A Model for the Thixotropy of Suspensions

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A model for the rheological behavior of thixotropic systems is presented. The model is intended for systems exhibiting no elastic or anisotropic effects. It is shown how the constants of the model can be determined by a systematic program of experimentation. It is also shown how the model can be tested and amended, if necessary, by the same program of experiments. The model is advanced for suspensions of rigid, solid particles in liquids; it is not expected to be valid for materials of polymeric constitution or for suspensions of elastic, deformable particles in liquids.

In a recent review of the literature on thixotropy, Bauer and Collins (*1*) state: "A thixotropic system exhibits a time-dependent, reversible, and isothermal decrease of viscosity with shear in flow." From this definition, and from their accompanying text, one can infer that a thixotropic system will exhibit the following phenomena:

1. Its viscosity will change with time when it is sheared at constant rate.
2. The change of viscosity will be a decrease provided that the shear rate applied is an increase over that previously experienced by the material for a long time.
3. The change of viscosity will be an increase provided that the shear rate applied is a decrease below that previously experienced by the material for a long time.
4. If an applied shear rate is maintained constant for a sufficient length of time, the viscosity will approach a limiting value, dependent only on the magnitude of the shear rate.

One can draw the further inference that in steady viscometric flow, thixotropic systems will exhibit the phenomenon of pseudoplasticity (shear thinning). They may also exhibit an apparent yield stress. That is, the graph of steady shear stress vs. steady shear rate may not pass through the origin, but, instead, the stress may approach a finite value as the shear rate approaches zero.

The examples of thixotropic systems cited by Bauer and Collins show that thixotropic phenomena are associated primarily with fairly concentrated suspensions of solid particles in appropriate liquids. For instance, they state that aqueous dispersions of ferric oxide, aluminum oxide, vanadium pentoxide, starch, and rubber latex, and other dispersions such as zinc oxide in paraffin and paint pigment in linseed oil, are thixotropic systems. Similar examples are cited by Weltmann (*12*). In view of the common occurrence and engineering importance of such materials, it is important to be able to make quantitative statements about thixotropic systems.

In one sense, the quantitative description of thixotropic systems is not conceptually difficult. One simply does a standardized rheological test (or series of tests) on the material, and from this obtains a number (or numbers) that one calls a *coefficient of thixotropy*. This procedure, while it undoubtedly has a certain amount of utility, suffers from the twin disadvantages that one does not thereby measure invariant properties of the material studied and one cannot use the data from one experiment to predict quantitatively the results of another experiment. Hence, what is required is a mathematical model of thixotropic phenomena. This model should contain definite constants (material properties) that one can measure, and the model should be capable, in principle, of predicting the results of any experiment once the material properties are known.

In this paper, we make some suggestions as to how such a model can be constructed for thixotropic systems composed of suspensions of solid particles in liquids.

THE MODEL

The model which is to be stated is based on plausible inference from the phenomena of thixotropy stated above. The model is intended to apply only to suspensions of rigid solids in liquids.

As the first item in the model, we assume that the material considered possesses no elasticity of shape. That is, the material is a viscous fluid and will not exhibit such viscoelastic phenomena as recoil or stress relaxation. Hence, the model will not hold for thixotropic systems exhibiting elasticity. Thixotropic phenomena in such systems, which include materials of polymeric constitution or suspensions of deformable particles in liquids, can perhaps be treated adequately by nonlinear models of viscoelasticity (*2*).

As the second item in the model, we assume that the material is isotropic and remains so upon application of shear. A subsidiary hypothesis is that the stress tensor for the material is symmetric.

These two items suggest that the constitutive equation of the material will be Newton's law of viscosity, but with a time-dependent viscosity. It will turn out that it is slightly more convenient to use the fluidity (the reciprocal of viscosity), so that the constitutive equation is

$$\boldsymbol{\tau}(P, t) = \frac{2}{\varphi(P, t)}\, \mathbf{d}(P, t) \qquad (1)$$

where (P, t) indicates that the proceeding quantity is evaluated at material point P at time t.

Since the fluidity φ depends explicitly on time, a second equation expressing this dependence must be found. For this purpose, we introduce the third item of the model: The rate of change of fluidity at a material point depends on the fluidity at that point and the rate of strain at that point. Hence, the required equation will be of the general form

$$\frac{D}{Dt}\varphi(P, t) = f[\varphi(P, t),\ \mathbf{d}(P, t)] \qquad (2)$$

The material or hydrodynamic derivative D/Dt must be taken, since by our third hypothesis, the fluidity at a material point is influenced only by conditions at that point, and so the derivative must follow the motion of the point. Rate theories of non-Newtonian viscosity, such as those typified by Equation (2), have been developed by Brodkey and his students [see especially Kim and Brodkey (*9*)].

As the fourth item in the model, we assume that the function f represents a balance between two processes. The first process is a spontaneous buildup of viscosity (breakdown of fluidity) which always occurs whenever the fluidity becomes greater than its minimum possible value φ_0. The second process is a breakdown of viscosity (buildup of fluidity) that occurs whenever shear work is done on the material and its fluidity is less than its maximum possible value φ_∞. Now, the rate of the first process must vanish when $\varphi = \varphi_0$, so that it is convenient to express this rate as a function of $\varphi - \varphi_0$ rather than of φ. Similarly, the rate of the second process must vanish when $\varphi = \varphi_\infty$, so that it is convenient to express this rate as a function of $\varphi_\infty - \varphi$ rather than of φ.

As the fifth item in the model, we assume that the rate of spontaneous buildup of viscosity is independent of the rate at which shear work is done on the material. The rate of breakdown of viscosity must be dependent on that rate, however. The rate at which shear work is done, per unit volume, is (3)

$$\boldsymbol{\tau} : \nabla \mathbf{v} = \boldsymbol{\tau} : \mathbf{d} = \frac{2}{\varphi}\,\mathbf{d} : \mathbf{d} = \frac{\varphi}{2}\,\boldsymbol{\tau} : \boldsymbol{\tau} \qquad (3)$$

where the symmetry of the stress tensor and Equation (1) have been used.

Under the hypotheses made, Equation (2) becomes

$$\frac{D\varphi}{Dt} = -\,g(\varphi - \varphi_0) + h\left(\varphi_\infty - \varphi,\ \frac{2}{\varphi}\,\mathbf{d} : \mathbf{d}\right) \qquad (4)$$

where g and h are nonnegative functions such that

$$\begin{gathered} g(0) = 0 \\ h\left(0,\ \frac{2}{\varphi_\infty}\,\mathbf{d} : \mathbf{d}\right) = h(\varphi_\infty - \varphi, 0) = 0 \end{gathered} \qquad (5)$$

Equations (1) and (4) are the mathematical statements of the proposed model of thixotropy. In order to apply the model to specific problems, one must also specify an initial condition, since Equation (4) is a differential equation.

In general, the nature of the functions g and h is to be determined by appropriate experiments. For the sake of illustration, however, let us assume as the sixth and last item that these functions have the simplest forms possible, namely

$$g(\varphi - \varphi_0) = \frac{1}{\lambda}\,(\varphi - \varphi_0) \qquad (6)$$

and

$$h\left(\varphi_\infty - \varphi,\ \frac{2}{\varphi}\,\mathbf{d} : \mathbf{d}\right) = 2k(\mathbf{d} : \mathbf{d})\,\frac{\varphi_\infty - \varphi}{\varphi} \qquad (7)$$

where λ and k are constants, the former having the dimension of time. Equation (4) can then be written as

$$\frac{D\varphi}{Dt} = -\frac{1}{\lambda}\,(\varphi - \varphi_0) + 2k(\mathbf{d} : \mathbf{d})\,\frac{\varphi_\infty - \varphi}{\varphi} \qquad (8a)$$

In some cases, it would be more convenient to write this in terms of stress; from Equation (1), we see that the required form is

$$\frac{D\varphi}{Dt} = -\frac{1}{\lambda}\,(\varphi - \varphi_0) + \frac{k}{2}\,(\boldsymbol{\tau} : \boldsymbol{\tau})\varphi(\varphi_\infty - \varphi) \qquad (8b)$$

In this simplest model, there are four constants: φ_0, φ_∞, λ, and k. The first three of these have direct physical significance; we shall show that the fourth parameter also has physical significance.

PREDICTIONS OF THE MODEL

We now apply the model to a number of specific cases. These will show that the model does indeed predict the kind of thixotropic phenomena that are actually observed. It will also be clear from the examples what experimental procedures will be necessary to test the model.

Steady Viscometric Flow

The prototype of this flow is Couette flow between parallel plates; other well-known examples are Poiseuille flow in a tube of circular cross section, or Couette flow between rotating, concentric cylinders. In such a flow, one can choose a coordinate system such that **d** has only two nonvanishing components; these are transposed, off-diagonal elements and equal to each other by the symmetry of **d**. Hence, if $\dot\gamma$ is the rate of shear, then

$$\mathbf{d} : \mathbf{d} = 2\,\dot\gamma^2$$

When the shear rate $\dot\gamma$ has been applied for a sufficient length of time, φ will approach a steady value $\tilde\varphi$. This will be obtained from Equation (8*b*) by setting $D\varphi/Dt$ equal to zero:

$$0 = -\frac{1}{\lambda}\,(\tilde\varphi - \varphi_0) + 4k\,\dot\gamma^2\,\frac{(\varphi_\infty - \tilde\varphi)}{\varphi}$$

The nonnegative root of this quadratic equation is

$$\tilde\varphi = \frac{-\,[4\,k\,\lambda\,\dot\gamma^2 - \varphi_0] + \sqrt{[4\,k\,\lambda\,\dot\gamma^2 - \varphi_0]^2 + 16\,k\,\lambda\,\dot\gamma^2\,\varphi_\infty}}{2} \qquad (9a)$$

and this gives the shear rate dependence of the fluidity. The material is non-Newtonian, obviously.

In many cases, it is convenient to express the fluidity in terms of stress rather than in terms of shear rate. The stress-explicit equation for the fluidity in viscometric flow can be found from Equation (8*b*) by putting $D\varphi/Dt$ equal to zero and by defining the shear stress τ by

$$\boldsymbol{\tau} : \boldsymbol{\tau} = 2\tau^2$$

One then obtains

$$\tilde\varphi = \frac{(k\,\lambda\,\tau^2\,\varphi_\infty - 1) + \sqrt{(k\,\lambda\,\tau^2\,\varphi_\infty - 1)^2 + 4\,k\,\lambda\,\tau^2\,\varphi_0}}{2\,k\,\lambda\,\tau^2} \qquad (9b)$$

Equations (9*a*) and (9*b*) are equivalent, of course.

We notice first that

$$\lim_{\dot\gamma \to 0} \tilde\varphi = \varphi_0$$

and

$$\lim_{\dot\gamma \to \infty} \tilde\varphi = \varphi_\infty$$

so that there is a progressive increase of fluidity (or decrease of viscosity) with increase of shear rate or shear stress. The material is, therefore, of the pseudoplastic type.

But consider the case where $\varphi_0 = 0$. We find that

$$\begin{aligned} \lim_{\dot\gamma \to 0} \tau &\equiv 2 \lim_{\dot\gamma \to 0} \frac{\dot\gamma}{\tilde\varphi} \\ &= \frac{1}{\sqrt{k\,\lambda\,\varphi_\infty}} \end{aligned} \qquad (10)$$

Thus, if $\varphi_0 = 0$, the material exhibits an apparent yield stress in the sense that the steady state stress does not pass to zero as the steady state shear rate does. The apparent yield stress is just $(k\,\lambda\,\varphi_\infty)^{-1/2}$. As will be shown, however, there is no true yield stress, nor is the case $\varphi_0 = 0$ realistic.

Figure 1 shows rheograms (plots of steady shear stress vs. steady shear rate) computed from Equations (1) and (9*a*). Constants used were $\varphi_\infty = 10$ poise^{-1}, $k = 10^8$ sec./poise, and $\lambda = 10^3$ sec. (These constants are used in all subsequent illustrations, also.) The figure shows rheograms for several values of φ_0. If φ_0 is zero, the plot is quite similar to that of a Bingham plastic. If $\varphi_0 = \varphi_\infty$, the fluid is Newtonian, and a straight line passing through the origin is obtained. If $0 < \varphi_0 < \varphi_\infty$, the fluid is pseudoplastic and shows a first Newtonian regime with viscosity $1/\varphi_0$ at low shear rates and a second Newtonian regime *(10)* with viscosity $1/\varphi_\infty$ at high shear rates.

Thus, the two constants φ_0 and φ_∞ can be determined from steady viscometric data. They are the limiting fluidities at low and at high shear rates, respectively.

It is of interest to notice the form of velocity profiles predicted by the model in steady, fully developed Poiseuille flow through a long tube. The axial velocity $u(r)$ at radial position r in a tube of radius R is given by (7)

$$u(r) = \frac{1}{2}\left(-\frac{dp}{dz}\right)\int_r^R \varphi(r')\, r'\, dr' \tag{11}$$

where dp/dz is the pressure gradient along the tube. The fluidity at radius r' can be found from the stress-explicit form of Equation (9) and the fact that

$$\tau(r') = \frac{1}{2}\left(\frac{dp}{dz}\right) r' \tag{12}$$

in tube flow.

Figure 2 shows the velocity profiles produced by a pressure gradient of 1,000 dynes/cc. in a tube of 0.50-cm. diameter. Constants used are the same as for Figure 1, and profiles for the same three values of φ_0 are shown.

Recovery of Consistency

Suppose that the material is sheared at constant rate γ for a length of time sufficient to attain the corresponding steady fluidity $\tilde{\varphi}$. When this has been attained, suppose that the material is brought to rest. According to Equation (8*a*), the fluidity will decay as

$$\frac{d\varphi}{dt} = -\frac{1}{\lambda}(\varphi - \varphi_0) \tag{13}$$

$$\varphi(0) = \tilde{\varphi} \tag{14}$$

Here, we write D/Dt as d/dt, since the terms in D/Dt involving velocity all vanish when the material is at rest.

The fluidity will then decay towards φ_0 according to the law

$$\frac{\varphi - \varphi_0}{\tilde{\varphi} - \varphi_0} = e^{-\frac{t}{\lambda}} \tag{15}$$

This experiment illustrates the physical significance of the parameter λ; it is the time constant for decay of fluidity in the resting material. Notice that if φ_0 were zero, the fluidity would ultimately decay to zero; that is, the material would gel or set up to a solid.

The foregoing simple experiment is complicated by two practical difficulties. In the first place, inertial effects render it impossible to bring a whole mass of material instantaneously to rest, as assumed in the idealized experiment. In Couette flow with a fluid sample of thickness L, a conservative estimate of the time required for the sample to come to rest is $10\,\varphi_\infty\,\rho\,L^2/\pi^2$. Hence, if

$$10\,\varphi_\infty\,\rho\,L^2/\pi^2 << \lambda \tag{16}$$

inertial effects can be ignored, and it can be assumed that the material comes instantaneously to rest. Unless λ happens to be very small (say of the order of 1 sec. or less), many viscometers currently used would satisfy the foregoing inequality.

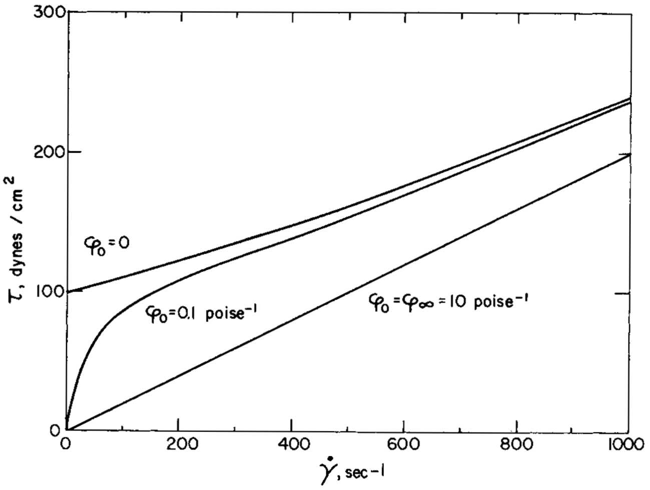

Fig. 1. Rheograms for steady state viscometric flow computed from Equations (1) and (9*a*).

The other difficulty concerns measurement of the time course of decay of fluidity. In order to measure fluidity, the material must be sheared; a static measurement of fluidity is a contradiction in terms. But if the material is sheared, the buildup term in Equation (8*a*) is not zero, and the ratio $(\varphi - \varphi_0)/(\tilde{\varphi} - \varphi_0)$ no longer follows strictly the law of exponential decay. In practice, one can minimize this difficulty by using a very small shear rate for measuring φ, but the design of a sensitive viscometer for low shear rate determination of viscosity is not an easy task.

An alternate procedure would be to study the time course of changes in fluidity accompanying step increases or decreases in shear rate. This procedure, while perfectly feasible, is not as clean as that of studying decay of fluidity in the resting medium, since the response to the step is complicated by the presence of the shear rate dependent fluidity buildup term.

Yield Phenomena

The preceding paragraphs considered the response of the idealized material to step changes in strain rate. It is also of interest to consider the response to step changes in shear stress. In particular, we consider the response to a sudden application of a constant shear stress τ to a material that has been at rest for an infinite length of time in the past. The material will then have its zero shear rate fluidity φ_0 at the instant of stress application. Assume that the stress is applied at time zero.

The buildup of fluidity will be given by the stress-explicit form of Equation (8). If we assume a homogeneous deformation (that is, if we neglect inertial effects), this becomes

$$\frac{d\varphi}{dt} = -\frac{1}{\lambda}(\varphi - \varphi_0) + k\,\tau^2\,\varphi\,(\varphi_\infty - \varphi) \tag{17}$$

and is to be solved subject to

$$\varphi(0) = \varphi_0 \tag{18}$$

The shear rate can be found from Equation (1) once the foregoing differential equation has been solved; that is

$$\dot{\gamma}(t) = \frac{1}{2}\,\tau\varphi(t)$$

Suppose first of all that $\varphi_0 = 0$, so that in steady viscometric flow, the material exhibits an apparent yield stress.

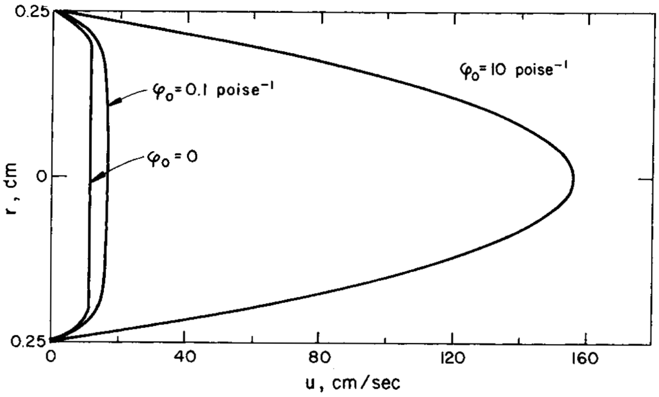

Fig. 2. Velocity profiles for steady tube flow computed from Equations (9*b*), (11), and (12). Pressure gradient = 1,000 dynes/cc.; tube diameter = 0.50 cm.

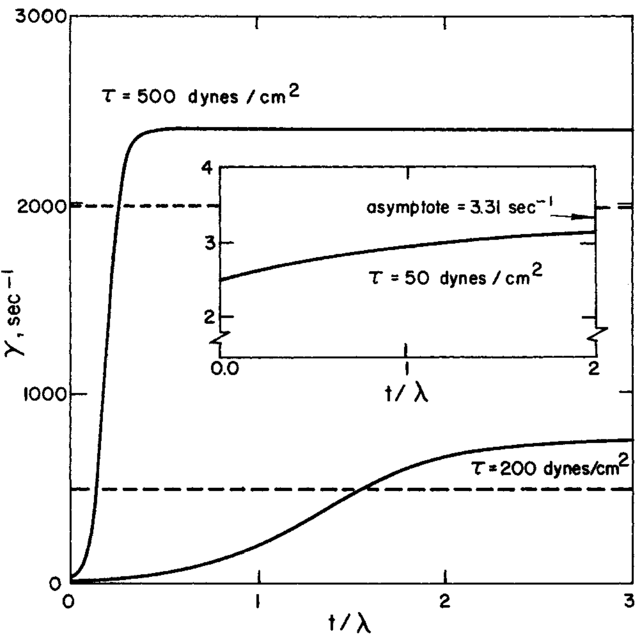

Fig. 3. Buildup of strain rate in response to suddenly applied shear stresses of various magnitudes. Solid lines: thixotropic material. Dashed lines: Bingham plastic material. Inset shows the buildup for the smallest stress used. The Bingham plastic does not flow under this stress.

Equations (17) and (18) show that if such is the case, application of a finite stress will not alter the fluidity, and the material will not flow. In other words, if $\varphi_0 = 0$, an infinite stress would be required to start building up the fluidity of the material. Thus, the case $\varphi_0 = 0$ does not produce a true yield stress, nor is this case physically reasonable. Hence, in the following we assume that $\varphi_0 > 0$.

Equation (17) can be solved in closed form by separation of variables, but the resulting form is so lengthy as not to be very useful. Hence, it is easier to solve Equation (17) numerically on an analogue or digital computer. Figure 3 shows the results of such calculations; the shear rates produced by three different applied stresses are plotted as functions of time. The constants used were as in the two previous figures, but φ_0 was taken to be 0.1 poise^{-1}. The dashed lines in the figure show the strain rate produced in a Bingham plastic with plastic viscosity equal to the reciprocal of φ_∞ (that is, the plastic viscosity is 0.1 poise) and yield stress 101 dynes/sq.cm. (the reason for this value is given later).

The lowest stress (50 dynes/sq.cm.) produces no flow in the Bingham plastic, of course. It does produce a very slow flow in our idealized thixotropic material. One notes that though the strain rate is increasing in this flow, its rate of increase is always decreasing. Thus, we say that a stress of 50 dynes/sq.cm. produces *primary creep* (*11*) in the material considered.

The stresses of 200 and 500 dynes/sq.cm. produce flow in both the Bingham plastic and our idealized thixotropic material. But the flow of the Bingham plastic starts immediately at its final value, whereas that of the thixotropic material builds up to its final value. The rate of buildup is greater the greater the applied stress. Thus, if one did not or could not make measurements of strain rate at small times, he could miss the initial transient in the thixotropic material and so infer that it exhibits a true yield stress.

Although the thixotropic material possesses no true yield stress, there is nonetheless a critical stress τ_c that plays a role similar to the yield stress of plasticity theory. We pointed out that the lowest applied stress produced a primary creep; that is a flow with decelerating strain rate. However, the two highest stresses produce a flow with a strain rate that accelerates for some time. The critical stress is that which produces an initial strain rate that neither accelerates nor decelerates.

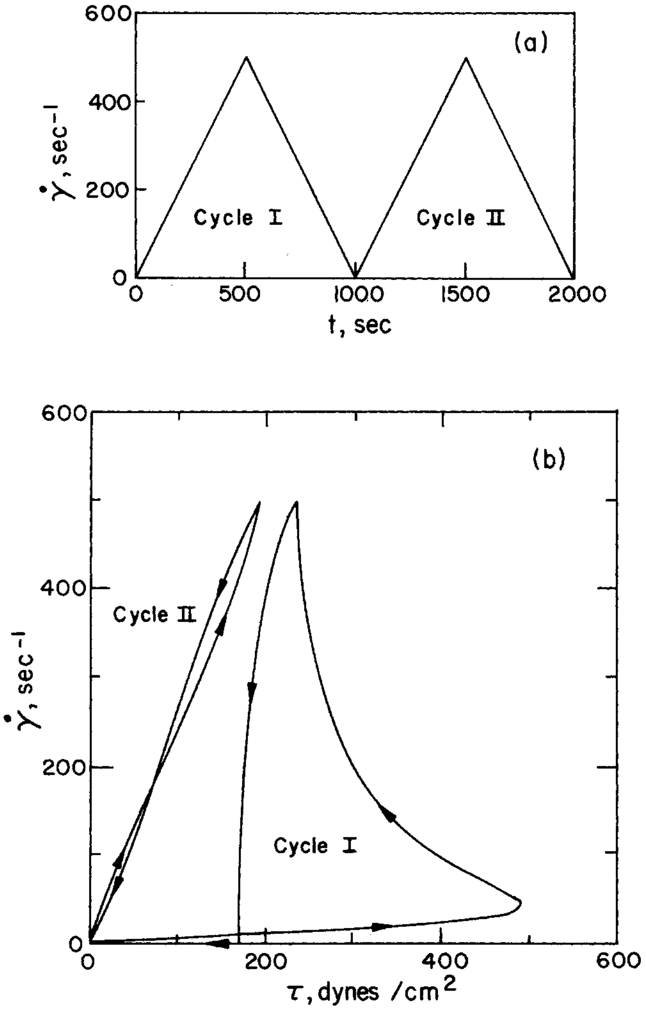

Fig. 4. Response to a time-varying program of a strain rate. *a*. The program of strain rate. *b*. The response. Corresponding cycles are marked I and II in both parts.

From Equation (17), we find that for constant shear stress

$$\frac{d^2\varphi}{dt^2} = \frac{d\varphi}{dt}\left[k\tau^2(\varphi_\infty - \varphi) - \frac{1}{\lambda} - k\tau^2\varphi\right] \tag{19}$$

Since $d\varphi/dt$ is always positive for finite times, we see that the fluidity (and so the strain rate) will be initially increasing at constant rate when

$$k\tau^2(\varphi_\infty - \varphi_0) - \frac{1}{\lambda} - k\tau^2\varphi_0 = 0$$

Hence, the critical stress that produces this condition is

$$\tau_c = \frac{1}{\sqrt{k\lambda\varphi_\infty\left(1 - 2\frac{\varphi_0}{\varphi_\infty}\right)}} \tag{20}$$

That is, if the applied stress is less than τ_c, the material will exhibit primary creep, but if the applied stress is greater than τ_c, the material will exhibit a strain rate that increases at an increasing rate for some time.

The value of τ_c resulting from the constants used in Figure 3 is 101 dynes/sq.cm. It is for this reason that we assumed that the yield stress of the Bingham plastic was 101 dynes/sq.cm. Notice that if φ_0 is zero, the value of τ_c given by Equation (20) is the same as the apparent yield stress in steady viscometric flow for that case.

The foregoing experiment provides the physical interpretation of the parameter k and suggests a sensitive means of measuring it. One does a series of these experiments with varying applied stresses and so determines the critical stress, τ_c. Equation (20) can then be used to calculate k, since the other parameters are presumably known from other experiments.

Hysteresis Loops

The three experiments discussed up to this point are sufficient (and convenient) to determine the four constants of our simplest model. One is not privileged to stop the investigation at this point, however, because one does not know that this particular four-constant model, or any four-constant model for that matter, is the right one. Hence, one must do further experiments to test the model.

An experiment that is often used in studies of thixotropic materials involves determining response to a time-varying program of strain rates. Figure *4a* shows a program of strain rates that is often used in such studies. One can imagine many variations on this program; the material could be allowed to rest between the cycles, for instance.

Figure *4b* shows the response of our idealized thixotropic material to the strain rate program of Figure *4a*. The material constants used are the same as those used for Figure 3. The fluidity was found as a function of time by solving the strain-rate explicit form of Equation (8) on the digital computer. It was assumed that $\varphi = \varphi_0$ initially.

The general features revealed are the existence of hysteresis loops—so characteristic of thixotropic materials—in the stress-strain rate curves, the generally lower level of consistency during the second cycle of strain rate, the sharp bend in the curve during the initial part of the first cycle, and the crossing of the curve during the second cycle. The first three of these phenomena are exhibited by the flow curves for a lithium sterate-oil dispersion given in Figure 3 of the review of Bauer and Collins (*1*); the last phenomenon also occurs [see Figure 8 of Weltmann's review (*12*)].

The fact that a simple, four-constant model predicts these rather complicated trends qualitatively is encouraging and suggests that quantitative testing of the model would be worthwhile.

A SUGGESTED EXPERIMENTAL PROGRAM

A detailed experimental program to test the kind of model developed here should proceed along the following lines. First, the assumption that the material possesses no elasticity of shape should be checked. This can be done in a number of ways; for instance, the recoil experiment (*8*) could be used, or one could subject the material to dynamic testing (*6*). If appreciable elasticity is found, the model will not be valid, of course.

Assume, however, that the test described above reveals no elasticity of shape. One should then test the hypothesis that the material is isotropic and remains so upon application of shear. In principle, it is not difficult to test this hypothesis, but in practice such a test is quite difficult. One possibility would be to use the kind of instrument used by Dierckes and Schowalter (*4*) in their helical flow studies. One could shear the material in Couette flow until a steady fluidity is achieved. One could then change over to very slow Poiseuille flow to see if the fluidity is the same when the direction of shear is changed. Experimental difficulties make it easy to simply assume that the material is isotropic, but, in fact, generation of anisotropy by shear would not be surprising, and the effect should be looked for.

Assume that appropriate tests reveal no generation of anisotropy. The third step in the program should be the performance of steady state viscometric tests. The results of these tests can be used to determine the two fluidities φ_0 and φ_∞. One could also estimate k and λ from such data by curve fitting, but it is better to determine these constants in the next stages of the program.

The fourth step in the program should be the determination of the time constant λ by studying the decay of fluidity in the resting material. According to the model, the ratio $(\varphi - \varphi_0)/(\tilde{\varphi} - \varphi_0)$ should decay exponentially. If this is found to be the case, one can find λ and proceed to the next step.

The fifth step in the program should be the determination of the parameter k. This can be done by studying the response to a suddenly applied stress, as described above.

The last step in the program is the testing of the constants obtained in the previous steps. One can start to do this without taking further data. For instance, the four constants should predict the shear stress-shear rate curve obtained in the steady viscometric test, and they should also predict the time course of increase of the shear rate when the material responds to a sudden application of stress. If, in fact, good fits of the model to these data can be obtained, one can reasonably hope to be able to get good agreement between prediction and observation in the acid test: response to a time-varying program of strain rate.

AMENDMENTS TO THE MODEL

Clearly, a real material can yield deviations from predicted behavior at any stage of the foregoing experimental program. The stage at which deviations are first encountered dictates the amendments to the model that must be made. Here, we indicate in a general way only what those amendments might be.

First, if elasticity of shape is indicated in the first stage of the experimental program, one might see if nonlinear viscoelastic models (*2*) can explain thixotropic phenomena exhibited by the material.

If the material passes the first test but exhibits anisotropy in the second stage of the program, a modification of the theory of Ericksen (*5*), involving a local orientation vector, could be tried. Failure of the model at either of these stages requires its complete rejection, of course; strictly speaking, we cannot amend the model in this case.

If the material passes the first three stages of the program but in the fourth stages fails to show an exponential decay of the ratio $(\varphi - \varphi_0)/(\tilde{\varphi} - \varphi_0)$, one can modify the function $g(\varphi - \varphi_0)$ used in Equation (4). The results of the fourth stage of the experimental program would, in fact, suggest what the modification should be.

If the material passes the first five stages of the program but fails somewhere in the sixth stage, a number of simple amendments might be tried. For instance, one could make the function g depend not only on $\varphi - \varphi_0$ but also on the volumetric rate at which shear forces do work on the material. Or different measures of the degree to which subcontinuum structure has been broken down or built up could be used. In the simple model, these were taken to be simply $\varphi_\infty - \varphi$ and $\varphi - \varphi_0$, respectively. But Kim and Brodkey (*9*) found different measures appropriate for polymer solutions.

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NOTATION

D/Dt = material derivative operator
$\mathbf{d}$ = rate of strain tensor $[= \frac{1}{2}(\nabla\mathbf{v} + \nabla\mathbf{v}^t)]$
f = function defined by Equation (2)
g = function defined by Equation (4)
h = function defined by Equation (4)
k = parameter in Equation (7)
L = thickness of sample in Couette flow
P = material point P
p = pressure
R = tube radius
r, r' = radial coordinate
t = time
u = axial speed
$\mathbf{v}$ = velocity vector
z = axial coordinate

Greek Letters

$\dot{\gamma}$ = shear rate
∇ = gradient operator
λ = time constant in Equation (6)
ρ = density
$\boldsymbol{\tau}$ = deviator of the stress tensor
τ = shear stress
τ_c = critical shear stress
φ = fluidity
$\tilde{\varphi}$ = steady state fluidity
φ_0 = steady state fluidity at zero shear rate
φ_∞ = steady state fluidity at infinite shear rate

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On the Numerical Solution of Problems in Multicomponent Distillation at the Steady State II

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A modification is presented of the K_b method described by Holland. This modified procedure exhibits substantially improved convergence characteristics when compared with the unmodified procedure or with the classical bubble point approach. Further, it provides by far the fastest algorithm known to the author. A second procedure for determining stage temperatures is also given. In this method, flow equations as well as equilibrium relations are satisfied by the temperature profile at each iteration. Next, an improved scheme for handling nonideal mixtures is given. Finally, it is shown that a positive solution to the convergence acceleration equations of Holland may not exist when this procedure is applied to a purity specification.

GENERAL PROCEDURE

In a previous paper (*4*), the author discussed certain aspects of the procedure recommended by Holland (*10*) for solving steady state multicomponent distillation problems. An improvement in this procedure is presented in this paper, and a comparison is made between this improved procedure and the method suggested by Boyum (*6*). Subsequently, certain theoretical results concerning the Holland correction procedure are obtained for the complex distillation column.

The problem under consideration is the computation of steady state values of liquid and vapor flows for each component on every stage of a perfectly insulated column having one or more feeds and perhaps side-draw product streams. Such a unit is termed a *complex distillation column* and is schematically illustrated in Figure 1. The scheme this author has found most effective for solving this type of problem is outlined below [compare with Amundson and Pontinen (*2*), Holland (*10*), Nartker et al. (*13*), Wang and Henke (*20*)]:

1. Initial estimates of the phase flow and temperature profiles are made. A standard initial estimate of the temperature profile is obtained by adding all feeds to the unit together component by component. The dew point and