# RHEOLOGY BULLETIN



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#### RHEOLOGY BULLETIN

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#### THE SOCIETY OF RHEOLOGY

Dedicated to the Development of the Science of the Deformation and Flow of Matter

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1.

The Leaflet Becomes The Bulletin. Commencing with this issue, the Rheology Leaflet becomes the RHEOLOGY BULLETIN. Commencing with this issue, too, we resume the numbering of volumes, etc.. to agree with the old Journal of Rheology, Vol. III of that journal having been issued in 1932. Fifteen issues of the Rheology Leaflet were published.

**The Annual Meeting.** The 1941 meeting of the Society of Rheology will be held in New York in October. The exact time and place of meeting are now being arranged. The members of the program committee are:

- F. C. Bingham; Dept. of Chemistry, Lafayette College, Easton, Pennsylvania.
- R. H. Ewell; Dept. of Chemistry, Purdue University, Lafayette, Indiana.
- W. F. Fair, Jr., Mellon Institute, Pittsburgh, Pa.
- A. I. McPherson; National Bureau of Standards, Washington, D. C.
- A. Nadai; Research Laboratory, Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pa.
- H. F. Wakefield; Bakelite Corp., Bloomfield, N. J.
- R. B. Dow, Chairman; New Physics Bldg., The Pennsylvania State College, State College, Pa.

This committee has been very active. It has eight good papers definitely promised so far and eight others are partly arranged for. All those wishing to offer papers should communicate at once with some member of the program committee and should enclose an original and two carbon copies of a 300 word abstract.

**The Civil Service Commission** (Room 220 Atlantic Bldg.. Washington, D. C.), asks us to call attention to various openings for rheologists, (fields of fuels, rubber, plastics, textiles), at salaries ranging from \$2,600 to \$5,600 per year. Applicants will not be given a written examination but will be rated on the basis of education and experience. Applications should be made at once, and in any case should reach the commission before December 31, 1941. For details see Bulletin No. 30 at any first or second class post office.

They Can't Keep the British Down. Your editor still receives notices of meetings of The Plastics Group of the Society of Chemical Industry. The latest notice tells of a meeting at a "temporary address" in London, February 6th. The only thing in the notice that doesn't look like "business as usual" is the omission of the customary luncheon or dinner.

**C. F. Kettering** at the Presentation Dinner of the **5th Annual Modern Plastics Competition** said "Whenever you do not know what a thing is in English, find out what it is in Latin or Greek and then you can get away with it . . Rheology is a word that slips in and you don't know why. You will find all through your industry just such words that mean absolutely nothing. It is to cover up the fact that you do not know what they are." He gives "photosynthesis" and "chlorophyl" as additional examples. Perhaps he wishes to encourage the use of ten words when one would convey the same meaning. One could then say, as he has, that an automobile is "a chemical device for making carbon dioxide and water".

The February Issue of J. Applied Physics contains an article on the Theory of Plastic Properties of Solids by F. Seitz and T. A. Read.

**The Measurement of Thixotropy** by Harvey A. Neville which appeared in The Rheology Leaflet No. 12, has been reprinted in Lehigh University Publication Vol. XV, Jan. 1941, No. 1.

The N. Y. Academy of Sciences, Section of Physics and Chemistry held a conference on "Viscosity" February 14-15. This well-attended meeting was held in the Academy quarters in the American Museum of Natural History. The large lecture hall and the comfortable office provide excellent facilities for the conferences which they hold about four times each year. The purpose of these conferences has been described by Dr. D. A. MacInnes in his introductory remarks at an earlier conference on "Electrophoresis" and, because they might also apply to the Society of Rheology, we are taking the liberty of quoting him in regard to "the ideas underlying the organization of the conference. It has appeared to the author and some of his associates that the older scientific societies, useful and effective as they are, fail in certain important respect. Due to crowded programs, not to mention crowded rooms, and the fact that they are in general organized around one branch of science, they fail to provide opportunities for the unhurried discussion of topics interesting to scientists representing a wide range of activities. This conference on electrophoresis was therefore arranged to provide (a) a short program of papers dealing, from widely different points of view with the subject of electrophoresis, (b ample time for discussion, and (c) an invited audience limited to those capable of taking part in the discussions.. It is of considerable interest that the selection of speakers and audience cut right across the usual divisions of physical science."

The program, which follows, conformed to that ideal. Friday, February 14.

- Introductory Remarks H. Mark. Conference Chairman, Polytechnic Institute of Brooklyn.
- "Forces and Molecular Arrangement in Liquids"—P. Debye. Cornell University.
- "Viscosity of Liquids"—H. Eyring, R. E. Powell and Ch. Clark, Princeton University.

#### Luncheon.

- "Distribution Functions in Condensed Systems"—J. E. Mayer, Columbia University.
- "Viscosity of Large Molecules in Solution"-R. Simha, Columbia University.

After the completion of the day's program the group joined in a cocktail hour arranged by the Executive Secretary, Mrs. Eunice Thomas Miner and her staff. Informal discussion of viscosity continued through the dinner which was held in the Museum restaurant where the guests were welcomed by Dr. Roy W. Miner, President of the Academy for 1940 and 1941. Saturday, February 15.

"Experimental Aspects of Viscosity, Diffusion and Sedimentation of High Polymers". E. O. Kraemer. Biochemical Foundation, Newark, Delaware.

E. O. Kraemer. Biochemical Foundation, Newark, Delaware. The collected papers will be published in an early volume of the Annals of the New York Academy of Sciences.

Professor H. Mark has been kind enough to write the following summary for the Rheology Bulletin.

## Report On the Conference On "Viscosity."

The aim of the conference was to present and discuss the present experimental and theoretical knowledge on the viscosity of liquids and solutions with particular emphasis laid on the viscosity of long chain molecules.

Prof. P. Debye pointed out how the diffraction of light and x-rays has been successfully used to get an insight into the arrangements of the molecules in a liquid. Very small changes in the wave length of scattered visible light allow one to determine the wave length and the rate of propagation of heat waves in a liquid and provide very interesting conclusions concerning density fluctuations in small volumes. X-ray scattering makes it possible to determine the average position of the atoms (Hg) or molecules (CCl<sub>4</sub>), which is best described by a curve indicating the probability of finding an atom or a molecule, expressed as a function of the distance from a given particle which has been chosen as origin. Prof. Debye further showed that rather similar molecules such as benzene or toluene seem to behave quite differently as soon as one is concerned with not only their mutual forces but also their geometrical packing effects.

Dr. Powell presented a paper, which was prepared by Prof. H. Eyring, Dr. Clark and himself. It shows that one can describe diffusion, viscosity behavior, surface tension and other properties of long chain molecules under the assumption that those molecules move as a whole (curled up) particle in sufficiently diluted solution, while they move in certain sectional sequence in more concentrated systems. If one takes the Eyring-Flory-Kauzmann equation for the viscosity of the pure molten high polymer as the extreme case in which the particles move in quasi-independent segments, and the Staudinger equation as the other extreme case in which the particles move independently as a whole, then one succeeds in explaining intermediate states (concentrated solutions) by combining these two relationships in a suitable manner. In order to reach agreement with the experimental facts, one has to assume segments of between 10 and 30 elementary units of the high polymer (glucose unit in case of cellulose, isoprene in case of rubber, etc.)

Prof. J. E. Mayer expounded the fundamental laws, which govern the distribution of molecules in liquids and solutions. He showed that for a complete satisfactory description, one would need to know the potential energy of any two not too remote particles as a function of the radius, then of any three of them and so on. As a good approximation, however, one can use the mutual interaction of two particles in which case, one is led to the distribution of molecules, which was derived by Debye from the angular intensity of distribution of scattered x-rays and which was discussed in the first paper.

These three papers gave a very comprehensive and up-to-date description of the statistical methods, which can be used to interpret the experimental results of viscosity measurements.

Dr. R. Simha completed the picture of the present situation from the hydrodynamical end. He discussed the different efforts to figure out how the viscosity of a liquid is increased if rigid (or quasi-rigid) particles of various number, size and shape are dispersed in it. The fundamental equation of Einstein (1906) has been extended to elongated particles and into the range of high concentrations. These considerations lead to expressions which are in fair agreement with measurements on model suspensions and with investigations on high polymers in the ultracentrifuge. The Staudinger rule appears as a statistical equation showing that in very diluted systems long chain molecules behave like independent, curled up, particles. Viscosity measurements allow a fair estimation of their average size, shape and interaction.

Finally, Dr. E. O. Kraemer described extensively the present state of experimentation and combined viscosity measurements with the investigation of osmotic phenomena, diffusion and sedimentation. Two experimental difficulties are outstanding:

a. In order to reduce the eventual interaction of the dispersed particles, one has to go to very diluted solutions; usually around 0.05 volume per cent, sometimes even still lower. Viscosity can still be measured in such systems with sufficient accuracy, but measurements of the other properties (diffusion, osmotic pressure, etc.) are extremely delicate.

b. All high polymers are more or less heterogeneous mixtures of molecules of different size, shape and sometimes even chemical composition. One has, therefore, always to deal with average values, which are of different nature if different experimental methods are employed and therefore must not be compared with each other without precaution.

The discussion centered on the points, which were put forward by the speakers and emphasized particularly, the necessity of better experimental data to check and improve the present concepts on the behavior of long chain molecules in the melt and in solutions.

#### A REPORT ON RHEOLOGICAL DEFINITIONS AND NOMENCLATURE.

#### Foreword.

In the following report by the Committee on Definitions and Nomenclature, an attempt is made to develop a logical and self-consistent system of classification of materials according to their rheological properties. The classification and the accompanying definitions have been developed in terms of idealized materials to which actual materials can be compared. In other words, ideal types of behavior and deformation are postulated which are susceptible of exact definition and classification. Actual materials can then be described in terms of the ideal types to which their behavior approximates. It should be borne in mind that an actual material with rheological properties coinciding exactly with those of a single idealized material is the exception rather than the rule. In applying to actual materials the quantitative definitions for idealized materials, great caution must be used.

It is recognized that the classification of a particular material may sometimes depend upon the method of measurement. This is particularly true as applied to the precision attained. The recognition of a measureable "yield stress," for example, may depend upon the precision of the measurements and upon the duration of the test. These uncertainties in the classification of materials result from the fact that it is sometimes either impossible or unimportant to determine for actual materials some of the characteristics which can be theoretically distinguished.

In this system of classification and definitions, only shearing strains and stresses are of interest, and the relations involved are expressed with reference to simple shear. Many of the concepts defined here in terms of simple shear are closely related to those usually defined by engineers in terms of more complex types of deformation, such as those arising in tension and compression tests. These deformations, while involving simultaneous shears in three dimensions and hence analytically complex, are often easier to produce experimentally than a simple shear. They therefore serve as a basis for many useful and practical concepts and definitions in the field of engineering. Where an analysis of the fundamental behavior of the material in deformation is required, these engineering tests may be reduced to a combination of shears and described in terms of the concepts used in this report.

A general relation between strain and stress applies to any point within a material, and except in extraordinary circumstances, these values will vary at different points. The quantities involved in these relations applying to individual points within the material cannot be observed directly. Observable quantities such as efflux-rate, pressure, etc., can be obtained by integrating the basic point relations and can then be compared with the values obtained experimentally. It is, however, always possible, at least formally, to devise experiments and methods of analysis by which the fundamental relationship can be completely determined from experimental data.

Although all materials exhibit the inertia effects associated with acceleration of the mass elements within the material, these effects are ignored as being irrelevant in the classification and definitions given below. It should be noted that turbulence and related hydrodvnamical properties belong in this category.

#### Descriptive Definitions.

**Plasticity** is that property of a body by virtue of which it retains a fraction of its deformation after reduction of the deforming stress to zero.

**Elasticity** is that property of a body by virtue of which it recovers its original size and shape after deformation.

**Thixotropy** is that property of a body by virtue of which the ratio of shear stress to rate of deformation is temporarily reduced by previous deformation.

**Strain hardening** is that property of a body by virtue of which the stress required for permanent deformation increases with the extent of previous permanent deformation.

A fluid is a substance which undergoes continuous deformation when subjected to shear stress.

A solid is a substance capable of remaining in static equilibrium under a shear stress, less than some value called the Yield Stress.

#### Quantitative Definitions

A simple shear strain is a deformation in which the material at any point has moved parallel to a fixed line in a reference plane by an amount which is proportional to the distance of the point from the plane. Such a deformation is shown in Figure 1, the full lines showing the initial shape and the dotted lines the final shape. 00 is the fixed line in the reference plane, P is the original position of a point in the body, and P' its position after deformation. The shear strain,  $\epsilon$ , is given by the ratio of the displacement ds to the distance dx of the point P from 00, or  $\epsilon = ds/dx$ . This simple relation does not apply if there is rotation of the reference line 00.



The **angle of shear** is the angle whose tangent is the shear strain. In Figure 1 the angle Q is the angle of shear ( $q = \tan^{-1} ds/dx$ ). The **rate of shear** is the time rate of change of shear strain. In Figure 1 the rate of shear is given by:

$$\frac{dv}{dx} = \frac{d(\frac{ds}{dx})}{dt}$$

A **complex shear** is the resultant of two or more simple shears. For simplicity, the definitions given in this report are stated in terms of simple shear, it being understood that the same definitions apply in the case of complex resulting from simple shears of the same type.

When the ratio of shear stress to rate of shear is constant, then the fluid may be called "simple." Under these conditions the constant may be called "coefficient of viscosity."

The **poise** is the unit of viscosity in the C. G. S. system.

The **fluidity** of a simple fluid is the reciprocal of the viscosity. The **rhe** is the unit of fluidity in the C. G. S. system.

The mobility  $\mu$  is the quantity defined by the equation

$$\mu = \frac{\mathrm{d}}{\mathrm{dF}} \left( \frac{\mathrm{d} \mathrm{v}}{\mathrm{d} \mathrm{x}} \right)$$

The **yield stress**  $F_0$  of a solid is the shear stress which must be equalled or exceeded to produce permanent deformation.

The **elastic limit** in shear of a solid is the maximum shear deformation that exhibits complete elastic recovery.

The **shear modulus of elasticity** (modulus of rigidity) of an elastic solid is the ratio of sheer stress to shear strain for values of the shear strain below the elastic limit.

#### Classification.

The classification of idealized types of materials is in terms of their behavior under stress, or the relation between strain and stress. The stress at any point within a material is a function of the strain and its time derivative, or rate of strain.

The stress may depend to some extent on the prior strain or deformation history of the material. Such dependence upon the prior strain is regarded for convenience as a secondary characteristic, materials being classified primarily by the actual relation between stress and instantaneous strain or rate of strain without regard to differences in this relationship that would result from a different strain history.

#### Classes of Fluids.

(a) A simple fluid (Newtonian fluid) is one for which the rate of shear is proportional to the shear stress. Symbolically:

$$\frac{dv}{dx} = \frac{1}{\eta} F$$
 (See note.)

(b) A **complex fluid** (Non-Newtonian fluid) is one for which the rate of shear is a function of shear stress only, this function being other than that of direct proportionality. Symbolically:

$$\frac{dv}{dx} = f(F) > O \neq \frac{F}{\eta}$$
 (See Note)

#### Classes of Solids.

(a) An **elastic solid** is one for which the shear strain is a single valued monotonic function of the shear stress for all values of the lat-

ter below the shear strength. Symbolically:

 $\xi = f(F) > 0, \frac{d\xi}{dF} > 0, 0 \lt F \lt F_{\infty}$  (See note) Reduction of the shearing stress to zero results in the immediate and complete disappearance of the strain.

(b) A **Hookean solid**, (ideal elastic solid), is an elastic solid for which the shear strain is directly proportional to the shear stress for all values of the latter below the shear strength. Symbolically:

 $\in = \frac{F}{G}, 0 \langle F \langle F_{\infty} \rangle$  (See Note)

Reduction of the shearing stress to zero results in the immediate and complete disappearance of the strain.

(c) A **plastic solid** is one which obeys the law of an elastic solid for shear stress below the yield stress, and for shear stress in excess of this value is permanently deformed without further increase in the shear stress. Symbolically:

$$\begin{aligned} E &= f(F) > 0, \quad \frac{dE}{dF} > 0, \quad 0 < F < F_{o} \\ E > 0, \quad \frac{dV}{dX} > 0, \quad F_{o} < F < F_{oo} \\ (See note) \end{aligned}$$

Reduction of the shear stress to zero results in an immediate recovery of the elastic portion of the strain. The strain in excess of that experienced up to the yield point remains as permanent deformation.

(d) A **plastico-viscous solid** is one for which the deformation for shear stress below the yield stress is that of an elastic solid, and which for shear stress above that value deforms continuously at a rate of shear which is a function of the shear stress. Symbolically:

$$E = f(F) > O, \frac{dE}{dF} > O, O < F < F_{o}$$

$$\frac{dV}{dX} = f(F) > O, F_{o} < F < F_{o}$$

(See note)

Reduction of the shear stress to a value below the yield stress results in the immediate reduction of the rate of shear to zero. The strain in excess of that experienced up to the yield point remains as permanent deformation.

(e) A **complex solid** is one for which the shear stress required for deformation is a function of both the shear strain and rate of strain. Symbolically:

$$\in = f(F, \frac{dV}{dX})$$

#### NOTE

The classification given above is without regard to prior strain. When the terms defined above are used without qualification it is implied that the stress-strain relation is independent of the strain previously experienced. Materials for which the stress-strain relation is dependent on prior strain should be described as **Thixotropic** or **Strain Hardening** in the senses in which these terms are defined above.

For purposes of easy comparison the following is recorded here.

# TENTATIVE DEFINITIONS OF TERMS RELATING TO RHEOLOGICAL PROPERTIES OF MATTER

### A. S. T. M. Designation. E 24-37 T

(Under the standarization of the Society, these definitions are under the jurisdiction of the A. S. T. M. Committee E-1 on Methods of Testing.)

Consistency-The resistance to deformation of material.

Quantitatively it is the ratio of the shearing stress to the rate of shear.

**Plasticity**—The ability of a body to retain a part or all of its deformation after reduction of the deforming stress to zero.

**Elasticity**—That property of a body by virtue of which it recovers its original size and shape after deformation.

Liquids—Substances which undergo continuous deformation when subjected to shearing stress.

**Simple Liquids**—Those substances in which the rate of shear is proportional to the shearing stress. The constant ratio of shearing stress to rate of shear of a simple liquid is the viscosity of the liquid.

**Complex Liquids**—Those substances in which the rate of shear is not proportional to the shearing stress.

**Solids**—Substances which undergo permanent deformation only when subjected to shearing stress in excess of some finite value characteristic of the substance.

**Plastic Solids**—Those substances which do not deform under a shearing stress until the stress attains a critical value (yield stress) when the solids deform so readily or so quickly that, except for inertia effects, the stress never exceeds the yield stress.

**Elastic Solids**—Those substances in which, for all values of the shearing stress below the rupture stress (shear strength), the strain is fully determined by the stress regardless of whether the stress is increasing or decreasing.

**NOTE:** Most solids exhibit combinations of properties. Metals, for example, are mainly elastic-plastic, while some petroleum residues, waxes and similar materials are plastic-viscous. Some

materials exhibit even more complex deformation, for example, rubber compounds.

### CORRELATED ABSTRACTS. VISCOSITY.

Viscosities of polyester solutions and the Staudinger equation. Paul J. Flory. J. Am. Chem. Soc. 62, 3032-8 (1940). The internal frictions of dilute solutions of decamethylene adipate polysters in diethyl succinate and in chlorobenzene have been compared with weight average molecular weights  $M_{w}$  determined from the relationship recently found by the author, connecting the viscosity of the molten polymer with its molecular weight (cf. Rheology Leaflet, No. 14, 14 (1940) ). in the range of mol. wts. examined --1500 =  $M_{w}$ =30000 -Staudinger's rule is not obeyed. Instead the equation

$$\lim_{C \to 0} \left[ \frac{/n}{C} r - \right] = K_w \cdot M_w + I$$

with  $K_{w}$  and I constants and c the concentration in gram/liter and  $\eta_{r}$  denoting the relative viscosity, is found to be valid. The value of the two constants depends upon the nature of the polymer and of the solvent.

The importance of investigations of this type has already been stressed by the reviewer.

#### P. J. Flory.

Relationships between viscosity and elastic properties of amorphous substances. W. Kuhn. Z. Phys. Chem. B. 42, 1 (1939). The total measured viscosity of a substance is considered as a sum of partial viscosities due to elastic bond mechanisms i, each having a known rigidity modulus  $G_{0}$ ; and a relaxation time  $\lambda$ ; observed if this particular bond only is present. Therefore according to Maxwell's relationship  $\gamma_i = G_{oi} \lambda_i$ . The relaxation of the shear created in the sample is therefore described by an equation  $G = G_{o1}e^{-\frac{1}{\lambda_1}} + G_{o2}e^{-\frac{1}{\lambda_2}} + \dots$  Experience shows that the sum  $G_{01} + G_{02} + \dots$  has the same value within two orders of magnitude. The great differences in the viscous-elastic behaviour of different materials are ascribed to the differnce in the distribution of the  $\lambda_i$  - values. Typical representatives for one class of substances are e. g. glass or glycerine, having  $\lambda_i$  - values not differing from each other for more than one or two orders of magnitude. In high molecular weight materials on the other hand widely differing  $\lambda_i$  's are present. Highly elastic behavior is characterized by a few large  $\lambda_i$  (causing elasticity) and a large set of small  $\lambda_i$  causing viscous effects. Further examples like polystyrene glasses are discussed.

Robert Simha.

The plastic deformation of metals depends upon two main factors, the ability of the metal to deform without fracture and the forces necessary to produce such deformation. Ordinary mechanical property tests usually do not give sufficient information to indicate the deformability of metals in the various ways in which they may be deformed. Considerable effort has been expended in trying to develop a test which will indicate the ability of sheets of a given material to be drawn into cups or shells. One type of test which has been proposed as a fairly reliable guide for the deep-drawability of metal sheet is that known as the Kayseler method. This method utilizes a wedge of sheet which is drawn out to a rectangular shape through a prismatic die. Apparently the advantage of the Kayseler method is that it makes possible a direct comparison between sheets of different thickness. Description of this method may be found in the following technical articles: Testing of Deep Drawing Materials by the Wedge-Draw-Cupping Test (Die Prufung von Tiefziehwerkstoffen durch das Keilzug-Tiefungsverfahren) Wilhelm Pungel. Stahl u. Eisen, Vol. 60, June 27, 1940, pp. 570-571. Review and Research. (For earlier work, see Metals and Allovs, Vol. 9, June, 1938, p. MA 369 L 5, and Vol. 10, June, 1939, p. MA 358 R 5.) Also see Metals and Alloys, Vol. 12, p. 832, December, 1940.

Most specifications for determining the tensile properties of materials specify limits for the rate of strain during the particular tests. Most tests, however, are not made at a constant strain rate but this rate usually varies appreciably during the test. In the Westinghouse Research Report No. R-9426- A. M. entiled "Strain-Rate Tests on Special High Temperature Hoskins 502 Alloy" dated December 4, 1940, W. E. Trumpler gives data showing the effect of strain rate upon the properties obtained for a high strength steel alloy.

Often it is desirable to have materials that will deform plastically under relatively low loads in order to provide smooth surfaces and protect hard shafts in bearings. In the A. S. M. E. Transactions for July 1A40 in a paper entitled "Properties and Performance of Plastic Bearing Materials," L. M. Tichvinsky shows that plastic material may be advantageous in bearings not only for the case of perfect fluid lubrication but also for that of semi-fluid lubrication. He discusses a number of uses of plastic materials in heavy duty bearings and gives an excellent bibliography on the subject. The discussion of this paper in the Transactions is more directly concerned with metals.

Perhaps one of the most significant rhelological phenomena encountered in the metal industry is that of extrusion of metals. A very interesting and informative series of articles on extrusion have appeared in Aluminium, June 1938, pp. 379-385; August 1938, pp. 556-559, anl July 1937, pp. 505-509 under the title (in German) of "Investigation of the Processes of Metal-Flow in Single and Multi-Strand Extruded Rods" by H. Walbert. This article not only discusses the properties of the material before extrusion and after extrusion but also gives information relative to the pressures and temperatures involved in the extrusion process. Two particular features of these articles are that they show photographs of etched longitudinal sections of the extruded ingot and extrusion piece. These etched cross sections quite clearly indicate flow lines of the metal. Searching comments on the investigation by Dr. A. Von Zeerleder and H. Hug of Neuhausen, Germany, are very interesting.

A fairly clear picture of the forces and power required for the extrusion of metals is obtained from the paper entitled "Recent Developments in Metal Extrusion" by Albert B. Cudebec which appears in Mechanical Engineering, January 1941. Mr. Cudebec discusses the extrusion of stainless steel, nickel alloys and bearing steels as well as nonferous metals. His article is based mostly on his experience with extrusion equipment and processes currently used in the British Isles.

#### R. G. Sturm.

#### GEOLOGICAL APPLICATIONS

Experimental Flow of Rocks Under Conditions Favoring Recrystalization by David Griggs, Bull. Geol. Soc. Amer. 51, 1001, 1940. In order that the results of experimental investigations of the flow of rocks may be applied with any degree of assurance to problems of rock deformation in nature, it is essential that the effects of all five of the varying environmental factors be investigated: (1) confining pressure, (2) shear stress, (3) temperature, (4) time, and (5) the presence of solutions. Pressure alone changes the behavior of rocks and simulates some types of natural deformation, but is shown to be inadequate to explain all natural flow because of the tremendous strength increase involved, its inability to produce plastic behavior in quartz, and the development of too intense mechanical twining in calcite aggregates. Temperature produced unimportant results in preliminary experiments at high pressure. Time seems to be inadequate as shown by creep tests on Solenhofen limestonc at low and high pressure. Some new experiments show the effect of solutions. The properties of quartz change markedly in the presence of solutions at elevated temperature. Marble flow is strikingly altered by the presence of solutions at elevated temperature. New creep tests on alabaster in the presence of solutions seem to demonstrate recrystalization flow and indicated the existence of two general laws governing this type of flow. These reconnaissance experiments indicate the important role that solution and recrystalization may play in rock deformation.

(Abstract by Author.)

#### THEORETICAL RHEOLOGY.

Flow in Stressed Solids: An Interpretation by Roy W. Goranson, Bull. Geol. Soc. Amer. 51, 1023, 1940. According to the hypothesis presented plastic flow in solids takes place by means of a change-ofphase transfer mechanism as solid  $\rightarrow$  fluid  $\rightarrow$  solid, or solid  $\rightarrow$  solution  $\rightarrow$  recrystalization of solid. Expressions are derived from consideration of the thermodynamic potential relations for different physical conditions. The quantity that has been related to the viscosity of a fluid is thus seen to be a function of the "activation energy." If the hydrostatic confining pressure be sufficiently high then release of the energy of deformation stored up in the crystal lattice can take place only by a change-of phase mechanism. The mathematical development is as follows: The expressions connecting compressive stress X and melting temperature in degrees absolute T<sub>rm</sub> of a solid are



(1) is for the "stressed face" and (2) for the "free face." h is the heat of melting (activation energy), the density and E is Young's Modulus for compression.

On the assumption that the number of free migrating atoms increases with temperature, and at the melting point this fraction of the total number becomes unity, the equation

$$9 = T/T_{m}$$

is used to correlate temperature-creep data. Combining (1) and (3) and integrating  $(\Theta)$ 

$$X - X_o = K' \ln \frac{V_s}{V_o}$$
 (5)

K is a physical constant and  $\bigvee_{S}$  the steady or minimum creep rate. The author states that (5) has been used for the past thirty years to express empirical creep rates for metal aggregates.

R. B. Dow.

(3)

#### PLASTICS.

Flow Temperature of Thermoplastics. L. W. A. Meyer. Modern Plastics. **18**, No. 4,59-61 (1940) Reprinted by courtesy of the American Society for Testing Materials.

Acrylate, polystyrene, vinyl co-polymer, cellulose ether and cellulose acetate were tested for flow characteristics in the Rossi-Peakes Flow Tester, Mooney Shearing Disc Plastometer, Dillon Extrusion Plastometer (modified) and the Williams Parallel Plate Plastometer (modified). The author concludes that it is possible to correlate the flow temperatures as determined by the Rossi-Peakes flow tester with the relative plasticity as determined by the Mooney shearing disc plastometer and with the extrusion temperature as determined by the modified Dillon apparatus for materials of similar compositions. No simple correlation could be found between data taken on these machines and the plastic temperatures as determined by the parallel plate plastometer.

**Crystalline Behavior of Linear Polyamides. Effect of Heat Treatment.** C. S. Fuller, W. O. Baker and N. R. Pape. J. Am. Chem. Soc. **62**, 3275 (1940) Although this article is devoted primarily to the crystal structure of these materials as shown by the x-ray examination one will find some data on the mechanical properties such as Young's modulus and shrinkage effects caused by various annealing temperatures.

**Cellulose Derivatives as Basic Materials for Plastics.** Emil Ott. J. Ind. Eng. Chem. **32**, 1641-7 (1940). This article is an excellent review of the existing knowledge concerning the effect of chemical composition upon physical properties. The influence of molecular size and shape, of side chains and of various plasticizers is covered and we also find viscosity curves for solutions of cellulose derivatives. Emphasis is placed upon the fact that in correlating physical properties with molecular weight one should use the weight-average molecular weights for the viscosity and that the important physical properties of cellulose are functions of the weight-average and not the number average. This is particularly important when one has no data regarding the molecular weight distribution.

**Protein Plastics from Soybean Products.** George H. Brother, Leonard L. McKinney and W. Carter Suttle. J. Ind. Eng. Chem. **32**, 1648-51 (1940). Soybean protein hardened with formaldehyde was used as a binder in a laminated sheet. Various physica! properties are presented, such as impact and flexural strengths and modulus of elasticity.

#### THE VISCOSITY OF HELIUM II.

#### A. D. Misener, University of Toronto.

Liquid Helium II is unique and therefore interesting. It is infinitely more interesting because it has proved to be an exception to the well established rules in two fields of physics considered as among those most thoroughly explored, the flow of heat through matter and the flow of fluids through tubes. The element, helium, liquefies under atmospheric pressure at a temperature of 42° Absolute, when all other substances are solid. By reducing the pressure over the liquid it may be made to boil and the temperature drops still lower. If we go on lowering the pressure and consequently the temperature, suddenly at 2.2° K a startling change occurs. The liquid appears to stop boiling, no bubbles rise through it, the surface is immobile. It is still evaporating rapidly and the temperature can be lowered by more rapid pumping and it is still a liquid but it remains quiescent. These two phases were christened, prosaically enough. Helium I, the first or high temperature modification, and HeliumII. the second or low temperature modification of the liquid.

Measurement of the density of liquid helium showed the difference between the states clearly. Helium II was found to have a **negative** expansion coefficient, i. e., an adiabatic expansion would **raise** its temperature. The phase diagram Figure I, shows an even more remarkable anomaly. Helium II apparantly exists **as a liquid** in equilibrium with its vapour at the absolute zero of temperature. Solid helium can exist only under an excess pressure of about 30 atm. From entropy considerations this means, simply, that Helium II must somehow have the same degree of order as a crystalline solid; yet all its physical properties are those of a fluid—and a very fluid fluid as we shall see.

In Fig. I it will be noticed that there is no triple point at which solid, liquid and gas are in equilibrium as is the case with the diagrams of other elements. The two liquid phases Helium I to the right and Helium II to the left are separated by the  $\lambda$ -line, and where this line meets the vapour line we have the  $\lambda$ -point, i. e., the temperature at which Helium I changes to Helium II when both are in equilibrium with helium gas. Table I gives a list of the physical properties of helium which have been studied to find possible changes at this  $\lambda$ -point.

# Table I... Behavior of the Physical Properties of Liquid Helium at the $\lambda$ -Point.

Change	Specific heat		
discontinuously	Viscosity		

#### Thermal conductivity Compressibility and velocity of sound Surface tension

Change in temperature coefficient Vapor pressure Density Internal energy Dielectric constant Refractive index Latent heats of fusion and vaporization

No change observed Electrical polarization Molecular refractivity Electrical conductivity Scattering of light X-ray structure

In this table we find changes we would not expect and some properties do not change when we thought they would. The fact must be emphasized that while there is no doubt that Helium I and Helium II are two distinct states they cannot be considered as two phases in the ordinary chemical sense, since there is no observable latent heat of transformation, and the measurements would have detected 0.001 times the specific heat.

Considering all its peculiar properties and its unique position in the scheme of things it is not surprising to find that Helium II has flow properties which distinguish it from all other liquids. The first attempt to measure its viscosity was made at Toronto in 1935 (1). The damping of an oscillating cylinder suspended in the liquid was observed. It was found that an abrupt change in viscosity occurs at the  $\lambda$ -point and that Helium II, though a liquid of specific gravity about 0.14, has a viscosity less than that of gases at ordinary temperatures. With such an unexpectedly low viscosity the Reynold's numbers involved in the measurements are far too high; but the observed logarithmic decrements are so closely linear that the data are probably fairly reliable.

The high Reynold's number had bothered others besides ourselves and simultaneously, in 1938, Kapitza (2) and Allen and Misener (3) published results on the flow of Helium II through fine channels which showed that it could not have a viscosity as great as  $10^{-9}$  c. g. s. units. Soon investigators in other places tried to find whether this "superfluid" had any viscosity at all. It soon became obvious, however, that the term "viscosity" could not be applied to Helium II as it disobeyed all the classical laws of flow.

This can be illustrated by one example. Helium II was made to flow through channels of about 0.12  $\mu$  width and 20 cm. length under

an impelling force which decreased from 160 dynes to 5 dynes. Under such conditions one might reasonably expect classical streamline flow, but instead of the rate of flow being proportional to the pressure it was absoluteely **independent** of the pressure. The rate was the same for a head of 5 dynes as for a head of 160 dynes to within 0.5%. What was equally astounding was that the comparatively dense liquid Helium II went through the capillary at from 10 to 15 cm sec. while we could force helium gas through at a rate of 8 cm sec. only by applying an excess pressure of 15 atmospheres, a pressure some 106 times that needed by the liquid.

Table II gives a summary of the results obtained up to about a year ago but before discussing their significance we must consider two new facts which were discovered concerning Helium II and which made us abandon all hope of dealing with it in any classical manner.

Experimenters	Method	Viscosity He II	
		T <sup>o</sup> K	7 x106
Wilhelm, Misener and Clark (1)	Oscillating cylinder	2.2	33
Allen and Misener (3)	Long capillary	$\left. \begin{array}{c} 2.17\\ 1.07 \end{array} \right\}$	<b>(</b> 0.004
Kapitza (2)	Flow between parallel plates		<0.001
Burton	Short capillaries	2.16	50 to 80
Keesom and MacWood	Oscillating disc	2.16 1.72 1.32	16 3.8 1.9
Giauque, Stout and Barieau	Flow through very small channel	2.2 1.8 1.4	15 0.35 0.07
Allen and Misener	Long capillary Short	2.18 1.15 2.16	~10 <sup>-3</sup> 78
	capillary		
Johns, Wilhelm	Various	2.08	29.3
and Smith (8)	capillaries	1.96	24.4
		1.81	19.4

# Table II. Summary of Experiments on the Viscosity of Liquid Helium II.

#### Allen and Various ~10 Misener (7) capillaries (for larger tubes)

Daunt and Mendelssohn (4) in a series of elegant experiments showed that whenever a solid surface came in contact with Helium II a film of the liquid quickly flowed over the surface and if the surface happened to connect two reservoirs of the liquid, this film would fill up the lower at the expense of the higher (see Fig. II, A and B). These films were found to be about 50 m  $\mu$  thick and to flow at a rate of about 20cm./ sec. They had many interesting properties but the most striking was that when flowing from one level to another these films moved at a steady rate no matter what the difference in level was. That is, the liquid in these films flowed in an absolutely pressure-independent manner; as did the liquid in our fine capillaries.

The second fact was discovered when we were measuring the flow of Helium II through emery powder tightly packed in glass tubes (5). We were trying to slow this superfluid down but it slipped through the powder almost independent of pressure head, even though we packed it as tightly as the glass tube would allow. Now when one is working at these very low temperatures one has to be very careful to remove all gases but helium from your apparatus, otherwise they will freeze solid and plug the tubes, etc. One of our tubes was behaving badly and I turned a small pocket flash light on it to see if I could locate the trouble. You can imagine my surprise when I suddenly saw a fountain of liquid helium spouting out of the top of one of the other tubes in the cryostat. Whenever the light fell on the emery powder in the bottom part of the tube a jet of liquid shot from the top of it several inches above the bath level (see Fig. II D).

Of course there was a great rushing about to take pictures of this direct transformation of heat into mechanical energy. We were afraid it might be hard to reproduce but it has proved one of the characteristic properties of Helium II. Place an open tube in the liquid, introduce heat at one end, an electric heater works as well as light (Fig. IIE) and the liquid will flow up the tube. That is, with a heat flow down the tube to the bath we have a flow of liquid in the opposite direction. It was logical to assume, and it has since been shown, (6) that a flow of this peculiar fluid generated a temperature difference and a consequent heat flow in the opposite sense.

Could this explain the pressure independent flow in our fine channels and in the films? Was their motion governed not by pressures but by the rate at which the temperature difference produced by their motion could be equalised? Probably the answer is not as simple as that. In spite of these complicating factors flow measurements were still carried on. At Cambridge (7) we concentrated on seeing how the rate of flow varied with channel size. Some of our results are summarised in Fig. III. Consider the results at one temperature, say  $1.5^{\circ}$ K. At first the velocity of fluid flow through the channel is decreased as the siz decreases but the channels of less than  $4\times10^{-4}$  cm, width the velocity rapidly increases for further decrease of size. Looking at the variation of velocity with temperature for the smallest channel we see that it is strikingly similar to that given by Daunt and Mendelssohn for their mobile surface films (see Fig. IV), even the velocity of flow is approximately the same.

Let us proceed in imagination from the wider tubes to the narrower remembering that the velocity of flow we have been considering is the average for the whole cross section and should perhaps be considered in terms of the volume per second per unit area passing a given point. As the tube narrows this volume is decreased but it appears that when the walls approach each other within 15  $\mu$  or so their proximity encourages the flow and the rate increases. We are lead to a flow cross section something like Fig. V.

The liquid does not slip at the walls, it flows in the form of a mobile film with the same velocity as if the solid were above the free surface of the liquid. Beyond this film we have something like the normal state of affairs, the outer layers being retarded by viscous forces and the central atoms slipping along faster. The big mystery in all this is how do the atoms just inside the film know that the wall is there to retard them through a layer of several hundred fast moving brothers.

At Toronto, Johns, Wilhelm and Smith (8) carried out flow experiments designed to separate the pressure dependent and pressure independent components of the flow. They found that by subtracting the pressure independent flow from the total flow they were left with a part proportional to pressure and obeying Poiseuille's Law. Their results are shown in Fig. VI. It is gratifying to see that the value of the viscosity they deduce for the pressure dependent part of the flow is in reasonable agreement with the early dynamical values.

All these flow measurements have done much more than bring us back to our starting point, they have revealed the presence of this pressure independent and frictionless "super-flow,"—a much more interesting problem. The theories advanced to explain this phenomenon all have their drawbacks. We shall here outline briefly one line that seems promising. This theory, advanced by F. London (9) and elaborated later by himself and also Tisza, (10) applied Bose-Einstein statistics to the energy distribution of the helium atoms. Essentially this means that the presence of one or more atoms in the lowest level of translatory motion increases the probability of other particles going into that level. These atoms are said to be in the "condensed" or "degenerate" state. These degenerate atoms are very peculiar in that their wave function must be spread uniformly over the whole volume and hence one can not say just where they actually are. It seems possible that the mobile surface films and the pressure independent flow in capillaries are due to these elusive atoms. They can also account for the "fountain effect" and the abnormally high thermal conductivity of this superfluid.

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#### Titles of figures:

- Fig. I. Density-temperature diagram of solid and liquid helium. Helium I to right of  $\lambda$  -line; helium II to left of  $\lambda$  -line.
- Fig. II. Transport phenomena in liquid helium II.
- Fig. III. Variation of flow with temperature for capillaries of different diameters, (from Allen and Misener).
- Fig. IV. Dependence of rate of flow of film on temperature, (from Daunt and Mendelssohn).
- Fig. V. Probable appearance of the variation of velocity across the diameter of a capillary. A represents the surface film; B represents the bulk liquid.
- Fig. VI. Viscosity of helium I and pressure-dependent component of flow of helium II.



Fig. I Ε B F A







#### THE TRANSIENT RESILIENCE OF SOME FLUIDS.

#### By J. M. Kendall,

#### Geophysical Research Corporation, Tulsa, Okla.

Many years ago Maxwell discovered that many fluids have elastic properties in shear. More recently the subject has been extensively considered in the "First Report on Viscosity and Plasticity," (Academy of Sciences, Amsterdam, 1935) and elsewhere. However, data on the elastic properties of actual fluids seem to be rather meager, even on the more viscous substances where the measurements can be made without much difficulty. The present work represents an attempt to investigate the elastic properties of several fluids with a viscosity of a few Poises or less.

In order to observe the elastic effects in a fluid when a shear is applied, it is necessary to apply the shear as suddenly as possible and to observe the instantaneous rate of deformation. In a strictly Newtonian fluid i. e., one which is entirely free from elastic effects, a suddenly applied shearing stress will produce a rate of shear proportional at all times to the shearing stress. On the other hand, a fluid having elastic properties gives a rate of shear which is initially in excess of that to be expected if only the viscosity and the applied stress are taken into account. The elastic effect, or resilience, is a rather elusive phenomenon in that it manifests itself only while the applied stress is changing; that is, it is transient in nature. In this paper the term "transient resilience" will be applied to this property. Resilience, of course, is defined as the reciprocal of rigidity.

In an apparatus designed for use in observing transient resilient effects in fluids, it is necessary to be able to apply the stress as suddenly as possible in order to accentuate the anomalous deformation. Furthermore, the anomalous deformation occurs with the greatest magnitude only when all mass effects involved in the system are reduced sufficiently. The apparatus shown in Fig. I was designed with these two ideas in mind. The clearance between the cylinder, which constitutes the moving part of the apparatus, and the aluminium block, which is stationary, is 0.003 inches both inside and outside. Fig. Ia shows the details of the arrangement. The diameter of the cylinder is 3-8 inch, the length 1-2 inch, and the wall thickness 0.0015 inch. The moment of inertia is 0.05 g. cm<sup>2</sup>.

The rotating cylinder is mounted on a rigid shaft which also carries a mirror and a small coil of copper wire. This entire rotating system is suspended on fine tungsten wires of negligible stiffness in torsion. The small mirror, in conjunction with the lamp, the lens system and the rotating drum carrying photographic paper, constitute the recording arrangement used for recording the angular displacement of the moving cylinder as a function of time. The electrical part of the apparatus has been designed so as to apply to the moving cylinder a torque with a time consonant of either 11 microseconds or 350 microseconds. The resulting torque can be regarded as impulsive in nature.

Fig. II shows the mechanical analogy for a fluid having transient resilience. There is a spring element R representing the resilience, and two dashpots representing the specific viscosity  $\eta_{sp}$  and the parallel viscosity  $\eta_o$ . The following relation expresses the shear at any time resulting from the application of an impulse of shearing stress to a fluid of the type represented by the above analogy.

$$\begin{aligned} \gamma_t &= \frac{\tau_i}{\eta_{sp}} \left[ \left[ + \left( \frac{\eta_{sp} + \eta_o}{\eta_o} - l \right) \right] e^{-\frac{\tau_i}{R\eta_o}} \right] \\ \gamma_t &= \text{Shear at time} \\ \gamma_s &= \text{Impulse of shearing stress} \\ \eta_{sp} &= \text{Specific Viscosity} \\ \eta_o &= \text{Parallel viscosity} \\ R &= \text{Resilience} = \frac{\tau_o}{\Omega_s} \end{aligned}$$
(1)

It is to be noted that, as the time  $t \rightarrow \infty$ , the exponential term  $\rightarrow o$  thus leaving only the specific viscosity and applied shearing stress implse in the right hand side of the equation. This, of course, is the condition under which the specific viscositv is usually measured with a capillary tube. The relation may be regarded as a more explicit definition of the term "transient resilience." Ths relation, however, neglects the mass of the fluid and the moving cylinder, and further, does not take into account the fact that the fluid constants are distributed rather than lumped. Moreover, most of the fluids having transient resilience are non-Newtonian, so that the relation will not hold above a certain rate of shear because of the non-linear relationship usually present in such fluids.

If a fluid with Newtonian viscosity is introduced into the apparatus the action is quite simple. The impulsive torque produced by the condenser discharge through the coil imparts an angular momentum to the moving cylinder. Because of the high viscous drag and negligible inertia, the cylinder quickly attains its final deflection. It should also be remembered in this connection that the torque due to the suspension is very small and its effect negligible during the time in which the record is taken. It follows that the deflection of the cylinder remains constant once the angular momentum has been dissipated by viscous forces.

If, however, the fluid between the cylinders is resilient, as well as viscous, the action is somewhat different. When the current impulse is applied to the coil, it impatts momentum to the moving system. The system continues to move until its momentum is expended both by the action of the viscous drag and the deformation of the resilient structure in the fluid. The energy absorbed by the viscous drag is immediately dissipated in the form of heat, but that absorbed by the elastic forces produces a stress within the fluid. This elastic stress is then dissipated by deforming the fluid, and it carries the cylinder with it toward its initial position. The record then has an "overshoot" which may be used as an indication of transient resilience in the fluid. Stated differently the overshoot is due to the partial recovery of the fluid after the sudden deformation.

The apparatus can also be used for the detection of very small shear yield strengths of materials which it is possible to introduce between the cylinders. This is done by applying a constant small torque to the cylinder and observing its motion. If the cylinder rotates at a slow, uniform rate, the yield strength of the material between the cylinders is too low to restrain the shearing motion produced by this particular torque. The torque may be decreased indefinitely by decreasing the current through the coil, and if the rotation decreases correspondingly without stopping completely, the yield strength is zero, and therefore the material is fluid. By this procedure a yield strength as low as 1 dyne/cm<sup>2</sup> can be detected.

Since our purpose is the measurement of viscosity and phenomena associated with it, inertia effects of the fluid must be reduced to as low a value as possible. This is accomplished by making the spacing between the moving and fixed cylinders sufficiently close. Simple theory of propogation of waves in a viscous fluid shows that this spacing must be made smaller than either of the quantities d or  $\lambda$ , which are defined by the following relations:

Distance for an amplitude decrease of 1/e

(2) (3)

Wave length:

$$\lambda = 2\sqrt{\frac{\pi\eta}{\rho}}$$

where  $\eta =$  viscosity

= density

If, for example  $\eta = 10$  Poises,  $q = 1.0 \text{ g/cm}^2$ , f = 1,500 cycles per second, then d = 0.0182 inches,  $\lambda = 0.114$  inches. It is clear that, in this case, the actual spacing used in the apparatus will lead to satisfactory performance.

# RESULTS.

Fig. III. shows a record for Primol D, a clear mineral oil having a viscosity of 1.25 Poises at 22° C as determined by a Fenske capillary tube viscometer. The record shows no observable overshoot, and therefore it may be inferred that, under the conditions of this test, this fluid has no transient resilience. The maximum rate of shear at the steepest part of this record was 5,800 cm/sec/cm.

Fig. IV. indicates the presence of transient resilience in a solution of "Vistanex medium" (Polybutene) in pseudo-cumene. This solution is a perfectly clear oily fluid. The proportions of the components are such that the specific viscosity is 0.87 Poises at 20° c as measured by the Fenske capillary viscometer. The overshoot indicates an appreciably transient resilience. The shear yield strength is zero.

Fig. V. shows a series of records taken for another solutio nof the same materials, but with a specific viscosity of 15.84 Poises at 20°C. This material also has zero yield strength in shear. The five different amplitudes recorded here give an idea of how the shape of the time-recovery curve varies with amplitude. The maximum rate of shear occurring in the steepest part of the largest amplitude is approximately 28,300 cms/sec/cm. The 350 microsecond impulse was used in making the four largest amplitude records. The 11 microsecond impulse was used on the smallest amplitude record only.

Data obtained from this series of records show that as the amplitude of the applied shear impulse is increased, the effective viscosity of the fluid decreases, which behavior must be attributed to the non-Newtonian characteristics of the fluid itself.

Maxwell concluded that relaxation phenomena should be exponential. Inspection of Fig. V. shows the time-recovery curves, and hence time-relaxation curves, are only approximately exponential in shape. The recovery rate is too rapid at the beginning of the record and too slow at the tail end of the record. Furthermore, even the shape of the curve changes when the amplitude is changed. Large amplitudes cause more trailing than small amplitudes.

The fluid used in taking these records has properties, which, except for the great difference of the time scale, are practically identical with the properties of much more viscous materials. Ferry and Parks\* found that pure polyisobutylene with a viscosity of  $8 \times 10^4$  Poises at 20 °C, gave a very similar sort of record, except that the times were measured in minutes rather than in thousands of a second. The principal result of adding a solvent to a thick substance seems to

\*Physics 1936, Vol. 6, p. 356.

be that of decreasing the time factor, but leaving other things pretty much as they were beforehand. Beyond a certain dilution, this statement is obviously not true.

Fig. VI. is a replot on a larger scale of the smallest amplitude record of Fig. V. The combination of inertia of the moving system and the transient resilience of the fluid form a resonant system. The natural frequency in this case is about 1000 cycles per second. The transient resilience, and hence the transient modulus of rigidity, may be estimated from these data. The transient modulus of rigidity comes out to be the order of  $10^4$  dynes/cm<sup>2</sup>. With the aid of relation (1) the parallel viscosity may also be estimated and is about 3.2 Poises, whereas the specific viscosity of the fluid is about 16 Poises.

The magnitude of the overshoot observed with a solution of Vistanex, as well as with other similar fluids, is a function of concentration and decreases as the solution is diluted. At a sufficient dilution, it disappears entirely. This occurs in the case of the Vistanex medium (m.w. 80,000) solution when the viscosity is between 0.25 and 0.15 Poises. For these low values of viscosity the inertia of the moving system of the apparatus and the inertia of the fluid itself are so great compared to the viscous and elastic effects in the fluid that they become the controlling factors and hence make it difficult or impossible to observe the overshoot.

Some experiments were performed to determine the effect of molecular chain length on the transient resilience. These experiments show that of two solutions diluted to the same viscosity, the one with are longer chain molecules has the greater resilient effect.

Fourteen fluids have been investigated. They are listed in Table 1. The table gives the approximate viscosity and the transient resilient effect, the latter qualitatively.

Several of the long chain molecules deserve some comment. It is not surprising, perhaps, to find that diluted rubber cement gave a large transient resilient effect, but it does seem somewhat surprising to the writer to find that a solution of Lucite (methyl methacrylate polymer) gave an even larger effect. Under ordinary conditions pure Lucite does not exhibit high elasticity. When the individual Lucite molecules are more or less freed from each other as they must be when in solution, they cause a very large resilient effect. The molecular weight of the sample tested is thought to be about 200,000 which fact alone may account for the large effect observed. Material No. 4, Polystyrene solution, showed an appreciable resilient effect. The time constant of its recovery, however, was considerably shorter than that of other fluids with about the same amount of resilience. Moreover, it appeared to be more nearly exponential than any other material investigated. The long chain molecules and the emulsions account for all of the resilient effects observed, with the single exception of a solution of G. E. Cable Compound (Solution No. 7). G. E. Cable Compound appears to be a refined asphalt. Only a small effect was found for a solution with a viscosity of about 20 Poises, quite a different order compared to the solutions of long chain molecules.

Among all the substances investigated, the emulsions were the only ones to show any yield strengths, and these yield strengths were quite small. The emulsions also showed very appreciable resilient effects. Thus they should really be classed as weak plastics, rather than as fluids, even though all of the constituents of the emulsions are themselves liquids. The resilient effect probably resides in the surface tensions of the small globules. The sudden shearing impulse must distort the spheres into spheroids, after which the surface tension restores them to the spherical form, thereby causing the overshoot in the record.

With the possible exceptions of the emulsions, none of the fluids investigated are what might be called thixotropic. Aside from the transient resilient effects, their viscosities are influenced neither by the duration of an applied shear nor by the past rheological history of the fluids. Rather they should be described as non-Newtonian.

# HYPOTHESES CONCERNING TRANSIENT RESILIENCE.

Some long chain molecules are supposed to be kinked while others are straight. The kinked molecules are probably more capable of stretching than the straight ones. On the other hand, both kinds are no doubt laterally quite flexible. Fig. VII shows assumed stress-strain diagrams for these chains. It is assumed that the molecules are much more easily compressed than stretched. The long chain molecules form an elastic structure when in solution. The structure, however, is continuously rearranging itself because of thermal motion, which fact can account for the zero yield strength. When a small amplitude impulse of shear is applied to such a fluid, the structure seems to yield without much alteration of the structural configuration, other than a temporary distortion. On the other hand, when a large amplitude impulse of shear is applied, the structure is completely disrupted and many of the chain molecules are crumpled. The crumpled chains, being weak in restoring force, slowly resume unstressed shapes. This fact can account for the previously made observation that the larger the amplitude of the applied impulse, the longer the recovery time. The non-linear stress-strain relation would account for the non-exponential recovery for the individual chains. The overall effect of the large impulse may be considered to be a whole spectrum of non-exponential elements, with the spectrum itself a function of the amplitude of the applied impulse.

#### ACKNOWLEDGEMENTS.

The writer wishes to thank Mr. W. T. Born, Director of the laboratory of the Geophysical Research Corporation, for permission to work on this problem. The writer also wishes to acknowledge the valuable suggestions made by Dr. Alfred Wolf, and the assistance of Mr. Fred C. McCullough, who prepared the sample fluids.

#### Table 1.

				Approx.		
Item		Sol	vent	Viscosity	Resilient	
No.	Material			Poises	Effect	Remarks
1	Vistanex Polyiso butylene	Pseudo	cumene	0.15	None	Approx. m.w. 80,000
		"		0.25	Trace	"
		**	"	1	Large	33
	2	"	32	16	Very Large	"
	r and an ar	"	"	1	Trace	Approx. m.w. 20,000
2	Lucite Methyl	Dichlor		1	Very Large	Approx. m.w.
	Methacrylate Polymer	Benzen	ө			200,000
3	N-Propyl Methacrylate Polymer	<b>1</b>		1	Small	
4	Polystryene	Pseudo	cumene	1	Appreciable	
5	Vinyl Acetate			1	Small	
6	Rubber Cement	Diluted	with	1	Large	
		Diamyl	Benzene			
7	G. E. Cable Com-	Pseudo	Cumene	1	None	
	pound	**	"	20	Small	
8	Glyptal Alkyd Resin	Pseudo	Cumene	0.3	None	
9	Linseed Oil Boiled				None	
10	LePages Mucilage	Water		1	None	
11	Glucose Emulsions	Water		1	None	
12	Dairy Cream				Appreciable	All of these
13	Petrol Agar diluted					emulsions
	with water					showed a slight
14	Glucose, Water, soap, and Mireral Oil					yield strength











FIS II



#### APPLICATION.

Mr. H. R. Lillie, Secretary Research Division Corning Glass Works Corning, N. Y.

I hereby apply for membership in the Society of Rheology commencing January 1 \_\_\_\_\_\_ as follows:

Sustaining membership (including subscription to Rheology Bulletin, Journal of Applied Physics, and Review of Scientific Instruments.) \$25.00 or more.

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