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A Thermodynamic Approach to Thixotropy

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The thixotropic behavior is discussed on the basis of the thermodynamics of irreversible processes. The fundamental equations are given for the thixotropic fluids by accepting the concept that the internal structure of the system is destroyed by the applied forces, and the general phenomenological equations are written for all the processes occurring in this system. The process by which the thixotropic recovery takes place is non-stationary. A method of specifying this process is proposed by introducing the concept of a fictitious pressure tensor; the data on a rubber latex suspension given by Mooney is analyzed by this method.

The isothermal process by which a system is softened by the disturbance of external forces and is hardened to the original state on settling is called thixotropy. This process is observed under appropriate conditions in the mechanical behavior of bodies showing the so-called structural viscosity. The thixotropy and the structural viscosity have been treated by many researchers since Freundlich[1]; it has been revealed that they are caused as a result of the breakdown and recovery of the internal structure of the system.

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[1] H. Freundlich and H. L. Löder, *Trans. Faraday Soc.*, **34**, 308 (1938).

In special cases, such as a suspension of rod-like particles, a detailed mechanism has been proposed for the behavior of anomalous viscosity under advanced treatment.[2] However, no general theoretical work is yet available, probably because the varieties and complexity are involved in terms of the internal structure.

Recently, a fundamental approach to the rheological behavior has been undertaken by Meixner[3] and by Kluitenberg[4] on the basis of the thermodynamics of irreversible processes. This treatment is phenomenological; for this reason, it is excellent, for it does not require detailed information on the internal structure. The latter author considered the thixotropic behavior to be a higher-order effect, introducing an internal degree of freedom, in his general theory of rheological processes. The purpose of this paper is to extend this approach and to interpret the thixotropy in terms of the general principles of thermodynamics.

General Equations of Thixotropic Fluids.— The viscous processes of isotropic fluids are described, on the basis of the thermodynamics of irreversible processes,[6] as follows. The Gibbs' equation reads;

$$T\frac{\mathrm{d}s}{\mathrm{d}t}=\frac{\mathrm{d}u}{\mathrm{d}t}+v\sum_{\alpha,\beta=1}^{3}P^{\mathrm{eq}}_{\alpha\beta}\frac{\mathrm{d}\varepsilon_{\alpha\beta}}{\mathrm{d}t} \tag{1}$$

where s is the specific entropy; u, the specific internal energy; v, the specific volume; T, the absolute temperature; t, the time; $P^{\mathrm{eq}}_{\alpha\beta}$, the equilibrium stress tensor, and $\varepsilon_{\alpha\beta}$, the total strain tensor. This is the equation that is applied to the Voigt model, i. e., the bodies having a parallel visco-elasticity; the fluid is one of special cases, as Kluitenberg has pointed out.[4]

It is assumed that the total pressure causes both the flow of the fluids and the destruction of the internal structure; that is,

$$P_{\alpha\beta}=P^{\mathrm{def}}_{\alpha\beta}+P^{\mathrm{des}}_{\alpha\beta} \tag{2}$$

Then, the balance equation for the total energy reads;

$$\rho\frac{\mathrm{d}u}{\mathrm{d}t}=$$

$$-\operatorname{div}\boldsymbol{J}^{\mathrm{q}}-\sum_{\alpha,\beta=1}^{3}P^{\mathrm{def}}_{\alpha\beta}\frac{\mathrm{d}\varepsilon_{\alpha\beta}}{\mathrm{d}t}-\sum_{\alpha,\beta=1}^{3}P^{\mathrm{des}}_{\alpha\beta}\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{3}$$

where ρ is the density (the reciprocal of the specific volume); $\boldsymbol{J}^{\mathrm{q}}$, the heat flow, and ξ, the degree of internal structure (a measure of the internal structure). The last term on the right-hand side of the equation represents the change in the internal structure of the fluid caused by the forces; it may be omitted in the case of the simple fluid with no structural viscosity, as Kluitenberg did.

The stress tensor for deformation, $P^{\mathrm{def}}_{\alpha\beta}$, is divided into two parts, the equilibrium stress tensor and the viscous stress tensor,

$$P^{\mathrm{def}}_{\alpha\beta}=P^{\mathrm{eq}}_{\alpha\beta}+P^{\mathrm{v}}_{\alpha\beta} \tag{4}$$

The equation for the entropy balance is derived from Eqs. 1, 3 and 4 as follows:

$$\rho\frac{\mathrm{d}s}{\mathrm{d}t}=-\operatorname{div}J^{\mathrm{s}}+\sigma^{\mathrm{s}} \tag{5}$$

where:

$$J^{\mathrm{s}}=J^{\mathrm{q}}/T \tag{6}$$

$$\sigma^{\mathrm{s}}=$$

$$\frac{1}{T}\left(-\frac{J^{\mathrm{q}}}{T}\cdot\operatorname{grad}T-\sum P^{\mathrm{v}}_{\alpha\beta}\frac{\mathrm{d}\varepsilon_{\alpha\beta}}{\mathrm{d}t}-\sum P^{\mathrm{des}}_{\alpha\beta}\frac{\mathrm{d}\xi}{\mathrm{d}t}\right) \tag{7}$$

The former is the entropy flow, and the latter is the irreversible production of entropy, which consists of three terms, the heat flow, the viscous flow and the rate of the breakdown of the internal structure.

The stress and the strain tensors are divided into a tangential part and a normal part as:

$$P_{\alpha\beta}=\widetilde{P}_{\alpha\beta}+P\delta_{\alpha\beta} \tag{8}$$

$$P^{\mathrm{v}}_{\alpha\beta}=\widetilde{P}^{\mathrm{v}}_{\alpha\beta}+P^{\mathrm{v}}\delta_{\alpha\beta} \tag{9}$$

$$\varepsilon_{\alpha\beta}=\widetilde{\varepsilon}_{\alpha\beta}+\varepsilon\delta_{\alpha\beta} \tag{10}$$

where $\delta_{\alpha\beta}$ is Kronecker's symbol and P, P^{v} and ε are traces of the corresponding tensors. It must be noticed that the tensors, $P_{\alpha\beta}$, $P^{\mathrm{v}}_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$, and also $\widetilde{P}_{\alpha\beta}$, $\widetilde{P}^{\mathrm{v}}_{\alpha\beta}$ and $\widetilde{\varepsilon}_{\alpha\beta}$ are all symmetrical. The same division is applied to the stress tensor for destruction. We set the trace of this tensor, P^{des}, as equal to zero. This implies that only the tangential force breaks down the internal structure of the system.

Under these procedures, Eq. 7 is rewritten as:

$$\sigma^{\mathrm{s}}=\frac{1}{T}\left(-\frac{J^{\mathrm{q}}}{T}\cdot\operatorname{grad}T-\sum\widetilde{P}^{\mathrm{v}}_{\alpha\beta}\frac{\mathrm{d}\widetilde{\varepsilon}_{\alpha\beta}}{\mathrm{d}t}-3P^{\mathrm{v}}\frac{\mathrm{d}\varepsilon}{\mathrm{d}t}\right.$$

$$\left.-\sum\widetilde{P}^{\mathrm{des}}_{\alpha\beta}\frac{\mathrm{d}\xi}{\mathrm{d}t}\right) \tag{11}$$

In this equation, the viscous flow term of Eq. 7 is separated into the shearing viscous and the volumetric viscous term. From this formulation of the entropy production, the following phenomenological equations are derived:

$$J^{\mathrm{q}}=-\lambda\operatorname{grad}T \tag{12}$$

$$\widetilde{P}^{\mathrm{v}}_{\alpha\beta}=-\eta\,\mathrm{d}\widetilde{\varepsilon}_{\alpha\beta}/\mathrm{d}t \tag{13}$$

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2) N. A. Scheraga, *J. Chem. Phys.*, **23**, 1526 (1955).

3) J. Meixner, *Z. Naturforschg.*, **4a**, 594 (1949); **9a**, 654 (1954).

4) G. A. Kluitenberg, *Physica*, **28**, 217, 561, 1173 (1962); **29**, 633 (1963).

5) S. R. de Groot and P. Mazur, "Non-equilibrium Thermodynamics," North-Holland Publ. Co., Amsterdam (1962).

$$P^{\mathrm{v}} = -\eta^{\mathrm{v}}\mathrm{d}\varepsilon/\mathrm{d}t \tag{14}$$

$$\tilde{P}^{\mathrm{des}}_{\alpha\beta} = -\zeta\,\mathrm{d}\xi/\mathrm{d}t \tag{15}$$

The first is the equation of the heat conduction, and the last, that of the breakdown and recovery of the internal structure.

When the fluid is not elastic on the shearing deformation, the equilibrium pressure tensor does not have non-diagonal components and the trace of this tensor, P^{eq}, is dependent on the volume (therefore, the trace of the total strain tensor, ε) and the temperature. Therefore, the linearized equation is assumed:

$$P^{\mathrm{eq}} = b\varepsilon + c(T-T_0) \tag{16}$$

where b and c are phenomenological constants and T_0 is the reference temperature. Using these relations, the phenomenological equations, 13 and 14, may be rewritten as:

$$\tilde{P}_{\alpha\beta} = -\eta\,\mathrm{d}\tilde{\varepsilon}_{\alpha\beta}/\mathrm{d}t \tag{17}$$

$$P = b\varepsilon - \eta^{\mathrm{v}}\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} + c(T-T_0) \tag{18}$$

The equation of entropy production is, by the use of these linearized phenomenological equations:

$$\sigma^{\mathrm{s}} = \frac{1}{T}\left\{\frac{\lambda}{T}(\mathrm{grad}\ T)^2 + \eta\sum\left(\frac{\mathrm{d}\tilde{\varepsilon}_{\alpha\beta}}{\mathrm{d}t}\right)^2 + 3\eta^{\mathrm{v}}\left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}t}\right)^2 + \zeta\sum\left(\frac{\mathrm{d}\xi}{\mathrm{d}t}\right)^2\right\} \tag{19}$$

The phenomenological coefficients defined in the phenomenological equations are positive, as the second principle of thermodynamics requires. λ is the coefficient of thermal conduction, η is the shearing viscosity, b is the volumetric elasticity and η^{v} is the volumetric viscosity; all are conventional terms. These coefficients depend on the state variables, $\tilde{P}_{\alpha\beta}$, T and ξ.

The structural viscosity and the thixotropy may be understood on the basis of the above formulation. In the first place, the apparent viscosity, η', which is measured experimentally, is defined as:

$$\tilde{P}_{\alpha\beta} = \tilde{P}^{\mathrm{def}}_{\alpha\beta} + \tilde{P}^{\mathrm{des}}_{\alpha\beta} = -\eta'\frac{\mathrm{d}\tilde{\varepsilon}_{\alpha\beta}}{\mathrm{d}t} \tag{20}$$

This quantity is expressed from Eqs. 15, 17 and 20 as:

$$\eta' = \eta + \zeta\left(\frac{\mathrm{d}\xi}{\mathrm{d}t}\right)\Big/\left(\frac{\mathrm{d}\tilde{\varepsilon}_{\alpha\beta}}{\mathrm{d}t}\right) \tag{21}$$

It should be noted that the ordinary viscosity, η, is not dependent on the rate of shear, $\mathrm{d}\tilde{\varepsilon}_{\alpha\beta}/\mathrm{d}t$, but is dependent on T and ξ. These formulations explain most of the viscous behavior of the fluids with internal structures.

When the internal structure is built up by deformation, i. e., $(\mathrm{d}\xi/\mathrm{d}\tilde{\varepsilon}_{\alpha\beta})>0$, the fluid exhibits the non-Newtonian viscosity of shear-rate hardening, i. e., $\eta'>\eta$. On the contrary, when the internal structure is broken down by deformation, i. e., $(\mathrm{d}\xi/\mathrm{d}\tilde{\varepsilon}_{\alpha\beta})<0$, the fluid exhibits the non-Newtonian viscosity of shear-rate softening, i. e., $\eta'<\eta$. When $\tilde{P}_{\alpha\beta}$, therefore $\tilde{\varepsilon}_{\alpha\beta}$, is very high, the internal structure of the fluids is broken down completely; then

$$(\mathrm{d}\xi/\mathrm{d}\tilde{\varepsilon}_{\alpha\beta})_{\tilde{P}_{\alpha\beta}\to\infty} \to 0, \quad \eta'=\eta \tag{22}$$

and the apparent viscosity becomes identical with the ordinary viscosity.

It should be noted that we have been considering the case in which the time-scale of the rate of change in the internal structure is sufficiently small compared to that of observation.

When the rate of change in the internal structure is comparable to or higher than the time-scale of observation, we observe a time-dependent behavior. This is the case when the thixotropic behavior takes place.

The Characterization of Thixotropic Fluids.—The simplest behavior of thixotropy is observed when the internal structure is destroyed instantaneously when force is applied, followed by stationary deformation and recovery, but the recovery of the structure into the stationary state is so slow sufficiently as not to be detected experimentally. This behavior is represented schematically in Fig. 1.

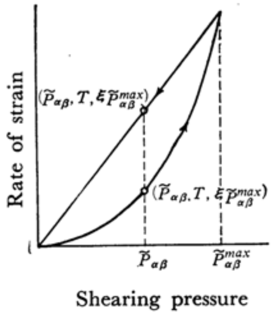

Fig. 1. A schematic plot of a simplest thixotropic behavior.

The up-curve of this figure is in the stationary state. The state variables of this fluid are $\tilde{P}_{\alpha\beta}$, T and ξ, and the following condition is required for the affinity of the change in the internal structure in the stationary thixotropic state from the theorem of minimum entropy production;⁶⁾

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{P}^{\mathrm{des}}_{\alpha\beta}(\tilde{P}_{\alpha\beta}, T, \xi) = 0 \tag{23}$$

By this equation the degree of internal freedom, ξ, is determined uniquely by $\tilde{P}_{\alpha\beta}$ and T.

From this consideration, it is clear that the state

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6) I. Prigogine, "Introduction to Thermodynamics of Irreversible Processes," 2nd. Ed., Interscience Publishers, New York (1961).

of the up-curve in Fig. 1 is stationary and that it is specified with the two variables of the three state variables, $\tilde{P}_{\alpha\beta}$, T and ξ. On the other hand, the state of the down-curve of Fig. 1 is not stationary. Since Eq. 23 does not hold in a non-stationary state, this state is specified by all three variables. That is, in the above case, the up-curve state is in $(P_{\alpha\beta},\ T,\ \xi_{\tilde{P}_{\alpha\beta}})$ and the down-curve state is in $(\tilde{P}_{\alpha\beta},\ T,\ \xi_{\tilde{P}^{max}_{\alpha\beta}})$, where $\tilde{P}^{max}_{\alpha\beta}$ is the maximum stress applied to the system.

However, no information is available on the degree of internal freedom in general. In order to overcome this difficulties, let us introduce the fictitious pressure tensor, $\tilde{P}^{\mathrm{f}}_{\alpha\beta}$; the fictitious pressure tensor is defined as the pressure tensor at which the non-stationary state of interest becomes the corresponding stationary one; i. e.,

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{P}^{\mathrm{des}}_{\alpha\beta}(\tilde{P}^{\mathrm{f}}_{\alpha\beta},\ T,\ \xi_{\tilde{P}^{\mathrm{f}}_{\alpha\beta}})=0 \tag{24}$$

By this relation the fictitious pressure is a function of T and ξ, and the non-stationary state is specified by the two variables, $\tilde{P}_{\alpha\beta}$ and $\tilde{P}^{\mathrm{f}}_{\alpha\beta}$. In the above case, the fictitious pressure is $\tilde{P}^{max}_{\alpha\beta}$.

The non-stationary state approaches the stationary one with the lapse of time. At the stationary state, only the flow conjugated with the forces fixed externally remains at a constant value; the other flows vanish, resulting their conjugated forces attaining constant values.[6] If the total force is fixed and the stationary viscous flow is established instantaneously, the system is non-stationary, as with the change in the internal structure. The entropy production of this non-stationary irreversible process is expressed as;

$$\sigma_{\xi}{}^{\mathrm{s}}=\tilde{P}^{\mathrm{des}}_{\alpha\beta}\frac{\mathrm{d}\xi}{\mathrm{d}t} \tag{25}$$

When the system is near to the stationary state, the following linear equation is assumed;

$$\begin{aligned}\tilde{P}^{\mathrm{des}}_{\alpha\beta}(\tilde{P}_{\alpha\beta},T,\xi) &= (\xi-\xi^{\mathrm{f}})\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\xi}\right)_{P_{\alpha\beta},\ T}\\ &= (\tilde{P}_{\alpha\beta}-\tilde{P}^{\mathrm{f}}_{\alpha\beta})\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\tilde{P}_{\alpha\beta}}\right)_{T,\xi}\end{aligned} \tag{26}$$

where ξ^{f} is the fictitious degree of internal structure, which is defined by the same consideration as the fictitious pressure tensor. Moreover, the signs of the quantities, $(\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}/\partial\xi)_{\tilde{P}_{\alpha\beta},T}$ and $(\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}/\partial\tilde{P}_{\alpha\beta})_{T,\xi}$, may be determined by simple consideration as follows:

$$\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\xi}\right)_{\tilde{P}_{\alpha\beta},T}<0,\quad \left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\tilde{P}_{\alpha\beta}}\right)_{T,\ \xi}<0 \tag{27}$$

From Eqs. 25 and 26;

$$(\tilde{P}_{\alpha\beta}-\tilde{P}^{\mathrm{f}}_{\alpha\beta})\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\tilde{P}_{\alpha\beta}}\right)_{T,\xi}=\zeta\left(\frac{\mathrm{d}\xi}{\mathrm{d}t}\right) \tag{28}$$

and, using the equation of total differential;

$$\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial t}=$$

$$\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\tilde{P}_{\alpha\beta}}\right)_{T,\xi}\frac{\mathrm{d}\tilde{P}^{\mathrm{f}}_{\alpha\beta}}{\mathrm{d}t}+\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\xi}\right)_{\tilde{P}_{\alpha\beta},T}\frac{\mathrm{d}\xi}{\mathrm{d}t}=0 \tag{29}$$

the equation

$$\frac{\mathrm{d}\xi}{\mathrm{d}t}=-\left\{\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\tilde{P}_{\alpha\beta}}\right)_{T,\xi}\Bigg/\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\xi}\right)_{\tilde{P}_{\alpha\beta},T}\right\}\frac{\mathrm{d}\tilde{P}^{\mathrm{f}}_{\alpha\beta}}{\mathrm{d}t} \tag{30}$$

is derived. Equation 28 then becomes

$$\tilde{P}_{\alpha\beta}-\tilde{P}^{\mathrm{f}}_{\alpha\beta}=-\left\{\zeta\Bigg/\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\xi}\right)_{\tilde{P}_{\alpha\beta},T}\right\}\frac{\mathrm{d}\tilde{P}^{\mathrm{f}}_{\alpha\beta}}{\mathrm{d}t} \tag{31}$$

By the integration of this equation, the final expression is obtained; that is;

$$\tilde{P}_{\alpha\beta}-\tilde{P}^{\mathrm{f}}_{\alpha\beta}=(\tilde{P}_{\alpha\beta}-\tilde{P}^{\mathrm{fo}}_{\alpha\beta})\exp(-t/\tau) \tag{32}$$

where the positive coefficient, τ, is defined as;

$$\tau=-\zeta\Bigg/\left(\frac{\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta}}{\partial\xi}\right)_{\tilde{P}_{\alpha\beta},T} \tag{33}$$

and $\tilde{P}^{\mathrm{fo}}_{\alpha\beta}$ is the initial value of the fictitious pressure tensor. As Eq. 32 predicts, the fictitious pressure, $\tilde{P}^{\mathrm{f}}_{\alpha\beta}$, approaches the real pressure, $\tilde{P}_{\alpha\beta}$, with the lapse of time. This is a process of the thixotropic recovery.

When the thixotropic recovery takes place and its relaxation time is larger than the time-scale of observation, a complicated behavior is observed, as we see in most of the colloidal suspensions. The above-described treatment can be applied to the interpretation of this behavior. For instance, if the stationary up-curve is obtained with the slow observation and if the measurement at the point A of Fig. 2 is made over the time-interval, Δt, in order to obtain the down-curve, the fictitious pressure changes from the initial value, $\tilde{P}^{max}_{\alpha\beta}$, to:

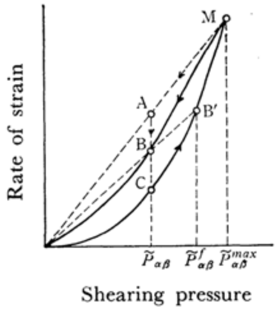

Fig. 2. Analysis of a flow curve of the thixotropic fluid.

$$\tilde{P}^{\mathrm{f}}_{\alpha\beta} = \tilde{P}_{\alpha\beta} - (\tilde{P}_{\alpha\beta} - \tilde{P}^{max}_{\alpha\beta}) \exp(-\Delta t/\tau) \qquad (34)$$

after the lapse of time Δt. Points A, B, B′ and C of this figure are specified by:

Point A, $\frac{\mathrm{d}}{\mathrm{d}t}\tilde{P}^{\mathrm{des}}_{\alpha\beta}(\tilde{P}_{\alpha\beta},\ T,\ \xi_{\tilde{P}^{max}_{\alpha\beta}}) \neq 0$,

Point B, $\frac{\mathrm{d}}{\mathrm{d}t}\tilde{P}^{\mathrm{des}}_{\alpha\beta}(\tilde{P}_{\alpha\beta},\ T,\ \xi_{\tilde{P}^{\mathrm{f}}_{\alpha\beta}}) \neq 0$,

Point B′, $\frac{\mathrm{d}}{\mathrm{d}t}\tilde{P}^{\mathrm{des}}_{\alpha\beta}(\tilde{P}^{\mathrm{f}}_{\alpha\beta},\ T,\ \xi_{\tilde{P}^{\mathrm{f}}_{\alpha\beta}}) = 0$, and

Point C, $\frac{\mathrm{d}}{\mathrm{d}t}\tilde{P}^{\mathrm{des}}_{\alpha\beta}(\tilde{P}_{\alpha\beta},\ T,\ \xi_{\tilde{P}_{\alpha\beta}}) = 0$

That is to say, Point B, which is measured by the experimental procedure, can be predicted by the fact that Point B′ is at the fictitious pressure, $\tilde{P}^{\mathrm{f}}_{\alpha\beta}$, on the stationary up-curve and that Point B is at the pressure, $\tilde{P}_{\alpha\beta}$, on the straight line, OB′.

If the recovery of the thixotropic structure is very fast and if the pressure is lower than $\tilde{P}_{\alpha\beta}$ before the measurement at $\tilde{P}_{\alpha\beta}$, the apparent negative thixotropy may be observed. The real negative thixotropy can, however, be observed only when $(\partial\xi/\partial\tilde{P}^{\mathrm{des}}_{\alpha\beta})_T > 0$. To this case the above treatment can be applied also. More generally, there may happen this behavior in case where the rate process occurs by the procedure of the up-curve measurement. The above treatment may easily be extended for such a case.

An Analysis of the Experimental Results and Discussion—Many efforts have been made by many researchers to elucidate thixotropic behavior. Although concrete discussions have been given for the mechanism of the thixotropic breakdown and recovery in some cases, a full quantitative description has not yet been successful. Of the researchers, Green and Weltmann made the most extensive study.[7,8] They proposed the hysteresis curve method for the characterization of thixotropic behaviors. However their experimental parameter is selected arbitrarily, and the comparison of the thixotropic behaviors of various samples is possible only under limited conditions; that is, their work is principally practical. In order to get a better description, Mooney,[9] Alfrey and Rodewald,[10] and Rehbinder[11] undertook to record the time-dependent shear-rate at a fixed shearing stress in order to characterize the thixotropic behaviors. By these studies, the thixotropic behavior is described by well-defined parameters, but their work has not had a general basis for the refined treatment.

The theoretical work described above provides a plausible basis for these studies. For example,

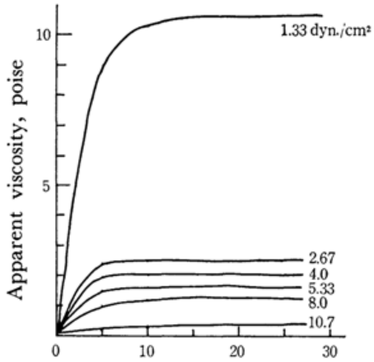

Fig. 3. Recovery curves of a suspension of a compounded rubber latex by Mooney.[9]

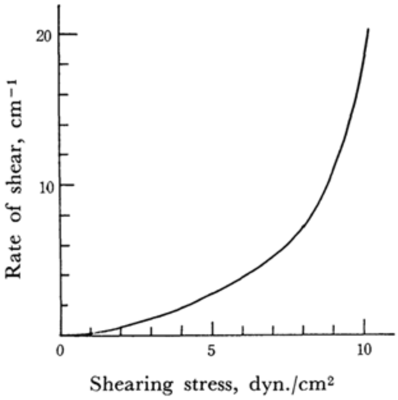

Fig. 4. The stationary curve of the rate of shear against the shearing stress of the latex suspension.

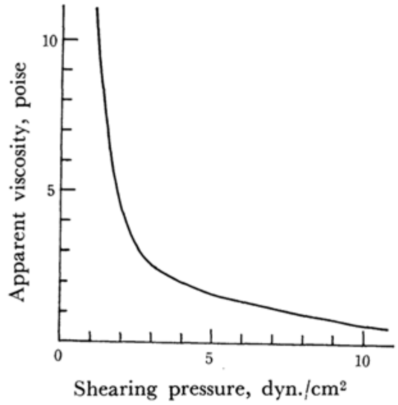

Fig. 5. Apparent viscosity vs. shearing pressure curve at the stationary flow.

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7) R. N. Weltmann, *J. Appl. Phys.*, **14**, 343 (1943); H. Green and R. N. Weltmann, ibid., **15**, 414 (1944); *Ind. Eng. Chem., Anal. Ed.*, **15**, 201 (1943); **18**, 167 (1946).

8) H. Green, "Industrial Rheology and Rheological Structures," John Wiley & Sons, New York (1949).

9) M. Mooney, *J. Colloid Sci.*, **1**, 195 (1946).

10) T. Alfrey, Jr., and C. W. Rodewald, ibid., **4**, 283 (1949).

11) P. Rehbinder, *Discussions Faraday Soc.*, **18**, 151 (1954).

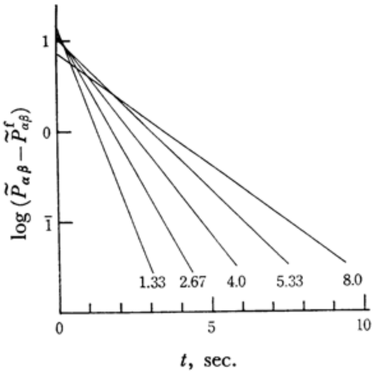

Fig. 6. Verification of the prediction of Eq. 32 using Mooney's data.

Mooney's work may be analyzed by this treatment as follows. Mooney measured the apparent viscosity of a suspension of a compounded rubber latex, the internal structure of which had been broken down completely beforehand, as a function of settling time at fixed shearing stresses; he thus obtained the results reproduced in Fig. 3. From this data the stationary shearing stress is drawn against the rate of shear in Fig. 4, while the apparent viscosity is replotted in Fig. 5.

When the fluid, the internal structure of which has been broken down completely, is fixed at a fixed shearing stress lower than that necessary for the complete destruction, the system is initially in the non-stationary state and approaches the stationary state. This non-stationary state is specified by the real and the fictitious shearing stress described in the preceding sections. The fictitious shearing stress is a function of the time at a constant shearing stress and becomes the real shearing stress as the time becomes infinite. The fictitious shearing stress is determined from the stationary stress vs. rate of shear curve as a value of the shearing stress at the corresponding value of the apparent viscosity or the rate of shear. The values calculated by this procedure are shown on the logarithmic scale against the time. This curve obeys to the prediction of Eq. 32, with the parameter, τ, varying with the stress; this is reasonable considering its definition given by Eq. 33.

From this treatment, all the stress vs. rate of shear curves may be constructed from the stationary curve and the parameter of the rate process of the thixotropic recovery. Green and Weltmann's hysteresis curve is also included in these curves.

In this treatment the fluids are assumed to be ideally viscous. Actually, the thixotropic fluids have yield values in most cases, as Freundlich first noted. This fluid may be treated by introducing the principle of relaxability in small proposed by Eckart[12] and by Kluitenberg[4]. However, this treatment is omitted here, for the extension of the present treatment to such a substances results in complicated expressions.

Lastly, it should be noted that the effect of the temperature on the thixotropic behavior is significant in most cases, as Lower, Walker and Zettlemoyer have already pointed out.[13] This effect is considered precisely in such fundamental equations as Eq. 19. However, no detailed discussions can be made here because of the lack of experimental data.

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[12] C. Eckart, *Phys. Rev.*, **73**, 373 (1948).

[13] G. Lower, W. C. Walker and A. C. Zettlemoyer, *J. Colloid Sci.*, **8**, 116 (1953).