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Annual Meeting of the Society of Rheology
October 30 and 31, 1942

at the

Hotel Pennsylvania, New York City

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RHEOLOGY IN THE WAR EFFORT

Eugene C. Bingham

Much has been accomplished in the petroleum industry in going from purely "national" to international units of viscosity. The A. S. T. M. has started an investigation under the direction of Dr. Mark on the possible correlation of some of the many empirical tests for rheological properties. Another committee of the same society is approaching the question from a different angle to meet immediate war needs.

The situation is that we have:—Empirical Tests, with results not expressible in absolute units; Relative Measurements, with results, through calibration, expressible in absolute units; and Absolute Measurements, where all of the dimensions are measured and calibration is not required for quantitative results. Absolute measurements are laborious but necessary for the establishments of our standards. Relative measurements are less laborious and not necessarily less accurate, when the required corrections and checks are faithfully made.

Empirical tests require the careful distinction to be made between the three rheological properties of elasticity, flow—either viscous or plastic, and ultimate strength. These tests, being subject to neither absolute measurement nor calibration are difficult to check and are therefore often ambiguous in the information which they give. This difficulty can be overcome by the more liberal use of Rheological Standards. The number of these, their distribution over the entire range is discussed and their use.

Substances which in their manufacture or use are judged principally on the basis of some rheological property, as is the case with glue, lubricating oil, gums, etc., should be placed in rheological grades which are as significant as possible. At this time, before this movement has made much headway, it is appropriate to discuss the simplest and most satisfactory method of grading. It is suggested that such a system may be obtained by an extension of the pH of acidimetry. This same system should be employed in the distribution of the rheological standards.

Liquid Sulfur; Viscosity and Equilibria

Richard E. Powell and Henry Eyring

The known equilibrium data make possible a quantitative treatment of the equilibrium between the ring S and the polymerized chain S. The theory explains the approach of the amount of S to the observed 50% upper limit.

Recent data on the viscosity of liquid sulfur and the effect of added impurities are treated in terms of current theories of the viscosity of long chains. The rapid decrease in viscosity of S with increasing temperature is due largely to a correspond-

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ing decrease in mean chain length as the theory shows. Impurities also decrease viscosity by decreasing chain length.

Rheological Properties of Rubber-like Materials

Arthur Tobolsky and Henry Eyring

A molecular model in terms of which the elastic-viscous properties of rubber-like substances can be interpreted will be presented. These substances can be thought of as networks of interpenetrating lattices, the vertices of which are points of entanglement or bridges between the long chain molecules. Relaxation of stress at constant extension and extrusion experiments are interpreted on the basis of the slipping at these entanglements. In certain vibrational experiments viscous damping is due to a different mechanism, namely the slipping past each other of adjacent segments of neighboring long chain molecules.

The Penetrometer Method of Determining Rheological Properties of Fluids Showing Complex Flow

Wesley W. Pendleton

The most rapid, accurate, and precise method of determining the flow characteristics of viscous fluids is by the use of the penetrometer. All other means of measuring these properties consume much time in preparing the test pieces and in making the tests, require difficult measurements of sample dimensions, and/or require elaborate flow measuring equipment.

Because of the difficult mathematical analysis of the movement of the needle in a complex fluid, simplified empirical formulas were developed only for simple fluid viscosities and the penetrometer has been used only as a device for comparing the consistencies of like materials. However, its extensive use in this limited capacity is proof of its simplicity and of the need for making it an absolute instrument.

In the penetrometer method proposed, a penetration-time curve under constant load is all that is required for determining shearing stress, rate of shear and viscosity at any rate of shear. The range of viscosities covered by the method is calculated to be from 10^4 to 10^{13} poises. Both simple and complex fluids are within the scope of the method. The method has been checked by rigorous mathematical theory and work is in progress on checking it with other viscometric methods.

An Analysis of Thixotropy in Pigment-Vehicle Systems

Henry Green and Ruth N. Weltmann

Pigment-Vehicle mixtures, such as printing inks, paints, enamels, etc., are almost invariably thixotropic. Their consistency curves consist of a hysteresis loop. The form of the up-curve arises from continuous thixotropic breakdown. The down-curve results from the attainment of a thixotropic level.

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An analysis is made of this loop showing how thixotropic breakdown can be represented graphically. Both theoretical and empirical equations are derived for the up-curve and for the area of the loop. Breakdown is shown to be proportional to the velocity gradient; and a coefficient of thixotropic breakdown is derived.

The down-curve follows the Reiner equation when a Couette type of viscometer is used. The formula for the up-curve in its most elementary form is:

$$T = \Theta \, (r.p.m) \ln \left[\, 1/K(r.p.m)^2 \right] \Big/ 9.55 \, S \cdot 4 \, \pi \, R^2 h + T_o$$

The area A of the loop is:

$$A = \Theta \, (r.p.m)^2 / 8 \, \pi \, R^2 hS$$

The coefficient of thixotropic breakdown,

$$\Theta = 4 \pi R^2 h \mathbf{U} \Big/ \mathbf{ln} \left[1/K(RPM)^2 \right] = 4\pi R^2 h \mathbf{U} / \ln \, (1/K^\circ A)$$

These equations are derived on the assumption that yield value is not affected by thixotropic breakdown. Actually there is a slight increase of the intercept on the force axis as breakdown increases. Corrections for this condition can be made but the equations given here are sufficiently complete for practical purposes.

R = radius for velocity gradient
h = immersed height of bob
U = plastic viscosity
r.p.m = top revolution per minute to which the flow curve is measured
S = instrumental constant
K, = inversely proportional to the square of the rate of shear at which U theoretically becomes zero.
K' = conversion factor equal to 10^{-6}
T = Torque
T = intercept on the torque axis.

The Fluidity of Electrolytic Solutions

Eugene C. Bingham and Robert T. Foley

The rheology of solutions and mixtures has perennial interest. Electrolytes having a common ion afford the simplest cases and therefore the clearest evidence. This evidence is clearly in favor of the additivity of fluidities. Solutions and mixtures of HCl, NaCl, KCl, NH Cl, BaCl and the data of Ruby and Kawai and of Brueckner are employed. The results are very consistent even up to 5 normal but those outside the experimental error are of interest.

The Solidification of Fluid Lubricants by Pressure

R. B. Dow

The apparent solidification of fluid lubricants at high pres-

sures as reported by Hersey and Shore, and by Kleinschmidt was determined by viscosity measurement, both studies being made with the rolling-ball viscometer. Some degree of solidification was assumed to have occurred when the ball ceased to roll at a certain pressure. The present investigation made use of a static, piston-displacement method in order to observe volume change which, with a knowledge of pressure and temperature, would enable the thermodynamics of solidification or freezing to be studied, e.g., application of the Clapeyron equation.

A Pa. Bright Stock sample at 32° and 100°, lard oil at 73° and 100°, sperm oil at 140°, and a typical hydraulic oil at 100°F were investigated over a pressure range of about 10,000 kg/cm². The freezing of mercury at 32° was observed for comparison purposes. The accuracy and precision was such that volume changes could be read off to within 0.1%, this figure representing also the greatest departure from a smooth curve of piston displacement versus pressure. No volume discontinuity within the experimental error was detected for the oils, but in the case of mercury the piston movement changed by about 6% with no permanent increase of pressure during freezing at 7640 kg/cm². However, in the case of lard oil at 73° it was found that solid material remained for a short while after the pressure was suddenly dropped from 5000 kg/cm² to atmospheric and the apparatus taken apart as soon as possible. It is concluded that solidification of Newtonian oils by pressure does not involve an appreciable volume discontinuity as observed during freezing at a definite temperature, but may result in the formation of a labile substance similar to the vaseline-like consistency obtained during a cold test.

Progress Report on the Viscosity of Oils as a Function of Temperature and Pressure

R. B. Dow

A previous report (paper read at Annual Meeting, N. Y. City, 1941) discussed the application of the A.S.T.M. Viscosity-Temperature Chart D 341-37T to viscosity-temperature-pressure relations for four typical hydraulic oils. The present report considers the adequacy of the Chart in representing these data for a wide variety of mineral oils that have been studied by the author and colleagues during the past five years. It has been found that the log log kinematic viscosity varies linearly with the log temperature at constant pressure over a pressure range of 20,000 lbs/in ² for some twenty different oils, and probably can be applied with some accuracy over a higher pressure range since the decrease of slope with increase of pressure is relatively small.

Flow and Recovery of Viscose Rayon Yarns

J. Press

This paper presents a description of some of the dynamic

properties of a typical linear high-polymer, normal viscose rayon, and gives a preliminary interpretation of the results.

Linear high-polymers, such as cellulose, rubber, wool, silk, etc., are characterized by a unique combination of toughness, long-range elasticity, and strength. These properties result from a more or less continuous network of long chain, flexible macromolecules having a random distribution of submicroscopic regions of varying degrees of inter-molecular organization.

Normal methods of analysis have given us a good picture of the molecular structure of the regions of extreme order and disorder. As yet, however, there is little in the literature bearing on the interrelationship of these regions of varying degrees of order despite the fact that it is this very interrelationship which is responsible for the great usefulness of linear high-polymers. Upon the application of an external force the regions of varying order tend to approach new equilibrium positions of higher order by slippage, stretching, orientation, and rotation.

The time-elongation test, under constant load, is the simplest type of experiment with which to study the dynamic properties of such materials. A number of load and recovery tests under varying loads is interpreted on the basis of differences in relaxation and retardation times of the regions of varying degrees of inter-molecular organization.

Comparative Viscosity and Osmotic Measurements with High Polymers

T. Alfrey and A. Bartovics

The osmotic pressures of a large number of polystyrene solutions in toluene were measured. The osmometer consisted of two brass chambers, separated by a semipermeable membrane which was mechanically supported by a metal screen. Each chamber was fitted with a filling tube with needle valve, and a vertical capillary tube. One chamber of the osmometer was filled with solution, and the other with pure solvent, after which the needle valves in the filling tubes were closed. The osmometer was then immersed in a constant temperature bath and the levels in the capillary tubes were read as a function of time.

The osmotic membranes were prepared from cellophane by swelling. Calcium thiocyanate solution was used for this purpose, followed by washing and stepwise transfer of the membrane to an environment of toluene.

Osmotic pressure determinations at a series of concentrations were made on polystyrene samples of different origin. In each case, the number average molecular weight was calculated from the limiting osmotic pressure-concentration ratio, which was determined as follows:

In a fairly wide range of concentration, the osmotic pres-

sure can be expressed as a power series in concentration, of which only two terms are significant:

$$\pi = a c + b c^2$$
$$\text{or } \pi/c = a + b c$$

was therefore plotted against c and the intercept at c = O was taken as the limiting π/C ratio.

The osmotic molecular weights were compared with the viscosity data for the various solutions, and K   constants were calculated.

Polystyrene samples which had been prepared by polymerization at various temperatures were fractionated by selective precipitation. After repeated fractionation, samples were obtained which had much sharper molecular weight distribution curves than the original samples. Representative fractions were chosen for the osmotic pressure-viscosity investigation outlined above.

It was found that a polystyrene sample which had originally been prepared by high temperature polymerization possessed a lower K   constant than a sample which originated from low temperature polymerization. That is to say, two fractions with the same osmotic molecular weight would exhibit different intrinsic viscosities, if one fraction came from a high temperature polymer.

A reasonable interpretation of this difference lies in the hypothesis of molecular chain branching. If, besides the ordinary chain propagation reaction, there is a high-activation-energy chain branching reaction, this latter reaction will be relatively more important at high temperatures than at low. The polymerization at high temperature will give a more highly branched polymer. A branched polymer would be expected to give a smaller viscosity contribution than an un-branched polymer of the same molecular weight.

This hypothesis is supported by certain other facts, the most significant being the shapes of the experimental molecular weight distribution curves of samples prepared at high and low temperatures. From theoretical kinetic considerations, one would expect a sharper distribution curve when branching is occurring than when only straight chain polymers are being formed. The experimental molecular weight distribution curves found for high temperature polystyrene are sharper than those for low temperature polystyrenes.

On Relaxation Effects in High Polymers

Robert Simha

In a perfect elastic body the deformation is, at any time, entirely determined by the stress alone. In a viscous body a constant stress results in a deformation increasing linearly with time. High polymers show a combination of elastic and viscous properties.

The Maxwell relaxation theory leading to the concept of a viscous-elastic body is briefy stated. Extensions to systems built up from several such components with different relaxation times are discussed. In the case of high molecular weight materials it is necessary to assume a distribution of widely differing relaxation frequencies. It is shown how this distribution can be determined from a knowledge of the applied stress and of the rate of deformation.

A molecular interpretation of the mechanical relaxation time is given. The various parts of the relaxation spectrum in high polymers can be correlated to the particular properties of long chain molecules. The connection with the corresponding distribution of dielectric relaxation frequencies is pointed out.

Mechanical Properties of Concentrated Polystyrene Solutions

John D. Ferry

Concentrated solutions of polystyrene in xylene are non-Newtonian liquids with no yield value. The viscosity of 25° (extrapolated to zero shearing stress) varies from 15.5 poises at a concentration of 15.4% polymer to 1.16×10^5 poises at 52.3%. The apparent fluidity is a linear function of the shearing stress, and this relation can be interpreted in terms of an internal modulus of rigidity. The dependence of viscosity upon temperature is characterized by the usual exponential relationship, with a heat effect which ranges from 3.8 to 10.7 keal. At the highest concentration, there is marked elastic recoil, which can be described by an internal modulus of rigidity and a mean relaxation time.

Although these solutions are liquids as far as slow deformation is concerned, when subjected to rapid oscillating deformation they support transverse vibrations. Such vibrations can be studied by observing the strain double refraction stroboscopically with polarized light. The modulus of rigidity calculated from the velocity of propagation (at 25°) varies from 0.83×10^4 dyn/cm² at 15.3% to 3.8×10^5 at 52.3%. It is much larger than the "internal" modulus of rigidity obtained from the viscosity measurements. The variation of the rigidity with frequency at intermediate concentrations, can be analyzed in terms of a mechanical relaxation time of 4×10^{-4} sec. The damping of the vibration, at high concentrations, can also be analyzed in terms of a relaxation time of the same value.

The viscosity and rigidity data can be interpreted by assuming two deformation mechanisms, which are tentatively identified as the unrolling of long chain molecules and the bending of carbon-carbon bonds.

The Gieseler Method for Measurement of the Plastic Characteristics of Coking Coals

Glenn C. Soth and Charles C. Russell

A description of a modified Gieseler plastometer together

with a procedure of operation is described. A method of calibration of the apparatus, to express the results of tests in absolute units is given. The problems met in the measurement of plastic characteristics of coking coals and the limitations in the use of absolute units to express the measurements is discussed.

Typical results are given for measurements of the plastic characteristics of different ranks of coal and the limits of reproducibility of results is shown. Generally, significant temperature points may be duplicated within 5°C, and maximum fluidity, expressed in divisions per minute, may be duplicated within 10–15%.

The plastic temperature range of usual coking coals is shown to be between 340° and 510°C. when the coals are heated at a rate of 3°C. per minute. The range of plastic properties measured by this modified Gieseler plastometer is shown to be equivalent to viscosities between 6.4×10^7 and 6.6×10^2 poises. By changing the load acting to turn the stirrer of the plastometer, this range may be increased.

Creep and Relaxation for Rubberlike Materials. An Automatic Relaxation Apparatus

Eugene Guth, R. H. Caston, S. L. Dart, and R. L. Anthony

The creep and relaxation phenomena show some general characteristics common to all materials. For creep the elongation versus time curve, and for relaxation the stress versus time curve can always hypothetically be resolved into a rapidly rising (creep) or rapidly decreasing (relaxation) transient part which asymptotically approaches a constant value and a linear steady-state part. The connection between creep and stress is, however, different for metals and rubber. For metals, the hyperbolic sine law holds in many cases. For rubber, this is not the case—according to our investigations.

Relaxation curves for different natural and synthetic materials will be shown and their significance in terms of molecular processes discussed briefly.

A machine was designed to draw a relaxation curve automatically, thus obtaining a more accurate curve and also saving much of the tedious work connected with the manual method. The machine operates on the principle of a chainomatic balance. This makes it possible to measure the force to a third of a gram and the time to within a few seconds. The machine is easy to operate and completely automatic during the run.

Symposium on "Flow under Abnormal Conditions"

At the occasion of the hundred and fourth meeting of the American Chemical Society held from September 7 to 11 in Buffalo, the Division of Physical and Inorganic Chemistry with the collaboration of the Society of Rheology arranged a Symposium on "Flow under Abnormal Conditions." Doctor Herman Mark

of the Polytechnic Institute of Brooklyn presided. The speakers were Doctor Elmer O. Kraemer of the Biochemical Research Foundation, Newark, Delaware, Doctor Robert Simha of the Polytechnic Institute of Brooklyn and Doctor Nelson W. Taylor of the Pennsylvania State College. Doctor William D. Harkins, of the University of Chicago, who planned to present a paper on "Flow in Two Dimensional Systems" was unfortunately unable to attend.

In the introduction Doctor Mark pointed to the variety of types of mechanical behavior of real materials as summarized recently in a series of graphs by Doctor Scott Blair.

The discussion was opened by Doctor Simha with a paper "On Anomalies of Elasticity and Flow and their Interpretation." He started with a most general stress-stress relation in which the shearing stress τ is a function of the shear γ, the shear rate $D = \frac{\partial \gamma}{\partial t}$, the time t elapsed since the start of the experiment, and the temperature T. By specialization one obtains the elastic solid and the viscous liquid. A superposition of these two types in the range of linear dependence upon γ and D leads to Maxwell's concept of the mechanical relaxation time λ, as determined by the tendency of the constituent particles to relieve the stress by jumping into more stable positions.

The behavior of threads or fibers of material and synthetic organic polymers or of inorganic glasses cannot be explained by the existence of a single constant relaxation time. The application of, e.g., a constant load to such systems causes them to exhibit so called "elastic after effect"; D at any time depends upon the values of previous deformations experienced by the body. The mechanical response of high polymers is characterized by a whole set or continuous distribution of mechanical relaxation times or frequencies similar to the dielectric response of polar high polymeric systems such as polyvinyl chloride or phenolic resins. Starting with the highest frequencies, the different regions of this spectrum can be related roughly to three different molecular mechanisms. First, to the response of the segments of the chain molecules to the orientational and dilatational tendency of the stress applied. Second to the fact that the whole shape of the flexible chain is changed by the stress. The relaxation time connected with the ability of a long molecule to assume varying shapes corresponding to varying values of the entropy is proportional to its molecular weight and inversely proportional to the intensity of the Brownian movement of one chain end in respect to the other. The corresponding band of frequencies is broadened by the forces operative in the system. A third group of frequencies originates from the relative translational and rotational displacement of whole chains. Because of the large forces involved in this process, the times are large. Flow is obtained after a period of time comparable or larger than these times. Cross linking and crystallization increase this part in particular. The latter process also narrows the width of the distribution curve. The inhomogeneity of the

sample influences the second and the third group. An experimental determination of the creep-time curve in the range of proportionality of τ and γ allows by Fourier analysis a calculation of the distribution of relaxation frequencies.

Dr. Taylor continued the symposium with a paper on "Anomalous Flow in Glasses." He pointed out that the flow of stabilized glass under constant stress may be resolved into a viscous part and an elastic part.

The elastic part is itself composed of an instantaneous or very rapid adjustment, followed by a delayed elastic displacement which is the sum of several exponential decay terms each having the form $l/l_o = e^{-kt}$ All the elastic processes are reversible. These conclusions were reached on the basis of experimental data on soda silica and potash silica glasses as well as on glasses of more complex composition. The interpretation is made that the several kinds of complex ions which make up the glass are individually and independently capable of adjusting themselves to the stress, and that the glass is not to be regarded as "homogeneous" material in the molecular sense but rather as a mixture of complex ions each having characteristic relaxation times. Under certain conditions it is possible to make one group of ions work against another so that apparently spontaneous reversals occur in the direction of movement or of the flow of electric current. Such effects are observed in the ageing of thermometers and in the dielectric absorption of glass condenser plates.

Where a glass is not stabilized, i.e., where insufficient time is given for the attainment of internal equilibrium with respect to association or dissociation processes, the release of stress takes place by two simultaneous processes one of which is the spontaneous relaxation following the exponential decay law, already described. The other process is one of molecular interaction analogous to the pairing of dipoles to reduce their stray fields. For this process the rate of strain release is proportional to the square of the strain, and is expressed by the well-known Adams-Williamson equation.

Dr. Kraemer finished the discussion with a paper on "Anomalous Viscosity of Solutions of Organic Macromolecules." He defined "ideal" behavior for the viscous properties of a colloidal solution as that of a very dilute suspension of rigid inert spheres relatively large compared to the molecular sizes of the solvent. For such, according to Einstein, the volumetric intrinsic viscosity is always 0.025. "Anomalous" behavior represents departures therefrom. Only for a few proteins do the intrinsic viscosities come within 25-50 per cent of the theoretical value, but the model experiments of Mark et al support confidence in Einstein's calculations. All macromolecular solutions therefore show anomalous behavior in flow.

The various manifestations of anomalous viscous behavior can be considered to fall into one of two groups, group I re-

ferring to cases where no mutual forces operate between the particles, and therefore generally involving extrapolations to zero concentration. Group II refers to cases where inter-particle forces occur. Group I effects may be referred back to changes in the individual particle; Group II effects involve in addition the play of particle interferences. Group I: (1) Variation in intrinsic viscosity with solute. The high intrinsic viscosity of some solutes cannot be due to solvation and must represent some sort of bulky or highly extended particle. In general, it is impossible to specify more accurately the character of the bulkiness, but there has been much speculation on this point.

In this connection, the question of Staudinger's rule requires consideration. The principal problem is that of measuring very large molecular weights (e.g., 25000 and up). There are only two absolute methods—osmotic pressure and ultracentrifuge — and, contrary to various reports, values by these methods can not be disproved by recourse to other methods. Unfortunately, there has been to date very few measurements by either method. More active interest has been shown during the last 3-4 years in making reasonably satisfactory osmotic measurements for solutes of high intrinsic viscosity, but because of the tremenduous deviations from Raoult's laws, the question of the best method of extrapolating to zero concentration is still unsettled. At present, different laboratories (Schulz and Gee) use different methods, with differences in the results, from the same data, of 50 per cent. It is however becoming clear that the relationship between intrinsic viscosity and molecular weight is not a straight line, as stated by Staudinger's rule, but is concave to the molecular weight axis. Furthermore, it has been found that Staudinger's constant may vary rather widely, depending upon the method of polymerization, and can not be calculated from the presumed chemical structure of the material. This means that Staudinger's relation needs careful calibration and proof for any new material for which it is to be used, and is unreliable for any new sample of a synthetic material unless samples prepared in the same way have previously been studied. Similarly, the relation for different products of similar chemical composition needs careful independent determination before the viscosity rule is of any value (e.g., cellulose, starch, and glycogen and derivatives). Staudinger assumes that such "anomalies" are due to different degrees of branching, but there is no convincing proof that this is the whole truth.

(2) Effect of solvent upon intrinsic viscosity. In different solvents, a given material may show a variation of 1 to 4 in intrinsic viscosity. This must be due to differences in the individual particles, and probably represents the effect of different solvate layers on the degree and compactness of coiling of extended molecules. Since the degree of solvation can not be measured, a quantitative discussion of the effect can not be given.

(3) Effect of temperature upon intrinsic viscosity. The

percentage change of intrinsic viscosity per degree increase of temperature is equal to ca. —0.2 to —1.5. Rise in temperature reduces solvation and therefore affects the degree of coiling. Also, since the thickness of many macromolecules is comparable with the size of solvent molecules, effects met with in ordinary solutions probably occur. Effect of temperature upon deformability and orientability of particles would lead to a positive coefficient and rarely occur.

(4) Effect of velocity gradient. Particles deform and orient in velocity gradients of sufficient magnitude and cause non-Newtonian behavior. Except for very long particles (e.g., tobacco mosaic virus) effect is very small in very dilute solutions, and it is questionable whether there are any measurements at sufficiently low concentrations to eliminate inter-particle interference. The same is true of streaming birefringence observations. There are equations relating these effects with the shape of ellipsoidal particles. The calculation of equivalent ellipsoidal shapes for some proteins have some meaning, although they depend upon the assumption of no solvation (which probably is never true) and usually gloss over the indistinguishability of prolate and oblate ellipsoids. For coiled-up molecules of high intrinsic viscosity there is the additional uncertainty of the degree of compactness of coiling (i.e., the effective density of the particle), and calculated axial ratios are of very questionable significance.

Group II (1) Effect of concentration on relative viscosity. This shows qualitatively the effect of inter-particle forces. Surprisingly, the rarity with which these curves cross, and the fact that they may be fairly well expressed by one-constant equations indicate an approximately common law of particle interference for many different types of materials. On closer examination, however, there are many irregularities that can not at present be explained.

(2) Since the nature of inter-particle forces can not be deduced from the viscosity-concentration data, especially for solutes of high intrinsic viscosity where particles are highly bulky or highly elongated, it is not surprising that theoretical discussions of the effect of concentration on the solvent effect, the temperature effect, non-Newtonian behavior, streaming birefringence, etc., where the mutual influence of particles must be taken into account, are at present lacking.

The following abstract from the paper "Flow in two-dimensional Systems" by Professor Harkins is reprinted from the "Abstracts of Papers" published by the American Chemical Society.

In general a two-dimensional system, or monolayer, cannot exist except when supported by a subphase, such as water, mercury, or a solid. The flow of a monolayer on a liquid subphase

is transmitted by intermolecular forces to the adjacent molecular layers of the three-dimensional phase, as shown by the last term in the expression for the flow of a monolayer through a deep canal:

$$\eta = \frac{\alpha a^3}{12 A} - \frac{a \eta'}{\pi}$$

in which a is the width of the canal, and η' is the viscosity of the subphase.

The normal relations of two-dimensional flow are similar to those in three dimensions. The viscosity (1) decreases with increase of temperature; (2) increases with increase of film pressure (F) according to the relation:

$$\text{Log } \eta = \text{Log } \eta_0 + KF$$

where η_0 is the viscosity at zero film pressure; (3) is Newtonian; (4) increases with the thickness of the film. With n-long chain paraffin acids, alcohols, amines, nitriles, etc., the viscosity of a condensed liquid film increases by equal increments for each additional carbon atom in the chain.

When the n-long chain alcohols of from 14 to 18 carbon atoms in the chain were investigated at 25°C., the behavior appeared to be entirely normal, but when the temperature range was increased from 2° to 70° the relations of flow were found to be extremely complicated and abnormal, with respect to variation both with temperature and with pressure.

The viscosity of high-pressure phases does not increase with pressure, and that of monolayers which have been designated as "solid" decreases with increasing length of chain.

The British Rheologists' Club

The British Rheologists' Club remains active in spite of the war. They now have received a package of application forms from the Society of Rheology and it is expected that a number of their members will join our society. If the British scientists can keep up their activities in these troubled times we should be able to hold our organization together. The following material is reprinted from Nature, Vol. 149, Page 702, June 20, 1942. It was forwarded by Dr. G. W. Scott Blair who asks for comment and criticism from members of the Society of Rheology.

Classification of Rheological Properties

At a meeting of the British Rheologists' Club held at the Imperial College of Science, London, on May 16, the accompanying chart was presented for discussion by the Committee. The discussion was introduced by Dr. V. G. W. Harrison (hon. treasurer).

It is believed that this classification marks a considerable advance on the earlier draft discussed at Birmingham, which

was reproduced in Nature of Feb. 14, p. 197. It incorporates many of the suggestions made by members at that meeting, and also the hatched "frame" enclosing those categories for which the rate of deformation is liable to increase or decrease with time for constant stress is eliminated. The Committee realized that the use of this frame added considerably to the complexity of the table and that, even with it, the picture was incomplete, since another "frame" would be required to allow for changes in the strain (σ)—time (t) relation with changes in stress (S).

In order to simplify the table, Mr. D. C. Broome had been asked to draw graphs relating σ/t, σ/S and $(d\sigma/dt)/S$ for each category showing, where necessary, the possible types of curvature which may occur in each category. These graphs, after slight revision by the Committee, have been included in the revised table. The table has also been re-arranged so that elastic deformations remain on the left-hand side throughout, the viscous and plastic deformations being on the right.

In the discussion which followed, Dr. C. A. Maunder Foster suggested that the Committee might proceed to consider the more detailed drawing of recovery curves and Mr. J. Pryce-Jones proposed that as soon as possible, examples of materials showing each type of deformation should be quoted. Mr. J. C. Gage doubted whether the insertion of the graphs had adequately replaced the "frame" of the earlier table.

Dr. J. Needham asked whether the complex rheological properties described by him in a paper read earlier in the day could be fitted into the table, and Mr. L. Bilmes submitted a circular form of the table, which the Committee will consider in the near future.

Replying on behalf of the Committee, Dr. G. W. Scott Blair (hon. secretary) said that he did not think that it would be possible to explain all kinds of complex rheological behaviour in terms of the present table. The Committee has taken as its first task the formulating of a table of types of deformation. It is hoped that with the help of members and of colleagues in the (American) Society of Rheology, the scope of classification of properties may be extended, but for the present the effective range of activity is limited. It is realized that the categories in the table cannot be regarded as hard-and-fast limits of behaviour, but rather as convenient land-marks, analogous in many ways to the psychologist's classifications of character and personality types. It would be rash to regard intermediate systems as, of necessity, mechanical mixtures of the simple types between which they lie. As soon as the categories are found to be acceptable, the Committee will consider the possibility of designating each type by means of a letter or number.

Any one who may wish to make criticisms or suggestions with regard to the above table is invited to communicate with the honorary secretary of the British Rheologists' Club, c/o Institute of Physics, University of Reading.
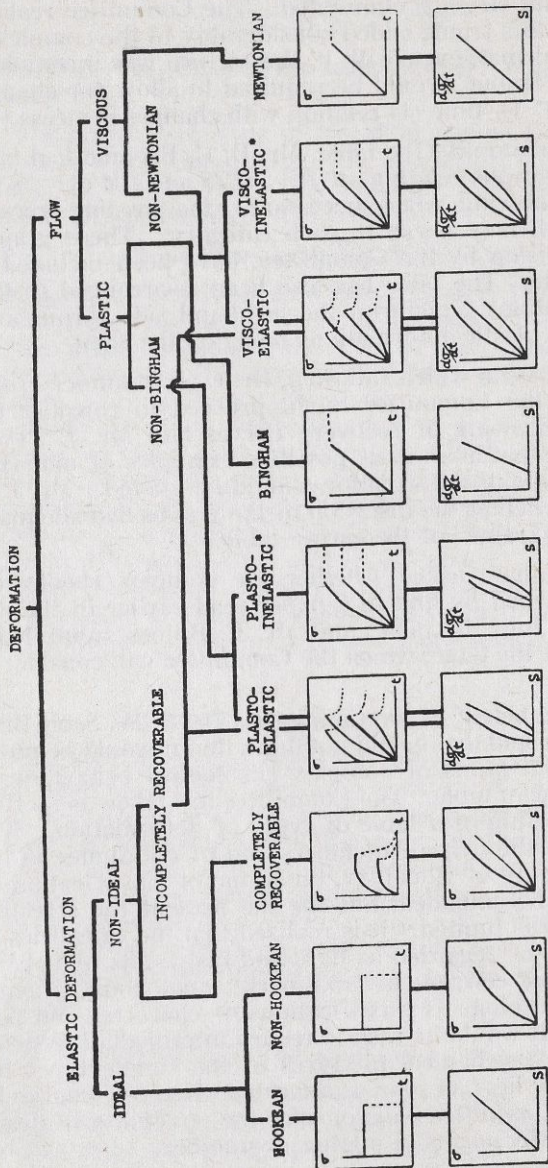
(1) σ represents shear strain.
 S ,, ,, stress.
 t ,, ,, time.

(2) Continuous curves represent deformation under stress.

(3) Dotted curves represent behaviour after removal of stress.

(4) Where two or more curves appear in a diagram, these indicate alternative types of behaviour.

(5) In cases marked * either the σ/t curve or the $\frac{d\sigma}{dt}/S$ curve may be a straight line, but not both, since in this case the systems would be Bingham or Newtonian, which are given separate categories.

(6) The upper series of diagrams in which shear strain is plotted against time represents deformations under constant stress.
 The lower series, in which $d\sigma/dt$ is plotted against stress, is for an arbitrary time.

Clays

Plasticity of Clays. E. A. Hauser and A. L. Johnson. J. Amer. Ceram. Soc. 25 (5), 223-7 (1942).

The clay minerals are characterized by (a) a typical layer or sheet lattice, (b) elastico-plastic properties, and (c) very fine particle size. This discussion concerns the importance of yield point and extensibility of kaolinite and their relation to the colloidal aspects of the clay-water system. Plasticity in clay systems is the result of the attraction and repulsion forces set up between the colloidal clay particles and the ions in the dispersion medium. These forces are explained in terms of the Gouy-Freundlich diffuse double layer, and are influenced by the number and nature of the counterions which swarm about the colloidal particle in an effort to neutralize its surface charge. The plasticity of industrial clays containing kaolinite as the principal mineral is ascribed to exchangeable calcium. A sodium-saturated clay shows more nearly viscous than plastic flow. The most economical way of enhancing the yield point of a kaolinite clay would be to replace the exchangeable cations by aluminum or hydrogen ions. The introduction of univalent hydrogen ions or of trivalent ions causes a reduction in the charges on the particles and results in an increase in the attraction forces between micellae. A study of the plastic properties of other clay minerals and of nonplastics might reveal that the proper adjustment of certain variables may change a nonplastic system to a plastic system. It should also be possible to change a plastic system to a nonplastic one.

E. C. HENRY

Visual Studies of Flow Patterns. A. E. Hauser and Davis R. Dewey II. J. Phys. Chem. 46, 212 (1942).

The streaming double refraction of dilute colloidal bentonite suspensions is used to make possible the observation of two-dimensional fluid flow patterns. The suspension flows through a channel containing the model to be studied. White or monochromatic light is polarized and a pattern of varying light intensity is observed which depends on the distribution of velocity gradients in the suspension around the model. Several photographs are shown of flow patterns formed around automobile models.

Liquids and Solutions

The Superfluid Properties of Liquid Helium

A. D. Misener, University of Toronto

Liquid helium, at temperatures below 2.2 degrees absolute, is the most peculiar fluid in existence. Not because it is the only substance that can remain a fluid at such low temperatures but because it completely violates all the long established rules gov-

erning the flow of fluids through tubes and the flow of heat through matter. The various experiments which show the departure of this fluid from laws of such universal scope are described. The unique effect in which a flow of heat through the fluid causes a flow of the fluid itself will be discussed.

Because the fluid obeys no existing laws the coefficient of viscosity, μ , and the coefficient of thermal conductivity, K , are meaningless. Nevertheless, it will be shown that liquid helium is a much better conductor of heat than copper and that it flows much more readily than any other substance known.

No completely satisfactory theory exists to explain these qualities but a very brief summary of the most suggestive of the numerous hypotheses will be given.

Polymers

The Influence of Temperature on the Mechanical Properties of Molded Phenolic Materials. T. S. Carswell, D. Telfair and R. U. Haslanger. A. S. T. M. 1942 Preprint No. 104. 10pp.

The rapidly growing use of plastic materials in the manufacture of military equipment has accentuated the need for quantitative data on the mechanical properties of these materials over a wide range of temperatures. Such data showing the variation of the impact, flexural and tensile strengths with temperature, were determined for compression-molded phenolic compositions containing wood flour, asbestos, macerated fabric, vegetable fiber, and cord fillers and for a pure resin composition. Impact values between –80°C. and 250°C. (–112°F. and 480°F.), flexural values between –80°C. and 180°C. (–112°F. and 355°F.) and tensile value between –80°C. and 230°C. (–112°F. and 445°F.) are tabulated and shown graphically.

The tensile strength of all materials studied, with the exception of the pure resin, decreases with increasing temperatures. The tensile strength of pure resin composition shows a maximum at about 25°C. and falls off both above and below this temperature. The tensile strength of asbestor-filled composition is less effected by temperature than is that of the other materials studied.

In general, the above conclusions apply to flexural strength also.

The impact strengths of pure resin and of the asbestos filled composition are practically unaffected by variations in temperature within the range studied. All compositions containing cellulosic fillers begin to lose impact strengths above certain temperatures which vary from about 120°C. for sisal fiber to 160°C. for wood flour and cord. The impact strength of wood flour-filled material is essentially unaffected by temperature below 160°C.: the other cellulosic-filled compositions studied show maxima as noted above, below and above which impact strength decreases. In general, the greater the impact strength

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of the composition, the greater is its rate of change of impact strength with temperature.

In an interesting graph, the impact strength-temperature relationships of these phenolic materials and of several thermoplastics are compared.

The practical importance of these data are pointed out.

<div align="right">H. K. NASON</div>

Mechanical Properties of Substances of High Molecular Weight. II Rigidities of the System Polystyrene—Xylene and Their Dependence Upon Temperature and Frequency. John D. Ferry, J. AM. Chem. Soc. **64**, 1323 (1942).

When the molecular weight of a polymer is sufficiently high, its solutions (in a completely miscible solvent) grade uniformly from viscous liquids through gelatinous or rubber-like consistencies to plastic solids. The mechanical properties of such systems depend upon the concentration, the molecular weight, and the solvent. These properties(such as moduli of elasticity and rigidity) can be measured only if the mechanical relaxation times are long compared with the time required to complete an experiment. In solutions of high polymers these relaxation times range from the order of a second to very much less; thus they behave statically (or when subjected to slow deformation) as viscous liquids. When under investigation with rapidly oscillating deformations they behave as rigid solids.

The propagation of transverse vibrations in solutions of polystyrene in xylene over a concentration range of 15.7 to 52.3% polymer between –5° C. and 40°C. and between frequencies of 200 to 4000 cycles/sec. has been measured by a mechanism previously described (Ferry, Rev. Sci. Inst. 12, 79, 1941). These solutions support transverse vibrations and therefore possess rigidity. The phenomena are analyzable in terms of a single relaxation time of about 4×10^{-4} secs. which to a first approximation is independent of temperature and composition. The modulus of rigidity varies from 10^4 to 10^6 dynes cm^{-2} in the range studied and decreases with increasing temperature. The results are discussed in terms of the molecular behavior of long chain polymers.

<div align="center">HOWARD A. ROBINSON</div>

Physical Properties of Polystyrene as Influenced by Temperature. T. S. Carswell, R. F. Hayes and H. K. Nason. Ind. Eng. Chem. **34**, 454—7 (1942).

Three samples of commercial polystyrene, whose average molecular weights, determined viscometrically by means of the Staudinger relation, were 60,000, 95,000 and 115,000, respectively, were injection-molded into standard test specimens. The tensile, flexural, impact, and hardness properties of these samples were determined at temperatures ranging from —75° to ✛ 100°c.

Tensile strength, elongation, and impact strength of injection-molded polystyrene increase as the average molecular weight of the polymer increases. Indentation hardness appears to be independent of molecular weight, within the limits studied, at temperatures below about 80°C.

This material undergoes a critical transformation with respect to mechanical properties at 80° to 85°C. which is analogous to the "second order transition range" of rubber at –71° to–67°C.

Polystyrene becomes tougher as the ambient temperature is reduced below the transformation range, and differs in this respect from most other plastics which generally are more brittle at lower temperatures.

H. K. NASON

Rubber

Molecular Structure and Rubber-Like Elasticity. III. Molecular Movements in Rubber-Like Polymers. C. W. Bunn, Proc. Royal Soc. 180, 82 (1942).

By analogy with atomic crystals, molecular crystals melt when the amplitudes of thermal vibrations of the molecules are roughly equal to the distances between molecules in the crystal. For flexible long-chain molecules, where segments move independently, the melting point should be lower than for rigid molecules of the same weight. In chain molecules the motion perpendicular to the chain resulting from rotation around single bonds accounts for most of the motion and therefore controls the melting. Rubber, polychloroprene and polyisobutylene melt below room temperature, while β —gutta percha melts at 65° C and polyethylene at 115° C. These differences are explained qualitatively in terms of the potential barriers opposing rotation.

"Free" rotation around a single bond does not occur but in a chain molecule there is a rapid switching from one equilibrium position to another. In gutta percha, rubber and polychloroprene, free rotation around the single bonds at the end of the isoprene and chloroprene groups can result in oscillation between two energetically equivalent positions. This is designated as molecular "wriggling," and this motion disturbs neighboring molecules sufficiently to result in melting.

Rotation around a single bond is controlled by two factors, bond orientation and steric hindrance. For polychloroprene, gutta percha and rubber the bond orientation forces are about equivalent. However, the C-Cl distance in polychloroprene is larger in the $C\text{-}CH_3$ distance in gutta percha and this allows rotation about the single bond at the end of the group to occur at lower temperatures. In rubber the corresponding motion is restricted by the same CH_3 group as in gutta percha, but the bond angles and the cis form of the molecule are more favorable.

The higher melting point of saturated chain polymers arises mainly from higher bond orienting effects. In unsaturated chains, the adjacent double bonds lower the potential barrier opposing rotation. Also, the molecular "wriggling" which occurs in rubber, gutta percha and polychloroprene cannot occur in saturated molecules because any rotation is toward higher energy positions. In polyethylene, repulsion between CH_2 groups favors a planar ziz-zag molecule which tends to raise the melting point still higher, while in polyisobutylene mutual repulsion between CH_2 groups opposes the staggered configuration with a lowering of the melting point.

Analysis of kinetic theories of elasticity indicates that the effect of intermolecular action is appreciable and possibly just above the melting point molecules may be aligned in roughly parallel positions in groups that correspond to very imperfect crystals. These groups may even be of approximately the same size as the crystals which exist below the melting point. Cohesion can occur by tying in the molecules between these imperfect crystals. It is suggested that on stretching, adjacent molecules, in addition to being aligned in the direction of stretch, are also under lateral compression, which would further aid crystallization.

Statistical Thermodynamics of Rubber. Frederick T. Wall, J. Chem. Phys. **10**, 132 (1942).

A theory of rubber elasticity is built assuming that the forces involved arise principally from straightening out curled up molecules rather than from intra—or intermolecular forces. Assuming free rotation about various bonds in the long chain molecules, it is seen that a large number of molecules left to themselves will assume a certain distribution of shapes. When a macroscopic piece of rubber is subjected to a stress, the original distribution is changed to one of lower probability, and hence of lower entropy. To determine the new distribution, it is assumed that a given molecule changes the components of its length in the same ratio as does the macroscopic piece of rubber.

From the difference in entropies of the stretched and unstretched configurations, it is possible to deduce an equation of state for a piece of rubber, namely:

$$f = \frac{NkT}{l_0} \left\{ \frac{l}{l_0} - \frac{l_0}{l} \right\}$$

where f is the force of stretching, l the length, l_0 the length when $f = 0$ and N the number of molecules. It is assumed in the derivation that the molecules change shape in only one direction (that of the stretching). Comparison with experiment gives a reasonable value for the molecular weight of rubber.

Statistical Thermodynamics of Rubber II. Frederick T. Wall. J. Chem. Phys. **10**, 485 (1942).

The theory of the preceding paper is extended by assuming

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that the volume of rubber remains constant during a stretching process. As a result all three components of the lengths of the molecules will change when a macroscopic piece of rubber is stretched in some direction. Comparing the probabilities of the stretched and unstretched states, there is calculated, through entropy considerations, the following equation of state:

$$f = \frac{NkT}{l_0}\left\{ \frac{l}{l_0} - \left(\frac{l_0}{l}\right)^2 \right\}$$

This equation differs slightly from the previous equation, but agrees better with experiment. The equation is compatible with, though not identical to, Mooney's equations derived from macroscopic considerations. (M. Mooney, J. App. Phys. **11**, 582, (1940)).

It is also shown by means of the theory that rubber should obey Hooke's law with respect to pure shear even though it doesn't obey Hooke's law for ordinary extension. This is in good agreement with observation.

The effect of vulcanization is also discussed. It is shown that the number of "molecules" must be taken as the number of molecular segments which are free to assume various shapes subject to fixed end positions. Assuming vulcanization involves cross-linking of molecules, it is seen that vulcanization increases the apparent number of "molecules" thus increasing the modulus of rigidity.

Theory

What Is Tack?—Henry Green. Paper Trade Journal **114**, 39-42, (1942).

In an attempt to find out what the practical ink man means by tack, the conclusion reached was that tack is pull resistance. Both cohesion and adhesion have been ruled out as direct factors and surface tension has been shown experimentally to be negligible in the case of printing inks. The author has described (Green, Anal. Ed., Ind. Eng. Chem. 13, 632-9 (1941)) in detail an instrument, the tackmeter, for measuring tack. The equation arrived at and experimentally verified is

$$T\,(\text{tack}) = \frac{\pi R^4 \mu}{D^2 t} + Cf$$

where R is the radius of contact area, μ the plastic viscosity, D the initial film thickness, t the time of break, f the yield value, and C a proportionality constant depending on D and R. The resistence is seen to be divided into two parts, (1) that due to the flow of the plastic and (2) that due to the yield value. The equation is only valid when the tacky material in question has the flow characteristics of a true liquid after the yield point has been exceeded.

The analysis of tack and the development of the tackmeter is a piece of work which has been carefully and accur-

ately executed. The definition of tack is rather narrow in scope in that the break must take place within the plastic material. Pressure sensitive adhesives, such as are used on cellophane tapes, have tacky surfaces and upon removal of the finger, the break occurs between the finger and the adhesive. None of the tacky material is left on the finger. The analysis of the latter type of tack, while similar to that treated by the author, is more complicated.

<div align="right">J. O. HENDRICKS</div>

The Viscosity of Dilute Solutions of Long-Chain Molecules, Dependence on the Solvent. Maurice L. Huggins, Kodak Research Laboratories. Presented before the Division of Paint, Varnish and Plastics Chemistry of the American Chemical Society, Buffalo, N. Y., September 8, 1942.

In a paper (**J. Appl. Physics. 10**, 700 (1939)) presented before the Society of Rheology in 1938, the author showed that, in general, the viscosity of dilute solutions of long-chain molecules should depend on the relative magnitude of solvent-solute attractions, on the one hand, and the solvent-solvent and solute-solute attractions on the other, this relative magnitude determining the average degree of coiling or extension of the solute chains. Later, Flory made the same observation and, recently, Alfrey, Bartovics and Mark have dealt with the subject in greater detail, presenting new experimental evidence in favor of this point of view.

In the present paper, a semi-quantitative treatment is presented, relating the viscosity constants to certain constants entering into the author's theoretical treatment of the thermo dynamic properties of solutions of long-chain compounds (**Annals N. Y. Acad. Sci., 43**, 1 (1942); **J. Am. Chem. Soc., 64**, 1712 (1942)).

The Viscosity of Dilute Solutions of Long-Chain Molecules Dependence on Concentration. Maurice L. Huggins, Kodak Research Laboratories. Presented before the Division of Colloid Chemistry of the American Chemical Society, Buffalo, N. Y., September 9, 1942.

It is shown that a simple, reasonable modification of the author's previous theoretical treatment of the viscosity of dilute solutions of long-chain molecules leads to the equation

$$\eta_{sp}/c = (\eta_{sp}/c)_{c=0} \cdot (1 + k'\eta_{sp})$$

for the initial concentration dependence of the viscosity. This is identical with an equation arrived at empirically by Schulz and Blaschke. The constant k' is characteristic of a given solute-solvent system, but is the same for solutions, in a given solvent, of different members of a polymer-homologous series.

At low concentrations (such as assumed in the theoretical derivation) this relationship is equivalent to

$$\eta_{sp}/c = (\eta_{sp}/c)_{c=0} + k'(\eta_{sp}/c)^2_{c=0} \cdot c.$$

Equations proposed by Baker, by Fikentscher and Mark, by de Jong, Kruyt and Lens, and by Martin all reduce to the same limiting equation, with k' different for different systems. Equations proposed by Arhenius, by Hess and Philippoff and by Bredee de Booys likewise reduce to this form, but with k' having the same value for all systems.

The Variation of Viscosity of Liquids with Temperature. M. K. Srinivasan and B. Prasad, Phil. Mag. 33, 258 (1942).

This paper is a comparative study of the various equations which have been proposed to represent the dependence of viscosity of liquids on temperature, and of their applicability to known data on organic and inorganic liquids. Equations of Andrade, Macleod, Silverman, Madge, Bingham, Souders, and Frenkel are considered. The hypotheses on which these various equations are based and their plausibility in the light of experimental data are discussed. The newer work of Eyring and coworkers of van Wyk and Seeder has been overlooked.

Andrade's simple equation.

$$\eta = A \exp(b/T)$$

reproduces experimental results as accurately as (if not better than) any of the other equations. The authors consider that it enjoys a better theoretical basis also. None of the equations can be applied satisfactorily to associated liquids having degrees of association which vary with temperature.

<div align="right">P. J. FLORY</div>

APPLICATION

R. B. DOW, Secretary-Treasurer
Ballistics Research Laboratory
Aberdeen Proving Ground, Maryland.

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.

Subscribing membership, (including subscription to Rheology Bulletin and Journal of Applied Physics.)
                                   $7.00 (foreign, $7.70)

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