# RHEOLOGY BULLETIN

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#### THE BINGHAM MEDAL, 1962

The Bingham Medal of the Society of Rheology for 1962 will be presented to Dr. Wladimir Philippoff of the Esso Research and Engineering Company, Linden, New Jersey. The recipient was chosen by the Bingham Award Committee consisting of the following members: T. G. Fox (Chairman), E. B. Bagley, S. Prager, T. L. Smith and J. P. Tordella.

The award is made to Dr. Philippoff in recognition of his outstanding contributions to the phenomenological rheology of viscoelastic materials. His dedication to experimental rheology over a period of almost thirty years has been manifested by his broad interests in new phenomena, in a wide range of materials, and in methods of measurement. His work has served as an inspiration, often the original motivation of interest in the science, to many outstanding rheologists during the last two decades. We honor him thus, both for his own pioneering accomplishments, and for his influence in attracting others to rheological problems.

Dr. Philippoff was born in Peterhof, Russia, in 1907, and moved to Germany in 1924. He took his technical training at the Technische Hochschule, Berlin, from which he received his Dr. Eng. (Elec. Eng.) in 1934. From 1932-1945 he was a Research Scientist at the Kaiser Wilhelm Institute of Chemistry where his work included dynamic testing and steady flow investigations on viscoelastic systems as well as studies of mechanical properties of soap solutions.

After a three year interlude working for the American Military Government he came to the United States in 1948. He spent one year as a Lever Brothers research fellow at Stanford University where he carried out fundamental research on soap micelles. This was followed by a two year period as Research Associate of the School of Mines of the University of Minnesota where he studied flotation and ore benefication processes. In 1951 he went to the Franklin Institute as a specialist in rheological, wetting and adhesion problems and remained there as a Section Chief and Principal Scientist until 1959. He is currently a Senior Research Associate at the Esso Research and Engineering Company, Linden, New Jersey, where he is engaged in general rheology studies, particularly in the field of polymer solutions.

### THIRTY-THIRD ANNUAL MEETING 1962

The Annual Meeting of the Society of Rheology will be held this year at The Johns Hopkins University at Baltimore, Monday, October 29, through Wednesday, October 31. All technical sessions except that on Monday evening will be in Shriver Hall at the University. The Monday evening session and the smoker on Tuesday evening will be held in the Sheraton-Belvedere Hotel.

*Meals.* On campus, lunch can be obtained at the student cafeteria. No tickets will be required.

*Hotel.* A block of rooms has been set aside at the Sheraton-Belvedere Hotel. Members of the Society will receive a registration card for hotel accommodation.

Registration. Registration cards for the Meeting will be sent to members to provide an opportunity of preregistering by mail. The cards should be forwarded to Professor J. L. Ericksen, Department of Mechanics, The Johns Hopkins University, Baltimore 18, Maryland. You will be able to pick up your registration badge, etc., at a desk which will be located Sunday evening, October 28, at the Sheraton-Belvedere Hotel and thereafter in Shriver Hall.

Publication. The Society encourages submission of papers presented at the Annual Meeting for publication in the Transactions. It would be helpful if authors would inform the Editor of such intent as soon as possible and certainly not later than at the Annual Meeting. Two copies of manuscripts, including a brief synopsis, must be submitted by November 15th to the Editor, Dept. of Engineering Mechanics, Stanford University, Stanford, California. Earlier submission would be appreciated since it would expedite the processing of papers and so contribute to earlier publication of the Transactions. Papers will be refereed by authorities in the field, and this will form the basis for the Editor's decision concerning suitability for publication in the Transactions. It is expected that the Transactions will be issued early next summer.

The details of the meeting are in the hands of the Local Arrangements Committee: Professors S. Corrsin and J. L. Ericksen.

#### RHEOLOGY BULLETIN E. H. Lee, Editor

Division of Engineering Mechanics Stanford University

Stanford, California

### PROGRAM OF THE MEETING

#### Monday Morning, October 29, 1962

#### 9:30-12:15

Opening of the Meeting: JOHN D. FERRY, President of the Society.

Welcome on behalf of the University: Technical Session. Chairman, DR. J. GAVIS

#### 1. Rheo-Optical Properties of Polymers. IV

D. G. LEGRAND, General Electric Research Laboratory, Schenectady, New York.

In previous papers we have presented data on the dynamic birefringence and light scattering from polyethylene. New studies of the dynamic birefringence of polytetrafluoroethylene, silicone rubber, polycarbonate, polymethyl methacrylate, and polyethylene as a function of frequency and temperature have been made. The results will be presented and interpreted in terms of various proposed theories. The relationships between the mechanical and optical relaxation spectrum will be discussed.

#### 2. Response of a Distributed, Thermally Activated System

J. ROSS MACDONALD, Texas Instruments Incorporated, Dallas 22, Texas.

For a linear, thermally activated system, a distribution of relaxation times may arise because of a distribution of activation energies, pre-exponential factors, or both. When these quantities and their probability densities are temperature independent, the expected situation within a limited temperature range, the temperature dependence of the distribution of relaxation times is completely determined. We shall consider the temperature, transient, and frequency response of such a system for a modified power-law type of relaxationtime distribution which leads to many results in qualitative or quantitative agreement with experiment. Both retardation and relaxation possibilities will be considered and rheological and geophysical implications emphasized. 3. PART 1: Rheology of Human Blood Measurement Near and at Zero Shear Rate

G. COKELET, E. W. MERRILL, E. R. GILLILAND, H. SHIN, Dept. of Chem. Eng., Massachusetts Institute of Technology, A. BRITTEN, General Hospital, R. E. WELLS, JR., Peter Brigham Hospital, Cambridge, 39, Massachusetts.

The yield stress  $\tau\gamma$  of static human blood as a homogeneous solid and its stress  $(\tau)$  — shear rate  $(\gamma)$  function under creeping flow as a homogeneous fluid were studied in a Couette-type viscometer. As normal blood tends to form a plasma-rich layer next to boundary surfaces, experimental artifacts easily arise. These are minimized by using vertically-grooved viscometer cylinders, and in the case of stress-shear rate measurements, determining the stress maxima in recordings of stress (at constant shear rate) as a function of time. Absolute measurement of yield stress requires careful interpretation of curves of stress versus time just after rotation ceases. Zero error is eliminated by using both clockwise and counter-clockwise rotation. When artifacts, caused by the disposition of normal human blood to form two phases, are eliminated, the yield stress and stress-shear rate function under creeping flow are well correlated by the same equation.

The importance of Casson's physical model to the structure of normal human blood is discussed. To be noted are the following: correlation of yield stress with volume percent red cells, temperature-independence of yield stress and of relative viscosity at shear rates above 1 sec<sup>-1</sup>, the possible physiological results of temporarily stopping blood flow in the living microcirculation, the rheologically-dominating effect of fibrinogen over other plasma constituents, and the role of rheological studies of blood in the biological investigation of the plasma membrane.

PART 2: A Rotational Viscometer Using an A.C. Torque to Balance Loop and Air Bearing

P. J. GILINSON, JR., C. R. DAUWALTER, E. W. MERRILL, Dept. of Chem. Eng., Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

A rotational (coaxial cylinder) viscometer is described for measuring non-Newtonian stress-shear rate functions between limits of shear rate and viscosity of, respectively,  $0.02 \text{ sec}^{-1}$  and 1 centipoise at maximum sensitivity and 100 sec<sup>-1</sup> and 200 centipoise at maximum load. Uniform precision of stress measurement of about 0.1% over this wide range of rheological interest is obtained by a novel means of measuring torque, coupled with essentially frictionless suspension of the stationary cylinder on an air bearing.

The torque applied by the rotational viscometer is measured by means of a closed-loop system which automatically develops an electromagnetic balancing torque. The feedback controlled excitation necessary to bring about this torque equilibrium is the measure of the applied viscometer torque. By the automatic control of the system dynamics, torques ranging from 0.0100 to 1000 dyne-centimeters can be measured with an uncertainty of  $\pm 0.0001$  dyne-centimeters.

4. Hydrodynamic Interactions of Submicroscopic Particles

HAROLD WAYLAND, DANIEL J. COLLINS\* and MARCOS INTAGLIETTA, California Institute of Technology, Pasadena, California.

Many biological systems, such as blood plasma, consist of solutions of several species of macromolecules of varying degrees of asymmetry. Studies have been made of the concentration dependence and shear dependence of viscosity of systems consisting of polystyrene latex spheres of 880 A diameter, tobacco mosaic virus rods, and mixtures of the two.

For the spherical particles, fluidity was linear with concentration up to the maximum studied, 1.2%. Comparison of the results for TMV alone with the rod-sphere mixture can most readily be interpreted as due to a breaking up of substructure units in TMV by the presence of the spherical particles.

This hypothesis is being further tested by studying the streaming birefringence of rod-sphere systems (TMV and Southern Bean Mosaic Virus).

\*Present address: Massachusetts Institute of Technology, Cambridge, Mass.

Monday Afternoon, 1:30 – 5:00

A Symposium on Problems Common to

Hydrodynamics and Hemodynamics

*Chairmen:* Dr. Edward A. Collins, Dr. Edward H. Bloch.

Introduction: FREDERICK R. EIRICH, Dept. of Chemistry, Brooklyn Polytechnic Inst.

The goal of this Symposium is to focus attention on the common problems of flow through tubes in the animal and in non-biological systems and indicate some of the unique advantages of studying the flow of blood.

This will be accomplished by presenting recent concepts of the flow of fluids through tubes, the special problems of the fluid mechanics of blood and to analyze the model systems which have been used to stimulate blood flow. The intention of this Symposium is to lift the problems of blood flow out of character in order to take advantage of the broad spectrum of disciplines present at the annual meeting.

5. Modern Theories of Flow in Tubes

CLIFFORD A. TRUESDELL, Dept. of Mechanics, The Johns Hopkins University, Baltimore, Maryland.

6. Physical Aspects of the Mammalian Circulatory System

R. H. HAYNES, Committee on Biophysics, University of Chicago.

- 7. The Flow of Blood Through Microscopic Vessels
  - EDWARD H. BLOCH, Dept. of Anatomy, Western Reserve University, Cleveland, Ohio.

8. A Survey of Attempts in the Mathematical Analysis of Blood Flow

EDWARD SAIBEL and EDWARD FOX, Dept. of Mechanics, Rensselaer Polytechnic Institute, Troy, New York.

9. Effects of Fibrinogen upon the Fluid Structure of Erythrocyte Suspensions

R. E. WELLS, JR., T. H. GAWRONSKI and R. D. PERERA, Depts. of Medicine, Harvard Medical School and Peter Bent Brigham Hospital, Boston, Massachusetts.

Red blood cells were suspended in solutions containing varying concentrations of the clothing protein, fibrinogen. Studies were conducted to determine the influence of these concentrations upon suspension stability, aggregate structure and viscosity. Fibrinogen, well established as the most active red cell aggregating protein fraction of blood, was made up in physiological saline solutions to concentrations of 0.3-5.0 grams percent (normal equals  $0.6 \pm 0.1$  grams percent). The rate and character of cell settling of the cell suspensions were studied. A photomicrographic technique (100 x magnification) was used to record the characteristics of cell aggregating phenomenon. Viscosity of the suspensions was measured by the GDM Viscometer, shear range 0.1 to 20 sec<sup>-1</sup>.

At the lower concentrations of fibrinogen, 0.6 grams percent or less, red cell aggregation and settling were within normal limits (0-6 mm/hr). Cell suspensions in fibrinogen solutions of 0.9 to 1.5 grams percent showed increasing rates of settling (40 mm/hr). The degree and rate of aggregation were markedly increased throughout the fluids as cells would first adhere face to face to form rolls (rouleaux) and the 5 to 10 cell rolls would then aggregate into small clusters. In suspensions of 1.5 grams percent fibrinogen and higher, aggregates formed rapidly and in large proportion, while rates of settling markedly decreased (15-20 mm/hr). Casson plots of shear stress versus shear rate were derived from viscometric data. All suspensions showed the characteristic curves of shear thinning fluids. Suspensions with fibrinogen concentrations from 0.3 to 0.9 grams percent revealed no apparent yield value or structural change during shear. Those suspensions with fibrinogen concentrations greater than 0.8 grams percent demonstrated a marked shift in slope at shear rates of 1-2 sec<sup>-1</sup>, strongly suggesting a marked structural change in fluid. Yield values for these fluids may be determined from data taken at low shear rates.

10. Detailed Characteristics of the Flow of Blood in Vitro

GEORGE BUGLIARELLO and JOHN W. HAYDEN\*, Carnegie Institute of Technology, Pittsburgh 13, Pennsylvania.

A microcinematographic study at 3000 frames/sec. of the motion of individual erythrocytes in human blood of various hematocrits flowing under macroscopically steady conditions through horizontal glass capillaries  $35 \mu$  to  $84 \mu$  in diameter has yielded direct quantitative information on the velocity profiles and other flow characteristics.

The velocity profiles were found to be affected by the unsteadiness and non-uniformity displayed by the flow on a microscopic scale, as well as by sedimentation effects, so that the flow features could be described in statistical terms only. The mean local velocity profiles were in all cases blunter than a laminar Newtonian velocity profile, and also blunter than a power-law non-Newtonian profile based on constant-shear concentriccylinder viscometer data. In general, other factors being equal, the degree of bluntness i) increased with hematocrit, ii) decreased as flow rate increased, iii) decreased as tube diameter increased.

Near the wall of the tubes, an average cell-free layer could be defined, which decreased in thickness as hematocrit increased, but was not appreciably or consistently affected by flow rates, except at the lower hematocrits and flow rates.

The presence of the layer was in agreement with the viscosity profiles obtained by differentiation from the velocity profiles. The viscosities increased rapidly toward the core of the flow from low values near the wall which were close to the values for plasma.

Monday Evening, 8:00 - 10:00 P.M.

Technical Session. Chairman, DR. D. J. PLAZEK

#### 11. Viscoelastic Properties of Dilute

Polyisobutylene and Polystyrene Solutions

NICHOLAS W. TSCHOEGL, J. E. FREDERICK and JOHN D. FERRY, University of Wisconsin, Madison, Wisconsin.

The storage and loss components of the dynamic shear modulus have been measured over a wide range of frequencies with the Birnboim-Ferry apparatus for dilute solutions of several polyisobutylenes and polystyrenes. Most of the polymers had sharp molecular weight distributions; the molecular weights ranged from 62,800 to 1,700,000. Concentrations varied from 1% to 4% and solvent viscosities from 0.2 to 100 poise. The frequency dependence in the polymers of lower molecular weight conformed very closely to the theory of Zimm, though the molecular weights calculated by this theory from the experimental data were somewhat too high and the discrepancy increased with polymer concentration and molecular weight. However, the samples with highest molecular weight conformed more closely to the theory of Rouse. This behavior is discussed in terms of a reformulation of the molecular theory based on a recent treatment by Kästner. The effect of molecular weight distribution was also investigated in a polystyrene with a distribution of the "most probable" form.

12. The Viscosity of Dilute Solutions of Linear Associative Colloids

WARNER L. PETICOLAS, International Business Machines Corporation, San Jose 14, California.

ABSTRACT: Although a great deal of work has been done on the viscosities of dilute solutions of polymers, very little work has been done on the viscosity of dilute solution viscosity of linear associative colloids (i.e., linear micelles). A large number of soaps, dyes and steroids are known to form rod-like colloids above certain critical concentration in dilute solution. The understanding of the rheological behavior of these linear colloids has been hampered in the past by the fact that both the average molecular weights and molecular weight distribution change with the monomer concentration. Recently, we have been able to calculate the molecular weight distribution of rod-like micelles as a function of concentration and temperature from a lattice gas model. Using this theory together with the theory for the dilute solution viscosity of rigid rods, it is possible to calculate the zero-shear rate viscosity of rodshaped colloids as a function of concentration and temperature. Comparison of predicted and measured viscosity behavior of a number of dyes and soaps are presented.

#### The Dynamic Mechanical Properties of Poly 4-Methyl Pentene-1

R. W. PENN, W. R. Grace & Co., Research Div., Clarksville, Maryland.

The dynamic mechanical properties of poly-4-methyl pentene-1 have been measured in torsion in the temperature range from 25° to 160°C at frequencies from 10<sup>-3</sup> to 10 cycles per second. Two transitions are found. The first, with a peak at 30°C at 1 cycle per second, is associated with the glass transition. The second, a lesser, very broad peak which appears between 100 - 130°C at 1 cycle per second may be attributed to crystallite relaxation. The dynamic compliance-frequency data can be superposed by the method of reduced variables for temperatures up to 100°C. The temperature dependence of the shiftfactors follows the WLF equation. Above this temperature, superposition can be achieved by applying simultaneous horizontal and vertical shifts to both components of the dynamic compliance. When the vertical shift is permitted the range of applicability of the WLF equation is extended to 160°C.

#### 14. An Instrument for Measuring Torsional Creep and Recovery

## DONALD J. PLAZEK, Mellon Institute, Pittsburgh 13, Pennsylvania.

A torsional creep instrument has been built to measure the viscoelastic properties of soft polymeric solids and liquids in the long time region. Special consideration was given to minimizing friction and undesired residual torques which introduce uncertainties in recovery measurements. The essential features are a reasonably low moment of inertia rotor which floats on a liquid and a torsional inductive drive. During measurements on crosslinked systems, gels, and viscoelastic liquids the only known undesired influences which exist are the viscous drag and the surface tension of the supporting liquid medium. In many cases these can be shown to be negligible. For viscoelastic liquids with much lower viscosities, centering is necessary and is accomplished using a pin which rides in a ring jewel. Illustrative results from measurements on different kinds of samples will be shown.

#### Session No. 1

#### Tuesday Morning, October 30

$$9:00 - 12:15$$

Technical Session on Polymer Entanglement. Chairman, Dr. N. NAKOJIMA

15. On the Question of Molecular Entanglements in Concentrated Polymer Solutions

W. PHILIPPOFF, Esso Research & Engineering Co., Linden, New Jersey.

The concept of entanglements between polymer molecules in concentrated solutions appears to be only a relatively minor factor in accounting for their viscoelastic behavior. There is undoubtedly some effect, based on flow birefringence experiments performed by different laboratories; especially, there is an effect on the change in the extinction angle with rate of shear. However, filtering of these solutions through a fine sintered glass filter removes these effects completely without influencing the viscosity. This would rule out such effects as a major influence in the viscosity of concentrated solutions. The change in viscosity with rate of shear over a large range of concentrations and a wide range of rate of shear does not show any break: the behavior of the concentrated solutions merge smoothly into the ones of viscosity only 6% greater than the solvent viscosity - the effects being only accentuated by increasing concentration. The flow birefringence behavior described by the stress-optical coefficient similarly does not show any break between  $\sim 30\%$  concentration and such low concentration that the molecules are essentially independent of each other. All these facts lead to the statement that the entanglements during the solution of a solid polymer into a concentrated solution undoubtedly occur, but they are a minor complication and do not lead to the well known enormous increase in the viscosity with concentration and the occurrence of elastic effects.

 Study of Entanglement of Polymers in Solution by Viscosity Measurements

SAMUEL H. MARON and THOMAS T. CHIN, Dept. of Chemistry, Case Institute of Technology, Cleveland 6, Ohio.

NOBUYUKI NAKAJIMA, W. R. Grace & Co., Research Div., Clarksville, Maryland.

In the previous paper was described a study of the flow behavior of solutions of a sample of polystyrene in five solvents in both the Newtonian and non-Newtonian flow regions at temperatures between 20° and 50°C. The concentration range covered was approximately  $0 \cdot 20\%$  by weight. In this paper we present a study of solutions of three samples of polymethyl methacrylate at 30°C in three solvents. The concentration range covered was approximately  $0 \cdot 16\%$  by weight.

These observations indicate that chain entanglement in solution is not probable, and the polymer chain curls on itself.

#### 17. Viscosity and Thermodynamics of Moderately Concentrated Polymer Solutions

R. SIMHA, Dept. of Chemistry, Univ. of Southern California, Los Angeles 7, California.

Most of the work on viscosity has been directed towards highly dilute solutions or bulk systems. In the course of investigating hydrodynamic and thermodynamic factors in the intermediate range of cencentrations we have been led to consider the existence of corresponding state  $\xi$  (e, T) relations where  $\eta$ , c, T represent suitable reduced viscosity, concentration and temperature variables respectively. On examining as a first step a single polymer (polystyrene) over a wide range of molecular weights in good and poor solvents. two conclusions are reached. First, universal  $\eta$  — c curves can be defined and the scale factors characteristically related to molecular weight and solvent. Secondly, in the  $\theta$ -solvent, the concentration factor is proportional to c<sub>crit</sub>, the solute concentration for phase separation.

We have studied also extremely poor solvents, T < 0. The Mark-Houwink exponent decreases slightly below 0.5, as is expected. Moreover, at  $T = T_{crit}$ , the volume fraction of polymer in the average coil at infinite dilution is approximately equal to the volume fraction  $v^2_{crit}$  of polymer. This suggests some tentative conclusions regarding the conditions for phase separation.

18. Viscoelastic Properties of Concentrated Solutions of Polyisobutylene in Cetane.

JOHN R. RICHARDS, KAZUHIKO NINOMIYA, and JOHN D. FERRY, University of Wisconson, Madison, Wisconsin.

Dynamic mechanical properties and shear creep compliance have been measured for five polyisobutylenecetane solutions ranging in concentration from 68.0% to 91.8%, as well as the pure polymer, to define the viscoelastic properties in the lower transition and terminal zones of the relaxation spectrum as functions of temperature and concentration. The dependence of the monomeric friction coefficient for segmental polymer motions on temperature and concentration, obtained from the viscoelastic data in the transition zone, is identical with that for the friction coefficient of the diluent cetane derived from diffusion measurements. The dependence of relaxation times in the terminal zone on temperature differs in a manner which can be interpreted formally by a small heat of dissociation of entanglement coupling points, which increases with decreasing polymer concentration. The dependence of terminal relaxation times on concentration is consistent with an average entanglement spacing inversely proportional to polymer concentration, a conclusion also reached from the depth of the minimum of the loss tangent as a function of frequency. The steady-state compliance is inversely proportional to polymer concentration.

#### 19. Theory of Viscoelasticity in Temporarily Crosslinked Polymers

PART 1: Treatment in a System with Single Relaxation Time

SHIZUO HAYASHI, Dept. of Physics, Faculty of Liberal Arts & Education, Gumma University, Maebashi, Japan.

A theoretical investigation about the viscoelastic properties of temporarily crosslinked polymers is presented using the concept of slipping of chains. Due to the slipping of chains, the deformation of chains is, in general, different from that of the system. Then we can introduce two kinds of deformation tensors, one is "observable" deformation tensor" of the system and the other is "inner deformation tensor" of chains.

In case of stationary simple elongation, retractive force decreases exponentially and the decrease of retractive force originates in the decrease of cross-sectional area. In stationary simple shear deformation, normal stress appears which relates to Weissenberg effect. The relation between tensile and shear viscosity coefficients satisfied so called Trouton's relation. At constant deformation stress nearly decays expoentially with time. For periodic shear deformation, normal stress also appears.

#### PART 2: Relaxation Spectrum and Steady Flow Viscosity

In order to explain the box type spectrum of high polymeric substances from a molecular theoretical standpoint we use a temporarily crosslinked network model, in which crosslinkages are created by secondary valancy of segments or by entanglement of linear polymers. Using the concept of slipping of chains for the said network model we want to obtain slipping theory of relaxation phenomena containing many relaxarion time. If we consider a motion of linear polymer molecule composed of many chains (chain means a part of linear polymer molecule between adjacent crosslinkages) we can consider many modes of motion of polymer molecule, therefore many different kinds of slipping processes of chains are suggested corresponding to the modes of motion. Assuming that each chain is Gaussian, we set up Rouse model corresponding to macro-Brownian motion of polymer molecule, in which chain corresponds to spring and friction of chain to bead without mass, this model is, however, a model for phenomena of pretty long time scale.

#### 20. The Effect of Molecular Weight Distribution on Polymer Rheology Near the Entanglement Region

ROGER S. PORTER and JULIAN F. JOHNSON, California Research Corporation, Richmond, California.

Viscosities have been measured on concentrated, > 10% polyisobutene solutions of defined broad molecular weight distribution,  $\frac{Mw}{Mn}$  >1.8. Equivalent data have been obtained for polyisobutene solutions containing the same concentrations and average molecular weights but of limiting narrow distributions,  $\frac{Mw}{Mn}$  > 1.02. The fractions and distribution determinations were derived from analytical and large-scale column chromatographic fractionation procedures. Viscosities were measured as a function of temperature and shear, to  $> 3 \ge 10^5$  seconds <sup>-1</sup>, for several polyisobutene concentrations. Measurements were made at low shear in capillary viscometers and with a rotational concentric cylinder viscometer at high shear rates. The effect of molecular weight distribution on reduced variables, flow activation energy, and the magnitude of non-Newtonian flow is evaluated for conditions near the entanglement transition. Results are compared with theory and with new interpretations of published data on other polymers.

#### Session No. 2

#### Tuesday Morning, 9:00 - 12:15

Technical Session on Mechanics of Continua. Chairman, Dr. J. L. ERICKSEN

21. A Recursive Approach to the Theory of Slow, Steady-State Viscoelastic Flow

W. E. LANGLOIS, International Business Machines Corporation, San Jose Research Laboratory, San Jose, California.

The slow, steady-state motion of an arbitrary Rivlin-Ericksen fluid is considered. By perturbing about a state of rest, equations governing the first, second, and third order flow fields are developed in such a way that the second order theory uses explicitly the first order results, etc. The first order equations are those of creeping viscous flow; the second order theory introduces two parameters associated with the viscoelasticity of the fluid; the third order theory brings in three more. Fluid inertia is neglected throughout. To facilitate application, the flow equations, derived in Cartesian tensor notation, are rewritten in general tensor notation; the equations are explicitly given both for cylindrical and spherical coordinate systems.

Several elementary flow problems of technological importance are solved: flow between parallel plates; the Poiseuille problem; helical flow in an annular region; torsional flow between discs.

It is shown that, in a rather fundamental sense, there is no fluid-film lubrication theory of viscoelastic flow. The components of stress differ among themselves, and vary across the film, by amounts comparable with the lubrication pressure. Hence, boundary conditions cannot be satisfied and it must be concluded that viscoelastic lubrication presents a fully three-dimensional flow problem.

22. Some Interesting Aspects of General Linear Viscoelastic Deformation

W. G. GOTTENBERG and R. M. CHRISTENSEN, Space Technology Laboratories, Inc., Redondo Beach, California.

Considerable interest is presently being shown toward the use of the general theory of linear viscoelasticity. in the solution of three-dimensional problems with time dependent material behavior. Adequate experimental techniques have not yet been developed to measure the material characteristics for use in a general analysis. However, in anticipation of these developments, it is interesting to consider the possible limits of variation of the parameters used in the theory of isotropic, linear viscoelasticity to describe the stress-strain characteristics of a material. A convenient form for these parameters is that of complex functions of frequency which relate the stress-strain behavior of the material in distortion and dilatation. Making use of the simple relations connecting these complex functions of frequency, their behavior in the limits is examined permitting some interesting conclusions to be drawn, particularly in the case of the complex Poisson's ratio. Hypothetical values of the real and imaginary parts of the complex shear and bulk moduli are assumed and the corresponding derived functions are shown to illustrate some of the results.

23. On Viscometric Flows of Simple Fluids

WALTER NOLL, Carnegie Institute of Technology, Schenley Park, Pittsburgh 13, Pennsylvania.

Recent investigations of the kinematics of "motions with constant stretch history" (also called "substantially stagnant motions") lead to an efficient treatment of "viscometric flows" in simple fluids. These viscometric flows make up the class of steady flows characterized by the property that the behavior of an incompressible simple fluid in such flows is determined by the shear stress function (or, equivalently, the shear dependent viscosity) and two normal stress functions. The most important viscometric flows are "curvilineal flows", which include almost all special flows that have ever been studied in connection with non-Newtonian fluids.

The method presented here is illustrated by an analysis and interpretation of experiments with a cone and plate viscometer.

24. PART 1: The Exact Solution of General Plane Strain Deformation of an Incompressible Neo-Hookean Body

P. J. BLATZ, California Institute of Technology, Pasadena, California.

The exact solution of the general plane strain deformation of an incompressible neo-Hookean body has been formulated. It develops that the displacement gradients of the undeformed body with respect to coordinates fixed in the deformed body are eigenvectors of the biharmonic operator. Several applications are discussed.

PART 2: General Formulation of the Homogeneous Thermomechanical Deformation of an Elastomeer

The problem of formulating the homogeneous thermal and mechanical deformation of an elastic body is considered. The first and second laws of thermodynamics are cast into a form in which the work done on the body is expressed in terms of stretch invariants and derivatives of the strain energy with respect to the stretch invariants. Some applications are discussed. Possible extension to a general thermomechanical field are considered.

#### Session No. 1

#### Tuesday Afternoon, 1:30 – 4:00

Technical Session. Chairman, DR. W. H. BAUER

#### 25. The Rheology of Primary and Secondary Consolidation

R. L. SCHIFFMAN, Rensselaer Polytechnic Institute, Troy, New York.

The theory of primary and secondary consolidation for fine grained soils is based upon the mechanics of a two phase system. The soil-water system consists of incompressible solids and incompressible fluids. The soil structure is considered to be elastic (primary consolidation) or visco-elastic (secondary consolidation).

This paper discusses the mechanical foundation of the theory of consolidation. The mechanical theory is reviewed and its physio-chemical basis is discussed. A distinction is made between primary and secondary consolidation based upon the viscosity of the soil structure.

General linear theories of secondary consolidation are presented in terms of rheological models. The theories presented are built-up from the observed and/or postulated rheological behavior of the soil components.

Non-linear theories are discussed in terms of physical implications and deviations from linear behavior.

Theories of primary and secondary consolidation for partially saturated soils are briefly discussed.

#### 26. Viscosity and Glass Transition Behavior of Polymer-Diluent Systems

L. J. GARFIELD and S. E. PETRIE, Eastman Kodak Co., Rochester, New York.

Recent theories of Ferry and Stratton, Fujita and Kishimoto, and Bueche and Kelley, based on free volume considerations yield relationships describing the concentration dependence of the glass transition temperature and of the viscosity of polymer-diluent systems. These theories, which permit the prediction of these properties over wide ranges of concentration from a knowledge of the expansion coefficients and glass transition temperatures of the pure polymer and of the diluent, are shown to be basically equivalent.

New thermal and viscocity data are presented for a number of polymer-diluent systems which provide a direct experimental test of the relationships and thereby support, in general, the underlying assumptions of these theories.

The glass transition phenomenon in monomeric liquids, a somewhat unfamiliar concept, is as much a determinant of their rheological behavior as it is observed to be in the case of amorphous polymers. Glass transitions of several diluents have been detected by differential thermal analysis, and the temperatures at which they were observed are given.

#### 27. The Determination of Weight Average Molecular Weight from Melt Rheology Studies

J. R. KNOX, AviSun Corporation, Marcus Hook, Pennsylvania.

E. B. Bagley has described a procedure for determination of  $M_w$  of polymers from their melt flow characteristics. The method is based on the measurement of the recoverable shear strain from the elastic portion of the end correction, and the use of Hooke's law in shear. Only two samples were characterized in this manner a linear and a branched polyethylene. We have applied this technique to polypropylene and have found it to be valid, provided two additional corrections are made to the measured pressure drop. One of these corrections is that due to the pressure drop across the barrel, which is a function both of the radii of the capillary and the barrel, and of the distance the plunger is from the capillary entrance. The second correction is that due to the compressibility of the melt, which is not negligible at high pressures. It is found that the apparent compressibility is inversely proportional to the square root of the length to diameter ratio.

28. Experimental Determination of the Molecular Weight Distribution of Linear Polymers from Stress Relaxation after Steady Flow

WARNER L. PETICOLAS, International Business Machines Corporation, Monterey and Cottle Road, San Jose 14, California.

Measurements on stress relaxation after steady flow in the melt on Ziegler-type polyethylenes are reported. The data has been analyzed by the method of Menefee and Peticolas to obtain an estimate of the molecular weight distribution. Comparison of the distribution curves obtained from rheological methods with those obtained from chromatographic fractionation shows that for the polyethylene samples tested, very close agreement for the two methods is obtained. Data from other laboratories on other polymers has also been examined with less satisfactory results. A summary of the advantages and disadvantages of characterizing polymers by this method in comparison with other methods is presented.

#### Session No. 2

#### Tuesday Afternoon, 1:30 - 4:00

Technical Session. Chairman, DR. D. J. PLAZEK

29. Determination of Transient Thermal Stresses in a Slab with Temperature — Dependent Viscoelastic Properties

JOHN S. HUMPHREYS and CHARLES J. MARTIN, Avco Corporation, Research and Advanced Development Div., Wilmington, Massachusetts.

The general problem considered is that of predicting thermal stresses in a thin layer of material whose mechanical properties vary with both time and temperature, due to temperature changes on the exterior. The analytical development followed falls within the framework of linear viscoelasticity and is based on recent work by R. Muki and E. Sternberg and by E. H. Lee and T. G. Rogers. The effect of temperature variation is accounted for using the Williams-Landell-Ferry logtime-temperature superposition hypothesis.

A specific case is worked through for a rigid aluminum slab covered by a layer of an epoxy resin heatshield material. Stress relaxation curves as a function of temperature are presented, determined by averaging the results of a series of relaxation experiments on this material. Then, using a prescribed exterior temperature drop and the heat conduction equation to determine a temperature distribution, inplane thermal stresses are found numerically on a high-speed computer. The results of direct elastic calculations and of simplified calculations using constant-temperature properties are compared with the more complete calculations including the variations of properties with temperature.

 Determination of Non-Flow Shrink Ratio in Oriented Fibers

D. PREVORSEK and A. V. TOBOLSKY, Textile Research Institute and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey.

A method for the determination of non-flow shrink ratio of oriented fibers is described. The dimensional changes accompanying the transition of an oriented semi-crystalline structure into an amorphous random coil state are shown for various polymers. The average number of segments per crystalline sequence, calculated by means of expressions derived by Tobolsky, is in good agreement with the estimates of crystallite sizes obtained by x-ray methods. Irradiation and fatiguing have a pronounced effect on fiber shrinkage, both in the magnitude of shrinkage and in the temperature range where the shrinking process terminates.

31. Viscoelastic Fluids: Development of a Simple Constitutive Equation

J. L. WHITE and A. B. METZNER, University of Delaware, Newark, Delaware.

A brief review of the available constitutive equations shows that most do not predict the properties of real materials correctly or are of such overriding complexity that they cannot be applied to the solution of any real problems.

A new constitutive equation in which all significant parameters may be evaluated from only two sets of experiments is developed. Under conditions of laminar shearing flow this equation is identical to Weissenberg's theory of viscoelasticity. The results obtained in this analysis should be regarded as a verification and extension of Weissenberg's theory. However, instead of working by analogy to the behavior of an elastic solid the analogy has been derived and the final form of the constitutive equation allows for extension to more complex problems.

Comparison with the available experimental results, while not entirely conclusive, indicates this equation may predict correctly the behavior of nonpolar materials and that it may work well on polar systems in the range of high deformation rates, i.e., the region of primary industrial interest. Several problems are worked to illustrate the use of such constitutive equations.

32. Velocity Profiles for Two-Dimensional Flow of

Milling Yellow Suspensions, as Determined from Birefringence Measurements

KEH-CHANG LIU and FRED N. PEEBLES, Dept. of Chem. & Metallurgical Engr., the University of Tennessee, Knoxville 16, Tennessee.

Use of the strain-optics laws for suspensions and the equation of continuity with birefringence measurements allows quantitative determination of the velocity profiles for steady, two-dimensional flow. This method of flow measurement was applied in the investigation of laminar flow of Milling Yellow dye suspensions in a converging channel, a diverging channel, a free-jet and a wall-jet. Satisfactory agreement between the measured velocity profiles and the profiles predicted from the equations of motion was found.

The method of determining the velocity profiles from birefringence data makes use of only the isochromates, and hence allows determination of the direction of principal strain rate independent of the isoclinic measurements. Comparisons of the directions of principal strain rates as inferred from the isochromates for the twodimensional flow fields with those indicated by measurement of the isoclinics will be presented and discussed in terms of prevailing theories on optical behavior of suspensions.

#### Session No. 1

#### Wednesday Morning, October 31

#### 9:00-12:15

#### Technical Session. Chairman, DR. W. L. PETCOLAS

33. A Dimensional Approach to Colloid Rheology

IRVIN M. KRIEGER, Dept. of Chemistry, Case Institute of Technology, Cleveland, Ohio.

The viscosity of a suspension of rigid spherical particles in a Newtonian medium can depend on many factors; a reasonably complete listing includes nine independent variables, all expressible dimensionally in terms of mass, length and time. The governing rheological law involves therefore seven dimensionless groups, some of which are already familiar, such as the reduced viscosity and the volume fraction. Of special interest are a "colloid number" which expresses the ratio of the rate of shear to the rotational Brownian movement, and an internal Reynold's number. Experimental measurements of non-Newtonian flow, thixotropic breakdown and the onset of turbulence are discussed from the viewpoint of the dimensional analysis.

#### 34. Rotational Flow Generator for Rheological Studies

W. H. HOPPMANN II, and C. E. MILLER, P.S.C., Rensselaer Polytechnic Institute, Troy, New York.

The paper presents a description of apparatus developed for the purpose of making a fundamental investigation of the flow in a cone-plate type rotational flow generator. It permits a study of lines of flow and rotational resistance for cones having semi-vertex angle from 0° to 90°. The usual viscometer limits the angle to less than 4°. Of special interest is a dynamometer capable of measuring extremely low torques. An optimum design of circuitry for resistance wire strain gages has been used for the purpose. Rotational speed control device and flow visualization techniques are fully described. Particular attention has been given to the design of vertical shafts which rotate the cone and the plate. The rotational system includes contact bearings, a vertically fixed shaft, and a vertically adjustable shaft. The latter makes it possible to adjust precisely the distance between the cone and the plate. Torque and angular velocity data are presented and comparisons are made with data existing in the literature. Also, there are included in the paper, photographs of fully developed flow lines which show interesting phenomena not reported upon before, as far as is known. Finally, some critical analysis is made of the flow equations in the light of experience gained with the apparatus.

#### 35. Mechanical Behavior of Raw Rubber in the Mooney Viscometer

KAZUHIKO NINOMIYA\* and SHUSAKU IDO, Japan Synthetic Rubber Co., Yokkaichi, Japan.

Time-dependent mechanical data were obtained for different kinds of raw rubber, both synthetic and natural, by using a Mooney viscometer. From the data obtained by rotating the rotor at a constant rate of rotation, it was found that the shearing stress in Mooney units could be approximately expressed by an exponential equation, irrespective of the species of rubber. Stress relaxation following sudden cessation of the rotation of the rotor at any given rotation period was found to be inversely proportional to the square root of the time.

The molecular weight — and the temperature dependence and the effects of plasticizer and filler were experimentally investigated for SBR samples.

\*Present address: University of Wisconsin, Madison, Wisconsin

#### The Extension of Unoriented Nylon 66 Filaments

MALCOLM F. BENDER and MALCOLM L. WILLIAMS, The Chemstrand Research Center, Inc., Durham, North Carolina.

The orientation of nylon 66 filaments usually occurs by a cold-drawing process. This process has been described, in phenomenological terms, by the adiabatic theory of cold-drawing of Müller and Jackel and of Marshall and Thompson. To explain the process in structural terms, we have performed tensile creep experiments under low loads in an atmosphere of controlled temperature and humidity. The extension first increases uniformly with long time; then there is a rather sharp yield point where the extension quickly increases by a large amount. The location of the yield point on the log time scale is quite sensitive to environmental conditions. Phenomenologically, the behavior is similar to the propagation of Lüder's bands in metals. The results are discussed in terms of both the adiabatic theory and the recent crystal defect model of nylon 66 proposed by Zaukelies.

#### The Rheology of Polyelectrolytes III – Experimental Determination of the correlation of M<sub>T</sub> with Other Average Molecular Weights

JOHN G. BRODNYAN and E. L. KELLEY, Research Laboratories, Rohm and Haas, Bristol, Pennsylvania.

It has been shown that plots of  $\eta/\eta_0$  versus log D, where  $\eta$  is the viscosity at the rate of shear D and  $\eta_0$  is the low rate of shear Newtonian viscosity, can be made to coincide for many polymer systems by shifting along the time, i.e., D, axis. Bueche has shown that a standard curve obtained by the above technique can be defined in terms of a relaxation time;  $\tau$ , given by:

#### $T = 12 \eta_0 MT/\pi^2 RTC$

The exact molecular weight average which correlates with  $M_{\rm T}$  is unknown.

In the investigation reported here, whole polymers of poly (acrylic acid) of different molecular weights were combined and the flow curves of the mixtures were measured over a wide range of rates of shear. Utilizing a mathematical technique developed by Peticolas and Menefee, we found that the relaxation time is apparently determined by the Z + 1 average molecular weight; and the high rate of shear Newtonian viscosity,  $\eta_{\infty}$ , is apparently determined by the Z average molecular weight. However, some experimentally determined values of  $M_{TT}$ are shown to be concentration dependent for C > 0.62g. ml.<sup>-1</sup> and in all cases lower than  $M_{z+1}$ . This implies that only melts or very concentrated solutions would give the correct value of M<sub>T</sub>. This is in contradiction to Bueche's results with rubbers. Data on melts also show experimentally determined values of  $M_T$  which are lower than M<sub>z+1</sub> and even M<sub>w</sub>. Thus, one questions the reliability of this technique for obtaining absolute molecular weights.

#### 38. The Method of Force (or Stress) Circuit Diagrams in Rheological Applications

NICHOLAS W. TSCHOEGL, University of Wisconsin, Madison, Wisconsin.

A method is presented which allows the analysis of mechanical systems in a manner which is analogous to the analysis of electric circuit diagrams. The force (or torque) circuit diagram setting forth the essential features of the mechanical system by the use of a set of conventional symbols may be drawn up by inspection, simply tracing the actual connection of the mechanical elements. A graphical method is available for converting the mechanical to the equivalent electrical circuit diagram.

Rheological models may be treated similarly, regarding them as parts of stress circuit diagrams. Session No. 2 - 9:00 - 12:15

Technical Session on Mechanics of Continua. Chairman, Dr. H. MARKOVITZ

39. An Experimental Method to Measure the Strain Energy Function "W"

A. SAN MIGUEL, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

A large class of materials such as rubbers may be reasonably described by a particular constitutive equation.

The experimental approach used in this paper is essentially to measure the principal strains at a point on the flat end surface of a circular cylinder subjected to a biaxial internal radial pressure.

The point principal strains and their corresponding directions are measured in a low reinforcing surface coating that exhibits birefringence upon deformation. This coating technique measures the two dimensional surface strains and their corresponding directions during loading. The third principal strain, which is normal to the free surface, is known from the longitudinal contraction of the circular cylinder. By varying the internal pressure or investigating neighboring points, the specified gradients can be determined. The point principal stresses are computed directly from the equilibrium equation.

Finally, the strain energy function is assumed to be a function of "three" invariants. The form of the strain energy function is empirically described for an elastomer loaded with crystal particles.

40. Viscoelastic Stress Analysis of a Spinning Hollow Circular Cylinder with an Ablating Pressurized Cavity

A. H. CORNELIUSSEN, Sperry Rand Research Center, Sudbury, Massachusetts, E. F. KAMOWITZ, Boston, Massachusetts.

E. H. LEE, Stanford University, Stanford, California and J. R. M. RADOK, Interscience, Inc., Vienna, Austria.

The viscoelastic stress and deformation analysis of a hollow circular cylinder, spinning about its axis, and subjected to internal pressure on the circular cylindrical ablating cavity is treated. Particular features of this problem: the ablating boundary varying with time, and the centrifugal body force due to spin, introduce difficulties which prevent the direct use of standard procedures of the theory considered: linear viscoelasticity with infinitesimal deflections. A method involving separate integration with respect to the time and space variables gives the solutions for particular viscoelastic materials represented by models with a finite number of springs and dashpots. A general method of solution is also developed which can be applied to general linear viscoelastic materials characterized by integral operators or the differential operator forms associated with model representation. Expressions for stress and deformation components are obtained for particular materials, and a selection of these is exhibited graphically. General and particular properties of the solutions are discussed.

#### 41. Thermal Feedback in Liquid Flow

I. J. GRUNTFEST, General Electric Co., Philadelphia, Pennsylvania.

A new dimensionless number or similarity criterion relating to rheological phenomena is developed from a consideration of the energy equations for the plane shear of viscous liquids. This parameter defines the range of stress in which Newtonian behavior is possible and provides an upper limit for the stability of laminar flow which is in general agreement with experiments.

As would be expected the new parameter increases monotonically with Reynolds number but it also includes additional properties of the fluid. Furthermore, the relevant length is unambiguously defined and time is introduced in a natural fashion.

In the enalysis the relevant instability is shown to arise from regenerative thermal feedback; that is, the initial viscous dissipation raises the temperature, decreasing the viscosity which increases the dissipation. The new parameter can be understood physically as the ratio of the thermal relaxation time of the sample of material undergoing shear to the time which would be required for the temperature to become infinite if the shearing process were ideally adiabatic.

This computation is relevant to the evolution of molecular theories of liquids because it permits the isolation of stress and time dependent effects in viscosity which are due merely to thermal feedback from those actually due to molecular orientation or deformation.

42. A theoretical and experimental investigation of finite deformation in viscoelastic media

PART 1: A Theory of Solids with Strain Energy and Memory

B. BERNSTEIN, E. A. KEARSLEY and L. J. ZAPAS, U. S. Dept. of Commerce, National Bureau of Standards, Washington 25, D. C.

A type of constitutive equation is discussed, in which memory functions are combined with strain energy functions. A theory is subsumed which should give an approximation to the general case for some range of finite strain, and which may be readily checked experimentally. It is also shown how this theory may be subsumed from the theory of Green and Rivlin. The problem of simple extension is then solved and the relation between load and extension is obtained for stress relaxation and equilibrium situations. This relation gives rise to two material parameters which do not appear in the stress-relaxation equations derived from the linear theory of infinitesimal viscoelasticity: The latter contains only one material function, whereas the former contains two material functions and a material constant.

PART 2: Stress-Relaxation Experiments and Comparison with Theoretical Predictions

#### L. J. ZAPAS, B. BERNSTEIN and E. A. KEARSLEY.

Simple extension stress-relaxation data have been obtained on plasticized PVC, on polyisobutylene (B-140) at 25°C and on vulcanized butyl-rubber at -50°C, at extensions up to 50% elongation.

A comparison with the theoretical predictions is presented. Simple extension equilibrium data were obtained on vulcanized rubber at 25°C and were correlated with the predictions of our theory for infinite times.

#### PART 3: A Theory of Fluids with Strain Energy and Memory

E. A. KEARSLEY, B. BERNSTEIN, and L. J. ZAPAS.

By generalizing the theory of viscoelastic solids a theory of fluids is developed in which the concepts of finite elasticity are combined with the notion of memory functions to give a simple constitutive equation without a preferred configuration, but with elasticity. Some simple steady flows are worked out and the consequences of this constitutive equation are examined.

#### Wednesday Afternoon – 1:30 – 4:00

Technical Session. Chairman, DR. E. B. BAGLEY

#### 43. A Comparison of Streaming Birefringence and Rotary Strain Birefringence Measurements

W. PHILIPPOFF and S. J. GILL, Esso Research and Engineering, Linden, N. J. and University of Colorado, Dept. of Chemistry, Boulder, Colorado.

A series of measurements on polyisobutylenes, solutions of polystyrene, and solutions of carbonmethylcellulose have been made using the basic method of flow (or streaming) birefringence and the newer method of rotary strain birefringence. This later technique does not approach the high accuracy of the flow technique but allows one to test the effect of amplitude and frequency of strain upon the induced birefringence.

In the Newtonian region, where angular measurements are at 45°, excellent correlation of birefringence is found for both techniques. For Non-Newtonian behavior the angular settings agree within a relatively large experimental error, and the birefringence gives good correlation at lower shear rates between 1-20 sec.<sup>-1</sup>. The birefringence is observed to be directly proportional to a geometrical factor of straining for the rotary birefringence technique.

#### 44. An Unusual Mechanism of Extrusion of Polytetrafluorethylene at High Temperature and Pressure

J. P. TORDELLA, Electrochemicals Dept., E. I. duPont de Nemours & Co., Inc., Wilmington, Delaware.

An unusual method was discovered for extrusion of polytetrafluoroethylene (PTFE) at temperatures above its normal, atmospheric pressure melting point but by a process which does not involve laminar, viscous flow. The method depends on the large elevation of the melting point of PTFE by pressure. Consequently, at high extrusion pressure unmelted polymer may be forced into capillaries at temperatures in excess of the atmospheric pressure melting point but below the actual melting point. Melting then occurs within the capillary and is accompanied by sintering of the powder to a tough filament. Rates of extrusion are many times larger than the limit imposed in laminar flow by onset of melt fracture. The effects of variation of temperature, pressure, capillary dimensions, and polymer pretreatment are given.

45. Die Wall Restriction on the Elastic Shear Deformation in Viscoelastic Flow of Polymer Melt

TEIKICHI ARAI — Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan.

Die wall restriction on the elastic shear deformation in steady flow is discussed. Experimental data on the Barus effect of polymer melts are cited. In a round tube extrusion, an access extrusion pressure which is unconnected with the mechanical equilibrium in the tube is formally calculated from the so-called end effect. The major part of this pressure contributes to an elastic solid type shear deformation of the flowing viscoelastic liquid in the reservoir and tube. But, when the melt flows out of the tube, the internal stresses are released from the die wall restriction to enlarge the ratio of the crosssectional area of the extrudate to that of the die. This value of the Barus effect with a number of short tubes is given as a function of the die wall elastic shear stress which is calculated by using the Couette's corrected tube length as the effective length. Accordingly, it may be said that the shear modulus in steady flow must be a function of elastic shear stress. Furthermore, the results with polyethylenese of different molecular weights show that the modulus tends to increase with molecular weight.

46. Flow Behavior of Dimethylpolysiloxane Fluids in a Cone-Plate Viscometer

W. H. BAUER and A. P. FINKELSTEIN, Rensselaer Polytechnic Institute, Troy, New York.

Flow studies were made, in a cone-plate viscometer, of dimethylpolysiloxane fluids with nominal viscosities of 10, 30, 60 and 100 stokes, at several temperatures and under different loading conditions. In all cases, as the shear rate was increased, climbing of the fluids onto the periphery of the cone occurred. At a critical rate of shear, the fluids were observed to clear the cone partially. This behavior is attributed to the development of normal stresses in the fluids. Normal stresses in these fluids were calculated, at selected rates of shear, from flow data obtained with a capillary viscometer, by means of the use of capillaries with a range of length to radius ratio, according to the method of Philippoff.

After correction of the capillary data for normal stress and kinetic energy effects, the shearing stresses at various rates of shear obtained in the capillary and the cone-plate viscometers were compared.

#### 47. Parallel Plate and Cone-Plate Normal Stress Measurements on Polyisobutylene-Cetane Solutions

HERSHEL MARKOVITZ and DAVID R. BROWN, Mellon Institute, Pittsburgh 13, Pennsylvania.

Normal stress measurements were obtained on a series of solutions of polyisobutylene in cetane. Pressure distributions were obtained in steady-state torsional shearing between two parellel circular discs and between a cone and disc. The use of a reduced variable treatment similar to that which is successful for the linear viscoelastic properties of moderately concentrated solutions serves as a useful approximation to the concentration dependence of the normal stress data over the range of experimental variables covered here.

## Large Longitudinal Retarded Elastic Deformation of Rubberlike Network Polymers. II Application of Nakada's Formulation

HERBERT LEADERMAN and FRANK MCCRACKIN, National Bureau of Standards, Washington, D. C. and — OSAMU NAKADA, Hitachi Central Research Laboratory, Kokubunji, Tokyo.

Measurements on the longitudinal creep under constant tensile load and recovery up to about 30% extension of a specimen of plasticized polyvinyl chloride have been fitted to the first three terms of the generalized functional proposed by Nakada. The measure of deformation is the conventional Hooke's law strain ( $\lambda$  -1), where  $\lambda$  is the relative length. The time-dependent material functions  $D_a(t_1)$ ,  $D_b(t_1, t_2)$  and  $D_c(t_1, t_2, t_3)$ are simply related to D(t), the longitudinal creep compliance of infinitesimal viscoelasticity theory. Values of D(t) obtatined from the creep data agree well with values obtained previously using a single Boltzmann type convolution integral with  $\left[\gamma - \frac{1}{\lambda^2}\right]/3$  as the measure of deformation. The inverse relationship giving nominal stress as a function of  $(\lambda - 1)$  involves only the longitudinal relaxation modulus E(t) of linear viscoelasticity theory.

### West Coast Regional Meeting of the Society of Rheology

The West Coast Regional Meeting of The Society of Rheology will be held on January 31-February 1, 1963, at Shell Development Company, Emeryville, California. Plans for the meeting include four technical sessions, which will begin at 9:00 A.M. and 1:15 P.M., and a social activity for Thursday evening, January 31.

Papers are being solicited for the meeting and prospective speakers are invited to send titles and a 200-word abstract to either Thor L. Smith, Stanford Research Institute, Menlo Park, California, or Paul J. Blatz, Guggenheim Aeronautical Laboratory, California Institute of Technology, Pasadena, California. Titles of papers are due on December 1 and abstracts on January 2, 1963. Abstracts will be duplicated prior to the meeting and mailed to participants and others upon request. In addition to contributed papers, it is anticipated that the program will include several review talks.

Local arrangements for the meeting are being made by Dale Meier of Shell Development Company. Overnight accommodations can be made at the Golden Bear Motel, 1620 San Pablo Avenue, Berkeley, or at the Claremont Hotel in Berkeley.

### Eleventh Annual Rheology Symposium in Japan

The Eleventh Annual Rheology Symposium will be held in Osaka at the Osaka Chamber of Commerce and Industry from 15th to 17th October 1962, under the joint auspices of the Chemical Society of Japan, the Physical Society of Japan, the Society of Polymer Science, Japan, the Japanese Society for Testing Materials, the Japanese Society of Mechanical Engineers, the Japanese Society of Civil Engineers and the Japanese Institute of Metals.

The discussion subjects will be grouped in 1) the rheology of metal, 2) the rheology of soil, rock and concrete, 3) the rheology of high polymer, including disperse system. A general lecture will be prepared for each main discussion subject. Contributions from other countries are cordially invited. Any inquiries about the symposium should be directed to:

PROFESSOR M. HORIO

CHAIRMAN OF THE ORGANIZING COMMITTEE

DEPARTMENT OF POLYMER CHEMISTRY

KYOTO UNIVERSITY, KYOTO, JAPAN

Since 1959 the Japanese Society for Testing Materials has published yearly a special rheology issue of its journal. The papers in these issues are normally written in Japanese, but all include abstracts in English. Also tables and captions of figures are always in English.

Copies of past issues may be obtained at a cost of U.S. \$1.00 including postage. Orders should be sent to:

THE JAPAN SOCIETY FOR TESTING MATERIALS c/o Kyoto University Sakyo-ku, Kyoto, Japan

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#### BIORHEOLOGY: An International Journal

An Important New International Scientific Research Journal to be published quarterly commencing July 1962.

#### Editors-in-Chief:

PROFESSOR A. L. COPLEY, New York Medical College, Dept. of Physiology and Pharmacology.

DR. G. W. SCOTT BLAIR, National Institute of Research in Dairying, Dept. of Physics, Shinfield, Reading, Berks.

Some of the papers to be published in the first issue:

- A. L. COPLEY and P. H. STAPLE: Haemorheological studies on the plasmatic zone in the microcirculation of the cheek pouch of Chinese and Syrian hamsters.
- M. JOLY: Dispositif pour la viscosimetrie précise de systems contenant des proteines.

S. OKA: A review on rheometry for biological studies.

H. HARTERT and J. A. SCHAEDER: The physical and biological constants of thrombelastography.

M. C. H. DODGSON: Colloidal structure of brain.

#### AIMS AND SCOPE OF THE JOURNAL

Biorheology comprises the study of deformation and flow of biological systems and of materials directly derived from living organisms. Such problems have recently assumed an increasing importance in physiology, medicine, surgery, botany and other biological disciplines. Since, by convention, rheology is not concerned with hydrodynamics, aerodynamics or the classical theory of elasticity, "Biorheology" will accept papers only on biological materials which are specifically concerned with the properties of the systems studied. For example, papers which deal entirely or almost entirely with haemo-dynamics would not be acceptable; haemorheological properties must form a significant portion of the work. Fourth International Congress on Rheology 1963

The Fourth International Congress on Rheology will take place from August 26 to August 30, 1963 at Brown University, Providence, Rhode Island, U.S.A. under the auspices of the International Committee on Rheology with the (U.S.) Society of Rheology as the host society. Rheologists who wish to present papers at the Congress are invited to submit, by March 30, 1963, abstracts of not more than 500 words, in a form suitable for publication, to:

PROFESSOR E. H. LEE

Editor of the Proceedings of the Fourth International Congress on Rheology

BROWN UNIVERSITY PROVIDENCE 12, RHODE ISLAND, U.S.A.

It is intended that twenty minutes will be allotted for the presentation and ten minutes for the discussion of each contributed paper.

In addition to contributed papers, the program of the Congress will include lectures of longer duration on fields of rheology of especial current interest and social occasions on which rheologists from the various countries represented may exchange views.

Accommodations for those attending the Congress and their spouses, consisting of single or double rooms, will be available in the dormitories of Brown University. Alternatively, some attendants may prefer to stay in one or the other of the hotels in the Providence area. Meals will also be available in the University. Information regarding the price of accommodations and meals will be given in later announcements.

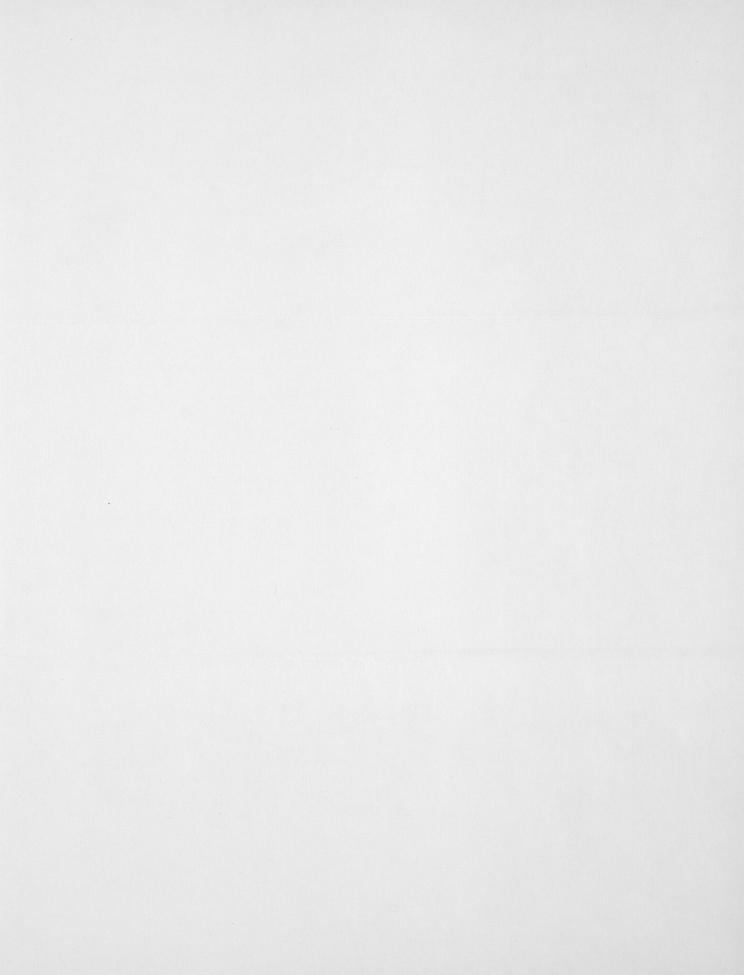
Those wishing to attend the Congress are requested to inform Professor R. S. Rivlin, Co-Chairman of the Congress, of their intention at the earliest possible date. This information, as well as any enquiries regarding the Congress should be addressed to:

PROFESSOR R. S. RIVLIN

Co-Chairman, Fourth International Concress on Rheology

BROWN UNIVERSITY PROVIDENCE 12, RHODE ISLAND, U.S.A.

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