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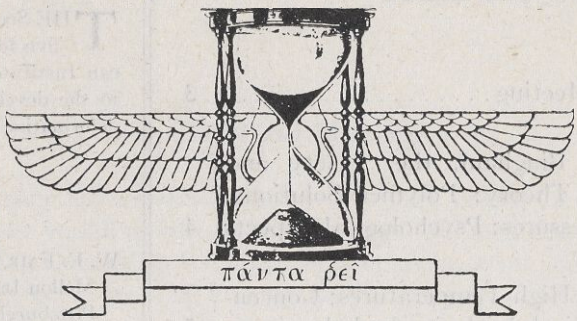
# RHEOLOGY BULLETIN




## REVIEW
## 1946 MEETING

PUBLICATION OF THE

## SOCIETY OF RHEOLOGY

VOLUME 17, NO. 3 NOVEMBER, 1946

# RHEOLOGY BULLETIN

Vol. 17, No. 3 November, 1946

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**Associate Editors**

A. Bondi
R. G. Fordyce
A. Gemant
H. K. Nason
J. A. Pask
W. W. Pendleton
B. R. Roberts
R. Simha

Published for the

## Society of Rheology

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# Rheology Bulletin

## Publication of the Society of Rheology

Vol. 17, No. 3 November, 1946

### The 1946 Meeting

THE Bingham Memorial Symposium set a new record for attendance, the enrollment equalled fifty-eight percent of the membership! Dr. Nason outdid himself in assembling the program, and much credit goes to Drs. Alfrey and Fair for excellent meeting arrangements that were comfortable and convenient.

The many details and last-minute tasks required for registration and conduction of such a meeting were most efficiently handled by Miss Margaret Griffin and her staff from the American Institute of Physics, to whom we are most indebted.

Although a success and a pleasure to all attending, the attendance at the "smoker" was not as great as at the technical sessions nor as large as anticipated. However, the mixing of the crowd was as stimulating as were the chemicals of a liquid nature, and all were fascinated by Dr. Nadai's description of his trip to Russia. We were glad to welcome Mr. Ronald Rivlin of the British Rheologists Club and hear him express the good wishes of that organization.

In this issue of the Bulletin appear the minutes of the business meeting as well as abstracts of all the papers presented. In addition, there are written discussions of some of the papers, prepared by Dr. Bondi.

The meeting was honored by the presence of Mrs. Eugene C. Bingham whose generous gift will be used as the first step toward the foundation of an annual "E. C. Bingham Memorial Award" for outstanding contributions to Rheology.

# First Session

FRIDAY, NOVEMBER 1, 9:30 A.M.

*Chairman*, H. K. NASON, *Monsanto Chemical Company*

**E. C. Bingham and the Society of Rheology Reminiscences.** A. NADAI, *Westinghouse Research Laboratories.*

This 1946 meeting of the Society of Rheology is the first one following the passing away of *Dr. Eugene Cook Bingham*, Professor of Lafayette College, Easton, Pennsylvania. The Program Committee arranging this meeting very appropriately suggested to call the 1946 meeting of the Society of Rheology the "E. C. Bingham Memorial Symposium on Rheology."

By dedicating it to the memory of the late Professor Bingham, the Program Committee felt certain that the high general esteem in which a large group of American physicists, chemists, and engineers looked upon him would be expressed best by this Symposium dedicated to the general problems of the flow of materials and the contributions to the Symposium would be a sign of the gratitude of those working in this field and would particularly honor his person whose inspiring work helped to establish this field as a special branch of science.

He proposed the name *Rheology* for the branch of science dealing with the physical, chemical, and mechanical problems of the flow of a large group of materials. He became the first editor of the first journal devoted to Rheology. Eugene Cook Bingham justly deserves to be honored today as the father of the Society of Rheology. In his modest manner he never considered himself as the founder of Rheology itself. The first copies of the *Journal of Rheology* (No. 1, Vol. 1 was published in October, 1929) offer a proof of this. He was keenly interested in the biographies of the early founders of the theory of the flow of viscous fluids and published in the Journal a biographic sketch of *Jean Leonard Marie Poiseuille* (1797–1869) from the pen of *Marcel Brillouin* and of *Sir George Gabriel Stokes* (1819–1903). In 1922 Professor Bingham published his *Fluidity and Plasticity* (McGraw-Hill Book Company, New York), a monograph dealing with viscous and non-viscous fluids and plastic solids. Bingham suggested the ideal stress-rate of flow law which received his name and in which a "Yield value" was introduced, below which no flow occurs and above which stress is increasing proportionally with the rate of flow.

He devoted much of his time to efforts in establishing better definitions for frequently used terms expressing mechanical properties of solids and fluids. He was for many years the Chairman of the Committee on Consistency of the American Society for Testing of Materials. He spent two years in studies in Europe, he was a student of Wilhelm Ostwald at the University of Leipzig around 1905 and went to the universities of Berlin and Cambridge. Concerning the viscosity of water in the vicinity of 20°C he arrived at the conclusion that the absolute viscosity of water was not sufficiently precisely known as the primary rheologic standard and devised improved methods for its determination. His efforts were always directed towards eliminating certain phenomenologic qualities which were in use describing properties of solids or fluids by suggesting definitions based on absolute values and clear in their dimensions. Further details are reported about his kind personality and his great merits of which a few are based on personal reminiscences of this writer.

**E. C. Bingham and the ASTM—An Appreciation.** W. H. FULWEILER, Philadelphia.

Dr. Bingham was a member of the American Society of Testing Materials for 28 years. Dr. Bingham's early work for the Society was in connection with the standardization of the Saybolt viscosimeter in 1922. In 1927 he was made Chairman of Technical Committee II of Committee E-1 on Consistency, Plasticity, and Related Properties. As Chairman of this Committee, Dr. Bingham made many contributions to the work of the Society. Among these may be mentioned

The adoption of definitions of consistency and plasticity;
Cooperation with the Bureau of Standards in the re-determination of the viscosity of water;
The study and development of new methods for the determination of softening point;
The symposium in 1937 on Consistency.

Dr. Bingham served as ASTM representative on the Study Committee on Viscosity of the International Society of Testing Materials. In addition to his committee work, he contributed some 6 papers, 7 discussions, and many committee reports to the proceedings of the Society.

**Present Status of Rheological Theory.** HENRY EYRING AND GEORGE HALSEY, *Textile Research Institute*, Princeton, New Jersey.

Relaxation data are satisfactorily explained by the three-element non-Newtonian model but the same success is obtained using the Wiechert multi-element linear model. The latter model fails to account satisfactorily for experiments at a constant rate, and when experiments at many rates are considered, proof of non-Newtonian behavior is realized.

When the criterion for the generalized three-element model exists, it is relatively simple to find the non-Newtonian law experimentally. Various laws that have been observed are discussed.

**The Effect of Solvent Composition on the Specific Viscosities of Polymer Solutions.** TURNER ALFREY, JR., *Polytechnic Institute of Brooklyn.*

At low concentrations the specific viscosities of solutions of a polymer such as polystyrene can be satisfactorily

represented by the first two terms of a power series in concentrations:

$$\eta_{sp/c} = [\eta] + k'[\eta]^2 c.$$

The intrinsic viscosity, $[\eta]$, is a measure of the hydrodynamic resistance offered by the polymer in an infinitely dilute solution, and thus reflects in some fashion the shapes or configurations assumed by individual polymer molecules. The second term, on the other hand, is an interaction term which measures the total interaction between different polymer molecules at low finite concentrations. Such interaction includes both the hydrodynamic interaction (interference between the patterns of flow around different molecules) and also any direct structural interaction (e.g., sticking together of polymer molecules to form small aggregates).

The simplest molecular picture of the effects of solvent composition upon the specific viscosity is perhaps the following: In an energetically indifferent solvent, the polymer molecules are distributed at random among their many possible configurations and will exert certain definite hydrodynamic interference. In a "poor" solvent (i.e., one exhibiting an endothermic heat of mixing with the polymer), polymer-polymer contacts among different segments of a polymer molecule will be favored, and hence the molecule will on the average be curled up in a more compact form. This should result in a lower intrinsic viscosity in a poor solvent than in a good solvent. On the other hand, in a poor solvent intermolecular as well as intra-molecular "agglomeration" of the polymer should be favored and hence the $k'$ constant should be *higher* in a poor solvent than in a good solvent. Finally, one would expect that changes in temperature should have very little effect on the intrinsic viscosity in a good solvent but that an increase in temperature in a poor solvent should tend to shake the structure loose and thus to result in increases in intrinsic viscosity.

In polymers such as rubber and polystyrene the above crude predictions seemed to be completely fulfilled in practice. Experimental results are reported for fractions of polystyrene in a number of pure and mixed solvents.

In the case of some other polymers, however, the effect of solvent composition is apparently more involved. Frith, for example, reports a number of cases in which the intrinsic viscosity is very insensitive to solvent composition but the slope of the $\eta_{sp/c}$ *vs.* $c$ curve is markedly dependent upon solvent composition. There are also cases known where inter-molecular agglomeration in poor solvents persists down to such extremely low concentrations that the observed intrinsic viscosity fails to isolate the shape properties of individual molecules. Possible explanations for effects of the above types are discussed.

*Written discussion of:*

"The Effect of Solvent Composition on Viscosity of Polymer Solutions" by Turner Alfrey, Jr.

Much of the speculation regarding the configuration of polymer molecules in solution could be reduced if viscosity data were supplemented by thermodynamic data, such as the temperature coefficient of the observed solubility, of the osmotic pressure in these systems, the heat of solution by the technique of Parks,[1] vapor pressure data, etc. Recent analysis of solubility data of paraffin chain compounds[2] showed that the cohesive energy density concept is entirely inadequate to describe the behavior of such systems even in a qualitative manner, mainly because the excess entropy of mixing assumes rather large values (negative in poor and positive in good solvents). One can deduce from those values that the state of order of the poor solvent is quite changed in the immediate neighborhood of the solute. A more important consideration in the case of ternary systems, such as presented by Dr. Alfrey, is the possibility of the existence of configurations which could not exist in binary systems and thereby materially increase the excess entropy of mixing (and the solubility) over that expected from a normal mixture law.

In the light of Kuhn's recent theory[3] much additional information about the solvent/solute interaction can be obtained from viscosity *vs.* rate of shear data.

—A. Bondi

[1] R. D. Rowe and G. S. Parks, J. Chem. Phys. **14**, 383 (1946).
[2] A. Bondi, to be published, J. Phys. Chem.
[3] W. Kuhn and H. Kuhn, Helv. Chim. Acta **29**, 609 (1946).

**Rheological Properties of Polymers and Plastics.** W. O. Baker, *Bell Telephone Laboratories.*

During the years of Professor E. C. Bingham's high activity, probably the most extensive rheological studies, in countless laboratories, were on high polymers. This does not mean that, for example, more measurements were not made on lubricating oils or low polymeric paints. Rather, it is significant that a particularly wide range of variables, such as shearing stress, rate of shear, temperature, and the time dependences of observations, was found to affect strikingly the flow of polymers. Often there was evidence of complex behavior. The apparently unique quality of long chain molecules allowing gross (several hundred percent) strain of a sample by *high elasticity* rather than *fluidity* has principally contributed this intricacy to polymer rheology.

Therefore, it was natural that the phenomenology first drew attention. The early suggestion of Maxwell has been widely modified and applied to polymers. Here

$$\Im = \gamma G e^{-t/\tau}; \quad \eta = G\tau,$$

where $\Im$ = shearing stress, $\gamma$ = strain, $G$ = modulus of rigidity, $t$ = time, $\tau$ = relaxation time. A more general expression includes a (perhaps quite artificial) series of terms $\Sigma_i e^{-t/\tau i}$ in which a distribution of relaxation times occurs. This general attack has at least aided statement of the problem of specifying the reaction of a chain polymer to external stress.

More recently, the detailed mechanism of polymer deformation has been probed. Stimulation has come especially from Eyring and co-workers. By happy coincidence, it has also lately become possible to prepare polymers of known structure and average molecular weight. Likewise, new techniques for studying very small displacements, such as the oscillations of a dipole in an alternating

electric field, the vibrations of small domains in a compressional, ultrasonic field, and very recently, in a field of ultrasonic *shear* waves, have come in. From these techniques, knowledge of the viscous contributions from specific chemical groups, such as C—Cl in polyvinyl chloride or the ester linkage in polyesters, is gained. In complementary fashion, molecular weights tell how the macromolecule as a whole influences viscosity, because of such relations as Flory's, wherein $\eta = K \exp aZ_w^{\frac{1}{2}}$, where $\eta$ = viscosity of polymer at given temperature, $a$ and $K$ are characteristic constants, and $Z_w$ is the weight average chain length of given polymer. The viscosity of long chains in *dilute solution* is also being interpreted in terms of chain configuration.

Hence, it is encouraging, in thinking of Professor Bingham's many contributions to "anomalous" viscosity, that the rheology of high polymers, the special realm of anomalies, is gradually being tied to their *molecular* traits. Next, it will be necessary only to understand the molecules!

**Summary of the Rheological Properties of Matter Under High Pressure.** P. W. BRIDGMAN, *Harvard University.*

The paper will be chiefly concerned with a review of my own experiments on the viscous flow of liquids and plastic deformation of solids under high pressure.

The viscosity of ordinary organic liquids increases under pressure at a continually accelerated rate above the first few thousand kilograms per square centimeter. The magnitude of the effect varies enormously from liquid to liquid, and probably is more dependent on the nature of the liquid than any other physical effect of pressure. Variations by a factor of $10^7$ fold have been observed. If temperature is combined with pressure, the temperature coefficient of viscosity is found to increase with pressure, which is unlike most other effects. The constant volume viscosity at high pressure decreases with increasing temperature. This is contrary to the demands of a simple theory. Some description is given of the more recent theories, which correctly reproduce the temperature dependence.

Solids such as steel may exhibit enormous increases in ductility under pressure. The increase of ductility with pressure is approximately linear. The work-hardening also increases approximately linearly with pressure, so that by straining under pressure it is possible to enhance the properties of steel beyond what is possible at atmospheric pressure. The elastic limit is raised by pressure, but not to as great an extent as the ductility. Studies have been made on a great many substances of the effect of combining shearing stress with hydrostatic pressure. Contrary to the elementary theories, the flow stress is not constant, but increases markedly with the increase in pressure. When some substances are sheared under pressure, phenomena such as internal fracture with self-healing or cold-welding may occur. The velocity of plastic flow under shearing stress is approximately independent of stress, quite unlike the case with a liquid. A simple picture is suggested to explain this effect.

*Written Discussion of:*

"Rheological Behavior of Matter at Ultra-High Pressures" by P. W. Bridgman.

Several of the phenomena described by Professor Bridgman have since found a fairly satisfactory explanation by application of Eyring's rate process theory of flow, e.g.: The finite magnitude of the temperature coefficient of viscosity at constant volume, when defined as an energy of activation

$$R\left(\frac{\partial \ln \eta}{\partial 1/T}\right)_V = \Delta H_{\ddagger}^{i}$$

could be ascribed to the restricted external rotation of the molecules in the liquid state. $\Delta H_{\ddagger}^{i}$ has been found numerically equal to another expression for restricted rotation in the liquid state, the excess energy of vaporization $T(\Delta S_{vap} - 20.2) = \Delta E_{vap}^{i}$ in many cases.[1] For cases where $\Delta H_{\ddagger}^{i} > \Delta E_{vap}^{i}$ assumption of actual deformation of the molecule moving past its neighbors leads to reasonable values for the potential energy barrier restricting internal rotation.

The concept of the "maneuver volume" $\Delta V_{\ddagger} = (\partial \Delta F_{\ddagger}/\partial_p)$ introduced by Eyring makes his theory predict, at least qualitatively, that hydrostatic pressure, by reducing the available volume, will increase the ductility, i.e., prevent rupture.[2] Professor Bridgman's data confirm this prediction.

—A. BONDI

[1] A. Bondi, J. Chem. Phys. **14**, 591 (1946).
[2] R. E. Powell, Ph.D. Thesis, Princeton, 1943, p. 62.

**The Role of Psychophysics in Rheology.** G. W. SCOTT BLAIR, *University of Reading, England.*

Rheology is primarily concerned with observing deformations in materials and derivatives of these deformations with time. States of stress are postulated to account for the interaction of one body with another and are usually measured either in terms of the deformations of associated prototype bodies (as when a spring is attached to a stretched strip of plastic) or in terms of the gravitational field, i.e., the weight attached to a test piece. Rheological properties are expressed as relationships between stress tensors and strain tensors and the time derivatives of the latter. Most of these relationships are not valid for anisotropic or otherwise complex conditions or for large strains.

Since an exact solution of many complex rheological problems is therefore not yet possible, "properties" are often assessed in industry by subjective handling judgments. Measurements have therefore been made of just noticeable differences for viscosity of true fluids ($\eta \sim 10^7$ poises) and for shear modulus of elastic solids ($n \sim 10^7$ dynes/cm$^2$). In spite of dimensional difficulties, subjective comparisons of firmness can also be made comparing highly viscous liquids with elastic solids or either of these with more complex materials. The results lead to simple algebraic relations from which the time exponent in Nutting's equation can be derived. This is found to agree within limits of experimental error with values from a constant stress compression rheometer. The nature of subjective

firmness judgments is tentatively discussed and the use of fractional differential expressions is introduced. The Nutting equation is shown as a special case of a more general equation and the fractional differentials involved are found to result from the conventional (Newtonian) definition of equality of time units.

## Second Session

FRIDAY, NOVEMBER 1, 1:30 P.M.

*Chairman*, H. MARK, *Polytechnic Institute of Brooklyn*

**Viscoelastic Properties of Resins at Elevated Temperatures.** G. J. DIENES, *Bakelite Corporation.*

A method of measurement and analysis, based on the parallel plate plastometer, has been developed for the determination of the viscoelastic properties of plastic materials at elevated temperatures. It is shown theoretically and verified experimentally that, for linear viscoelastic materials, measurements from constant load and constant plate separation experiments may be expressed, by using the appropriate normalization factors, as deformation-time and stress-time curves, respectively. The necessary criteria for interpreting such measurements in terms of a mechanical model are discussed. The method has been applied to vinyl chloride-acetate resin, polyethylene resin compounds and a cellulose ester compound. The data show that these compounds are linear viscoelastic materials, that is, the deformation (or any of its components) is proportional to the applied stress at a fixed value of the time. Data are presented which show that at elevated temperatures the viscoelastic properties of these materials are representable by a simple mechanical model consisting of a pure elastic spring, a retarded Voigt element and a pure viscous dashpot coupled in series. The elastic, delayed elastic, and viscous components of the deformation are, therefore, quantitatively separable and are completely characterized by four constants, two elastic moduli and two viscosity coefficients. High temperature stress-strain curves at various rates of loading, and recovery behavior after periods of continuous deformation are predicted theoretically and verified experimentally. The variation of the viscoelastic constants with temperature and composition has been evaluated. The principal viscosity (viscosity of pure dashpot) is the only viscoelastic constant which obeys a linear log $\eta_3$ *vs.* $1/T$ relation over wide ranges of temperature, thus permitting the calculation of activation energies for viscous flow. It is shown that the disappearance of elastic effects is associated with a sharp decrease of the retardation time (time constant of the delayed elastic deformation). A study of polyethylenes of various molecular weights shows that the effect of increasing molecular weight is to increase the resistance to both the elastic and the viscous types of deformation and to increase the temperature at which elastic effects become negligible. The principal viscosity varies with the molecular weight according to Flory's relation (linear log $\eta_3$ *vs.* $M^{\frac{1}{2}}$). The variation of the other viscoelastic constants with the molecular weight is more complex.

**Concentrated Solution Viscosity of Polystyrene.** R. S. SPENCER AND J. L. WILLIAMS, *The Dow Chemical Company.*

Data are presented on the viscosity, under various conditions, of solutions of polystyrene in the range from a few percent to 50 percent polymer. It is shown that Martin's equation represents the effect of concentration rather well up to about 20 percent polymer, and that Flory's relationships for the individual effects of concentration and molecular weight hold over the entire range covered. A study of the simultaneous effects of temperature, molecular weight, and concentration on the viscosities of isopropylbenzene solutions of polystyrene shows that both the temperature coefficient and molecular weight coefficient depend on the concentration. This influence of concentration on activation energy has been noted by other workers for the cases of rubberlike elasticity and dielectric relaxation.

Extrapolation to obtain the activation energy of viscous flow of pure polystyrene is discussed, and a comparison is made between the values thus obtained and those reported in the literature. It is concluded that this quantity has a value in the neighborhood of 12 kcal.

**Statistical Analysis of Plasticity Measurements of Natural and Synthetic Rubber.** M. C. THRODAHL, *Monsanto Chemical Company.*

A simple statistical analysis is made of the three types of plasticity measurements—parallel plate (Williams), extrusion (Dillon-Johnston), shear (Mooney)—on crude Hevea and GR-S rubbers. Based on the method of preparation of 256 samples used for the measurements, it was found that shear plasticity data were most precise of the three types, with parallel plate and extrusion types following in that order. The coefficient of variability in parallel plate and extrusion type measurements was less for GR-S than for Hevea; however, this coefficient was less for Hevea than for GR-S in shear plasticity measurements.

**Rheology of Asphalt.** J. W. ROMBERG AND R. N. TRAXLER, *The Texas Company.*

The difficulties encountered in evaluating the rheological properties of asphalts possessing complex flow are discussed

and a new method for measuring viscosity at a constant power input is described. Methods for measuring elastic effects are reviewed and relaxation one-half time data based on Maxwell's equation are given for several different kinds of asphalt.

Nutting's stress-strain-time relationship is discussed and data are given which indicate that it is not satisfactory for evaluating the flow properties of asphalts.

*Written discussion of:*

"Rheology of Asphalt" by J. W. Romberg and R. N. Traxler.

The writer finds it very gratifying that the authors place so much emphasis on the limitation of the energy input into the system, the viscosity of which is to be measured, in order to minimize the disturbing effects of temperature gradients. Despite the fact that Umstatter[1] has more than 10 years ago directed attention to the danger of temperature gradients in the evaluation of high shear stress viscosity data, and actually determined the temperature increase in an asphalt viscometer, and despite the fact that more than half a dozen authors have contributed mathematical analyses of the temperature distribution in highly stressed liquid to the literature during the past decade, even outstanding rheologists are still presenting viscosity data which are uncorrected for temperature effects. Quantitative and even qualitative misinterpretation of their data is the regrettable result of this surprising neglect.

—A. Bondi

[1] H. Umstatter, Koll. Beih. **37**, 287, 421 (1933); **39**, 265 (1934).

## Third Session

### Business Meeting

*Chairman*, W. F. Fair, Jr., *Mellon Institute*

#### Annual Report of the Secretary-Treasurer

November 1, 1946

Because of the absence of the Secretary-Treasurer from the last Annual Meeting, no report of the Secretary was submitted to the Society. The Treasurer's report appeared later in the May issue of the *Rheology Bulletin*. A copy of the report is included in the present report.

The membership continues to grow at a steady rate. The totals for the past five years are as follows:

| 1942 | 1943 | 1944 | 1945 | 1946 |
|---|---|---|---|---|
| 161 | 171 | 201 | 212 | 231 |

The rate of growth of the membership has been practically constant since 1940.

Non-member bulletin subscriptions this year are 43 against 35 for 1945.

The Society suffered an irreparable loss in the death of Professor E. C. Bingham on November 6, 1945, shortly after the last annual meeting which he attended and in which he took an active part. Messages of condolence were sent to Mrs. Bingham and Lafayette College, and were printed in the May Bulletin which was a Memorial Edition to Professor Bingham.

The reorganization of the American Institute of Physics, of which the Society of Rheology is a Founder Society, has been followed with much interest. The By-Laws were re-written by the Policy Committee of the Institute on January 26, 1946, and unanimously approved by the Governing Board on March 1, 1946 to be the proposed Amendment No. 1 to the Constitution.

As outlined on page 5 of the August Bulletin, the Amendment provides for the Founder Societies to continue as Member Societies, and additionally provides for personal membership either as Member or Associate Member. Under this plan, Members must be members of a Member Society whose annual dues are not less than $4.00. The representation on the Board of Directors of the Institute will be determined for a Member Society on the basis of its own membership. The Society would be represented by 1 Director since it falls in the class having up to 500 members, whereas now it has three members on the Governing Board. It has been reported to the Secretary that the rest of the Founder Societies have approved the Amendment, hence the vote of the Society of Rheology will only be a token one. However, a decision in the matter should be determined by the Society at the present business meeting.

During the year the members have been asked to vote on matters of policy by casting two written ballots which were published in the May and August Bulletins. Copies of both ballots are appended to this Report. The results of the May ballot were as follows:

| *Question* | *Result* |
|---|---|
| 1 | Yes |
| 2 | No |
| 3 | Yes |
| 4 | No |
| 5 | Yes |
| 6 | Yes |

From the results of this return, the officers of the Society decided to continue the Bulletin in its present form for this year, and in the meantime to prepare a suitable publication program which would fit into the program of A.I.P. and its proposed new journal *Physics*. The Smoker planned for this meeting was the action taken on the vote on question 6.

The August ballot was to determine the attitude of the membership on the proposed Amendment No. 1 to the Constitution of the A.I.P. as discussed above. The results

showed a large majority of those voting to be in favor of accepting the amendment.

As outlined in the August issue of the Bulletin, the Executive Committee has tentatively planned a publication program which appears to be satisfactory for the present needs of the Society. Members would receive *Physics* and 1 issue of the *Journal of Colloid Science* for their dues. This plan will be submitted for further consideration at the present annual business meeting.

Respectfully submitted,

R. B. Dow
*Secretary-Treasurer*

### Minutes of Annual Meeting

November 1, 1946

One hundred and thirty-six persons registered for the Annual Meeting before which 17 papers and 3 abstracts were read. After the introductory remarks by President W. F. Fair, Jr., Mrs. E. C. Bingham was introduced as a guest of the Society. A short period of silence was observed in memory of Professor E. C. Bingham. A Symposium of invited papers opened the meeting which was dedicated to Professor Bingham. The Symposium and session of contributed papers were given on November 1 and 2 in the Keystone Room of the Hotel Pennsylvania.

The Annual Business Meeting was called to order by President Fair in the Keystone Room at 4:00 P.M. on November 1. The Minutes of the 1945 Annual Meeting, the Secretary's, and the Treasurer's Reports were accepted as read. The President explained the necessity of revising the Constitution of the Society to conform with Amendment No. 1 of the Constitution of the American Institute of Physics, and asked for a motion to appoint a Committee to do this task. After a favorable vote, Messrs. Markwood (Chairman), Alfrey, and Dow were appointed to the Committee. Editor Markwood spoke briefly on the Publication Plan of the Society which had been published in the Bulletin and approved prior to the Annual Meeting. Dr. La Mer stated the publication policy of the *Journal of Colloid Science*, and assured the members that the Symposium Papers would be published in January, or in March at the latest. All necessary space would be available for good material.

The status of the National Bureau of Standards project on the determination of the absolute viscosity of water was reviewed by the Secretary. He was authorized by vote to write to the Director to express the interest of the Society in seeing the work continued.

President Fair announced Mrs. Bingham's gift of $100 to the Society. It was suggested that it be used to establish an award in rheology in memory of Professor Bingham. President Fair spoke of a tentative plan whereby a medal with possibly a small cash award could be given each year by the Society. After considerable discussion on the matter from the floor, Dr. Mooney proposed a motion that the Executive Committee be empowered to examine the possibility of obtaining further funds for this purpose, and to solicit them if it appeared feasible in order to establish the fund. Dr. Spurlin suggested the amendment that the Executive Committee be authorized to award a medal next year, irrespective of the drive for funds. The amended motion was passed. President Fair stated that the assistance of an additional committee would be asked to help work out the details of the award.

The Nominating Committee for officers for 1947–49 was announced by the President to be: Messrs. Dow (Chairman), Nason, Spencer, Nadai, and Huggins.

Dr. Barton, Director of the American Institute of Physics, spoke briefly on individual membership in the reorganized Institute. Announcements about the new journal *Physics* will be made in about a month. The lack of paper and good editorial personnel have delayed the journal. President Fair announced that a new Membership Committee would be appointed in the near future and asked the help of all members in increasing the membership in the Society. The meeting was closed with the announcement that the next Annual Meeting would be held in New York City, and upon vote of the Society the Secretary was instructed to send the greetings of the Society to Professor Wheeler P. Davey of Pennsylvania State College who could not be present on account of ill health.

A Smoker was held on the evening of November 1 which provided a general get-together for the members and their guests. Dr. Nadai gave an excellent, illustrated talk on his recent travel to a scientific conference in Russia.

Respectfully submitted,

R. B. Dow
*Secretary-Treasurer*

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## Fourth Session

### Social Evening

FRIDAY, NOVEMBER 1, 8:00 P.M.

*Master of Ceremonies*, TURNER ALFREY, JR., *Polytechnic Institute of Brooklyn*

**Trip to Moscow and Leningrad to Attend Celebrations of the 220th Anniversary of the Foundation of the Academy of Sciences of the U.S.S.R. June 15 to July 1, 1945.** A. NADAI, *Westinghouse Research Laboratories.*

In this trip 16 Americans and 1 gentleman from Mexico participated. The trip was made by Army plane from New York over the Azores, Casablanca, Cairo, to Teheran, with short stop-overs in these last two cities; then by

Russian Army plane to Moscow. Perhaps 160 foreign delegates participated in the two weeks meetings in Soviet Russia together with some 800 scientists of the Russian Soviet Republics. The Russian Academy was founded by Tsar Peter the Great in 1725. The delegates of this International meeting were received by the Academy of Sciences in Moscow on June 15, in a beautiful building situated along the Moscow river, by President V. L. Komarow and by Dr. Bardin, Dr. Joffe and Dr. Orbeli, Vice Presidents. During a 10-day sojourn in Moscow a series of general meetings were held and members of the congress were invited to visit various scientific institutions in and near Moscow. The writer made the acquaintance of a number of outstanding Russian engineers working in the field of theoretical mechanics, including strength of materials. Among these were N. N. Davidenkov, member of the Ukrainian Academy of Science and Drs. Ilyushin, Ishlinsky, and Sokolovsky. The writer was greatly surprised to discover that the Academy of Sciences in Moscow had published during the last 10 years a *Journal of Applied Mechanics and Mathematics*. The editor of this Journal, Mr. Talitskich, kindly gave the writer information concerning many most valuable papers which had been published in this journal on the theory of the flow of metals, theory of elasticity, hydrodynamics and other subjects. The writer was presented, to his further surprise, with a copy of a Russian translation of his book on *Plasticity* which had been published in 1936. The members of the Congress were taken by two special trains from Moscow to Leningrad where the laboratories of the great Russian physiologist, Pavlov, and of Dr. Joffe, physicist, were visited. All members of the American party were unanimous in their praise of Russian scientific work, particularly in the theoretical branches of the various sciences. This was particularly the case in theoretical rheology. The Russians have developed the mathematical theory of plasticity during the past 10 years, numerous important exact solutions of which are entirely unknown to American readers. In the institute of Joffe and Davidenkov much very interesting work could be seen, for example, on the problems of the brittle failure of materials, on the statistical theory of fracture, on impact problems. The Academy has in Moscow an Institution of Applied Mechanics which the writer visited. It is well known that the Russian Academy is the central organization in Soviet Russia guiding and organizing practically all scientific research in that country. Thus, the Academy has scientific laboratories in all branches of science throughout the country, including some remote cities of the Union.

The members of the Congress were lavishly entertained during the $2\frac{1}{2}$ weeks sojourn in Moscow and Leningrad. They were given wonderful performances in the Bolshoj opera house in Moscow and in the opera house in Leningrad, mostly operas of Russian composers. One evening the Congress was the guest of the Central Government in the Georgian Hall of the Kremlin Palace at which most members of the Russian Government were present, including Stalin, Molotov, and others. The American party was also guest twice of Ambassador Harriman, Spassow House.

The return trip was made by Russian Army plane from Moscow crossing over Siberia with stops in Novosibirsk, Kerensk, and Jakutsk, crossing the Bering Straits to Fairbanks, Alaska, returning from there to Minneapolis on July 5, 1945.

A. NADAI

## Fifth Session

SATURDAY, NOVEMBER 2, 9:00 A.M.

*Chairman*, W. H. MARKWOOD, JR., *Hercules Powder Company*

**Mechanism of Brittle Fracture.** NELSON W. TAYLOR, *Minnesota Mining & Mfg. Company.*

A new equation has been derived from fundamental principles, which connects the stress, $f$, required to break a brittle material in simple tension, with its duration of application, $t$. This equation is

$$t = t_0 e^{2E\theta/fT}$$

where $E$ is Young's modulus, and $\theta$ is a small number having the dimension of temperature. It is related to the heat capacity by the equation $k\theta = \frac{1}{2}$ (heat capacity per molecule for one degree of temperature), $k$ being Boltzmann's constant, and $T$ being the absolute temperature. By using common logarithms this equation becomes

$$\log t = \log t_0 + 2E\theta/2.3fT.$$

This equation is identical in form with the empirical equation $\log t = -a/m + 1/fm$ developed for glass by J. L. Glathart and F. W. Preston.[1] The theoretical equation permits quantitative treatment of the effect of temperature on the breaking strength and also on the strength-time relation.

The rate controlling process appears to be the orientation or displacement of the atomic network in the direction of maximum tension. The elementary step in this process requires the participation of a "unit segment" of solid whose length is inversely proportional to the stress. Fracture takes place when the elongation of this unit reaches a critical value, and is (by thermal agitation) momentarily concentrated in a single bond of that segment.

The theory permits calculation of the surface tension

or specific surface energy of the solid from breaking strength data. It also offers an explanation of the great strength of small fibers or of small areas under load.

A parallel treatment of the problem of breakdown of electrical insulators under high voltage will be published elsewhere.

[1] J. L. Glathart and F. W. Preston, J. App. Phys. **17**, 189–195 (1946). See also F. W. Preston, Nature **156**, 55 (July 14, 1945).

**A Review of the Rheology of Bituminous Materials.** R. N. TRAXLER, *The Texas Company.*

Methods for evaluating the consistency of bituminous materials in absolute units are reviewed with emphasis on procedures for measurement of high viscosities. It is pointed out that since such materials may be either simple or complex liquids the use of rheology diagrams is helpful. Methods for calculating viscosity and degree of complex flow are discussed. Published work on age-hardening and its relationship to the degree of complex flow in a bitumen is reviewed. Various methods that have been proposed for evaluating temperature susceptibility are mentioned. Data are given which indicate the relationship between elasticity and degree of complex flow of different asphalts. References are cited to fundamental work on the theology of filled asphalts.

The rheological aspects of the tests commonly used on bitumens such as softening point (R & B), A.S.T.M. penetrometer, and ductility test are discussed at some length. A short review is given of published investigations concerning the colloidal properties of bitumens as related to their rheological characteristics.

**The Rheology of Processing Quality of Raw Rubbers.** M. MOONEY, *United States Rubber Company.*

Departures from perfect processing in calendering and extruding of raw rubber stocks are enumerated and briefly discussed. They include shrinkage, or elastic recovery from the forming operation, roughness, slow extruding, tearing, and scorching, or partial curing during the forming operation.

Rheological tests useful in studying processing defects are briefly described. These include principally "plasticity" or viscosity measurements of the compression, extrusion and shearing type, together with the corresponding measurements of elastic recovery. Measurements of tack, or adhesion strength, can also be made, but are not yet generally used.

The rubber industry is only beginning to find empirical correlations between rheological measurements and processing defects. In such work, quantitative measurements of various defects are coming into vogue. These include calender and extruder shrinkage, rate of extrusion, and surface roughness.

**The Rheology of Lubricants.** R. B. DOW, *Bureau of Ordnance, Navy Department.*

The commercial development of the new organo-silicon oxide polymers and fluocarbons has opened up a new field of lubricants of remarkable chemical stability. The rheological properties of some of these new compounds will be discussed briefly. The chemistry of additives to lubricants has been greatly broadened during the past five years due to the remakable success of these compounds in improving "oiliness" of lubricants. Studies have been continued on the chemical nature of oxidation in lube oils, and it has been shown that greater stability in service is not necessarily attained by the practice by using an oil of higher viscosity. The marked effect of gases under pressure in reducing the normal viscosity of a lube oil has been further demonstrated at several temperatures over a gas pressure range of 3000 psi.

Interest continues in the field of high pressure effects, notably illustrated by the publication recently of two extensive surveys on viscosity and allied effects under pressure. The previously reported use of the A.S.T.M. chart to represent viscosity-temperature-pressure data for lube oils is further discussed. New data on viscosity-temperature-pressure relationships for high V.I. hydraulic oils are presented, also a similar study of Burma oils to conclude a survey of this pressure effect on typical foreign oils. On searching for a readily measured characteristic of a lube oil which might be correlated with the pressure coefficient of viscosity, it has been found that the aniline point offers some promise in this respect. Some of the other possibilities of more fundamental significance, e.g., molecular weight, paraffinic content, index of refraction, $H/C$ ratio, etc., have been found to bear no detailed or consistent relationship to the pressure coefficient of viscosity of petroleum oils. The extremely high thrust-shear technique of Bridgman has been applied to a very interesting examination of the friction properties of thin films of various lubricants. Another rheological property of some interest at high pressures is the solidification of lubricants which will be mentioned briefly. Some of the interesting theoretical developments of late will conclude the review of rheological properties of lubricants.

*Written discussion of:*

"Rheology of Lubricants" by R. B. Dow.

It appears most probable to the writer that more careful observation of the volume *vs.* pressure curves will reveal a compressibility increase in the pressure range in which a second phase is precipitated, just as careful investigation under isobaric conditions led to the discovery of both volume and heat effects in the temperature range in which a second phase appears in lubricating oils.[1] The inverse relationship between Aniline point, a measure of the aromaticity of petroleum fractions, and viscosity-pressure coefficient, which has been discovered by Dr. Dow, is quite well understandable from the point of view of the rate process theory of flow,[2] since the cyclic component of the oil molecules due to its rigidity increases the size of the kinetic unit of flow, and thereby $\Delta V_{\ddagger}$, the viscosity-pressure coefficient. This explains also the scatter points on Dr. Dow's graph, because naphthene rings will act kinetically like benzene rings and likewise increase $\Delta V_{\ddagger}$,

but will decrease the aniline point very much less than the latter.

—A. BONDI

[1] A. Bondi, Petroleum Zeits. **33**, 14 (1937), Petro. Refiner **22**, 287 (1943).
[2] A. Bondi, J. Chem. Phys. **14**, 591 (1946).

**Rheological Properties of Paints, Varnishes, Lacquers and Printing Inks.** HENRY GREEN, *Interchemical Corporation.*

The bulk of the work done in "pigment-vehicle" rheology has been carried out mainly in industrial laboratories. In order to find out what has been accomplished in the study of the rheological properties of materials like paints and printing inks (usually Bingham-bodies) it is necessary to turn to industry for information rather than to our colleges or to textbooks.

The displacement of single-point methods by consistency curves, as a method of measurement, has been slow and by no means complete. Progress in this direction has been made, however, and the situation is not discouraging.

The Bingham concept of plastic flow has been accepted. If it is not in universal usage, that is largely because there are no satisfactory commercial viscometers available that can produce the necessary types of curves. Reiner and Rivlin have deduced the equation of flow of Bingham-bodies in rotational viscometers. This equation gives the rheological factors, yield value, and plastic viscosity. The amount of thixotropic breakdown can be determined from the area of the loop formed when the up- and down-curves of a thixotropic material are plotted together. This loop is produced only by means of rotational viscometers.

Materials like heavy bodied oils, and varnishes act like Newtonians under low rates of shear, but form thixotropic loops under high rates. The accumulated heat is insufficient to explain this fact. Pseudoplastics cannot be reduced to yield value and plastic viscosity, or to analogous parameters. Their measurement, therefore, for the present consists only of their consistency curves.

*Written discussion of:*

"Rheological Properties of Paints, Varnishes, Lacquers, and Printing Inks," by Henry Green.

The controversy about the reality of the yield value to which Dr. Green referred broke out shortly after Professor Bingham presented his differential equation 30 years ago. It could very well be made an entirely non-controversial issue. We all realize today that there is, strictly speaking, probably no such thing as a yield value, for as we refine our methods of velocity measurement we can observe a substance to flow at lower and lower "yield values." There is no question, on the other hand, but that the technical rheological behavior of lubricating greases, printing inks, etc. is characterized by something that amounts to the same as a yield value. It appears therefore most desirable and would eliminate further controversy to *qualify* observed derived *yield value* by the (arbitrary) shear rate value for which it has been found. Several authors have already adopted the practice to define the yield value reported by the minimum observable shear rate or velocity under the condition of tes. Vold,[1] e.g., defined his "practical yield values" by a minimum observable velocity of $10^{-4}$ cm/sec.

—A. BONDI

[1] R. D. Vold and L. L. Lyon, Ind. Eng. Chem. **37**, 497 (1945).

**The Bingham Viscometer and Viscosity Standards.** J. F. SWINDELLS, *National Bureau of Standards.*

The paper deals with a technique which has been found to be satisfactory for the use of Bingham viscometers in evaluating the viscosities of the National Bureau of Standards standard viscosity samples based on the value of 0.01005 poise for water at 20°C. This includes a discussion of the various possible errors involved and methods used in minimizing their effects. Other standards are discussed including sucrose solutions and the American Petroleum Institute Oil Standards. A table of what seem to be the best values for the related viscosity of water in the range 10–60°C is also included.

**The Fundamentals of Tackiness and Adhesion.** J. J. BIKERMAN, *Merck and Company.*

The paper compares the importance of "molecular" forces with that of "rheological" forces on different stages of making and breaking adhesive joints.

Adhesives usually are applied in liquid form, and the perfection of the contact between the adhesive and the solids to be joined depends above all on the wetting power of the liquid toward the solids. This wetting power is primarily a "molecular" phenomenon. The resistance which must be overcome to separate two solids jointed by a liquid adhesive is tackiness. Its mechanism is purely rheological, and tackiness is a function of viscosity. When, in the course of its setting, the viscosity of the adhesive becomes very high, the resistance to separation is still rheological, but is smaller than would be expected from the viscosity. Some new experiments concerning this intermediate region between tackiness and final strength are reported. When the adhesive has "set," the resistance to separation is determined by the final strength of the adhesive, which (for tensile tests) is identical with the tensile strength of the adhesive film of the given thickness; the final strength, too, is a rheological property. The experiments which are claimed to prove disagreement between final strength and tensile strength are given a different interpretation. The rupture occurs usually within the set adhesive, not between the adhesive and a solid, and, consequently, molecular forces are not involved in the determination of final strength, probably because of the universal roughness of solid surfaces.

**The Initiation and Propagation of the Plastic Zone along Tension Specimen of Nylon.*** JULIUS MIKLOWITZ, *Westinghouse Research Laboratories.*

This paper presents a study of the mechanical factors influencing the initiation and propagation of the plastic zone in Nylon. Nylon is a material that exhibits a well-defined yield point. Upon drawing a fiber of this material from a state in which its long-chain molecules are in random

orientation into one in which the molecules are parallel to the tensile axis, a stress-strain diagram is produced which shows an upper and lower yield stress and a large yield-point elongation. The yield-point elongation is produced by the formation of a plastic discontinuity on the fiber (in the shape of a neck or constriction) during the drop from upper to lower yield load, and by the travel of the boundaries of the discontinuity along the fiber under a constant tensile load. These characteristics of Nylon make it an extremely valuable material in studying localized yielding (the well-known property of mild steel), since with its enormous strain values, the details of discontinuous flow are greatly magnified.

Specifically, studies were made of the influences of the speed of stretching and rigidity of the testing machine on the initiation and propagation of the plastic zone and the accompanying phenomena. Under constant conditions of machine rigidity and speed of stretching, the progressive yieldings produced by one and two traveling boundaries were compared.

The results of the tests gave conclusive evidence of, and data on, the factors influencing the shape of the plastic boundary and the extent of the yield-point elongation. Mechanical effects on the yield stresses were also noted.

It was found that the full yield-point elongation of Nylon is composed of two parts: first the strain in a section of material due to the plastic boundary passing over it, and second a small amount of strain due to the continuous action of the load on this section as the plastic disturbance advances to yield other sections of material; the longer the load remains on the section, the greater the strain of that section becomes. As the speed of deformation increases, the length of the plastic boundary decreases, or stated in other words, the maximum strain of a cross section of material, due to the boundary passing over it, occurs more abruptly. This maximum strain increases with an increase in speed of deformation. The yield-point elongation, which depends in main on this maximum strain, increased almost three times for a ten thousandfold increase in speed. Yielding by two plastic boundaries progressed under a mean strain rate one-half as great as that in the single boundary yield. Following in line with the speed effect found, the maximum strain in the two-boundary yield was less than the single. The shape of the plastic boundary remains approximately the same throughout the yielding process, provided the relative speed between the heads of the specimen remains constant.

The upper yield-load stress increased almost two times over a ten thousandfold increase in speed. The true yield stresses, occurring at any strain within the yield-point elongation, increased almost two times over the same speed range. The test results gave proof that as the rigidity of the testing machine became greater the upper yield-load stress increased. The load drop from upper to lower yield point became steeper with an increase in rigidity.

* See footnote to next paper.

**The Stress-Strain Relationship of Nylon under Biaxial Stress Conditions.*** JULIUS MIKLOWITZ, *Westinghouse Research Laboratories.*

In this paper a method is described by which the stress-strain characteristics of Nylon under equi-biaxial tensile stress were investigated. The results of the tests made are used for comparison with the applied single-stress condition, under which Nylon showed a well-defined yield point and localized yielding.

In comparing the ordinary load stress-conventional strain curve of the Nylon fiber with that of the equi-biaxial load stress-conventional strain curve of the membrane, it may be said that both show practically the same flow point. The essential difference is the drop in stress during the yield point elongation of the membrane, whereas the fiber yields under a constant stress.

The true stress curve of ordinary tension lies above that of the true stress of equi-biaxial tension.

* These papers are based on an investigation done for the National Defense Research Committee (Division 2) of the Office of Scientific Research and Development under O.S.R.D. Contract OEMsr-891 (O.S.R.D. Report No. 3864 (1944)). Acknowledgments are due Dr. A. Nadai of the Westinghouse Laboratories for guidance in this work and Division 2 for permission to publish parts of the investigation.