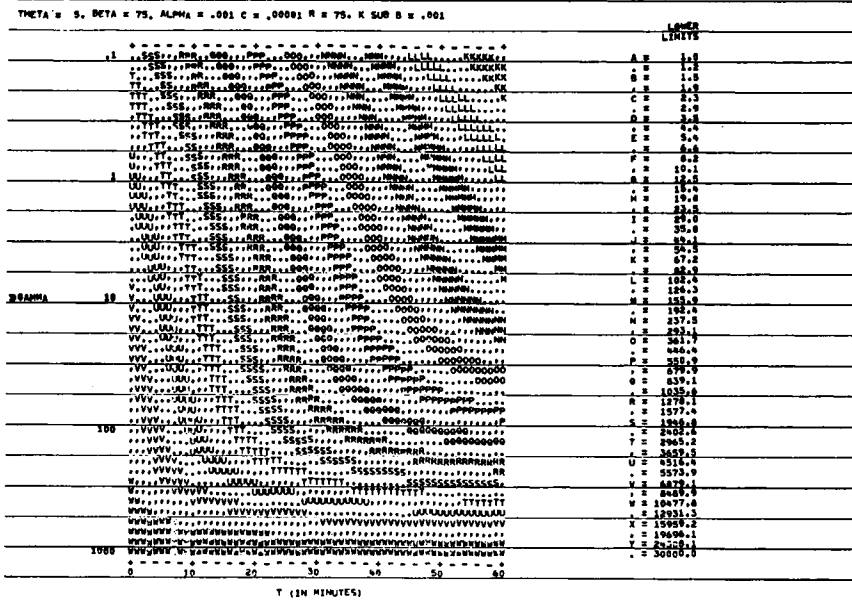
The Coefficient of Thixotropy

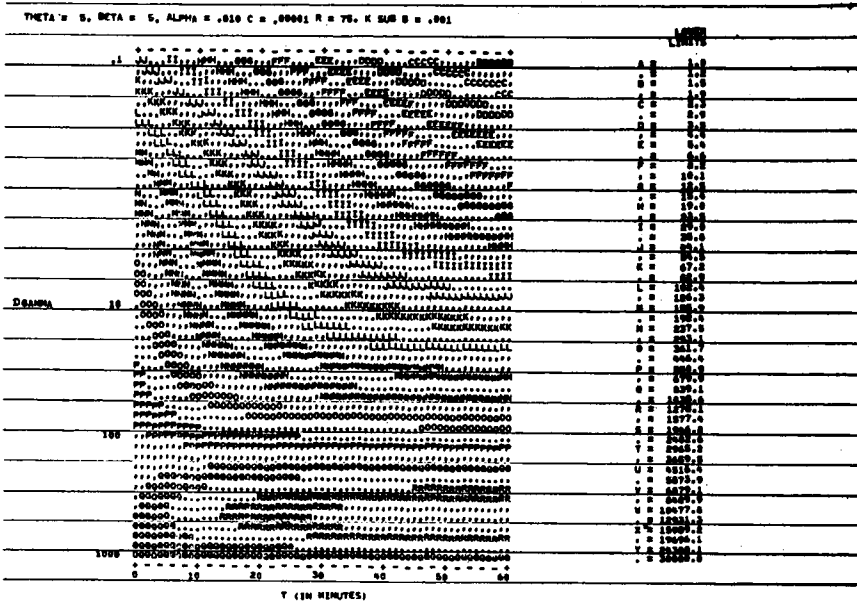We shall define a coefficient of thixotropy, λ, by the following equation:

$$\lambda = \frac{F_0 - F_\infty}{F_\infty}. \tag{12}$$

This is the ratio of the stress corresponding to the degradation of the structure A to the stress due to the viscosity of the system with structure B.

The former is variable with time, while the latter is time independent. Both F_0 and F_∞, and thus λ, can be conveniently determined, as shown in Figure 2. Obviously for all thixotropic systems, the coefficient is larger than zero.

THETA's 5, BETA = 75, ALPHA = .001 C = .00001 R = 75, K SUB B = .001

T (IN MINUTES)

(a)

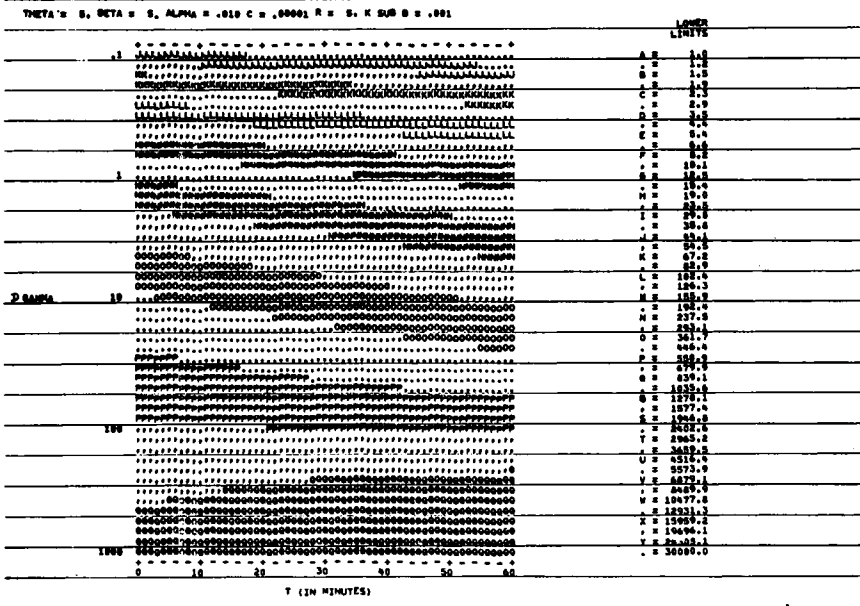THETA's 5, BETA = 5, ALPHA = .010 C = .00001 R = 75, K SUB B = .001
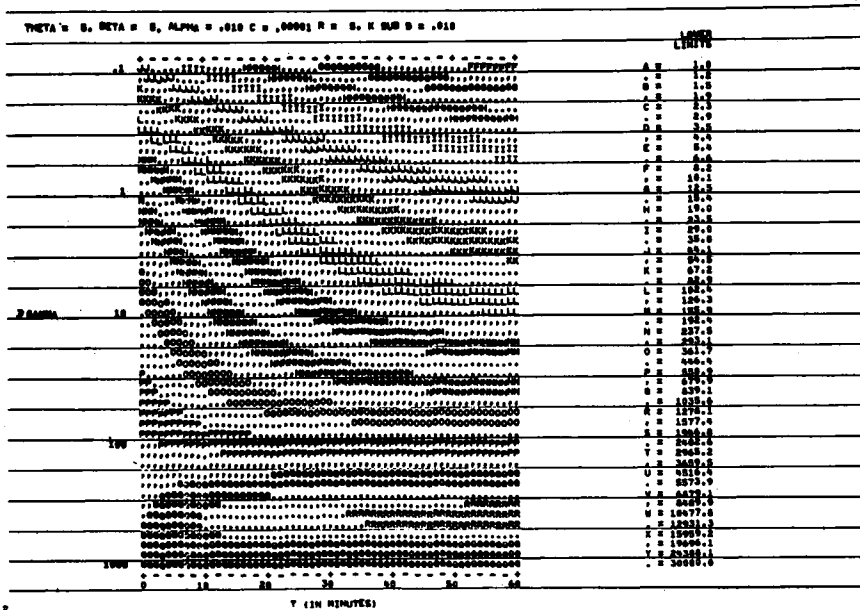
T (IN MINUTES)

(b)

Fig. 4 (*continued*)

(c)

(d)

Fig. 4. Change of shear stress as a function of shear rate and time of shear according to eq. (11) $(X = 10^{-5}, L_B = 5$ dynes-sec/cm^2): (a) $k_b = 10^{-3}$ sec^{-1}, $k_b/k_f = 5$, $\beta_A = 75$ sec, $\alpha_A = 10^{-3}$ cm^2/dyne; (b) $k_b = 10^{-3}$ sec^{-1}, $k_b/k_f = 75$, $\beta_A = 5$ sec, $\alpha_A = 10^{-2}$ cm^2/dyne; (c) $k_b = 10^{-3}$ sec^{-1}, $k_b/k_f = 5$, $\beta_A = 5$ sec, $\alpha_A = 10^{-2}$ cm^2/dyne; (d) $k_b = 10^{-2}$ sec^{-1}, $k_b/k_f = 5$, $\beta_A = 5$ sec, $\alpha_A = 10^{-2}$ cm^2/dyne.
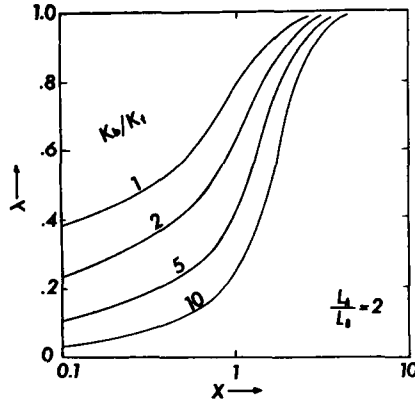
Fig. 5. Change of λ with x as a function of k_b/k_f at constant L_A/L_B.

Substituting eqs. (11b) and (11c) into eq. (12), one obtains

$$\lambda = \frac{\left(L_A \dfrac{\text{Sinh}^{-1} \beta_A \dot{\gamma}}{\beta_A \dot{\gamma}} - L_B\right)\left(\dfrac{k_f e^x}{m}\right)}{\left(L_A \dfrac{\text{Sinh}^{-1} \beta_A \dot{\gamma}}{\beta_A \dot{\gamma}} - L_B\right)\left(\dfrac{k_b e^{-x}}{m}\right) + L_B} \tag{13}$$

If measured at low shear rate, such that $(\beta_A \dot{\gamma})$ approaches zero,

$$\lambda = \frac{(L_A - L_B)\, k_f e^x}{L_A k_b e^{-x} + L_B k_f e^x} \tag{14}$$

since

$$\lim_{(\beta_A \dot{\gamma}) \to 0} \lambda \frac{\text{Sinh}^{-1} \beta_A \dot{\gamma}}{(\beta_A \dot{\gamma})} = 1.$$

Further, since all the parameters are positive and $L_A > L_B$, $k_b > k_f$, it can be shown that

$$\lim_{x \to 0} \lambda = \frac{(L_A - L_B)k_f}{L_A k_b + L_B k_f} \geq 0 \tag{15}$$

$$\lim_{x \to \infty} \lambda = \frac{L_A}{L_B} - 1 > 0. \tag{16}$$

Notice that the coefficient equals zero when $L_A = L_B$. This is a special case where A and B are equal in the ratio of relaxation time to geometrical dimension and are thus indistinguishable. The slope, $d\lambda/dx$, is always positive and approaches zero at both low and high shear rates. The general behavior of λ, as expressed in eq. (14), can be further illustrated in Figures 5 and 6. It is clearly shown that large L_A/L_B and large k_b/k_f lead to large thixotropy as expected.

A detailed theoretical calculation of λ, as of F, is difficult since it would require the knowledge of every molecular parameter involved. However,
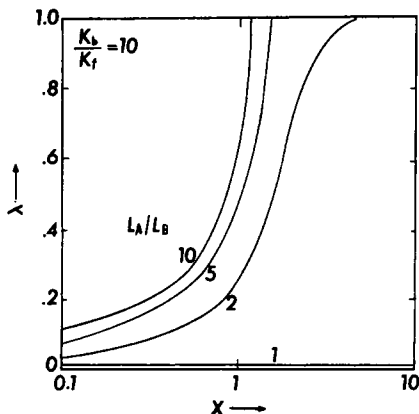
Fig. 6. Change of λ with x as a function of L_A/L_B at constant k_b/k_f.

λ is easily obtained from the experimental F-versus-t relationship and can thus be used as a measurement for practical characterization of thixotropy of colloidal systems.

EXPERIMENTAL

Shear stress was measured in a Haake Rotovisko rotational viscometer. Results were occasionally checked by duplicating the experiments using a Weissenberg rheogoniometer, Model R18. In either case, the change of shear stress with time at constant shear rate was automatically recorded. All measurements were done at 25°C.

Several gelling dispersions were used in this study. They were of two types: organic solvent based and water based. The solvent-based dispersion consists mainly of an acrylic copolymer prepared by free-radical polymerization and dispersed in a poor solvent such as toluene. The aqueous dispersion consists mainly of an acrylic latex, prepared by emulsion polymerization and stabilized by Duponol-type surfactants. Both dispersions were pigmented with TiO_2. They were formulated to be used as surface coatings.

To ensure that the observed variation of stress with time was not due to delayed response or erroneous responses of the viscometer used, standard viscosity oils of broad viscosity range (from 0.12 to 230 poises) purchased from Cannon Instrument Company were used for calibration. This is particularly important when the slope of F versus t is needed, such as in the calculation of the elastic modulus.

To measure λ for different shear rates, a standard three-step procedure was adopted. After the sample was placed in the viscometer, it was (a) sheared under high shear rate, 1370 sec^{-1}, for a period of about 2 min until all thixotropic behavior disappeared, as indicated by a constant shear stress with further shearing; (b) left undisturbed for 30 min to allow recovery of the structure; (c) sheared again at a chosen shear rate for thixotropic deg-

radation. This cycle was repeated using a different shear rate at step (c) each time. The reason for repeating (a) and (b) was to ensure the samples studied were at identical deformational state and history. The stress recorded during step (a) was used as a means to detect any change in the rheological state. For different types of dispersions, the length of the recovery period in (b) has to be adjusted.

RESULTS AND DISCUSSION

Typical results on the change of shear stress with the time of shear of a water-based colloidal dispersion are shown in Figure 7, which was obtained from the Weissenberg rheogoniometer. In this particular experiment, the first normal stress difference, $F_{11} - F_{22}$, was also measured. Clearly, both the shear stress and the normal stress difference exhibit thixotropic behavior. This came as no surprise since from molecular theories normal stress difference can be interpreted in terms of the networks structure.[9] Thus, any change in the structure will reflect on the shear stress as well as the normal stress difference. The variation of shear stress with time at various shear rates for sample 2629, which is typical of aqueous dispersions, is shown in Figure 8. The maximum value of the shear stress is taken as F_0 for the calculation of λ. The change of λ of this sample with shear rates is shown in Figure 9. It can be seen that the way λ changes with shear rate follows the general pattern of the theoretical curves of Figures 5 and 6. The experimental point at high shear rate is a deviation from this general pattern and will be discussed later. Figure 10 shows the change of λ with shear rate of two other aqueous dispersions. The general pattern is also observed.
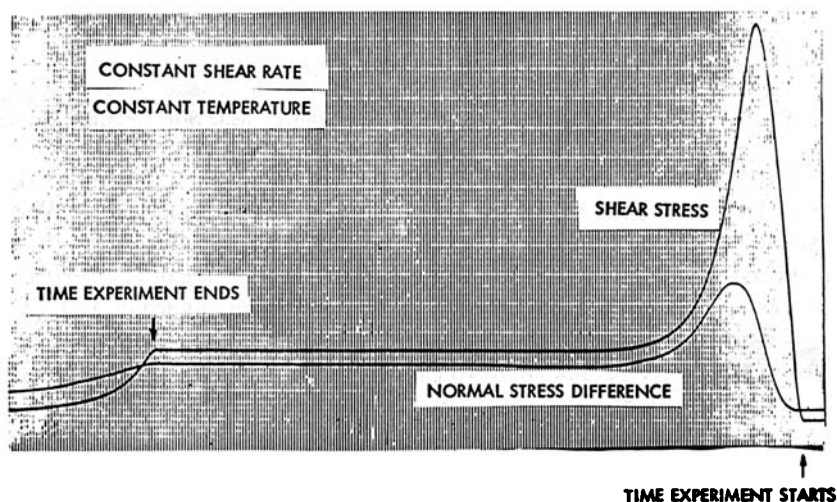

Fig. 7. Change of shear stress and normal stress difference with time of shear under constant shear rate and temperature.
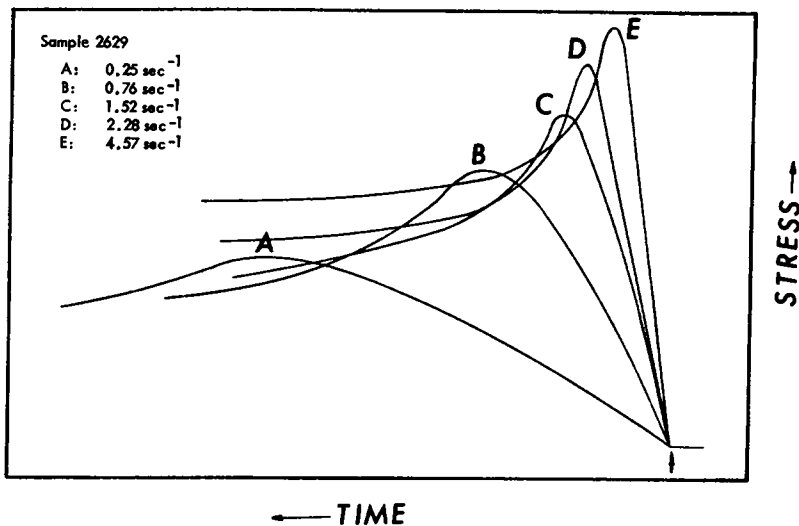
Fig. 8. Change of shear stress with time of shear of an aqueous dispersion (sample 2629).
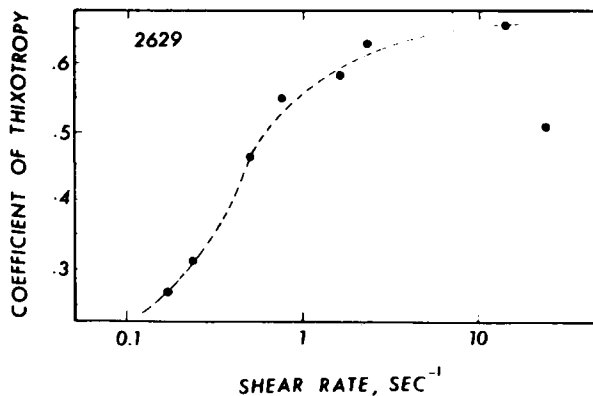

Fig. 9. Change of coefficient of thixotropy as a function of shear rate (sample 2629).

As discussed in the theoretical section, an assumption was made that, prior to the yield point, the material can be treated as an elastic body. This assumption is verified in Figure 8. The various curves in this figure have been shifted in such a way that the starting time of shearing of each experiment coincides, as indicated by the arrow. The point at which the material yields is taken to be at the maximum stress. During the initial period, the stress is linearly proportional to t as would be expected for an elastic body, since, by Hooke's law, $F = G\dot{\gamma}$. Thus,

$$F = (G\dot{\gamma})t \qquad (17)$$

where G is the shear modulus which can be evaluated from this part of the $F(t)$ curve. The result of the evaluation for sample 2629 is shown in Table I. The agreement in G from data at different shear rates is excellent.

TABLE I

Calculation of G from Steady-State Thixotropic Measurements

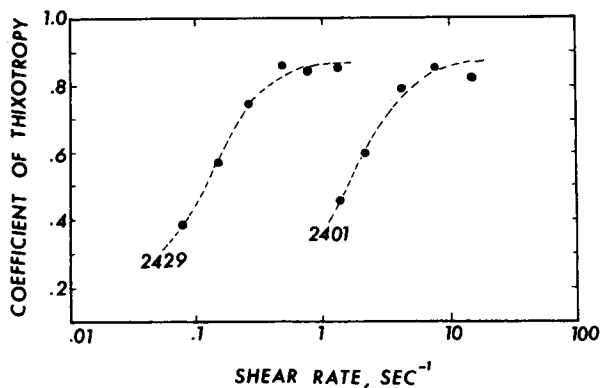| Shear rate, sec^{-1}	F_0, dynes/cm^2	F_∞, dynes/cm^2	λ	Slope	G, dynes/cm^2
0.25	225	177	0.27	3.5	14.0
0.76	309	200	0.55	11.1	14.6
1.52	357	225	0.58	22.0	14.5
2.28	396	242	0.64	32.2	14.1
4.57	428	290	0.47	64.5	14.1

Fig. 10. Change of coefficient of thixotropy as a function of shear rate (samples 2429 and 2401).

The relatively low value of G is typical of most aqueous dispersion studied and indicates that the initial state of the dispersion is a weak gel. Although the G value so calculated can be used as an indication of the elastic modulus of a thixotropic system in the gel state, its use in correlating with other viscoelastic parameters should be cautioned until further investigation.

The assumption of elastic body appears to be valid only for low shear rates. Since if the shear rate is sufficiently high, the yield stress is exceeded within a very short time after the application which may be beyond the present limit of detection. Thus, the true peak stress corresponding to the applied shear rate may not be observed. It is also possible that before the macroscopic flow takes place, certain molecular orientations or arrangements occur.[10] The application of large deformation in a short time may lead to the breakage of certain weak intermolecular interactions resulting in the absence of a true peak stress. In either case, a low apparent F_0 and, consequently, a low λ will be observed.

The assumption made in considering the flow behavior at region II, namely, that the system can be represented by two groups of flow units A and B, does not imply that A and B are necessarily two discrete, monodisperse phases. It has been pointed out by Ree and Eyring[8] that each group can be composed of many kinds of flow units which have different
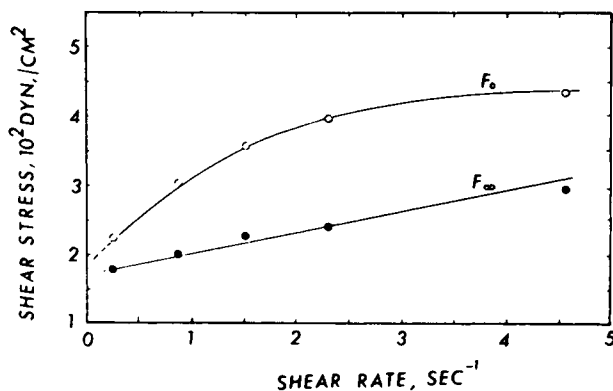
Fig. 11. Changes of shear stress F_0 and F_∞ as a function of shear rate (sample 2629).

relaxation times but are sufficiently well described by an average value for the group. Judging from the experimental data, F_0 and F_∞, which are reflections of A and B, are sufficiently different in the range of shear rates studied.

One of the advantageous features of the Ree and Eyring theory is that it assumes no specific molecular configurations or conformations of the flow units. It also recognizes the discrete boundary of the units relative to the medium and to each other. Thus, the theory is applicable for polymer solutions, diluted and concentrated,[8] polymer emulsions of various volume fractions,[11] and composite system of industrial interest.[7,12] One major disadvantage, however, is that the theory is too rich in adjustable parameters. Thus, a unique resolution of the parameters is often very difficult in complex systems.

The phenomenon represented by $F(t)$ as discussed here is similar to that of stress overshoot of polymer solutions and polymer melts which is a subject arousing much interest recently.[13] However, the appearance of a constant G over different shear rates in these dispersions does not fit with the recent theories of stress overshoot.

In Table I, F_0 represents the maximum shear stress the material can withstand before viscometric flow starts at a certain shear rate. By extrapolating F_0 to zero shear rate, one would obtain the "yield stress" as conventionally defined: the minimum stress to initiate flow. This is shown in Figure 11. Yield stress has long been recognized as an important parameter in determining the degree of leveling, or the smoothness of a coating.[14,15] However, accurate experimental evidence has been lacking due to problems associated with its measurement. Briefly, it is practically impossible to measure the yield stress under experimental conditions such that the rheological state of the coating is identical with that as the coating reaches equilibrium during the leveling process.[16] It appears that the yield stress obtained by this method may offer a better correlation with leveling than one would have by measuring the stress after cessation of steady state flow.[17] This method will be further improved if a convenient scheme can

be developed for the calculation of F_0 at various shear rates from the theory. Such a calculation would avoid the absence of a true peak stress as discussed and circumvent the uncertainty that exists in the process of extrapolation.[5] The various factors involved in the leveling of paints are of much concern to the coating industry and have been discussed by many authors recently.[16,18,19]

CONCLUSIONS

1. The thixotropic behavior of gel was interpreted by a model which separates the change of shear stress (or viscosity) with time under constant shear rate to two regions. Region I covers the growth of shear stress from the application of shear to the yield point, as represented by a peak stress. At this region, the material is assumed to be elastic. Region II covers the decay of the shear stress from the peak stress to the point the stress attains an asymptotic value. At this region, the system is represented by a dynamic equilibrium between two types of rheological structures A, which is non-Newtonian, and B, which is Newtonian. The transition from A to B represents thixotropic degradation; the transition from B to A represents thixotropic recovery.

2. By solving the differential equation representing the net rate of transition, the concentrations of A and B at any time during the stress decay can be evaluated. The concentrations depend mainly on the shear rate. At very low shear rates, it is shown that $X_A \gg X_B$; whereas at high shear rates, $X_B \rightarrow 1$.

3. The shear stress at region II can be evaluated based on the theory of Ree and Eyring. Numerical analysis shows that the predicted effects of the equation are in good qualitative agreement with experimental observations. Thus, it is explicitly shown that the thixotropic behavior of a system is dependent on two types of variables: a—rheological such as relaxation times, molecular dimensions, elastic energy, and reaction rate constants; and b—experimental such as temperature, shear rate, and time. Due to the number of parameters involved, a unique identification of each variable from an observed shear stress–time relationship is as yet impossible.

4. The ratio $(F_0 - F_\infty)/F_\infty$, defined as λ, the coefficient of thixotropy, is proposed for practical characterization of thixotropic systems. The influences of many rheological parameters are illustrated. The coefficient can be easily evaluated in a steady state experiment as shown in Figure 2.

5. The shear modulus of the material at the gel state can be calculated from the slope of the stress growth at region I. It was shown to be constant at low shear rates. Thus, the assumption of elastic body appears to be valid over the range of shear rates studied. If the shear rate is sufficiently high, a true yield point may not be observable due to both experimental and theoretical factors. Consequently, the apparent coefficient of thixotropy tends to be lower than it should be. By extrapolating the peak stress to zero shear rate, the yield stress of the material may also be evaluated.

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