

RHEOLOGY BULLETIN

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THE BINGHAM MEDAL, 1960

The Bingham Medal of the Society of Rheology for 1960 will be awarded to Dr. Bruno H. Zimm, of the School of Science and Engineering, University of California at LaJolla. The recipient was chosen by the Bingham Award Committee consisting of the following members: F. D. Dexter (Chairman), W. Busse, J. H. Dillon, H. Eyring and B. Maxwell.

Bruno H. Zimm was born in Woodstock, N. Y., in 1920, son of Bruno L. Zimm, a well known sculptor. He attended Columbia University, receiving an A.B. degree in 1941 and a Ph.D. in chemistry in 1944. His doctoral thesis, on the vapor pressure of alkali halides, was directed by Professor Joseph E. Mayer. He worked on several war projects, including one on aerosols under V. K. LaMer at Columbia, and one on plastics under Herman F. Mark at Brooklyn Polytechnic Institute. He taught briefly at Brooklyn Polytechnic, for four years at the University of California at Berkeley, and for a year at Harvard before joining the General Electric Research Laboratory in 1951. He stayed at General Electric for nine years until 1960 when he joined the University of California, School of Science and Engineering, at La Jolla. In the spring of 1960 he was a visiting professor of chemistry at Yale.

His research interests have included the theory of liquids, solutions, and long-chain molecules, as well as experimental researches on various phases of high polymer physical chemistry. He is known as the originator of the "Zimm plot," a method of plotting light scattering data on a grid of parallel lines to determine molecular size and shape. His work in the rheological field has been concerned principally with the theory of high polymer solutions. He has further developed the method of normal coordinates, originally devised by P. E. Rouse, Jr. and F. Bueche, and has applied it to problems of non-Newtonian flow, double refraction of flow, and dielectric behavior. He has also developed a viscometer for determining the viscosity of high polymer solutions as a function of frequency with oscillating shear at acoustical and ultrasonic frequencies.

THIRTY-FIRST ANNUAL MEETING 1960

The 31st Annual Meeting of the Society of Rheology will be held in Pittsburgh, Pa. on October 31 through November 2. The six technical sessions and the business meeting will convene in the Auditorium of Mellon

Institute. Registration will take place in the Bellefield Avenue lobby of Mellon, beginning at 9:00 A. M. on October 31. The conference room, adjoining this lobby, has been reserved for informal discussions among those attending the meeting. *Please use the Bellefield Avenue entrance to Mellon Institute, for all sessions.*

The Bingham Medal will be awarded in the evening of November 1 during a smoker which will be held in the University Room of the Hotel Webster Hall beginning at 8 P. M. There will be no extra charge for this evening.

All members are urged to take advantage of the opportunity to preregister by returning the registration card sent to all members *together with the registration fee* to Hershel Markovitz, Mellon Institute, Pittsburgh 13, Pa. before October 25. The Executive Committee has set this fee at \$3.00 for members and speakers and \$6.00 for non-members. Please make your check payable to *Society of Rheology—Pittsburgh Meeting.*

The Hotel Webster Hall, across the street from Mellon Institute, has set aside a number of rooms for our members. Those who wish to stay there are urged to send in their reservations as soon as possible. There may not be enough space at this hotel for all those desiring accommodations. There are many other hotels in downtown Pittsburgh, about 3 miles away.

The details of the meeting are in the hands of the Local Arrangements committee: Drs. R. M. Arnold, H. Markovitz (chairman), D. J. Plazek, H. L. Toor, and N. Weber.

PROGRAM OF MEETING

All technical sessions will be held in the Auditorium of Mellon Institute (please use the Bellefield Avenue entrance). There will be four general sessions and two symposia. On Tuesday morning, November 1st, the Symposium on the Rheology of Suspensions will be held, and on Wednesday afternoon, November 2nd, the Symposium on Mechanics of Continua. Abstracts of the papers to be presented are given below.

Monday Morning, October 31

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| 9:00 | Registration Begins: Bellefield Avenue Lobby |
| 9:45 | Opening of the Meeting: John H. Elliott, President of the Society |

RHEOLOGY BULLETIN

E. H. Lee, Editor

Division of Applied Mathematics
Brown University
Providence 12, R. I.

10:00-12:00 Technical Session (John H. Elliott,
Chairman)

The Normal Forces and Their Thermodynamic Significance

H. H. HULL, *R. R. Donnelley & Sons Company, Chicago,
Illinois.*

As a test of the concept that the isothermal strain energy is a Gibbs free energy and that this is indicated by the normal stresses, a manometer was placed in the face of a band viscometer. A Newtonian type fluid showed a negative pressure while a viscoelastic type fluid showed a positive pressure. This positive pressure is a measure of free energy (with certain corrections) just as osmotic pressure is a measure of free energy.

This is consistent with the published data on flow birefringence, which indicates that Newtonian fluids under simple shear are placed in tension at 45° to the direction of shear while with viscoelastic fluids the direction of maximum tension moves asymptotically toward the direction of shear.

This is also consistent with published data on the shape of suspended droplets in a shear field (from which it will be shown that relationship between the forces and their direction can be calculated), published data on the Weissenberg Rheogoniometer, etc.

A shear field orientates particles and the entropy associated with this orientation can be calculated $\Delta S = \frac{R}{N} \ln P$ where P is the probability that the orientation can be reached by chance alone. The orientation can, hence, be calculated from the free energy.

A Direct Method for Measuring the Normal Stress in Simple Shearing Flow

A. B. METZNER, W. T. HOUGHTON, R. A. SAILOR*
University of Delaware, Newark, Delaware

A technique has been developed in which the capillary jet experiment is used to measure the normal stress in the direction of shear, P_{11} . The capillary jet experiment consists of forcing the fluid in laminar flow through the capillary and measuring the diameter of the emerging jet as a function of shear rate. Application of Newton's second law to the liquid at the capillary tip and the emerging jet shows that the normal stress is a function of shear rate and the ratio of the diameter of the capillary tube to the diameter of the jet. If the relationship between shear stress and shear

rate is known, then the normal stress, P_{11} , can be determined directly from the diameter ratios as a function of shear rate without assuming any normal stress—shear rate relationship at all.

A momentum balance for a Newtonian non-elastic fluid predicts that the tube diameter to jet diameter should be 1.155 and invariant with respect to shear rate. Capillary jet experiments for water and ethyl alcohol have confirmed this value of the diameter ratio.

The effects of tube diameter and tube length to diameter ratio on the tube diameter to jet diameter ratio have been studied. Results for a 5% solution of polyisobutylene in decalin in tubes of ratio L/D of 138 to 367 will be presented.

In addition preliminary results for aqueous solutions of C.M.C. and polyethylene oxide in water will be presented.

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Socony Mobil Oil Company, Inc., Paulsboro, New Jersey.

Experimental Tests of Symmetry Conditions in Laminar Flow

WLADIMIR PHILIPPOFF, *Esso Research and Engineering
Company, Linden, N. J.*

Using new flow-birefringence devices it could be shown that flowing polymer solutions, probably consisting of deformable coiled molecules, are isotropic in the 2-3 plane, normal to the direction of flow, but are anisotropic in the 1-3 plane parallel to the direction of flow. Weissenberg's statement of $P_{22} = P_{33}$ (equal normal forces) is therefore confirmed. Suspensions of rigid particles are anisotropic in the 1-3 and in the 2-3 plane and give a "cross of isoclines" in the 2-3 plane due to a radial (uniaxial) symmetry. Results of the measurements of the flow birefringence of the suspensions in the 1-2 plane are given together with a description of a model of the mechanism of deformation in plane simple shear. The combination of deformational mechanics, optics, and the analysis of the motion of individual particles forms a powerful tool for the description of the phenomenon of flow.

Flow Birefringence of Molten Polyethylene

F. D. DEXTER, J. C. MILLER, *Union Carbide Corp.,
Bound Brook, N. J., and —*

W. PHILIPPOFF, *Esso Research and Engineering Co.,
Linden, N. J.*

Flow birefringence measurements in molten polyethylene in the 1-3 plane at three temperatures were compared with the stress optical coefficients of molten polyethylene in tension.

Using the concept of normal stresses, the recoverable shear S , was calculated from the birefringence data and compared favorably with experimental data from a rotational viscometer. The comparison establishes that the optical coefficient in three dimensions and the tensorial distribution of stresses, assuming $P_{33} = P_{22}$, is applicable to molten polyethylene.

Monday Afternoon, October 31

2:00-5:00 Technical Session (E. A. Collins, Chairman)

Molecular Weight—Temperature—Concentration Relationships for the Viscosity of Polyvinyl Acetate and its Solutions in Diethyl Phthalate and in Cetyl Alcohol

H. NAKAYASU and T. G. FOX, *Mellon Institute, Pittsburgh, Pennsylvania.*

Previous measurements of the viscosity of linear polyvinyl acetate fractions in a thermodynamically good solvent, diethyl phthalate, have been extended to lower molecular weights; measurements have been made as well in a thermodynamically border line solvent, cetyl alcohol, at the Θ temperature (123°C) and above. These cover the range in molecular weight from 8×10^3 to 1.3×10^6 , in temperature from 160 to 35°, and in concentration from 0.1 to 1.0 volume fraction of polymer. The observed viscosities, ranging from 2×10^{-2} to over 2×10^6 poises are represented by simple empirical equations and interpreted in the light of current molecular concepts of flow.

The Rheology of Polyelectrolytes. I. Flow Curves of Concentrated Polyacrylic Acid Solutions

J. G. BRODNYAN and E. L. KELLEY, *Rohm & Haas, Inc., Philadelphia, Pa.*

Flow curves of a polyacrylic acid of 1.8×10^5 viscosity average molecular weight were obtained at various degrees of neutralization and concentrations over a wide range of rates of shear. A biconical rotational viscometer was used at low rates of shear and a high-pressure capillary viscometer at high rates of shear. The range covered was sufficient in most cases to give not only the low shear stress Newtonian region but also the high rate of shear Newtonian region.

Yield Stresses and Flow Properties of Carboxypolymethylene-Water Systems

WALTER H. BAUER, WILLIAM H. FISCHER, and STEPHEN E. WIBERLEY, *Rensselaer Polytechnic Institute, Troy, New York.*

Dispersions of carboxypolymethylene (Carbopol) in water were found to exhibit sharply defined yield stresses, rapidly restored after imposed flow, as shown by stress relaxation measurements made with a cone and plate viscometer. Flow curves, rate of shear versus shearing stress, exhibited marked shear rate thinning, with little or no hysteresis. Effects of variation of concentration, pH, and temperature were investigated. A relation between shear stress and rate of shear involving yield stress as a parameter is discussed.

Upper Newtonian Regime in Polymer Solutions

EDWARD W. MERRILL, *Massachusetts Institute of Technology, Cambridge, Massachusetts.*

The display of an upper Newtonian regime of flow, at shear rates near 10^5 inverse seconds, in solutions of various whole polymers of polyisobutylene, takes widely differing forms according to the solvent. As shear rate increases, the apparent viscosity of the solution may decrease to the upper Newtonian level, or increase to it, or decrease from above to below and then finally increase to it. In all solutions the upper Newtonian viscosity corresponds to a viscosity number (n_{sp}/C) that is, in the limit, independent of concentration. In cyclohexane and benzene, the viscosity number for a single whole polymer of polyisobutylene is identical, and these viscosity numbers correlate with the 0.5 power of the average molecular weight of the polymer. In decalin and dichlorobenzene solutions of one whole polymer of polyisobutylene, the viscosity number is half the value found in cyclohexane and benzene, but in decalin, fragments of a second upper Newtonian regime are found of which the viscosity number is equal to that found in cyclohexane and benzene. In connection with the interpretation of the upper Newtonian regime, the observation of shear thickening (viscosity increasing with time of shear) is discussed, as well as the question of whether molecular scission occurs in the course of measurement of the upper Newtonian regime. Experiments are cited that suggest disentanglement of macromolecules without chain scission occurs in the annulus of the coaxial cylinder viscometer used for these studies.

An Equation for Non-Newtonian Flow

ALBERT M. MATTOCKS, *University of Michigan, Ann Arbor, Michigan.*

A rotating-cup viscometer, equipped with automatic program controls and two types of recording, an X-Y recorder and digital print-out, was developed. Using this equipment numerous non-Newtonian systems have been measured, and various equations for describing non-Newtonian flow have been tested. The available equations were found inadequate, and a new equation, called the Structure Equation, was developed. The equation is as follows:

$$F = f + n_a S - b_v e^{-aS}$$

where F is shearing stress, S is rate of shear, f , n_a , b_v and a are constants for a given system. The asymptote to the flow curve at high rates of shear is defined by its intercept, f , on the stress axis and its slope, n_a . Yield value is interpreted as $f - b_v$, a is an undefined constant which has the value of 0.001 for all systems yet studied. The viscosity at extremely low shear is defined as $\lim_{S \rightarrow 0} dF/dS$ which is $n_a + a b_v$.

Application of this equation to aqueous systems, consisting of polymer solutions, emulsions and suspensions will be presented.

Tuesday Morning, November 1

9:00-12:00 Symposium On the Rheology of Suspensions (F. H. Gaskins, Chairman)

Application of the Method of Composition and Linear Regression Analysis to a Problem Involving a Pseudoplastic Suspension

W. F. AMES and V. C. BEHN, *University of Delaware, Newark, Delaware.*

Experimental data obtained for a digested sewage sludge has been obtained relating shear stress to shear rate at varying concentrations by weight of solids. Examination of the data leads to two hypotheses which are used in a "method of composition" to obtain a "generalized power relation"

$$\sigma = b_0 C^{b_1} \left(\frac{du}{dr} \right)^{b_2 + b_3 \log C}$$

where σ = shear stress, C = concentration by weight of solids in the pseudoplastic suspension and du/dr is shear rate. Statistical regression analysis is used to obtain the coefficients from the data and to test the adequacy of the model. The results are highly satisfactory yielding predictive and analytical information in a concise and useful form.

Flow Properties of Attapulgitic Suspension In Water

A. F. GABRYSH, TAIKYUE REE, H. EYRING and I. CUTLER, *University of Utah, Salt Lake City, Utah.*

The results reported here were obtained using a rotational viscometer constructed at this Laboratory, and concern the study of the flow and deformation properties of Attapulgitic suspension in water. More particularly, the stress-strain-time relations with respect to variables of temperature, concentration and pH are given in terms of (a) isothermal structural change brought about by the mechanical disturbance and (b) partial recovery after an initial transition is achieved by the first cyclic deformation. The flow curve (shear rate, 0 to 700/sec, versus shear stress) exhibits first a rheopectic and subsequently a thixotropic hysteresis loop.

The observed flow properties of the suspension are described in terms of the Ree-Eyring theory of non-Newtonian flow. The transition of the rheopectic flow curve to a thixotropic flow curve is explained on the basis of structural break-down (evidenced by electron micrographs of material taken from the shear region and compared with material taken from a non-sheared region of the viscometer cup) in the needle-like bundle-shaped crystal structure.

The Differentiation Method in Rheology

J. G. SAVINS, G. C. WALLICK, and W. R. FOSTER, *Socony Mobil Oil Co., Inc., Dallas, Texas.*

In most instances the approach to the problem of interpreting the non-Newtonian flow behavior of various

systems has been in terms of what is referred to as the *Integration Method*. It consists of expressing flow properties in terms of an ideal model which is substituted into an integral equation relating observed kinematical and dynamical parameters. On integrating, the rheological parameters descriptive of the ideal model appear in an equation relating the pairs of observables.

A more general method of rheological analysis is to make no assumptions regarding the character of the function relating the observables to rheological parameters. This is the *Differentiation Method*. One differentiates the integral equation with respect to one of the boundary conditions; the result contains the pair of observables, their derivatives, and the rheological function evaluated at that boundary. These derivatives can be obtained from the experimental data by graphical or computer techniques and then substituted into the differential equation to produce the unknown function in graphical form.

Since these methods basically represent different modes of analysis, considerably more insight into the probable response of real data obtained by the Differentiation Method can be obtained from a dual Differentiation Method-Integration Method analysis of the characteristics of ideal flow models. Such a procedure has been applied to suites of flow models representing a variety of Generalized Newtonian and Viscoplastic behavior using machine processing and computation methods for Poiseuille and Couette flows. We believe this study represents one of the earliest reported instances of computer analysis in problems of this kind.

The salient features of this dual method of viscometric analysis are illustrated in the suites of predicted characteristic derivative functions which have been developed, and in the treatment of data on a variety of non-Newtonian suspensions and solutions.

Rheological Properties of Blood

ROBERT H. HAYNES, *University of Chicago, Chicago, Illinois.*

Blood is a complex fluid of various cell types suspended in a solution (plasma) containing dissolved salts, carbohydrates, lipids, and proteins. It has several interesting rheological properties, the most important of which is its ability to form a dense clot under certain conditions, as in hemorrhage. However, from the standpoint of hemodynamics, certain other rheological properties, which arise primarily from the presence of the red cells in suspension, are also of considerable interest; these are the dependence of the apparent viscosity on the rate of shear and the tube size in which the blood is flowing. (In the circulatory system one finds a wide range of shear rates and vessel sizes.) The shear-dependent viscosity can be explained in terms of the axial accumulation of the red cells with concomitant formation of an effectively cell-free marginal zone at the tube or vessel wall. The dependence of viscosity on tube radius can also be explained in terms of such a cell-free marginal zone. In this paper, some of the

experiments and theoretical approaches that have been used to elucidate these phenomena will be discussed, together with their physiological implications.

Shear Viscosities and Stress-Relaxation Viscosity Parameters of Gelled Oils

DEAN W. CRIDDLE and JAY CORTES, JR., *California Research Corporation, Richmond, California.*

The viscosities of gelled oils (lubricating greases) were measured in capillary viscometers and in a falling cylinder viscometer to cover a shear rate range of 10^{-5} to 10^{+5} sec^{-1} . Stress-strain curves were obtained for the initial deformation in falling cylinder viscometers for shear rates of 10^{-5} to 10^{+2} sec^{-1} . Shear stress relaxation curves were obtained by observing elastic after-effects following deformation at various strain rates and initial stresses. Elastic shear moduli were found to be independent of shear rate. Stress relaxation depends upon the deformation rate and the initial applied stress. Stress-relaxation viscosity parameters were calculated from elastic after-effects of the gels for a variety of stress relaxation conditions. Relaxation shear rates were defined and calculated for the stress-relaxation viscosity parameters. The viscosity-shear rate curves obtained from relaxation of greases from their ultimate yield shear points overlap and extend those curves obtained from shear experiments; hence, under some conditions the viscosity parameters characterizing the gel and the fluid states are identical.

Tuesday Afternoon, November 1

2:00-4:00 Technical Session (M. L. Williams, Chairman)

Frequency and Temperature Dependence of Dynamic Mechanical Properties of a High-Density Polyethylene

H. NAKAYASU, H. MARKOVITZ, D. J. PLAZEK, *Mellon Institute, Pittsburgh, Pennsylvania.*

Dynamic mechanical measurements were carried out on an unannealed sample of a high-density polyethylene with a forced oscillation torsion pendulum. The data were obtained at frequencies between 2×10^{-4} and 9 cycles per second. The temperature range extended from -30 to 80°C , above which significant changes of crystallinity occur. The results, within experimental error, were found to be independent of amplitude over a five fold range. A constant low tension was applied to the sample. At appreciably higher tensional stresses, an effect on the dynamic parameters was observed. A simple temperature superposition can not be applied to these data. It appears that two mechanisms with different temperature dependences contribute to the dynamic behavior in the range of variables studied.

Dynamic Mechanical Properties and Creep of Poly-2-Ethyl Butyl Methacrylate

THEODORE P. YIN and JOHN D. FERRY, *University of Wisconsin, Madison, Wisc.*

The real (J') and imaginary (J'') components of the complex compliance have been measured between 0.05 and 3600 cycles/sec. in the temperature range from 20° to 151°C . for a fractionated poly-2-ethyl butyl methacrylate with molecular weight 2.20×10^6 . The creep compliance, $J(t)$, and creep recovery were measured from 101° to 151° . The glass transition temperature was determined to be 11°C . The method of reduced variables gave superposed curves in the transition zone with shift factors following the WLF form of equation; the WLF parameters were $f_g = 0.021$, $\alpha_f = 1.8 \times 10^{-4}$ deg^{-1} . In the plateau zone (including the creep) an additional f -reduction for temperature dependence of entanglement was necessary, with $\Delta H = 4.4$ kcal. The retardation and relaxation spectra was calculated; the latter is almost identical in shape throughout with that of the n -butyl polymer. The logarithm of the monomeric friction coefficient is -3.69 at 100°C . and 4.79 at T_g . The average degree of polymerization between the entanglement coupling points is calculated to be 83, 115, and 178 respectively from the plateau in the spectra, from the height of the maximum in J'' , and from the position of the latter on the frequency scale. In general, the viscoelastic behavior of the 2-ethyl butyl polymer resembles that of the n -butyl much more closely than that of the n -hexyl which has the same side chain molecular weight.

Bulk Creep and Recovery in Free Volume Dependent Viscosity Systems

A. J. KOVACS — *Centre de Recherches sur les Macromolécules, Strasbourg, France.**

Viscoelastic bulk deformation under pressure is calculated for a special Kelvin body which consists of (1) a dashpot whose viscosity depends on the free volume, and in parallel (2) a Hookian spring with a constant bulk modulus. Starting with Doolittle's formula relating the bulk viscosity to the fractional free volume we have shown that the time dependence of the bulk deformation of this body is entirely asymmetrical with respect to the sign of the hydrostatic pressure: (a) If pressure is applied abruptly, the typical exponential decrease of volume becomes approximately linear with respect to the logarithm of time (except for the initial and the final part of the deformation, near the equilibrium). (b) If pressure is suddenly removed the volume increase will be a recovery of the autocatalytical type.

Some examples of these typical features are illustrated by the behaviour of supercooled liquids near the glass transition temperature. Tentatively the anomalous diffusion of small molecules through polymers can also be related to the same phenomena.

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A Theory For the Occurrence of Intrinsic Resonances in Stressed Solid Materials

SOL R. BODNER, *Brown University, Providence 12, R. I.*

Recent experimental work on the measurement of the compliance of initially stressed materials has supplied strong evidence that at least some of the additional resonances (i.e., those not predicted by classical theory, and specifically, those observed by E. R. Fitzgerald), are inherent in the material. A theory is presented to explain these resonances and the low values of the elastic modulus obtained with the Fitzgerald apparatus. The resonances are viewed as self-excited oscillations caused by nonlinear characteristics of the motion of dislocations in the materials.

4:00-5:00 *Business Meeting*

8:00 Smoker at Hotel Webster Hall—Presentation of the Bingham Medal

Wednesday Morning, November 2

9:00-12:00 Technical Session
(J. T. Bergen, Chairman)

The Distribution of Pressures in the Roll Application of Newtonian Fluids

RAYMOND R. MYERS and RAY D. HOFFMAN, *Lehigh University, Bethlehem, Pa.*

An analytical treatment is developed for the passage of a finite thickness of liquid through a roll nip, which heretofore had been characterized only by means of an overall pressure profile. The contact area between a roll applicator and a planar substrate is divided into four contiguous regions: bank, shear, cavitation, and filamentation; pressures are calculated for the shear and cavitation regions in terms of the velocity-viscosity product, the distance of travel, and geometrical parameters. Two experimental factors are introduced: the first is the recognition of tensions in the film prior to cavitation and the second is the existence of a finite film thickness between the two surfaces. This paper shows that both of these factors can be accommodated in the general theory and shows the magnitude of their effects on the pressures attained in the nip. The resulting complex function is broken down into a coefficient and two characteristic terms which are plotted separately in order to show their physical significance. Effects introduced by changes in certain operating conditions are pointed out and natural limits of operation are discussed.

Capillary Rheometry as a Technique For Predicting Processing of Elastomers

C. C. McCABE and N. N. MUELLER, *E. I. duPont de Nemours & Company, Inc., Wilmington, Delaware.*

The flow properties of elastomers provide a basis for predicting processing characteristics and are usually determined by measurements which relate a shear stress

to some shear rate. Many instruments are available for obtaining such measurements. In this paper the use of a capillary rheometer is described, and data obtained from it are used to predict processability of neoprene. Limited results for other elastomers are also included.

The capillary rheometer to be discussed consists of a constant temperature chamber with a circular orifice described by its diameter and its length to diameter ratio. A piston coupled to a driving mechanism through a force measuring gauge is used to extrude polymer through the orifice. Shear stress-shear rate data are collected for various elastomers at selected temperatures over a wide range of shear rates. Characteristic curves are then drawn for each elastomer and form the basis for processability comparisons. Interpretation of the data enables one to predict extrusion rates, die swell, and extrudate smoothness.

Similar curves are obtained for each individual elastomer containing increasing amounts of fillers or specific compounding ingredients in a given formulation. The quantitative effect of interaction between compounding ingredient and polymer is established from comparisons of these curves. It is then possible to predict processing characteristics for specific compounds by determining only the characteristics of the base elastomer and applying a suitable correction based on the interaction effects previously determined.

Effect of Die Entry Geometry on Polymer Melt Fracture and Extrudate Distortion

E. B. BACLEY and H. P. SCHREIBER, *Canadian Industries Limited, Central Research Laboratory, McMasterville, Quebec, Canada.*

When a polymer melt is extruded through a flat entry capillary (180° included entry angle) extrudate distortion is observed above a critical shear stress, σ_a , and critical shear rate, G_a . This is believed to be the result of polymer melt fracture at the die entry. With steeply tapered dies, however, much higher values of σ and G can be achieved without any apparent filament distortion. Work by Clegg in which the internal structure of the extruded filament was examined showed that flow irregularities can exist even though the extrudate is ostensibly undistorted. The work reported here confirms the observations made by Clegg and further shows that melt fracture in fact occurs at values of σ_a and G_a which are independent of die entry geometry. Some details of the melt fracture mechanism in tapered dies are illustrated by a short movie from which certain conclusions, in basic agreement with suggestions of Schott and Kagan, can be drawn.

Some Elastic Effects in Polymer Flow

E. B. BACLEY, *Canadian Industries Limited, Central Research Laboratory, McMasterville, Quebec, Canada.*

In certain polymer systems the applicability of Hooke's law in shear, coupled with the quantitative relationship given by Philippoff and Gaskins relating end corrections and recoverable shear strain in capil-

lary flow, permits the calculation of recoverable shear strains, S_R , in flowing polymer melts over a wide shear rate range. It is found that the onset of melt fracture, which results in extrudate distortion in capillary flow, occurs at a constant value of recoverable shear, essentially independent of molecular weight or polymer type provided no long chain branching is present. It can be shown that interesting similarities exist between polymer melt and polymer solution behaviour over a wide range of recoverable shear values.

In computing the apparent viscosity of a flowing system, n_{app} , the simple ratio of shear stress to shear rate is usually taken. In elastic systems, however, when the recoverable shear strains become large, Weissenberg has pointed out that the main directions of stress and strain velocity ellipsoids no longer coincide. Under these circumstances a more realistic viscosity value, n_{max} , is given by the relationship

$$n_{max} = n_{app} \sqrt{1 + S_R^2/4}$$

where S_R is the recoverable shear strain. When this correction is applied to polymer melts for which S_R values are available it is found that a large part of the non-Newtonianism of the melts vanishes. A large part of the apparent non-Newtonian behaviour is thus directly and simply related to the elastic characteristics of the melt. This result agrees with the work of Jobling and Roberts on solution behaviour.

Flow and Shape of Drops in Non-Newtonian Fluids

A. FARAROUÏ and R. C. KINTNER, *Illinois Institute of Technology, Chicago, Illinois*

The dimensionless correlation of the drag coefficient for motion of a drop falling through non-Newtonian fluids, similar to that which has been suggested for Newtonian fluids, has been studied. A relationship, analogous to that for flow through a pipe, between an average shear stress at the surface of the drop and its shear rate was defined. Then a second equation for the drag coefficient of a drop, falling in a Stokes region, as a function of a Reynolds number has been derived. Finally, by mathematical development, an expression for the average shear rate at the surface of a drop moving in a fluid, for Newtonian and all non-Newtonian except thixotropic and rheopectic fluids has been obtained. This type of shear rate, which is similar to the shear rate given by Rabinowitch's expression should be entirely independent of fluid properties.

Moreover, the shapes of liquid drops falling through highly viscous fluids have been observed in both Newtonian as well as non-Newtonian fields. The relation of eccentricity and terminal velocity of drops with their equivalent diameter has been plotted. For small size drops (diameters 0.3 cm. to 1.3 cm. of nitrobenzene mixture falling through C.M.C. and corn syrup) as the size of the drops was increased, a change in drop shape from spherical to vertical ellipsoidal and then back to spherical has been observed. On the other hand, for very large drops (equivalent diameters around 5 cm.) of water falling in castor oil, the upper sur-

face began to fold inward and a depression at the rear stagnation point was observed.

Wednesday Afternoon, November 2

2:00-4:00 Symposium on Mechanics of Continua
(H. Markowitz, Chairman)

Variational Principles For Non-Newtonian Flow

M. W. JOHNSON, JR., *University of Wisconsin, Madison, Wisconsin.*

A new variational theorem is formulated which has as its Euler equations and natural boundary conditions all of the differential equations and boundary conditions of the problem of the steady, incompressible flow of a non-Newtonian fluid. No conditions of admissibility on trial functions other than those of differentiability are required. Other variational theorems, including the classical theorems for the Newtonian fluid of von Helmholtz, are derived from this fundamental theorem by adding some of the natural conditions as admissibility conditions. Conditions under which some of these theorems are minimum or maximum principles are discussed.

Applications of Variational Principles In Rheology

M. W. JOHNSON, A. J. ZIEGENHAGEN, and R. B. BIRD, *University of Wisconsin, Madison, Wisconsin.*

Several illustrations of the variational principles of von Helmholtz,¹ Tomita,² Bird,³ and Johnson⁴ are discussed. Applications to flow in non-circular conduits and flow around submerged objects are given. For flow in annuli the results may be compared with previous analytical solutions.⁵

¹H. L. F. von Helmholtz, *Wissenschaftliche Abhandlungen*, Vol. 1, pp. 223-230 (1882).

²Y. Tomita, *Bull. of the Japan Soc. of Mech. Engrs.*, 2, 469-474 (1959).

³R. B. Bird, *Physics of Fluids*, *in press*.

⁴M. W. Johnson, *Physics of Fluids*, *in press*.

⁵A. G. Frederickson and B. B. Bird, *Ind. Eng. Chem.*, 50, 347-352 (1958).

Conservation Laws For Liquid Crystals

J. L. ERICKSEN, *Johns Hopkins University, Baltimore, Maryland.*

Commonly used forms of the laws of conservation of linear momentum, moment of momentum and energy seem inadequate for describing liquid crystals. We present reasoning which leads to forms which seem more appropriate.

On Constitutive Relations For Materials With Memory

BARRY BERNSTEIN, *U. S. Naval Research Laboratory, Washington, D. C.*

Two approaches have been followed in formulating constitutive relations for materials with memory. One

approach has been through the use of functionals. The other has been through the use of differential equations. The latter approach is a special case of the former, but leaves unanswered certain questions concerning initial conditions. These questions may be resolved using certain simple mathematical devices such as equivalence classes. It is then indicated how to define symmetry properties of a material defined by differential equations.

Functionals determined by analytic differential equations may be expressed as series of integrals, in a manner analogous to Taylor series. Thus constitutive relations given by analytic differential equations form special cases of those given by analytic functionals.

On the Foundation of Linear Viscoelasticity

BERNARD D. COLEMAN, *Mellon Institute, Pittsburgh, Pennsylvania* — and

WALTER NOLL, *Carnegie Institute of Technology, Pittsburgh, Pennsylvania.*

The classical linear theory of viscoelasticity should perhaps be called *infinitesimal viscoelasticity*, because it is a theory which can be applicable only to those physical situations in which the deformation, computed relative to a fixed configuration, has been infinitesimal at all times in the past. In this paper we work within the framework of the general theory of simple materials, i.e. materials for which the stress depends in an arbitrary way on the history of the deformation gradient. We formulate a differentiability assumption in function space and use this assumption to prove that infinitesimal viscoelasticity is indeed valid for simple materials when the deformation has been infinitesimal for all times in the past. We also derive a new theory of linear viscoelasticity which is more general than the classical infinitesimal theory. This new theory, which we call *finite linear viscoelasticity*, is shown to be a complete first-order approximation to the theory of simple materials. Finite linear viscoelasticity should be valid when the deformation, computed relative to the present configuration, has been *small in the recent past* but not necessarily in the distant past. The theory applies, in particular, in the limit of *slow* but finite deformations. In this the finite theory linear viscoelastic fluids can be related to the theory of Newtonian fluids.

Visit of a Group of German Rheologists to U.S.A.

A team of Rheologists from Germany is visiting this country to study activities in the field of "Rheology—

Research and Applications in Lubrication." The visit has been arranged by the Council for International Progress in Management (USA) Inc. The group of participants includes specialists in theoretical aspects, research and application. They will be here until October 14th, having arrived on September 6th. Many members of the Society will have an opportunity of meeting this group, since they are engaged on an extensive tour of industrial laboratories and research institutes from coast to coast. The participants are:

PROFESSOR I. U. AUGUSTIN

Technical University of Berlin

DR. G-H GÖTTNER

Institut für Erdölforschung Hannover

ALEXANDER VON HOYNINGEN-HUENE

Esso A. G., Hamburg

WERNER H. KARA

Deutsche Shell A.G., Pinneberg

KURT KIRSCHKE

Bundesanstalt für Material Prüfung, Berlin

FRIEDRICH KROEG

Caltex Oil GmbH, Hamburg

RICHARD WEBER

Metallgesellschaft A.G., Oberursel

International Symposium on Macromolecular Chemistry

There will be an International Symposium on macromolecular chemistry under the auspices of the International Union of Pure and Applied Chemistry at Montreal, Canada, July 27th to August 1st, 1961. The Symposium will embrace all aspects of high polymer science. Details can be obtained from:

THE ORGANIZING COMMITTEE

INTERNATIONAL SYMPOSIUM ON

MACROMOLECULAR CHEMISTRY

P. O. Box 816

SARNIA, ONTARIO, CANADA

Lubrication Conference

The Seventh Annual Lubrication Conference sponsored by the Lubrication Division of the American Society of Mechanical Engineers and the American Society of Lubrication Engineers will be held at the Statler Hilton Hotel, Boston on October 17, 18, 19, 1960. The eight technical sessions are concerned with: surface films in lubrication, gear lubrication, unusual environments, fluid film journal bearings, friction and wear, fluid film thrust bearings, hydrodynamic gas bearings, and hydrostatic gas bearings.

List of National Societies of Rheology

Britain:

DR. M. F. CULPIN
Hon. Sec., British Society of Rheology
8 The Broadway, Pontypool, Monmouthshire, U. K.

France:

PROF. H. WEISS
Office National des Universities et Ecoles Francaises
96, Boulevard Raspail, Paris VIe, France

Germany:

DER RHEOLOGISCHE GESELLSCHAFT DRG EV
Berlin Dahlem, Unter den Eichen 87, Germany

DR. MESKAT
Deutsche Rheologen—Vereinigung e.v.
Geschäftsstelle, Dormagen, Bahnhofstrasse 9, Germany

Japan:

DR. B. TAMAMUSHI
1321 Shimo-Ochiai 3, Shinjuku—Ku
Tokyo, Japan

Netherlands:

DR. P. G. MEERMAN
Wienweg 28, Brunssum (L), The Hague, Holland

Nederlandse Reologische Vereniging
Kring Reologie
Bond Voor Materialenkennis, Gravenhage
Koninginnegracht 41, The Netherlands

U.S.A.:

MR. W. R. WILLETS, Secretary Society of Rheology
c/o Titanium Pigment Corporation
99 Hudson Street, New York 13, N. Y., U.S.A.

Sweden:

DR. J. KUBAT
Svenska Traforskningsinstitutet
Drottning Kristinas Vag 61, Stockholm (0), Sweden

List of Representatives from Countries Having a Group of Rheologists

Australia:

DR. P. U. A. GROSSMAN
19 Mountain View Rd., Nunawading, Victoria, Australia

Brazil:

PROF. B. GROSS
Instituto Nacional de Tecnologia
Avenida Venezuela 82, Rio de Janeiro, Brazil

Israel:

PROF. M. REINER
21 Kiriya Sefer, Ahnza, Haifa, Israel

India:

DR. B. R. SETH
Indian Institute of Technology, Kharagpur, India

Yugoslavia:

PROF. A. PETERLIN
Inst. Jsef Stefan, Ljubljana, Yugoslavia

AMERICAN INSTITUTE OF PHYSICS, INCORPORATED
FOR SOCIETY OF RHEOLOGY

Statement of Account — At December 31, 1959

Balance in account, December 31, 1958.....	\$ 7,103.57	
Receipts, year ended December 31, 1959:		
Dues — 1958.....	\$ 4.40	
Dues — 1959.....	933.20	
Dues — 1960.....	<u>2,214.80</u>	3,152.40
Interest on U. S. Government Series "G" bonds.....		17.50
		<u>\$10,273.47</u>
Disbursements, year ended December 31, 1959:		
Contribution to A.I.P.	\$ 218.49	
A.I.P. charge for collecting dues.....	264.72	
Membership Committee.....	116.61	
Secretary-Treasurer's office.....	76.58	
Editor's office.....	10.69	
Ballot mailing — Election of Officers.....	43.82	
Annual Meeting expense.....	96.20	
Bingham Medal.....	6.51	
Bulletins:		
Fall 1958 — printing.....	\$ 178.75	
Spring 1959, Vol. 28, No. 1:		
Printing.....	\$125.07	
Addressing, stuffing, mailing, and postage.....	<u>46.10</u>	171.17
Summer 1959, Vol. 28, No. 2:		
Printing.....	\$135.60	
Addressing, stuffing, mailing, and postage.....	<u>63.16</u>	198.76
Fall 1959, Vol. 28, No. 3:		
Addressing, stuffing, mailing, and postage.....	<u>79.99</u>	628.67
Transactions, Volume 2:		
Printing.....	\$1,375.00	
Editor's expense.....	21.00	
Addressing, stuffing, mailing, and postage.....	<u>94.59</u>	1,490.59
Transactions, Volume 3:		
Editor's expense.....	\$ 11.91	
Addressing mailing list.....	<u>1.75</u>	13.66
Total Disbursements.....		<u>\$ 2,966.54</u>
Balance in account, December 31, 1959.....		<u>\$ 7,306.93</u>
Bingham Fund:		
U. S. Government Series "G" bonds.....		\$ 700.00