# RHEOLOGY BULLETIN

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### THE BINGHAM MEDAL, 1956

The Committee for the Bingham Medal has once again chosen to honour a man in the prime of his career. This year's medalist, Arthur V. Tobolsky, is well known to all rheologists for his work in the field of polymerization mechanisms and the correlation of structure with properties of polymers.

Born in New York City in 1919, Dr. Tobolsky received his A.B. degree from Columbia University in 1940 and the Ph.D. in Physical Chemistry and Physics at Princeton University in 1944. In the same year he joined the faculty of Princeton and is now Eugene Higgins Associate Professor of Chemistry. He has also served as Adjunct Professor at the Polytechnic Institute of Brooklyn, from 1945 to 1950 and Assistant Director of the Textile Research Institute from 1948 to 1950. In addition to his teaching and research activities at Princeton he is also a member of the Board of Editors of American Scientist and engaged in private consulting work. The results of his research have been presented to the public in two books and over eighty papers on the rheology of visco-elastic materials and the kinetics of polymerization.

The awarding of the Bingham Medal will take place during the Social Hour, Thursday evening, November 8th at the Annual Fall Meeting of the Society. The presentation will be made by Sir Hugh Taylor, Dean of the Graduate School, Princeton University.

### THE ANNUAL FALL MEETING, 1956

The Mellon Institute in Pittsburgh will be host to the Society at this year's Annual Meeting. Members should enter the Institute by the Fellfield entrance. Technical sessions will start at 10:00 A.M., Wednesday, November 7th and continue through Friday, November 9th. The Webster Hall, 5th Avenue, Pittsburgh 13, will be the meeting hotel and those planning to attend should write directly to the hotel to secure reservations as early as possible since this is the only hotel convenient to the Mellon Institute. A Social Hour Smoker is planned for the evening of November 8th at the Pittsburgh Athletic Association.

The following is a tentative program for presentation of papers. As this bulletin goes to press two of the papers listed are awaiting company approval. If additional, appropriate papers are received in time, there will be a sixth session on Friday afternoon.

### TENTATIVE PROGRAM FOR THE FALL MEETING

Session 1, 10:00 A.M., Wednesday, November 7. "THE TACKINESS OF LIOUID ADHESIVES"

J. J. BIKERMAN, DEPT. of CIVIL & SANITARY ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.

The tackiness of liquid adhesives is a purely rheological property and is not influenced by the molecular adhesion between the adherends and the liquid, in accord with the view of Stefan 1874 and Bikerman 1947. For a given liquid (a hydrocarbon oil) it is independent of the nature of the solid (stainless steel, nickel and copper were tested). It is greater the flatter the surfaces of the adherends. For the liquid amounts used, tackiness is smaller for rougher surfaces. The temperature coefficient of tackiness is similar to that of the viscosity of the liquid. For Newtonian liquids, tackiness is the product ft, f being the tensile stress required to separate the adherends during time t, if a liquid is present between and around the adherends. If there is no liquid around the adherends, capillary attraction in addition to viscosity must be overcome, and the product ft increases with t and is always greater than in the previous instance.

# "THE STRUCTURE OF ADSORBED POLYMER LAYERS"

### F. R. EIRICH, BROOKLYN POLYTECHNICAL INSTITUTE, BROOKLYN, NEW YORK

Flow processes at interfaces, or in narrow channels, are strongly influenced by the structure of adsorbed layers. It may, therefore, be of interest to report the results of a detailed experimental investigation of the adsorption of high polymers and of polyvinyl acetate in particular on metal surfaces.

From the adsorption equilibria and conformance of the equilibrium to a Langmuir isotherm, it has been deduced that the adsorbed layer consist of chain molecules which are held in form of loops in a rather loose structure that reaches to an appreciable distance from the surface. Solvent and temperature play a very decisive part as regards the details of the structure of the layer, and rate phenomena are very pronounced. Consequently, the flow of solvent RHEOLOGY BULLETIN Bryce Maxwell, Editor The Princeton University Plastics Laboratory Princeton, New Jersey

parallel to surfaces carrying adsorbed macromolecules must be considered as being impeded up to distances which may reach a considerable fraction of the molecule contour length.

### "THE VISCOSITY OF SUSPENSION OF SPHERES. III. SEDIMENTATION VOLUME AS A DETERMINING PARAMETER"

### JAMES V. ROBINSON, THE MEAD CORPORATION, CHILLICOTHE, OHIO

Equations expressing the dependence of the viscosity of suspensions of spheres upon the concentration of the solid phase have most recently been proposed in terms of relative viscosity or natural logarithm of relative viscosity. When an alternate equation, in terms of specific viscosity, is applied to experimental data, the parameter of the equation is numerically consistent with the necessary condition that the upper limit of volume concentration for a suspension is the reciprocal of the relative sedimentation volume. The parameter of the viscosity equation expressed in terms of the natural logarithm of relative viscosity is not so consisten. Analysis is made of new data, and of data taken from the literature, to illustrate the point.

# "NEW METHOD FOR DETERMINATION OF THE SURFACE VISCOSITY"

### R. BULAS AND C. A. KUMINS INTERCHEMICAL CORPORATION, RESEARCH LABORATORIES, NEW YORK, NEW YORK

All methods of measuring surface viscosity of detergent solutions and/or insoluble films spread on a liquid require separate determination of the viscous drag exerted by the pure liquid and by the corresponding solution. This is no serious detriment when working with homogeneous solution. However in attempting to investigate the presence of surface structure in pigmented systems it is impossible to separate the viscous drag of the surface from any resistance occasioned by the surface concentration of materials at the air-liquid interface. This paper describes a technique which we plan to use in the study of possible surface structure in pigmented media.

The oscillating disk method has been modified in such

a way that both measurements can be carried out on a single solution. For a pure liquid the logarithmic decreament of the damping increases asymptotically with the increased submergence of the disk and, for all practical purposes, can be assumed constant at a certain critical depth (h). The log decreament at the critical submergence has been found to be twice as large as that obtained with the disk in the plane of the surface. If the log decreament of a detergent solution is determined with the disk submerged at the critical depth, its half-value can be subtracted from that obtained with the disk in the plane of the surface, the difference being the log decreament due to surface viscosity alone.

The critical depth h has been found to be related to the bulk viscosity of the solution in the following manner:

h = K x viscosity of the bulk to the a pawer Where K and a are constants.

Results obtained in determination of the surface viscosity with the above described method showed a good agreement with those obtained using conventional technique. Session 2, 2:00 P.M., Wednesday, November 7.

### "NORMAL STRESS MEASUREMENTS ON POLYISOBUTYLENE SOLUTIONS IN A CONE AND PLATE INSTRUMENT"

# HERSHEL MARKOVITZ AND R. BRADY WILLIAMSON, MELLON INSTITUTE, PITTSBURGH, PA.

Normal stress measurements have been made on concentrated solutions of an unfractionated polyisobutylene in decalin in an apparatus with a cone and plate geometry. The data taken at various concentrations can be superposed in a way similar to that used for the dynamic rigidity. The functional relationship between the normal stress and rate of shear is related to that between the dynamic rigidity and the frequency. The results are discussed in terms of recent rheological theories.

#### "A MEASUREMENT OF DYNAMIC NORMAL STRESS"

### ROBERT S. MARVIN, RUBBER SECTION, NATIONAL BUREAU OF STANDARDS, WASHINGTON 25, D. C.

Some preliminary measurements of the normal stress during dynamic deformation in simple shear have been made. Samples were strained in the NBS Twin Transducer at frequencies between 50 and 400 cps and strain amplitudes (RMS values) up to about 6%. The RMS stress normal to the alternating strain was detected with a piezoelectric crystal in the form of a ceramic cylinder which held the sample against the moving plate. The normal stress magnitudes were proportional to the squares of the shear strains, and independent of the frequency within the precision of the measurements.

### "ON NORMAL STRESSES; FLOW CURVES, FLOW BIREFRINGENCE AND NORMAL STEESS DATA FOR POLYISOBUTYLENE SOLUTIONS"

W. PILIPPOFF, FRANKLIN INSTITUTE, PHILADELPHIA, PENNSYLVANIA

### "STRAIN AGING HYDROGEN EMBRITTLEMENT IN TITANIUM ALLOYS"

# HARRIS M. BURTE, WRIGHT AIR DEVELOPMENT CENTER

### AIR RESEARCH AND DEVELOPMENT COMMAND, WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Hydrogen contamination in the alpha-beta class of titanium alloys leads to a very pronounced strain rate sensitivity of the ductility of these materials, and to low stress, premature fracture under sustained tensile loading (creep). The effects of strain rate, hydrogen concentration, temperature, stress concentrations, alloy composition, and microstructure are described.

A mechanism for this strain aging embrittlement is suggested which involves plastic deformation inducing microsegregation of interstitially dissolved hydrogen to the grain boundries of these two phase polycrystalline materials. This microsegregation involves diffusion of the hydrogen and proceeds at a finite rate. Properties measured under various conditions of loading depend upon whether the rate of deformation is fast or slow relative to the rate of microsegregation and consequent embrittlement.

### "INTERNAL FRICTION IN THE RANGE 4°-300°K OF IRON WIRES CONTAINING HYDROGEN"

# W. R. HELLER, SHELL DEVELOPMENT CO., EMERYVILLE, CALIFORNIA

Internal friction effects in iron due to interstitial carbon and nitrogen are now well known and increasing in use as a tool for study of cold-working and aging phenomena. Analogous studies of the internal friction associated with hydrogen in iron are of interest in connection with ratedependent embrittlement phenomena. Measurements have been made of the damping at low temperature of a torsion pendulum whose suspension was chosen from variously treated iron wires charged cathodically with hydrogen. By appropriate theoretical considerations it is possible to correlate the damping with the diffusion of hydrogen and the effects of cold-working the wires.

### Session 3, 9:30 A.M., Thursday, November 8. "A STOCHASTIC PROCESS MODEL FOR MECHANICAL BREAKDOWN PHENOMENA"

### BERNARD D. COLEMAN, E. I. DU PONT DE NEMOURS AND COMPANY, CAROTHERS RESEARCH LABORATORY,

### WILMINGTON, DELAWARE

The classical approaches to the problem of determining the functional form of tensile strength distributions are based on static statistical models which can be treated by the methods of the theory of extreme value statistics. These approaches are not applicable to oriented polymeric fibers which show a very strong dependence of tensile strength on time allowed for failure. To overcome this difficulty, a molecular model has been developed which accounts for the time dependence, the size dependence, and the extreme autocatalytic nature of mechanical breakdown phenomena. Most of the work done to date on this model has been concerned with a "perfect" fiber that can be divided up into a set of non-interacting slabs. Methods have been developed for calculating the distribution of breaking times under constant stress for a single slab and a long fiber composed of many slabs. Some progress has been made in generalizing these results so as to estimate the effect of stress-concentrating flaws on the distribution of breaking times.

### "ON IDEAL LOCKING MATERIALS"

## WILLIAM PRAGER, BROWN UNIVERSITY, PROVIDENCE 12, R. I.

A solid with a non-linear stress-strain law is classified as "soft" or "hard" depending on the nature of the deviation from linearity. For a soft material, the stress increment required to produce a specified strain increment diminishes with progressing deformation; for a hard material, on the other hand, this stress increment grows as the deformation progresses. Cork composition materials and foam rubber are examples of hard materials.

The paper is concerned with an ideal hard material, which deforms readily under negligible stresses until a limiting state of strain is reached when "locking" occurs in the sense that certain types of stress increase can be supported without change in strain. A general relationship between locking strain and admissible stress increase is stipulated, and a material exhibiting this relationship is called an "ideal locking material". The following problem is treated: can a body made of an ideal locking material accommodate itself to specified displacements of the points of its surface, or will the attainment of these surface displacements be prevented by locking? It is shown how the intensity of the surface displacements that produce locking can be bounded from below and above.

#### "THE DEPENDENCE OF THE ULTIMATE PROPERTIES OF GR-S RUBBER ON STRAIN RATE AND TEMPERATURE"

### THOR L. SMITH, JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

The tensile strength and ultimate elongation of a viscoelastic material depend on both strain rate and temperature. The tensile properties of an unfilled GR-S rubber have been measured using an Instron tensile tester at strain rates between  $1.7 \ge 10^{-1}$  sec. <sup>-1</sup> and at thirteen temperatures between -68 and 88°C. The tensile strength and ultimate elongation data at the various temperatures and strain rates were combined to give composite curves which are functions of a reduced strain rate. From superposing the data at the different temperatures, the temperature dependence of the ultimate properties was obtained. Below 25°C, the temperature dependence was found to be essentially identical with that for small deformations and is given by the Williams, Landel and Ferry equation which is a nearuniversal function of the glass-transition temperature. From the composite curves and the temperature function, the tensile strength and ultimate elongation can be predicted at any strain rate and temperature, provided wave-propagation and heating effects are negligible.

### "ON THE MOTION OF PLASTIC MASS" COSIMO TORRE, SYRACUSE UNIVERSITY, SYRACUSE, N. Y.

Motion of a plastic mass is considered in terms of the equation of motion of a continuum with a limit condition and certain stress-rate of strain relations. The possibility of working with the acceleration terms in the equation of motion of solids and computations in plane problems is discussed.

# "THE EFFECT OF VISCOSITY ON CRYSTALLIZATION IN GLASS"

# WEBSTER CAPPS, GLASS SECTION, NATIONAL BUREAU OF STANDARDS.

The role of viscosity will be discussed in crystallization in glass melts as will be surface tension, nucleation and energy difference between glass and crystal phases. The means of control of these properties will be described for a variety of processes such as enamelling of metals, controlling color in certain signal and filter lenses, annealing of glassware and in drawing of glass fibers.

Session 4, 2:00 P.M., Thursday, November 8.

"TRANSVERSE WAVE PROPAGATION AND NON-NEWTONIAN FLOW IN SOLUTIONS OF PARTIALLY POLYMERIZED FIBRINOGEN"

### JOHN D. FERRY AND FRANCES E. HELDERS, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.

Non-Newtonian flow and transverse wave propagation have been studied in solutions of intermediate polymers of bovine fibrinogen, formed by thrombin at pH 9.4, ionic strength 0.5, in the presence of 0.5M hexamethylene glycol. The results conform approximately to the behavior of rigid rods or elongated ellipsoids as predicted by the theories of Kirkwood, Saito, and Cerf. From the thories, relaxation times are calculated, and from these molecular lengths of about 2000 Angstroms and 7000 Angstroms for wave propagation and non-Newtonian flow, respectively. The magnitude of the length agrees with values derived from flow birefringence; the discrepancies may be associated with a distribution of lengths.

### "RELATION BETWEEN STRESSES AND STRAIN RATES IN A SUSPENSION OF RIGID RODS"

# STEPHEN PRAGER, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA.

The method of Kuhn and Kuhn has been used to develop relations between stresses and strain rates for a dilute suspension of rigid rods being deformed in an arbitrary fashion at a steady, spacially homogeneous rate. It appears that if the flow is not irrotational, the vorticity enters in an essential manner into the non-Newtonian stress-strain rate relations. One result of this is that the Wiessenberg effect vanishes, at least in simple shear flow.

The above calculations are compared with general phenomenological relations which have been proposed during the past decade by various authors. The effects of temporal and spacial variations in the strain rates have also been examined.

### "HYDRODYNAMIC THEORY FOR THE FLOW OF A VISCOELASTIC FLUID"

### Y. H. PAO, POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & COMPANY, INC., DU PONT EXPERIMENTAL STATION, WILMINGTON, DELAWARE.

A hydrodynamic theory for the flow of a viscoelastic fluid is formulated and applied. The viscoelasticity is specified in terms of the conventional and well-known relaxation and retardation spectra. Time dependent recoverable strains are defined with respect to convected rotating coordinate axes. The theory is linear to the extent that these strains are small although the over-all displacement gradients of the fluid may be large. The theory is applied to two dimensional steady state simple shear flow to predict the variation of the apparent viscosity and the steady state elastic compliance with shear rate. Pressure flow through a pipe of circular cross section has also been treated.

Previous work of similar nature is reviewed.

# "A NEW THEORY OF THE VISCOSITY OF SIMPLE LIQUIDS"

## M. MOONEY, UNITED STATES RUBBER COMPANY, PASSAIC, NEW JERSEY

The Eyring picture of the mechanism of viscous flow is open to serious criticism as to the postulated molecular movements in the neighborhood of a hole. Consequently a new thory is proposed which, following Maxwell's concept of flow, is based on a detailed mechanical picture of the stress relaxation process in an elastic material subjected to continuous external stress. According to this theory small regions in the liquid containing 4 or more molecules are temporarily expanded, by chance concentrations of thermal energy, above a critical value of the specific volume where the elastic rigidity disappears. As a result there is movement and partial release of stress in the surrounding region.

Quantitative analysis of this stress relesase is based on theoretical work by J. M. Dewey. Analysis of the frequency of creation of expanded regions follows Debye's analysis of thermal vibrations as a sum of high frequency elastic waves. It turns out that the adiabatic modulus of compression is a major factor determining the viscosity of a liquid.

Tested on a variety of different simple, non-associated liquids, the theory is found to be correct in order of magnitude.

#### "HEAT GENERATION AND CONDUCTION IN THE FLOW OF A VISCOUS COMPRESSIBLE LIQUID"

## H. L. TOOR, CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH 13, PENNSYLVANIA.

The energy equation has been solved for the case of a compressible non-Newtonian liquid entering a tube at temperature equal to the wall temperature. It is shown that the temperature in the center of the tube initially decreases with distance due to expansion of the liquid while away from the center it increases with distance due to frictional heat generation.

For most polymers the heat generation eventually predominates and at some distance along the tube the centerline temperature begins to rise. The increase continues until the steady temperature profile is reached.

A simple equation is presented which gives distance required to closely approach the steady profile.

#### Session 5, 9:30 A.M., Friday, November 9.

"VISCO-ELASTIC FLOW IN CONVERGENT PIPES AND CHANNELS"

### WILLIAM E. LANGLOIS, DIVISION OF APPLIED MATHEMATICS, BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND.

#### Present address E. I. DuPont DeNemours & Co.

The visco-elastic flow generated by a line sink at the vertex of a wedge-shaped region and its axially symmetric analogue, the flow generated by a point sink at the vertex of a cone, are considered. It is pointed out that purely radial flow occurs only in rather special circumstances; the flow is usually characterized by eddies near the vertex of the wedge or cone.

### "A HIGH SHEAR RATE CAPILLARY VISCOMETER FOR POLYMER MELTS"

### E. H. MERZ, R. E. COLWELL, B. H. WOOD, MONSANTA CHEMICAL COMPANY, PLASTICS DIVISION, SPRINGFIELD, MASSACHUSETTS.

An instrument has been developed to measure the flow characteristics of polymer melts at shearing rates in the range 1-10,000 sec.  $^{-1}$  and over the temperature range 70-600°F. The derived flow parameters obtained are independent of the capillary length and diameter used. At least three parameters are necessary to classify typical polymer melts: (1) a reference state viscosity, (2) a temperature coefficient, and (3) a shear rate parameter. Additionally, one might require a measure of the melt elasticity and a pressure coefficient. Such parameters can be deduced from data obtained on the instrument.

A sensitive strain gage mounted in the cross head of an Instron Testing Machine is used to measure the force required to drive a piston at constant speed into a reservoir containing the polymer melt. The melt is extruded thru capillary tubes of 32 to 188 length/diameter ratio. Flow anomalies such as melt fracture, non-equilibrium flow, and "lubricated surface" flow are evidenced by the force trace.

### "THE MEASUREMENT AND COMPUTATION OF THE MECHANICAL MODULI OF VISCOELASTIC SUBSTANCES"

### J. R. PARKS, J. R. VAN WAZER, AND L. COOPER, MONSANTO CHEMICAL CO., INORGANIC DIVISION, DAYTON, OHIO

The viscoelastic properties of doughs have been studied using an apparatus similar to that described by H. Markovitz et al. The instrument uses rotary differential tranformers as input and output transducers. The signals are registered by a Sanborn two-channel recorder and a Dumont Dual-Beam scope. The experimental data are reduced by numerical integration of the differential equation representing the behavior of the sample by a modified Runge-Kutta method. The inverse of the dynamic modulus of rigidity appears as a factor in the eigenvalue of the differential equation. An iterative procedure was found by which the computer could converge on the eigenvalue that satisfies the differential equation and boundary conditions. Some results will be shown and discussed.

#### "AXIAL FLOW OF NON-NEWTONIAN FLUIDS IN CYLINDRICAL ANNULI"

### ARNOLD G. FREDRICKSON AND R. BYRON BIRD, DEPT. OF CHEMICAL ENGINEERING, UNIVERSITY OF WISCONSIN, MADISON 6, WISCONSIN

In order to make deductions from flow data concerning the range of applicability of various non-newtonian flow models, it is essential that there be available good experimental data and accurate analytical solutions for flows

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in various geometrical arrangements. There are already such results for axial flow in cylindrical tubes and for radial flow in cylindrical annuli. This paper deals with the analytical solutions for the equations of motion of nonnewtonian fluids which are flowing parallel to the axis of a cylindrical annulus. Complete numerical results are given for the power-law model.

### "FLOW OF POLYETHYLENE IN CAPILLARY INLETS AT STRESSES ABOVE THOSE AT WHICH MELT FRACTURE OCCURS"

J. P. TORDELLA, POLYCHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC., DU PONT EXPERIMENTAL STATION, WILMINGTON, DELAWARE

Motion pictures were made of the flow of polyethylene in glass extrusion apparatus. At stresses above a critical stress, flow in the inlets of the capillaries was not uniform. Incidence of this non-uniform flow was accompanied by corresponding irregularity of the shape of the extrudates. The work appears to substantiate the hypothesis that the cause of the irregularity of extrusion of viscoelastic liquids at and above a critical stress is fracture or rupture of the liquid in inlets of the capillaries.

### SOCIETY NEWS

#### Constitution

In accordance with Article VIII "Amendments to the Constitution" and Article VIII "Amendments to the By-Laws" of the Constitution and By-Laws of the Society, a

letter ballot and proposed revision of the Constitution and By-Laws was submitted to the membership in June. The Secretary-Treasurer has certified the results of this letter ballot to be as follows:

For the revision	160
Against the revision	2
Blank Ballot	1

Since, by far, the majority of those members voting have approved the revision as submitted, the revised Constitution and By-Laws become effective at the date of this canvass of letter ballots, September 17, 1956.

#### Society of Exploration Geophysicists

The Governing Board of the American Institute of Physics has been petitioned by the Society of Exploration Geophysicists for membership in the Institute. The Executive Committee of the Society of Rheology has been polled by the President and voted to recommend to the Governing Board that this petition be received with favorable consideration.

#### Edwin W. Tillotson

Dr. Edwin W. Tillotson, a member of the Society of Rheology, retired as Director of Research of the Mellon Institute on July 31st after forty-three years of association with the Institute.

President of the American Ceramic Society in 1925 and an honored Fellow of that Society since 1931, he received the Albert V. Bleininger Medal in 1949. Specializing in the field of the chemistry and technology of glass, his publications have laid the foundation for much future work in this field.