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Instrumentation for the Rheological Investigation of Viscoelastic Materials*

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1. INTRODUCTION

The investigation of the mechanical properties of viscoelastic materials generally requires special instrumentation. The ordinary viscometers that are used for the study of simple viscous liquids and the tensile testers, etc., that are employed for elastic solids are not completely satisfactory for these "in-between" materials, whose properties may traverse the entire gamut between solid and liquid, depending only on the time and temperature of the experiment. Furthermore, viscoelastic materials are quite often investigated as molten bulk polymer or concentrated polymer solutions. Therefore, rheologists have had to develop suitable apparatus that are more nearly machines than instruments.

The present discussion deals with instruments presently in use in the Franklin Institute Laboratories that are representative of most of the types of apparatus used for viscoelastic investigation. That instrumentation which we designed was developed with the dual aim that (a) as wide a range in the experimental parameters as possible be obtainable with each instrument, and (b) the experimental data be correlatable on a rheological basis with the results from the other instruments. We are concerned with determining the force, deformation, and rate of deformation relationships existing under stationary or quasi-stationary conditions. Most of the instruments have been described, at least in part, previously. This presentation must, of necessity, be limited to a survey of the principles of design and the *modus operandi* of the instruments.

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2. CONI-CYLINDRICAL ROTATIONAL VISCOMETER

The investigation of mechanical properties under "steady-state" conditions is probably the most general technique used in rheology. "Steady-state conditions" means that the material is sheared unidirectionally and continuously until an equilibrium value for the rate of shear is obtained under a constant shear stress, or the converse. It is desirable that the instrumentation be so designed that the parameters can be precalculated from the geometry and cross-checked against the calibrated values. One of the primary instruments used for this purpose is the rotational viscometer, of which there are many types.

In our investigations the coni-cylindrical assembly is employed. The assemblies have been designed according to the development of Mooney and Ewart[1] in order to obtain a reasonably constant distribution of the rate of shear profile across the annulus. Four assemblies are available: two are biconical concentric cylinders; two are monoconical concentric cylinders having a cone on the bottom of the inner cylinder. In all of these, the inner cylinder rotates under an applied force determined by suspended weights. The latter assemblies were designed to be especially suitable for work with high-consistency materials; this means that large shear stresses can be applied in the available range of rates of shear. These two instruments have been described in detail.[2]

The biconical cylinders are modifications of the Mooney-Ewart design, in that the inner cylinder contains cones at both ends. These viscometers contain a given volume of material in an almost completely closed system; therefore, volatile solvents can be used without complication. The operating procedure is generally the same as that given previously.[2] Figure 1 shows one of these assemblies.

The two biconical rotors are hollow and float, due to their buoyancy, in the fluids being investi-

1 UPPER BEARING (SLEEVE)
2 COLUMN
3 PLATFORM
4 MIRROR BRACKET
5 PULLEY VERNIER
6 SPECIMEN CUP BEARING
7 BELT RETAINER
8 COVER
9 CONE
10 SPECIMEN CUP
11 LOWER PLATFORM
12 SHAFT
13 BEARING RETAINER
14 BEARING SUPPORT
15 BEARING SUPPORT BRACKET
16 LOWER COLUMN
17 WASHER
18 PULLEY
19 PULLEY BUSHING
20 CUP STUD
21 CONE BEARING

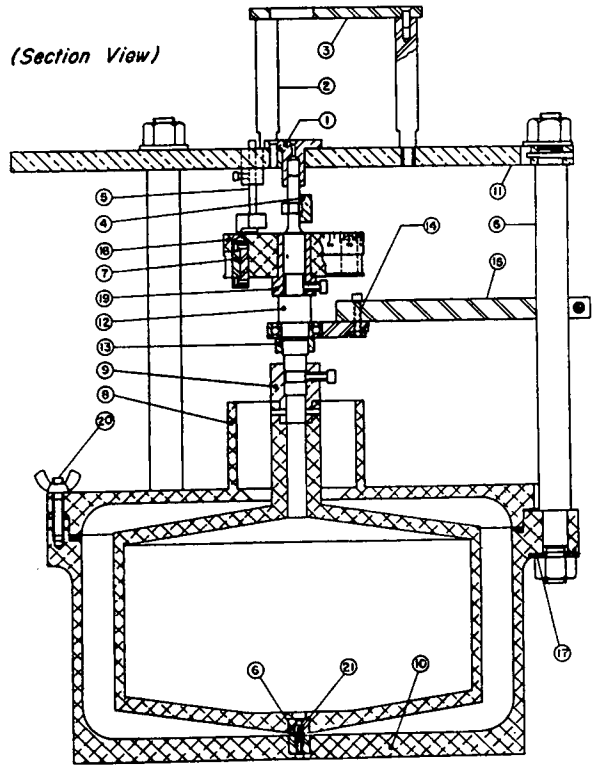

Fig. 1. Assembly drawing of rotational (coni-cylindrical) viscometer.

gated. The buoyancy is counteracted by means of additional weights selected so as to produce a minimum friction in the assembly. The effective friction force is generally equivalent to approximately one gram of applied load.

In operation, a load is attached to a supporting line. The angular motion as a function of time is recorded until stationary flow is attained. If elastic recoil is to be determined, the load is removed and the reverse motion of the rotor is noted until no further movement occurs. The range of motions obtainable is from $^1/_{70}$th of a degree to several revolutions in respective time intervals. The maximum speed is approximately $4^1/_2$ revolutions/sec.

We have suitable temperature controllers available that allow measurements to be made over a range of -15 to $+300$°C.

The constants for the rotational viscometer assemblies have been derived according to the theory of Mooney and Ewart,[1] with a modification to take the two cones into consideration for the case of biconical rotors. Three primary rheological parameters are determinable: the shearing stress, the rate of shear, and the "recoverable" shear strain (See Appendix).

The shearing stress τ (in dynes/square centimeter) is calculated as the maximum value which exists at the rotor.

$$\tau_{max} = (T/2\pi R_i^2 L_0) \tag{2.1}$$

where T is the torque (in dyne-centimeters), R_i is the radius of the inner cylinder (in centimeters), and L_0 is the "equivalent" length of the conical cylinder (in centimeters).

The rate of shear D (per second) is calculated as the maximum value occurring at the same point of reference:

$$D_{max} = 2\omega/(1 - c^2) \tag{2.2}$$

where ω is the angular velocity of the rotor (in radians/second) and c is ratio of radii of inner to outer cylinders.

For non-Newtonian fluids, a correction must be applied to the nominal rate of shear which takes into account both the ratio of the radii and the properties of the material, this correction, leading to the rate of shear to be obtained for infinite planes and referred to τ_{max} is:

$$\dot{\gamma}_{max} = [n(1 - c^2)/(1 - c^{2n})]D \text{ (per second)} \tag{2.3}$$

where $n = (d \log D/d \log \tau)$ is the differential slope of the flow curve ($\log D$ vs. $\log \tau_{max}$). An evaluation of the bracketed correction factors has been given in reference 2.

The total shear deformation γ, which is customarily discussed in rheology, can be infinite for a Newtonian liquid. With viscoelastic materials, the shear deformation under stress is taken up both by the flow (an irreversible process) and by storage due to the elasticity (a reversible process); upon removal of the stress, recovery of the stored energy occurs dependent upon the elastic properties of the fluid under the particular conditions of investigation. It is this recovery, termed the "elastic recoverable shear strain"[3] or "retarded elastic recovery"[4] that is important to rheological analysis.

The recoverable shear s is calculated from the

geometrical factors similarly to the calculation of the total shear as the dimensionless quantity

$$s = 2\phi_e/(1 - c^2) \qquad (2.4)$$

where ϕ_e is the angle (in radians) passed through by the rotor *under elastic recoil.*

The instruments have been calibrated with Newtonian liquids of known viscosity to cross-check the calculated values for the constants.

The range of operation of the various assemblies depends on the properties of the material and the temperatures employed. Practically, the limits of operating conditions for the rotational viscometer can be stated as: angular velocity from 1 degree of revolution in 70 hours to 1 revolution/sec.; net load from 0.5 g. to 100 lb. The values of D and τ given by these ranges will be shown. The range of recoverable shear, which is not shown graphically, goes down to about 0.002 shear units (0.2%) shear), while the upper limit depends solely on the material; thus far, values of s up to about 100 shear units (10,000% shear) have been measured in these instruments. Numerous experimental results obtained with this instrumentation have been published; they will only be referred to here.[5]

3. CAPILLARY VISCOMETER

The capillary tube viscometer is the other primary instrument for the investigation of mechanical properties of viscoelastic material under "steady-state" conditions. Among the types of capillary viscometers in use, only the applied pressure or the driven capillary tube viscometers are completely satisfactory for studying viscoelastic materials. (In the hydrostatic devices the pressure head, and hence the shear stress, decreases continuously. In the glass bulb devices, the rate of shear varies continuously due to a nonuniform cross-section.) To determine the non-Newtonian characteristics of viscoelastic fluids for which the rate of shear is generally a variable function of the shear stress, either τ or D should be constant.

The high-pressure capillary viscometer in use at FIL has been described in detail.[6,7] It is a gas pressure-operated device consisting of a stainless steel capillary tube mounted between two reservoirs. Both reservoirs are filled with the fluid which is then pushed alternately from one chamber to the other. A sketch of the assembled viscometer is shown in Figure 2.

Any number of strainless steel capillary tubes can be used with the viscometer. At the moment,

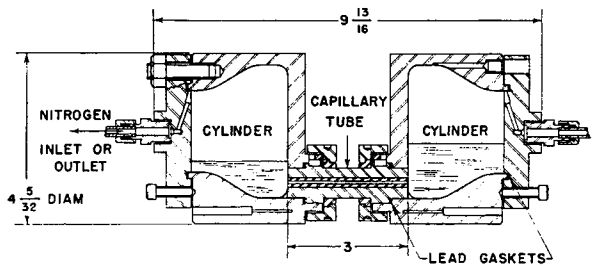

Fig. 2. Detail of capillary viscometer (assembled with 3-in. capillary).

19 units are available ranging in diameter from 1.27 to 0.019 cm. and in length from 30.5 to 0.038 cm., with length/radius ratios of 5.3 to 497. The capillary tubes are too numerous to list, but the ranges of operation in terms of shear stress and rate of shear are described in the next section.

The parameters for the capillary viscometer have been derived from the Poiseuille equation; a detailed account of its derivation has been published.[6] The result of these investigations is that three primary rheological parameters can be determined with the capillary instrument: shearing stress, rate of shear, and recoverable shear strain.

The shearing stress at the rim of the capillary (in dynes/square centimeter) is

$$\tau_T = R\Delta P/2L \qquad (3.1)$$

where R is the radius of the capillary (in centimeters), ΔP is the pressure gradient (in dynes/square centimeter), and L is the length of the capillary (in centimeters).

This equation is completely valid only for Newtonian liquids when the pressure is entirely utilized by viscous flow inside the tube; furthermore, the capillary must be of such a length that entrance effects are small compared to the viscous losses. This equation assumes laminar, stationary flow, which means that the liquid is sheared in concentric cylinders at velocities of flow corresponding to Reynolds numbers below 2000 and that an equilibrium value of volume flow rate Q is obtained. Generally, a portion of the energy input due to the pressure will be converted to kinetic energy, the correction for which is well established. This value must be deducted from the total shearing stress determined under the stated conditions in obtaining the net shearing stress which acts on the fluid.

The mean rate of shear across the capillary radius is likewise calculated from an equation valid for viscous liquids of constant viscosity. Vis-

coelastic fluids may have a viscosity differential with respect to the radius; therefore, the frame of reference is significant. The most logical frame of reference is the capillary wall, where τ_{max} is calculated and at which point the Newton viscosity relationship, $\eta = \tau/D$, is valid. The equation is:

$$\dot{\gamma} = [(n + 3)/4]D = (n + 3)Q/\pi R^3 \quad (3.2)$$

n, which is discussed in more detail in reference 7, was defined as $(d \log D/d \log \tau)$. It may take any value from 1 to ∞. For Newtonian liquids, n always equals 1, hence $\dot{\gamma} = D$. For non-Newtonian materials subjected to slow shearing, $\tau \propto D$ and $n = 1$, giving an initial viscosity η_0; at higher levels of D and τ, n becomes larger than 1; $\dot{\gamma}$ becomes larger than the mean rate of shear.

The recoverable shear strain s of a viscoelastic material may be evaluated in capillary viscometer experiments by either one of two methods: the elastic recoil after shearing and the "capillary length technique."

The elastic recovery after shearing is determined in a manner similar to that employed for the conicylindrical viscometer; that is, after equilibrium conditions are obtained and the rate of deformation or volumetric rate of flow is constant, the shear stress is removed. If the viscoelastic material has a large enough s at the rate of flow involved, it will be seen to retract in a direction reverse to that of the flow. The recoverable shear is calculated from the volume of material which recovers elastically (see reference 6) as

$$s = 4V'/\pi R^3 \quad (3.3)$$

where V' is the volume recovering elastically (in cubic centimeters).

The "capillary length technique" for determining the τ–s–D relationship has been treated extensively in a previous publication.[6] This treatment deals with elastic potential energy in the stationary flow of viscoelastic fluids. Derivations of the equations are presented for evaluating the elastic energy from a comparison of the pressure vs. capillary length–radius ratio relationships for two or more capillary tubes of equal radii (i.e., in the same rate of shear range.)

The capillary length technique is of extreme importance for the evaluation of the three parameters τ, s, and D. It is not limited by the factors which interfere in the direct determination of elastic recoil, e.g., the capillary radius must be large enough to allow accurate determination of the volume of material which retracts elastically and the rates of shear must be sufficiently low that the recoil can begin immediately after the stress is removed, with insignificant overshoot in the direction of flow due to the momentum of the flowing solution.

The tubes are calibrated with Newtonian liquids of known viscosity, direct measurement of R and L, and, for the larger tubes, determination of R from the volume of mercury contained in the tube. The calibration is particularly important because it leads to the so-called "hydrodynamic radius" which incorporates the geometrical effects on the viscous liquid, such as the entrance effect. The overall range of operation of the capillary viscometer, in terms of τ and D, will be shown. The limits are based on applied pressures of 0.05–1400 psi and rates of flow of 10^{-3} to 1 cm.^{3}/sec. The recoverable shear s has a minimum value of about 1 shear unit (100% shear) in recoil or in the capillary length effect. There is no practical limit to the maximum values obtainable except as dictated by the properties of the material; the largest values determined experimentally so far are approximately 400 shear units. Experimental data are given in references 5–8.

4. THE RHEOGONIOMETER

The Weissenberg rheogoniometer was conceived as an instrument which, in ideal form, "would yield a complete specification of rheological data by measuring for any given material the development with time of the stresses and strains present throughout the whole solid angle."[9] It has been designed with a flexibility of operation that permits both steady-state (continuous unidirectional shear) and dynamic (harmonic oscillatory shear) experiments to be performed. A complete description of the rheogoniometer has been given previously.[9,10] Jobling[9] presents a discussion of the theoretical foundation as formulated by Weissenberg and a description of the instrumentation and accessories together with the methods for calibration and operation.

The rheogoniometer at FIL has been used only for steady-state investigations of viscoelastic materials. Thus utilized, this instrument is essentially a cone-and-plate viscometer. The upper flat plate is connected to the frame by a torsion bar by means of which the torque set up on the plate due to the shearing action can be determined. The deflection of the torsion bar is detected by a change in capacitance between two plates, one of which is fixed in space while the other rotates with the plate.

Fig. 3. Photograph of Weissenberg rheogoniometer.

The specified procedure has been modified in that a standard variable capacitor has been incorporated in parallel to the plates. Hence, use of the Proximity Meter and the Bridge and Standardize Unit for null point indication only, the change in capacitance due to the torsioning can be counterbalanced by a standard capacitor which has been calibrated in terms of shear stress units. Alternatively, a flat plate, fixed rigidly in space, can be used as the top plate so that the normal forces can be measured independently with no distortion in the plane of shear due to the torsion rod. The lower plate consists of one of several cones which are connected by flexible diaphragms to a chuck which is driven by a motor operating through three decade gear selections at 1 to 3000 r.p.m., providing a fixed rate of shear in the gap of the viscometer. In addition, gear reductors have been added up to a ratio of 150:1 which enable us to measure to $^1/_{150}$ r.p.m. The cones are free to move vertically, due to the flexible connection, with the result that the downward force exerted by the normal stress developed in the material acts on a calibrated spring through a shaft. The spring's deflection can be counteracted by a micrometer gauge which has been so calibrated that a direct calculation of the normal stress can be made from the downward thrust. The assembled rheogoniometer is shown in Figure 3.

The cone-and-plate design unmodified is not completely satisfactory for studying semiviscous solutions which may tend to flow out of the gap; also, difficulty is experienced with highly elastic materials which ball up and are sheared out of position. These difficulties could be alleviated by the inclusion of rings on the lower plate to form a cup; however, the effect of the additional shear surfaces must be taken into account.

A humidifier has been incorporated so that hygroscopic solutions can be investigated without undue moisture adsorption. Temperature-control equipment was not included with this instrument; however, it is possible to provide for it.

When the rheogoniometer is used solely as a steady-state cone-and-plate viscometer in the way described, three primary rheological parameters can be determined: the rate of shear, the shearing stress, and the normal stress.

The rate of shear (per second) is calculated as the mean value imposed across the annulus as

$$D = \omega/\sin \alpha \tag{4.1}$$

where ω is the angular velocity (in radians/seconds) as calculated directly from the motor speed and α is the angle of the cone (in degrees).

The shear stress (in dynes/square centimeter) is calculated from the torque imposed on the top plate as

$$\tau = T/(2/3)\pi R^3 \tag{4.2}$$

where T is the torque (in dyne-centimeters) and R is the radius of the surface under shear (in centimeters).

The normal stress is calculated from the thrust on the bottom plate (cone) as

$$P_{11} = 2F/\pi R^2 \tag{4.3}$$

(in dynes/square centimeter), where F is the force in dynes). (Note: The derivation of the normal stress equation was given by Jobling.[9] Our further development, which takes a somewhat different approach, has been presented in detail.[3a,5d]

The shear stress is determined from a graph which contains a plot of stress units (dynes/square centimeter versus the change in capacitance caused by the torsioning of the torque bar. This graphical construction is required because the capacitance changes in a nonlinear manner; therefore, the

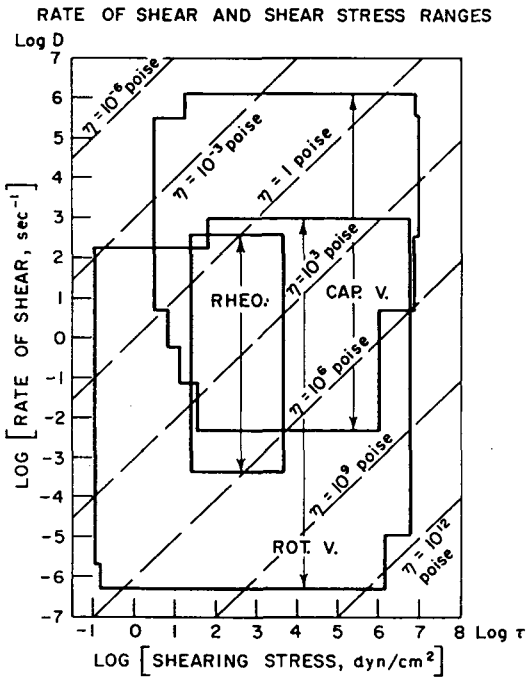

Fig. 4. Rate of shear and shear stress ranges.

amount of closure of the plates represented by a given ΔC value depends on the initial value C_0.

The calibration of the rheogoniometer is quite involved, in that many factors have to be checked out. These include: (*1*) determination of the constant for the torque bar (This is carried out by measuring the resonant frequency of the torque assembly with and without added weight, then calculating its moment of inertia. By this means the torque constant was calculated as $T = 1.65 \times 10^7$ dyne-cm./radian, as compared to 1.66×10^7 dyne-cm./radian found by Jobling.) (*2*) correlation of the capacitance change ΔC between the plate on the torque bar and the fixed plate to the amount of torque on the bar, starting from different initial values C_0 to obtain varying degrees of sensitivity to torque changes; (*3*) comparison of shear stress values calculated from ΔC with experimentally determined shear stresses of Newtonian oils; (*4*) calibration of the springs; (*5*) correlation of motion of bottom plate to upward thrust of spring.

The operating range of this instrument is based on the particular assemblies used. The maximum ranges in shear stresses and rates of shear are shown in Figure 4. Normal stresses, which are not included on that plot, can be measured from about 10^2 to 1.5×10^5 dynes/cm.^{2} The shear stress range is based on the minimum capacitance change measurable with accuracy up to the maximum closure of the plates. The rates of shear are based on a 150:1 reduction at 1 r.p.m. of the motor up to 3000 r.p.m. These ranges are calculated from 2° and 4° cones with which two upper plates are used. Reference has been made in the two previous sections to the experimental results obtained.

5. JET EXTRUSION INSTRUMENT

Among the properties of viscoelastic materials that are of interest is the behavior of these fluids in free-flying jets. This behavior has an obvious direct bearing on such things as extrusion conditions. The parameters which control the jet's behavior are rheological. Past work has defined them for simple viscous liquids; however, little work has been done on viscoelastic fluids. Having interest in such investigations, we developed a jet extrusion instrument.

The instrument, in brief description, consists of a cylinder and piston. The test fluid is forced through the cylinder at a preselected fixed rate and expelled through a cylindrical nozzle. The jet extrusion apparatus, which has been described in detail in recent publications,[11] is shown in Figure 5.

The nozzles used with this instrument are capillary tubes of various diameters and lengths. These enable us to work in a wide range of impressed velocities and rates of shear (the dimensions, etc. are given in the references cited above).

The investigations conducted with this instrument are concerned, primarily, with the general topic of the determination of the influence of the rheological properties of viscous and viscoelastic fluids on the fluids' behavior in extruded jets. Needless to say, this topic covers such aspects as

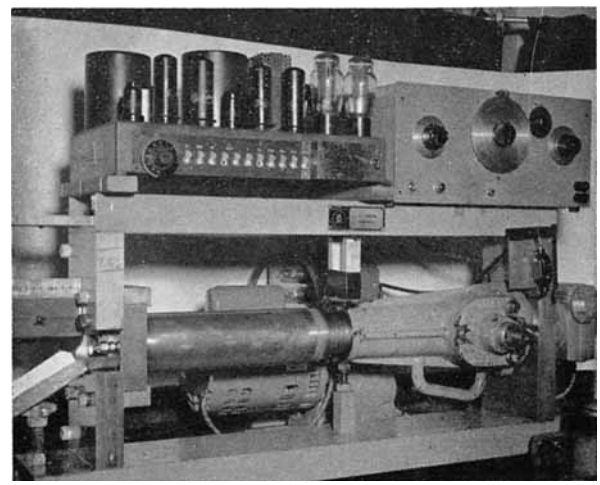

Fig. 5. Photograph of jet extrusion instrument.

the mechanism of jet disintegration, the control of jet breakup, and the relationship between the flight velocities obtained to the rheological properties existent at the extrusion.

These investigations have led to the development, in incomplete form, of equations for calculating the rheological properties of viscoelastic fluids from the velocity relationships obtained on extrusion. This offers the possibility of eventually correlating the jet extrusion parameters to the other rheological parameters.

6. VIBRATION TESTER

Since the investigations of Philippoff in 1934,[12] viscoelastic liquids have been known to have mechanical properties depending on the frequency of shear vibrations. The viscosity termed η' decreases with increasing frequency, and the elasticity described by the shear modulus G' increases with frequency. These measurements have been made possible by a number of instruments termed dynamic or vibration testers. The dynamic tester, which has been developed at the Franklin Institute, has been partially described in several papers.[13] It is shown in Figure 6.

The basic principle of this tester lies in the use of a mechanically-driven cam shaft, the rotation of which is transformed into a reciprocating motion; the cam has a variable eccentricity. This motion is transferred through a strain gage to the sample holder, and the displacement of the sample relative to the frame of the instrument is recorded. The energy is transferred from the sample holder to the frame of the instrument only through the sample without any other possibility of loss through friction, etc. We measure the direct force on the sample and the displacement of the sample independent of the possible deformation of the strain gage and of the instrument. In a strict sense, we are not operating at constant stress or with a constant amplitude in investigating a large range of frequencies, but the amplitude impressed on the strain gage and sample remains constant. The frequency can be changed over a wide range by means of gear boxes, the highest frequency being determined by the resonance of the samples and by the necessity of filtering out the 60-cycle stray current up to about 10 cycles/sec. Under these conditions, the inertia is either negligible as compared to the elasticity of the sample, or it can easily be taken into account. The sensing elements for both the strain gage and the deformation measurements are so-called differential transformers, which are energized by $4^1/_2$ v. at 1600 cycles/sec. The output of the differential transformer is amplified and rectified in a phase-sensitive bridge and, after being passed through a suitable filter, is impressed on an oscillograph. The force deflection is vertical, the deformation deflection, horizontal; this leads to a hysteresis loop on the oscillograph. The same voltage that energizes the differential transformer is subdivided by a step-attenuator; and this voltage then activates a suitable motor-driven switch, allowing us to record four dots on the picture, the distance of which from the axes on the screen can be calibrated directly in force and deformation. The range in double amplitudes is 6 to 900 μ for the deformation and 60 g. to 35 kg. for one of the strain gages; the other strain gage withstands up to 90 kg. (200 lb.).

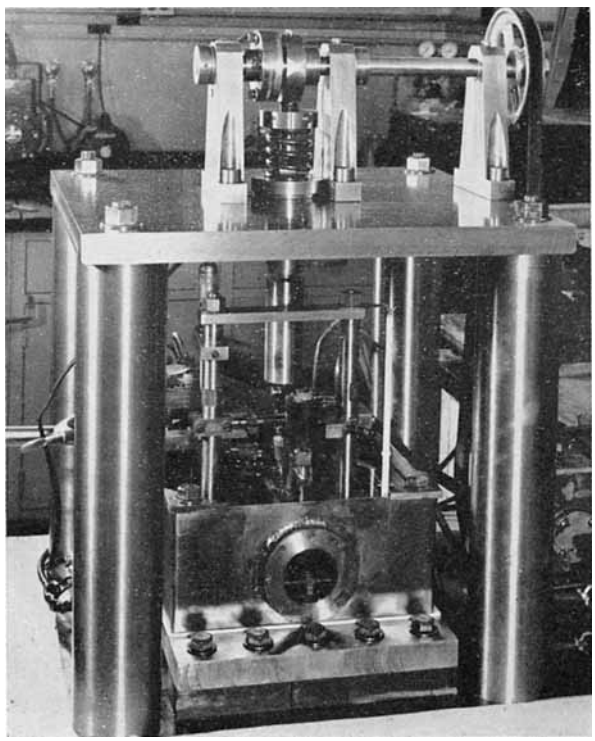

Fig. 6. Photograph of vibration tester.

The instrument accommodates a number of stressing devices. For rigid plastics, a bending arrangement in which a beam, clamped at the ends, is flexed in the middle, is more suitable. The shear arrangement calls for samples, 1 in.^{2} and $^1/_4$ in. in thickness, symmetrically placed in a three-plate arrangement, the middle plate being moved by the reciprocating movement, while the sides are held rigid. For liquid materials, a pump arrangement is used with two inner cylinders for viscosities of 1

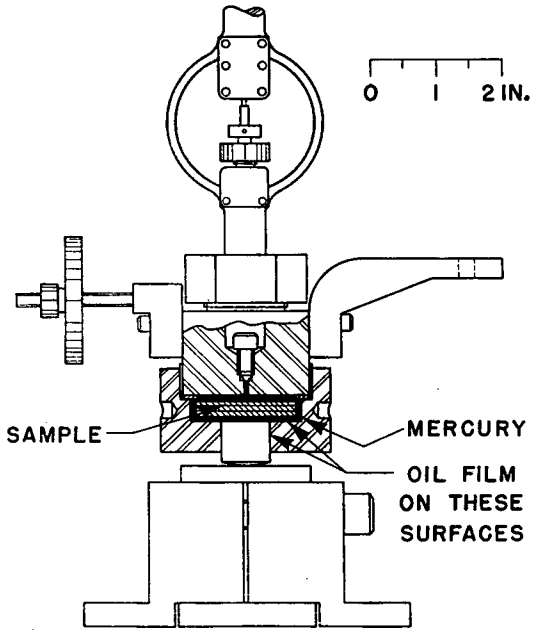

Fig. 7. Compressibility tester.

poise up to 2×10^6 poise. The results with these three devices have been correlated so that, for example, for asphalts, whose properties change to a very large extent with temperature, a continuous curve from all three types of tests can be obtained. The pumping arrangement is especially suitable for the measurements of molten plastics.

The vibration tester has been used for a wide variety of materials, e.g., asphalts, polyisobutylene solutions, etc., in a range of temperatures between −20 and +300°C. and at frequencies between 10 cycles/sec. and 1/50 cycle/hr. For periods longer than 30 sec./cycle, a two-pen recorder is used which traces the amplitude and the force as a function of time. This makes possible a very exact harmonic analysis, should it be necessary. When different vibration amplitudes are obtained at one frequency, the force required varies by considerable amounts, and the amplitude dependence on the mechanical properties can be investigated.

In addition, we have used a compressional arrangement for rubber and a compressibility cell for measuring the dynamic compressibility or bulk modulus as a function of frequency and temperature;[14] this arrangement is shown in Figure 7.

For calibration purposes we have used oils of 1 poise viscosity as well as steel bars. This large range is necessary because of the three arrangements available and the relatively free choice of sample dimensions for the shear and bending experiments.

The experimental quantities involved in dynamic testing are: G^*, the stiffness (or total) modulus (in dynes/square centimeter) calculated from the force applied and the sample geometry, δ, the loss angle between the force application and the deformation response (in degrees), and $\omega(= 2\pi f)$, the circular frequency imposed (in radians/second), where f is in cycles/second.

The rheological parameters which can be calculated from the above quantities are:

$G''(= G^* \sin \delta)$ the loss modulus (in dynes/square centimeter),

G' $(= G^* \cos \delta)$ the storage (or dynamic elastic) modulus (in dynes/square centimeter),

η' $(= G''/\omega)$ the dynamic viscosity (in poise), and η^* $(= G^*/\omega$, the so-called 'absolute' viscosity (in poise). This last parameter is of interest in certain cases.

The rheological parameters are usually evaluated in terms of G'', G', and η' vs ω or f (plotted logarithmically) at various temperatures. Also, the loss or damping factor, $\tan \delta$ $(= G''/G')$ vs. ω is often considered.

7. TORSION CRYSTAL

The torsion crystal apparatus, which was designed according to the principles established by Mason[15] has been described rather completely previously.[16] It consists of a cylindrical quartz crystal, about 10 cm. long and 1 cm. in diameter. The crystal is connected electrically and held at the four quadrants about the nodal point (approximately midway along its length). The crystal is fully immersed in the fluid under investigation, and excited into resonance; then a comparison is made of the resonant frequencies and the electrical resistance of the crystal in the test fluid and in either the pure solvent, if the fluid is a solution, or in air. From the change in resonant frequency and resistance, the dynamic properties G', G'', etc., can be calculated.

The present setup allows measurements to be made at a fundamental frequency of about 20 kcycles/sec. Resonant frequencies of 40, 60, and 100 kcycles/sec. are obtainable with some additions to the instrument. The temperature can be varied as much as desired, then the data can be treated by Ferry's "Method of Reduced Variables."[17] Some torsion crystal measurements correlated to other dynamic data have been published (see reference 13b).

8. BIREFRINGENCE TESTER

The investigation of flow birefringence is very important in rheology as an independent means of ascertaining changes in flowing liquids. Until recently, no one had tried to correlate the results of flow birefringence measurements, namely, the degree of birefringence Δn and the extinction angle χ, with mechanical properties. In 1938, Buchheim and Philippoff[18] pointed out that the viscosity decrease with increasing rate of shear is similar but not identical to the decrease of sin 2χ with the rate of shear. The newer investigations of Peterlin and Signer[19] and Lodge[20] brought this question up again. Our numerous investigations then showed the importance of measurements of the extinction angle which allow calculation of the recoverable shear s according to the formula

$$s = 2 \cot 2\chi \tag{8.1}$$

The flow birefringence instrument of the Franklin Institute has been designed according to the principles employed for the past one hundred years. It has a concentric cylinder arrangement with an inner rotating cylinder and a beam of linearly polarized light travelling axially in the annulus. However, the design of the instrument has several novel features that merit description. The instrument has been made with double walls for temperature control, and it forms a compact unit. Three inner cylinders are used. The internal diameter of the outer cylinder is 2 in., the length 3 in., and the gaps 3.5, 1, and 0.4 mm. The bores of the outer cylinder and the inner cylinders are highly polished and are made out of hardened stainless steel. The inner cylinder is mounted on two pairs of prestressed ball bearings and held on the driving shaft with a cone. This arrangement could be made so precise that the eccentricity would be less than the sensitivity of a 1/10,000-in. dial gage. The windows, which admit the light beam, are made out of 0.2 mm.-thick, strain-free microscope covers. The birefringence tester with its water connections is mounted in a cradle which allows it to be swung in and out of the beam of light.

The optical arrangement is mounted on a very rigid optical bench (1 m. in length). The illumination with short focal length lenses was adapted from Cerf.[21] The light source is a Sylvania 25-w. concentrated arc lamp. The condenser is a 1:1.5 opening, 15-mm., Dallmeyer movie projector lens. The image of the arc is projected on Bjornstahl wide-angle Anastigmat slits that pass parallel beams of light of a much higher intensity than can be obtained by use of completely parallel light. Another lens (20-mm., 1:1.9 Berthiot) gives an image of the first slit on the entrance of the instrument and an image of the second slit on the half-shadow arrangement mentioned below. The determination of χ is made with the Bravais plate introduced by Cerf; Δn is measured by a Senarmont compensator. The polarizer (a Glan–Thomson prism) is mounted on a 200-mm. divided circle near the second lens and connected by a rigid pipe to the analyzer, which is mounted on the optical bench behind the instrument. Both the polarizer and analyzer can be locked together and swung around the beam of light over $\pm 45°$. The plane of polarization of the instrument was chosen to be 45° from the vertical so that the angle of 45° that occurs for normal liquids would require a vertical position for the analyzer and polarizer. The half-shadow as well as the Bravais plate can be observed through a microscope on the same optical bench.

The Senarmont instrument can compensate for about one wavelength in phase difference. We have a Soleil compensator that can replace the Senarmont and allow measurements of 6λ phase difference. An interference filter of $\lambda = 5420 \pm 15$ A. can be placed in front of the lenses to give monochromatic light when required.

The optical arrangement gives a sensitivity for the measurement of Δn of 4×10^{-8} units per degree of the Senarmont compensator. Depending on the color and transparency of the solution, the adjustment of the compensator can be made as close as from 2 to 10 min., which means a sensitivity of around 10^{-9} units in Δn. The Bravais plate gives good operation with colorless solutions and allows χ to be measured at values of Δn of 1×10^{-8} to 2×10^{-8}, as has been mentioned by Cerf. With higher degrees of birefringence, the cross of isoclines gives measurements that are accurate enough even with colored solutions. The angle can be determined down to one minute on the divided circle but the actual precision depends on the condition of the solution and the magnitude of Δn, the probable error being between $1/4$ and $1/2$ degree; sometimes, however, even better precision is obtained. The inner cylinder is driven by a synchronous motor of 1800 rpm at $1/2$ horsepower, whose rotation can be electrically reversed; the latter is attached to a decade gear selector. The gear selector is connected to the inner cylinder by timing belts which give smooth operation with rigid control of speed. Furthermore, decade re-

duction gears can be inserted between the motor and the gear selector, permitting a 30,000,000:1 change of speed. This arrangement allows us to precalculate the rate of shear for each inner cylinder. Therefore, once the gear is selected, the rate of shear can be found from a table. The highest rate of shear used was 34,600 sec.$^{-1}$ with the 0.4-mm. gap; the lowest was 0.0008 sec.$^{-1}$ with a 3.5-mm. gap. The instrument is shown in Figure 8.

We deliberately avoided measuring the shearing stress in this instrument, since this would have complicated the instrument and probably made its operation less stable. The shearing stresses were therefore measured in the viscometers described previously. This made the operation much more flexible. A check of the results with several cylinders showed that the birefringence does not depend on the particular gap used; this was previously determined only by Sadron in 1937[22] for normal liquids.

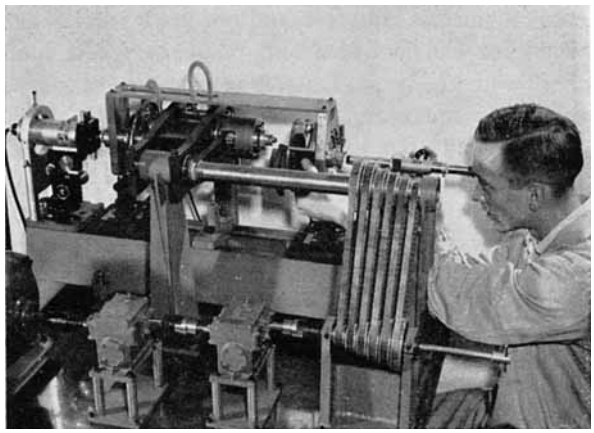

Fig. 8. Photograph of flow birefringence instrument.

Further discussion of the flow birefringence instrument, together with many experimental results, has been presented.[3,5,23]

9. SUMMARY

A survey has been presented of some of the instrumentation applied to the investigation of viscoelastic materials; detailed analyses of the same have not been attempted here. We have used the instrumentation available at the Franklin Institute Laboratories to illustrate the breadth of experimental techniques required for a reasonably complete rheological treatment.

APPENDIX

Part I. Shearing Stress on Coni-cylindrical Rotor

The maximum value of the stress at the rotor (in dynes/square centimeter), according to Mooney[1] is:

$$\tau_{max} = T/\{2\pi R_i^2[L_0 + (R_i/3 \sin \phi)]\} \quad (A1)$$

where T $(=R_p mg)$ is the torque (in dyne-centimeters), R_p is the radius of the main pulley (in centimeters), m is the applied load corrected for friction (in grams), g is the gravitational acceleration $(= 980.7$ cm/sec.$^2)$, R_i is the radius of the inner cylinder (in centimeters), and L_0 is the "equivalent" length of the cylinder.

a. Monoconical cylinder:

$$L_0 = L_c + [(R_0 - R_i)/(2 \sin \phi)](1 - \cos \phi) \quad (A2)$$

where L_c is the geometrical length of the cylinder (in centimeters) ϕ is the half-angle of the cone (in degrees), and R_o is the radius of the outer cylinder (in centimeters)

$$\tau_{max} = R_p mg/\{2\pi R_i^2[L_{01} + (R_i/3 \sin \phi)]\} \quad (A3)$$

(in dynes/square centimeter).

b. Biconical cylinder:

$$L_0 = L_c + 2[(R_0 - R_i)/(2 \sin \phi)](1 - \cos \phi) \quad (A4)$$

where the factor of two in the numerator takes into account the two cones. Also, a factor $(R_h/3 \sin \phi)$ must be included to account for the unsheared area at the top of the cup (see Fig. 1), where R_h is the radius of the hole, in cm.:

$$\tau_{max} = R_p mg/2\pi R_i^2\{L_{02} + [(2R_i - R_h)/3 \sin \phi]\} \quad (A5)$$

Part II. Rate of Shear for Coni-cylindrical Rotor

The "fluidity" in a coni-cylindrical viscometer (see Mooney[1]) is:

$$F_{max} = (\omega/T)[4\pi R_i^2 R_0^2/(R_0^2 - R_i^2)][L_0 + (R_i/3 \sin \phi)] \quad (A6)$$

(in square centimeters/dyne-second), where ω is the angular velocity of the inner cylinder (in radians/second). Then, the maximum rate of shear (per second) is

$$D_{max} = \tau_{max} F_{max} = \frac{T}{2\pi R_i^2[L_0 + (R_i/3 \sin \phi)]}\left(\frac{\omega}{T}\right) \times \frac{4\pi R_i^2 R_0^2}{(R_0^2 - R_i^2)} L_0 + (R_i/3 \sin \phi)$$

$$= \left[\frac{2\omega R_0^2}{R_0^2 - R_i^2}\right] = \left[\frac{2\omega}{1 - (R_i^2/R_0^2)}\right]$$

$$= \left[\frac{2\omega}{(1 - c^2)}\right] \text{ where } c = R_i/R_0. \qquad \text{(A7)}$$

Equation (A7) is applicable to both mono- and biconical cylinders, only the relatively small unsheared area in the latter case being neglected. In any event, this is accounted for by the calibration.

Part III. Recoverable Shear for Coni-cylindrical Rotor

The basic relationship for the rate of shear and shear strain is:

$$D = d\gamma/dt \qquad \text{(A8)}$$

where γ is the shear strain (dimensionless), and t is the associated time interval (in seconds).

The equation relating angular velocity and angular motion is:

$$\omega = d\phi/dt \qquad \text{(A9)}$$

where ϕ is the angular motion of the inner cylinder, (in radians).

Combining eqs. (A8) and (A9) in integrated form with eq. (A7), we obtain:

$$\gamma = Dt = [2\omega/(1 - c^2)]t = 2\phi/(1 - c^2) \qquad \text{(A10)}$$

For ϕ defined as the angle traversed by the inner cylinder under elastic recoil, we have the recoverable shear s:

$$s \equiv \gamma_e = 2\phi_e/(1 - c^2)] \qquad \text{(A11)}$$

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Synopsis

In the investigation of the rheological properties of viscoelastic material, a variety of instruments may be employed. The investigation may be concerned either with mechanical properties under "steady-state" or dynamic conditions or with optical properties such as are determined by flow birefringence techniques. This paper describes representative instrumentation (available at the Franklin Institute Laboratories) suitable for making the above types of determinations. The types of instruments are: (*1*) a coni-cylindrical rotational viscometer, (*2*) a high-pressure capillary tube viscometer; (*3*) the Weissenberg rheogoniometer, (*4*) a jet extrusion instrument, (*5*) a vibration tester, (*6*) a torsion crystal instrument, and (*7*) a flow birefringence instrument. The fundamental principles underlying the instruments which have not been described previously, are discussed.

Résumé

Dans la recherche des propriétés rhéologiques des produits viscoélastiques, on peut employer une grande variété d'instruments. La recherche peut porter sur les propriétés méchaniques dans des conditions de stationarité dynamique soit sur les propriétés optiques telles qu'elles sont déterminées par les techniques de biréfringence d'écoulement. Cet article décrit un ensemble d'appareils que l'on peut

employer pour faire les déterminations du types émumérés ci-dessus, en employant les instruments disponibles à Franklin Institute Laboratories comme modèles. Ces types d'instruments sont: (*1*) un viscosimètre cylindrico-conique (rotationnel); (*2*) un tube capillaire viscosimétrique à haute pression; (*3*) un rhéogoniomètre de Weissemberg; (*4*) un appareil à extrusion rapide; (*5*) un testeur à vibration; (*6*) un instrument à torsion à fil de cristal; et (*7*) un instrument de biréfringence d'écoulement. Des principes fondamentaux concernant ces instruments, n'ont pas été décrits ou préalable, mais ils sont discutés.

Zusammenfassung

Bei der Untersuchung der rheologischen Eigenschaften viskoelastischer Stoffe kann eine Vielfalt von Instrumenten verwendet werden. Die Untersuchung kann entweder die mechanischen Eigenschaften unter den dynamischen Bedingungen eines "stationären Zustandes" betreffen oder sie kann auf die optischen Eigenschaften, wie sie durch Strömungsdoppelbrechungsmethoden bestimmt werden, gerichtet sein. In der vorliegenden Arbeit wird eine repräsentative Instrumentenausstattung beschrieben, die zur Ausführung der oben angegebenen Typen von Bestimmungen goeignet ist, wobei die am Franklin Institute Laboratories zugängliche Instrumente als Modell dienen. Die Instrumenttypen sind die folgenden: (*1*) ein konisch-zylindrisches (Rotations-)-Viskosimeter; (*2*) ein Hochdruckkapillarviskosimeter; (*3*) das Rheogoniometer nach Weissenberg; (*4*) ein Strahlextrusionsinstrument; (*5*) ein Vibrationstester; (*6*) ein Kristalltorsionsinstrument und (*7*) ein Strémungsdoppelbrechungsinstrument. Für die Instrumente, die früher noch nicht beschrieben wurden, werden die zugrunde liegenden fundamentalen Prinzipien diskutiert.

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