

## Automatic Rotational Viscometer and High-Pressure Apparatus for the Study of the Non-Newtonian Behavior of Materials

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The automatic concentric-cylinder rotational viscometer described here records flow curves of shear stress versus rate of shear. It provides an automatic means of increasing and decreasing the applied rates of shear and an automatic control of the time that each shear rate is applied to the sample. In as much as flow properties may change rapidly with time and shear rates, this automatic control is important for materials which are time dependent. Presently, with proper selection of the axle and transmission gears, the cup's rotational speed can be automatically varied from zero to 1830 rpm. A switch permits the operator to select a constant shear rate and record shearing stress changes as a function of time at any point of this range. By simply replacing the gear sets, a speed of approximately 2750 rpm can be achieved. The time required for the speed to change from zero to a preset maximum, at constant acceleration, is controlled by voltage

### I. AN AUTOMATIC CONCENTRIC-CYLINDER ROTATIONAL VISCOMETER FOR RHEOLOGICAL MEASUREMENTS OF NON-NEWTONIAN FLOW

#### INTRODUCTION

AMONG the various types of viscometers, the rotational viscometer is one of the more commonly used instruments for measuring viscosities. It consists of two concentric cylinders, and the liquid to be tested is contained in the annular space between the two cylinders. Either the external (Couette type) or the internal cylinder (Searle type) is rotated, while the other is kept in position. The viscometer reported here belongs to the Couette type. Although the principle of the Couette type viscometer is well known, a brief description is given below, since it will serve for a better understanding of its use, especially for non-Newtonian fluids.

#### 1. Variables for Newtonian Flow

When the cup (external cylinder) is rotated the liquid is sheared in the annular space, and attains a steady state for a given angular velocity. The torque acting on every molecular layer of the liquid is the same, otherwise the condition of the steady state does not hold.<sup>1</sup> The torque on a molecular layer located at a distance  $r$  from the common axis is given by  $\tau$  and it should be the same as the torque acting on the surface of the bob (internal cylinder). The total torque (measured by a transducer) is given by

$$\tau = 2\pi r^2 h f, \quad (1)$$

where  $h$  is the height of the bob immersed in the liquid, or an equivalent height if there are end effects, and  $f$  is the

<sup>1</sup> M. Reiner, *Deformation and Flow* (H. K. Lewis and Company Ltd., London, 1949), pp. 27-34.

changes through a Variac which affords a continuous range from 11 to 300 sec. Shear rates of up to 4090 sec<sup>-1</sup> are obtained. The cup and bob are aligned coaxially and mechanically fixed. Added cup-bob features for bob-flushing effectively control effects of frictional heating within the sample. Other apparatus described here provides a means to measure the consistency of greases, near the "pseudo solidification" point induced by high pressures. The flow curves of greases which have a critical solidifying pressure reveal characteristics suggesting stiffer consistencies at increasingly high pressures. A 6-tank "reservoir" of hydraulic fluid is used where the fluid under compression and the tensile stresses in the steel of the tanks are used to completely eliminate the antagonistic "ripples" in the pressure which are caused by the action of the pump. Pressures of 0-50 000 psi are easily and safely obtainable with this apparatus.

shear stress (force per unit area) acting on the molecular layer under consideration. Under a shear stress  $f$  successive molecular layers shear with respect to the neighboring layer. The rate of shear (velocity gradient)  $\dot{s}$  is given by

$$\dot{s} = dv/dr = r(d\omega/dr), \quad (2)$$

where  $v$  is the linear velocity and  $\omega$  is the angular velocity. Generally,  $\dot{s}$  is a function of  $f$ , i.e.,

$$\dot{s} = F(f) = r(d\omega/dr). \quad (3)$$

From Eq. (1),  $dr/r = -df/2f$ ; substituting into Eq. (3) one obtains

$$\omega = \int_{\omega=0}^{\omega} d\omega = -\frac{1}{2} \int_{f_b}^f F(f) \frac{df}{f}. \quad (4)$$

Here,  $f_b (= \tau/2\pi R_b^2 h)$ , where  $R_b$  is the radius of the bob, is the shear stress on the surface of the bob, and  $f (= \tau/2\pi r^2 h)$  is the stress on the representative molecular layer a distance  $r$  from the axis of the bob.

For Newtonian fluids, the relation,  $F(f) = f/\eta$ , ( $\eta =$  viscosity, which is independent of  $f$  or  $\dot{s}$ ), is introduced into Eq. (4) and by integrating the latter from  $f_b$  to  $f_c$  (shear stress on the surface of the cup), one obtains

$$\Omega = \frac{\tau}{4\pi\eta h} \left[ \frac{1}{R_b^2} - \frac{1}{R_c^2} \right], \quad (5)$$

where  $\Omega = 2\pi n/60$ ,  $n$  being rpm (revolutions per minute). From Eqs. (1) and (5) one obtains

$$\eta = f_b \left/ \frac{4\pi n}{60[1 - (R_b^2/R_c^2)]} \right. \quad (6)$$

Defining  $\eta$  as  $f/\dot{s}$ , the  $f$  and  $\dot{s}$  on the bob surface are

$$f = \tau/2\pi R_b^2 h \quad (7)$$

and

$$\dot{s} = 2\Omega / (1 - \alpha^2) = 4\pi n / 60(1 - \alpha^2), \quad (8)$$

where

$$\alpha \equiv R_b / R_c.$$

Reiner,<sup>1</sup> Philippoff,<sup>2</sup> and Green<sup>3</sup> fully develop Eqs. (6), (7), and (8) for Newtonian liquids.

## 2. Variables for Non-Newtonian Flow

For non-Newtonian fluids, the integration of Eq. (4) is more difficult than shown above, since  $\eta$  in  $F(f)$  [ $= f/\eta$ ] is a function of  $f$  or  $\dot{s}$ . Here  $\dot{s}$  [ $= F(f)$ ] is calculated as follows. For non-Newtonian fluids, (4) yields

$$\Omega = -\frac{1}{2} \int_{f_c/\alpha^2}^{f_c} F(f) df/f, \quad (9)$$

where  $f_b$  has been replaced by  $f_c/\alpha^2$  from the relation

$$R_b^2/R_c^2 = f_c/f_b = \alpha^2 \quad (10)$$

which is derived from Eq. (1). From Eq. (9) one gets

$$[\partial\Omega/\partial\alpha]_{f_c} = -F(f_b)/\alpha. \quad (11)$$

The quantities,  $f$  and  $\dot{s}$ , given by Eqs. (7) and (8) are exactly calculable even for non-Newtonian fluids. The apparent fluidity  $\phi_{ap}$  is defined as

$$\phi_{ap} = 2\Omega / f_b(1 - \alpha^2) \quad (12)$$

giving

$$\Omega = -\frac{1}{2}\phi_{ap}f_c(1 - 1/\alpha^2). \quad (13)$$

Introducing  $(\partial\Omega/\partial\alpha)_{f_c}$ , from (13) into (11) one gets

$$\frac{F(f_b)}{f_b} = \phi_{ap} + \frac{1}{2}\alpha(\alpha^2 - 1) \left[ \frac{\partial\phi_{ap}}{\partial\alpha} \right]_{f_c} \quad (14)$$

which is readily transformed to

$$F(f_b) = f_b\phi_{ap} \{1 + \Delta(f)\} = \frac{2\Omega}{1 - \alpha^2} \{1 + \Delta(f)\}, \quad (15)$$

where

$$\Delta(f) = \left[ \frac{\partial \ln\phi_{ap}}{\partial \ln(1 - 1/\alpha^2)} \right]_{f_c}. \quad (16)$$

The relation (15) shows that when  $\Delta(f) \ll 1$  the shear rate,  $\dot{s} = [F(f_b)]$ , is given by (8). Thus,  $\Delta(f)$  is the correction,<sup>4</sup>

<sup>2</sup> W. Philippoff, *Viskosität der Kolloide* (Verlag von Theodor Steinkopff, Dresden and Leipzig, 1942).

<sup>3</sup> H. Green, *Industrial Rheology and Rheological Structures* (John Wiley & Sons, Inc., New York, 1949).

<sup>4</sup> Equation (15) is similar to an equation originally derived by Rabinowitsch for non-Newtonian flow in a capillary. The original derivation was modified by Saal and Koens. Later the correction  $\Delta f$  was studied first by Mooney, later by Krieger and Maron, and by Fritz and Kroepelin. The final form of the original (Rabinowitsch) equation, given by (15), is due to the work of Krieger and Maron.

for the non-Newtonian behavior of the liquid, which was studied by several investigators.<sup>5-10</sup>

The correction  $\Delta(f)$  is obtained by measuring  $\phi_{ap}$  at a constant  $f_c$  with cylinders of various  $\alpha$ . Since the method using many cylinders is very inconvenient, two methods have been devised<sup>7</sup>: one uses two bobs with one cup (the double bob method), and the other uses only one bob with one cup (the single bob method). The details of these methods are given by Krieger.<sup>6</sup>

Even for non-Newtonian fluids,  $\dot{s}$  is calculated using Eq. (8), since the  $\Delta(f)$  is frequently within 10% of the Newtonian  $\dot{s}$ . For exact studies, however,  $\dot{s}$  should be calculated from Eq. (15).

Occasional slippage occurs on the surfaces of the cup and bob. The correction for the slippage effect was studied by Mooney.<sup>5</sup> If slippage is evident, the corresponding correction should be incorporated in calculating  $\Omega$ , before the above  $\Delta(f)$  correction is made.

## 3. Shortcomings of the Rotational Viscometer

The Green-Weltmann type of viscometer<sup>2,11</sup> is convenient for studying thixotropic and rheopectic (dilatant) substances. However, it also has formidable shortcomings. Among others, the temperature rise due to frictional heating was frequently criticized.<sup>12,13</sup> For example, Lower, Walker, and Zettlemyer<sup>12</sup> found that heavy mineral oil did not show a thixotropic hysteresis loop when it was studied in an apparatus where the temperature was carefully controlled, while Weltmann<sup>14</sup> found a thixotropic loop in her experiment using the rotational viscometer (Couette type). Thus, the authors claimed that the hysteresis loops found by Green and Weltmann are not due to thixotropy (structural breakdown), but due to softening of the materials caused by the rise in temperature. However, Hahn<sup>15</sup> showed their concept is only partly right, since some thixotropic substances are destroyed by a very small mechanical disturbance.

In view of the fact that the frictional heating plays a large role in viscosity studies, careful attention was paid to minimize this effect in constructing the viscometer. Water from the thermostat, in which the cup-bob part of the viscometer was immersed, was circulated through the

<sup>5</sup> M. Mooney, *J. Rheology* **2**, 210 (1931).

<sup>6</sup> I. M. Krieger and S. H. Maron, *J. Appl. Phys.* **23**, 147 (1952).

<sup>7</sup> W. Fritz and H. Kroepelin, *Kolloid-Z.* **140**, 149 (1955).

<sup>8</sup> R. Rabinowitsch, *Z. Physik. Chem.* **A145**, 1 (1929).

<sup>9</sup> R. N. J. Saal and G. J. Koens, *Inst. Petroleum Tech.* **19**, 176 (1933).

<sup>10</sup> I. M. Krieger and S. H. Maron, *J. Appl. Phys.* **25**, 72 (1954).

<sup>11</sup> R. H. Weltmann, *N. L. G. I. Spokesman* **20**, No. 3, 34 (1956).

<sup>12</sup> G. W. Lower, W. C. Walker, and A. C. Zettlemyer, *J. Colloid Sci.* **8**, 119 (1953).

<sup>13</sup> R. N. Weltmann, *Ind. Eng. Chem.* **40**, 272 (1948).

<sup>14</sup> R. N. Weltmann, *J. Appl. Phys.* **14**, 343 (1943).

<sup>15</sup> S. J. Hahn, T. Ree, and H. Eyring, *N. L. G. I. Spokesman* **23**, 129 (1959).