

RHEOLOGY BULLETIN



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EDITORIALS

Rheology Reviews

With this issue we inaugurate a new feature, Rheology Reviews, being broad surveys designed to furnish a perspective of a wide field of knowledge. In this way we can hold symposia without having to travel on wartime congested trains. Such surveys require the breadth of interest and maturity of experts. We are fortunate in this first Review. Its title is, "Some Rheological Properties of Matter under High Hydrostatic Pressure." The author is Dr. Richard Dow, of the Ballistic Research Laboratory, Aberdeen Proving Ground, Aberdeen, Maryland. Dr. Dow is also the very efficient Secretary-Treasurer of The Society of Rheology. He has for many years been engaged in high pressure studies, and was formerly a Research Associate of Professor P. W. Bridgeman of Harvard University. Other Reviews will be published from time to time as conditions permit. The Editor will welcome suggestions as to topics and experts.

Our Abstract Service

A very satisfying response has already developed as a result of the appeal for help in the last issue of the Rheology Bulletin. The following journals have already been assigned definitely to certain people who will supply us with abstracts regularly.

American Paint Journal
Angewandte Chemie
Bell Laboratories Record
British Plastics and Moulded Products Trader
Chemistry and Industry
Helvetica Chimica Acta
India Rubber World
Industrial Engineering Chemistry
Instruments
Journal of the American Chemical Society
Journal of Applied Physics (rubber articles only)
Journal of Chemical Physics (rubber articles only)
Journal of the Franklin Institute
Journal of Physical Chemistry
Journal of the Society of Glass Technology
Kolloid Zeitschrift
National Bureau of Standards Journal of Research
Naturwissenschaften
Oil and Gas Journal
Petroleum Engineer
Rubber Age
Transactions of The Faraday Society

This is a good start, but there are dozens more of good journals in which papers on rheological subjects may appear. Pick out your favorites, write the Editor, and thereby boost the Bulletin. It's fun when you get going, and you'll meet a lot of other Good Friends.

Abstractors in this Issue

The following are the names and addresses of our Good Friends who have cooperated in making this August 1943 Rheology Bulletin a success:

- A. Bondi, 1800 Baronne St., New Orleans 13, La.
- Neill M. Brandt, Bausch and Lomb Optical Co.,
Rochester, N. Y.
- John D. Gerry, Woods Hole Oceanographic Institution,
Woods Hole, Mass.
- Andrew Gemant, The Detroit Edison Co., 2000 2nd Ave.,
Detroit, Mich.
- R. H. Kelsey, Physics Research Division, The Firestone
Tire and Rubber Co., Akron, Ohio
- Wesley W. Pendleton, Research Laboratories, Westing-
house Electric and Manufacturing Co., East
Pittsburgh, Pa.
- H. G. Schurecht, Professor of Research, The New York
State College of Ceramics, Alfred, N. Y.
- Robert Simha, Department of Chemistry, Howard
University, Washington, D. C.
- Kuan Han Sun, Research Laboratories, Eastman Kodak
Co., Rochester, N. Y.
- R. N. Traxler, Refining Department, The Texas Co.,
Port Neches, Texas
- L. E. Welch, Bakelite Corporation, 230 Grove St.,
Bloomfield, N. J.
- Ruth N. Weltmann, The Research Laboratories, Inter-
chemical Corporation, 432 West 45th St., N. Y. C.

PROGRAM

ANNUAL MEETING OF THE SOCIETY OF RHEOLOGY

October 29 and 30, 1943

at the

Hotel Pennsylvania, New York City

Friday Morning

9:00-9:30 Registration

1. 9:35-10:05 The Optimum Fluidity, or the Rheological Homeostasis, E. C. Bingham, Lafayette College, Easton, Pa.
2. 10:10-10:40 The Pore Size of Brick, W. H. Herschel, National Bureau of Standards, Washington, D. C.
3. 10:45-11:15 Exploring Stress - Strain Relations of Isotropic Plastic Solids, W. Prager, Brown University, Providence, R. I.
4. 11:20-11:50 Non-Homogeneous Stresses in Viscoelastic Media, T. Alfrey, Monsanto Chemical Company, St. Louis, Mo.
5. 11:55-12:25 Solution Viscosity Relationships of Some Commercial Cellulose Acetates, T. S. Lawton, Jr., Monsanto Chemical Company, Plastics Division, Springfield, Mass.

Luncheon

6. 2:00- 2:30 The Importance of Flow Phenomena in Plastics Engineering, Robert Burns, (Chairman, Committee D20 on Plastics, American Society for Testing Materials), Bell Telephone Laboratories, Inc., New York, N. Y.
7. 2:35- 3:05 Rheological Properties of Asphalt, R. N. Traxler, H. E. Schweyer and J. W. Romberg, The Texas Company, Port Neches, Texas.
8. 3:10- 3:40 Rheological Properties of Solid Suspensions in Resin Solutions, E. N. Harvey, Jr., and E. K. Fischer, Interchemical Corporation, New York, N. Y.

9. 3:45- 4:00 Uncertainty in Rheology, E. C. Bingham, Lafayette College, Easton, Pennsylvania.
10. 4:00- 5:00 Annual Business Meeting
Saturday Morning
11. 9:00- 9:30 Viscosity and Osmotic Measurements with Fractionated High Polymers, W. Badgley, J. Hansen, W. Zybert and H. Mark, Brooklyn Polytechnic Institute, Brooklyn, N. Y.
12. 9:35-10:05 The Brittle Point of Polystyrene, W. Berman, G. Goldfinger and H. Mark, Brooklyn Polytechnic Institute, Brooklyn, N. Y.
13. 10:10-10:30 Rigidities and the Kinetics of Setting of Gelatin Gels, J. D. Ferry, Harvard Medical School, Boston, Mass.
14. 10:35-11:05 Second Order Transitions in High Polymers, R. F. Boyer and R. S. Spencer, The Dow Chemical Co., Midland, Mich.
15. 11:10-11:40 A New Theoretical Treatment of Rubberlike Elasticity, M. L. Huggins, Kodak Research Laboratories, Rochester, N. Y.
16. 11:45-12:15 The Effect of Thixotropy on Plasticity Measurements, H. Green and Ruth N. Weltmann, Interchemical Corporation, New York, N. Y.
17. 12:20-12:50 Elastic Properties of Some High Polymers at Different Frequencies, H. S. Sack, in collaboration with J. Motz and R. N. Work, Cornell University, Ithaca, N. Y.

THE OPTIMUM FLUIDITY OR THE RHEOLOGICAL HOMEOSTASIS

Eugene C. Bingham

In lubrication a certain amount of viscosity is desirable to keep surfaces from touching but too great a viscosity is objectionable. It would appear therefore that there is an optimum fluidity beyond which it is dangerous to go. We desire our highways to be smooth to avoid noise or jolting but we fear the slipping or skidding of too little friction. So the body fluids, particularly the blood, contain a high percentage of water giving the suppleness and movements in the organism. There are a series of equilibria maintained in the human body, which Dr. W. B. Cannon in his volume on the Wisdom of the Body has denominated homeostases. There is not only this homeostasis of water, but of sugar, salt, proteins, fat, calcium, oxygen, temperature and pH. It is not surprising that the fluidity optimum depends upon conditions to some extent, but the truly remarkable thing is that with irregular intake of nourishment there should be equilibria which are recognizable.

A consideration of the blood of a large number of healthy adult men shows that whereas the number of red blood cells as measured by the hemoglobin content (H) varies widely, the fluidity in rhes (ϕ) may be calculated by the simple formula

$$\phi = 53 + 0.24 H$$

which holds good to 3.3 per cent, which is about the accuracy of the method (Sahli) used for measuring the hemoglobin. The conclusion that we reach at once is that the fluidity has to be adjusted to the hemoglobin content, i.e. the number of blood cells. If athletes require a heavy meat diet, it may suggest a connection with the fact already noted that meat eaters have blood which is less fluid than vegetarians. It is also known that for sudden and severe exertion it is important for the blood to be rapidly aerated, which can only be possible when the blood has plenty of red cells. Confirming the above, it is found that persons going from sea-level to a high altitude suffer from the lack of sufficient oxygen and during the process of acclimatization the number of red blood cells increases.

Women normally have blood with higher fluidity, on the average, than men but they also have a lower hemoglobin content too in accordance with the above formula. May we ask if that may be taken as evidence that women, on the average, are accustomed to less sudden and violent exertion than men? Might we not also ask whether with more viscous blood the heart of an athlete might not wear out more quickly than that of his healthy but slightly more anemic spouse? We might even ask whether a hemoglobin requirement might not be advantageously added to the long list of desiderata for aviators in the stratosphere.

THE PORE SIZE OF BRICK

Winslow H. Herschel

On the basis of Peek and McLean's value of 38.5 dynes per cm for the adhesion tension, the pore radius in cm may be found from the equation,

$$R = \frac{5.2}{t} \cdot \left(\frac{V_a}{V} \right)^2 \quad (1)$$

where t is the time of submersion in seconds, V is the per cent porosity and V_a is the absorption per cm^2 , or the total absorption divided by the area, in cm^2 , of one face of the brick. For simplicity, it is assumed that the pores are straight and cylindrical, and that the water enters entirely from one end.

When the vacuum used in forming the brick is increased, R increases and the number of cycles of freezing and thawing at failure decreases. It was concluded that the pores become clogged in freezing and thawing tests so that it is questionable whether it is worth while to redetermine R after failure. A more promising field for investigation would be the adhesion tension method, i.e. determining pore radius by forcing the water out of a saturated specimen. This might clarify points now in doubt regarding relation between thickness of specimen and effective length of pores, and the value of adhesion tension when water enters a dry pore.

EXPLORING STRESS - STRAIN RELATIONS OF ISOTROPIC PLASTIC SOLIDS

W. Prager

In testing of materials it is impossible to measure local stresses and strains; only certain stress resultants (e.g. tensile force, torque) and certain global deformations (e.g. elongation, angle of twist) are accessible to measurement. The empirical relations between these stress resultants and the corresponding global deformations will permit the establishment of reliable stress-strain relations only if fairly uniform distributions of stress and strain are set up in the test specimen. Torsion of solid bars and bending being thus excluded, combined tension and torsion of thin-walled tubes recommends itself as one of the few tests in which a fairly general state of uniform stress can be realized without too great experimental difficulties. A manner of representing graphically the results of such tests is suggested. Well known theoretical stress-strain relations are represented in this manner and compared with results of experiments on mild steel. The possible effects of isotropic and anisotropic strain hardening are discussed.

T. Alfrey

The visco-elastic properties of a material can be considered known if the fundamental differential equations which govern deformation are known. These equations describe how an infinitesimal volume element of the material will respond to stress during an infinitesimal element of time. Such information, no matter how exact, is by itself unsatisfactory. From the practical standpoint, we are interested in the properties of materials only as a steppingstone to the behavior of objects. The ultimate aim of rheology is not only to know the governing differential equations for a material, but to be able to solve them subject to any desired set of boundary conditions - i.e., to be able to predict the response of an object, constructed from the material in any shape, to any arbitrary sequence of forces.

Previous attempts to treat this problem have been largely confined to one or the other of two special cases:

1. For materials whose time-behavior is simple (e.g. ideal solids and Newtonian liquids), it is possible to treat the spatial complications thoroughly (Theory of elasticity, hydrodynamics).
2. Where the stress and strain are spatially simple, it is possible to treat complicated time behavior. (Simha, Alexandrov and Lazurkin, Leadermann, etc.)

The purpose of this paper is the simultaneous treatment of spatial and temporal complications. The governing partial differential equations are too complicated to be of much use in the general case. It will be shown, however, that in a wide variety of problems, the space and time variables can be separated, so that the complete solution is no more difficult than the special cases (1) and (2) above.

SOLUTION VISCOSITY RELATIONSHIPS OF SOME COMMERCIAL CELLULOSE ACETATES

T. S. Lawton, Jr.

Two series of commercial cellulose acetates, differing in viscosity but not appreciably in chemical composition, were studied in concentrations ranging from one to two hundred grams per liter in anhydrous acetone at 25°C. Capillary viscometers of the Fenske type were used.

For moderate concentrations (up to 8 grams per liter), the relationship

$$\eta_{sp/c} = [\eta] + K' \cdot [\eta]^2 C$$

proposed by Huggins, is valid. However, K' may not be the same for all members of a series of cellulose acetates differing only in molecular weight, but increases as the molecular weight increases. For acetates of medium molecular weight (35,000-40,000 by Staudinger's method), K' is about 0.7, as reported by Mark. However, values as low as 0.3 and as high as 0.9 have been found for low molecular weight and high molecular weight products, respectively.

Shearing-stress versus rate-of-shear data were obtained for both series of acetates. For the concentrations used, and at shearing stresses up to 7500 dynes per sq. cm., typical Bingham flow curves, showing no definite yield point, were obtained. At high rates of shear, the curves appear to be linear.

20% solutions of the two series of acetates were investigated by five different falling-ball methods now in commercial use, and correlative relationships between these methods were established. It was not possible, however, to correlate results obtained with dilute solutions in capillary viscometers with the falling-ball data.

For technical control purposes, the replacement of 20% solution, falling-ball methods by dilute solution, capillary viscometer methods seems undesirable. Materials which differ greatly in viscosity in 20% solution may differ only very slightly in dilute solutions. In addition, the extreme care necessary to assure precision in work with dilute solutions is not practical for most control work.

THE IMPORTANCE OF FLOW PHENOMENA IN PLASTICS ENGINEERING

Robert Burns

The use of plastics as engineering materials has become increasingly evident in production of material of war, and will no doubt continue into the post-war period. Starting with celluloid about 75 years ago, becoming modernized by the introduction of phenolics for electrical applications 30 years ago, and then followed by the introduction of thermoplastics for decorative-structural purposes, we now find all types of plastics engaged in the grim business of war.

A few years ago the Bell System plastics technologist, who was forced by the intricate design of precision electrical apparatus to worry about flow, was considered somewhat of a sadist who spent his time looking for trouble instead of contemplating the pleasanter phases of life. Now, with plastics being used in the far North, involving the possibility of breakage from lack of flow (brittleness), and in the tropics with the continual hazard of failure due to too much flow, control of this property becomes of vital importance.

This informal presentation will cover the practical significance of elastic and plastic flow, recovery, "elastic memory," and related phenomena. Standard and special test methods used by the plastics industry for qualification and procurement purposes will be reviewed.

RHEOLOGICAL PROPERTIES OF ASPHALT

R. N. Traxler, H. E. Schweyer and J. W. Romberg

The flow characteristics of 25 asphalts from different sources and processed by various methods were evaluated in a rotary viscometer of a type suitable for the measurement of high consistencies at a constant rate of shear. Consistencies of each asphalt at fixed temperatures were determined at two or more mean rates of shear. If an asphalt is a complex liquid the measured consistency decreases as the rate of shear is increased. The magnitude or degree of complex flow may be evaluated by "c" in the equation:

$$M = F/S^c$$

where F = Shearing Stress, dynes per sq. cm.

S = Rate of shear, reciprocal seconds

M and c are constants.

The constant "c" may be calculated from two experimentally determined values of rate of shear and shearing stress by the equation:

$$c = (\log F_1 - \log F_2) / (\log S_1 - \log S_2)$$

The value of "c" is unity for asphalts that are simple (Newtonian) liquids but less than unity for those that are complex liquids.

It is shown that these equations for evaluating the flow of complex liquids are valid over a considerable range in rate of shear and are not limited to one type or size of viscometer.

Data are given which show that certain asphalts are simple liquids at service (atmospheric) temperatures while others have the characteristics of complex liquids. Evidence is given that the type of flow (and if complex, the degree thereof) depends on the source of the asphalt, the method and degree of processing, the age of the sample and the temperature at which the evaluation is made. Further, it is shown that some asphalts retain their complex flow characteristics at temperatures as high as their Ring and Ball softening point.

A discussion is given of the relationships between the fundamental rheological characteristics of asphalts and the empirical tests commonly used by bituminous technologists.

RHEOLOGICAL PROPERTIES OF SOLID SUSPENSIONS IN RESIN SOLUTIONS

Edmund N. Harvey, Jr. and Earl K. Fischer

The rheological properties of pigment suspensions in resin solutions are intimately connected with the application conditions and appearance of protective coatings. In the analysis presented here, the flow properties of typical pigment suspensions are correlated with various processing procedures, application methods, and end-effects such as "orange peel", "sagging", and other surface imperfections.

For spray gun application, plastic viscosity and yield value determine the delivery from the gun and the region in which proper atomization are obtained. Size distribution counts of the particles from the spray gun showed that adequate atomization is obtained over a wider range of viscosities than is sometimes considered practicable. While most of the compositions initially exhibit Newtonian flow of low viscosity, after spraying they show pseudoplastic and, in some cases, plastic flow. This arises from an increase in the relative content of the suspended phase through evaporation of solvent. Orange peel results from all types of flow when the plastic viscosity increases to a value outside the limits for uniform levelling. The time necessary for smooth flow out is directly proportional to the viscosity and inversely proportional to the film thickness. Sagging results from excessively low viscosity of the material on the coated surface, abnormally thick films, or both. An appreciable yield value in the composition after spraying leads to low surface gloss.

Although the durability of the finished coating is determined largely by the properties and balance of the ingredients, wide variations in practical formulation present an essentially similar rheological picture.

UNCERTAINTY IN RHEOLOGY

Eugene C. Bingham

This is not a discussion of the "Uncertainty Principle". It concerns the development of the Science of Rheology and is therefore non-mathematical but is intended to be very definite and concrete.

The Society of Rheology was started in 1929 growing from a series of Plasticity Symposia dating back to 1924. We have no reason to be satisfied with the progress that has been made.

Much uncertainty then existed as to how best to measure viscosity and no value was accurate enough to serve as a standard. Attempts made to remedy the situation have not come to fruition. The practical utility of Rheology in various fields such as medicine and physiology remains clouded. The reasons for this may be stated in the hope that thereby a way for overcoming them may eventually be made plain.

In the analogous science of electricity, no one need any longer be in doubt as to whether resistances are additive or not, provided the arrangement of the conductors is known. Knowing the law, the resistance of the system may be calculated even when the arrangement is not simple. In Rheology, the fundamental law is still a subject for opinion and debate. This is a stumbling block in the treatment of the theory of mixtures, of which blood is one of many examples.

The definition of viscosity established a volume relationship and it should be agreed upon as to what sort of a relationship should be expected when two inert liquids are mixed by volume or weight or by molar weights. There is no doubt in regard to the property of specific gravity; why should there be an opportunity for doubt in the case of viscosity?

The accuracy and reliability of electrical measuring instruments, ammeters, voltmeters and the like are assumed without question. How different in rheological measurement? Aside from the use of "National units" such as Engler, Saybolt Redwood which are not fully convertible, we are now moving to the kinematic Centistoke and for no good reason an English unit of viscosity has been added, to increase the confusion in practice.

The author would like to be able to leave relative viscosities out of consideration, but that is impracticable. For example almost the entire body of data on the viscosity of blood is expressed as relative viscosities based upon the viscosity of water at the temperature of measurement taken as unity. This is a vicious system for many reasons, one being that it involves the use of a multiple standard but the most important one being that relative units of this sort are not additive and cannot be regarded as viscosities, as is done.

We do not want to be querulous. On the other hand, we want full discussion of the conclusions drawn from the available facts, but when conclusions are inescapable, it is our duty to make those decisions known to those who may be concerned. This program is both practical and practicable.

1. Let us ask the proper authorities to make it possible for the National Bureau of Standards to bring to an early conclusion the important determination of the absolute fluidity of water over a wide range of temperatures, one or more of

these values to be used as fundamental rheological standards.

2. At the same time agreement of opinion might be demonstrated in regard to satisfactory methods for absolute measurement, and the necessary corrections.

3. With the above great achievement already made, it would be a natural step to the establishment of secondary standards of viscosity over the entire industrial range of viscosities. This would make it easy to employ very simple instruments for measurement and yet make possible the accurate estimation of rheological properties in absolute units, as is not feasible at present.

4. We should, ourselves, assume responsibility for reaching conclusions on the moot questions as soon as possible. The problem of separating the various rheological variables, e.g. elasticity, yield value, mobility, tensile strength and thixotropy is admittedly difficult but that is all the more reason for concerted attack. We may first of all ask for suggestions as to the best method of attack. Is our present lack of certainty due to an insufficiency of crucial data of an experimental nature, or are papers of a fundamental theoretical character the greatest present need; or is rheological science too disorganized among physicists, chemists, metallurgists, engineers, physiologists, etc? Those who hold this last view might argue that it is difficult to get a fundamental paper on rheology published without a strong journal in the world devoted to that particular field. Yet there are some five hundred papers published each year on some phase of rheology. This at any rate indicates that there are enough papers each year to fill a journal, there must be a public with an interest in this field. The question then is as to whether a strong journal of rheology would serve as a cohesive bond among such diverse workers, to such an extent that they would join in the unified development of the Science. Could the diverse groups of rheologists be welded together, there is little doubt but that the necessary financial support could be found for a journal. In time the public would take the trouble to become informed as to the progress of rheological opinion.

VISCOSITY AND OSMOTIC MEASUREMENTS WITH FRACTIONATED HIGH POLYMERS

W. Badgley, J. Hansen, W. Zybent and H. Mark

Polystyrene was prepared under various experimental conditions, such as different solvent, temperature, catalyst concentration and degree of conversion into the polymer. The polymers were fractionated and the fractions investigated. Specific viscosity measurements were carried out at various concentrations in the range between 0.20 and 0.80 per cent

volume concentration. The intrinsic viscosities and k' constants were determined for the various fractions. It appears that only fractions of one and the same sample can be represented by one single k' value. As soon as the conditions of polymerization are changed, the hydrodynamical characteristics of the material, as expressed in the k' value, also change.

Osmotic pressure measurements were carried out with the fractions at various solute concentrations in the range between 2 and 10 gr solute per kg solvent. The molecular weights (M) and μ -values of the various fractions were determined.

Thus one has four quantities to characterize a high polymer in dilute solution: the two hydrodynamical quantities $[\eta]$ and k' and the two thermodynamical quantities M and μ . Experiments have shown that only M (molecular weight of the solute) is independent of temperature and nature of the solvent; all other values depend upon the interaction between solute and solvent and hence change with temperature and nature of the solvent. They can be used to characterize a given polymer in respect to its internal structure, such as branching, ring closure, etc.

Various relationships between the four quantities M , $[\eta]$, k' and μ have been studied. One is the relation between intrinsic viscosity and molecular weight which was found to obey the expression:

$$[\eta] = K \cdot M^a \quad (1)$$

where a assumes different values for different systems solvent-solute.

Equation (1) should be used instead of the Staudinger equation if one wants to compute molecular weights from viscosity measurements; it shows that in general unfractionated polymers are bound to give complicated molecular weight averages if one uses the viscosity method.

This was checked experimentally. Fractions of a polystyrene with an a -value of 0.70 were mixed in known proportions and the intrinsic viscosities of the mixtures determined. It was found that the averages observed are neither the number nor the weight average, but the "viscosity" average as computed from equation (1) with $a = 0.70$.

THE BRITTLE POINT OF POLYSTYRENE

W. Berman, G. Goldfinger and H. Mark

The volume-temperature relationship of polystyrene was investigated and the rate of attainment of equilibrium volume was measured. The apparent second order transition point of

polystyrene seems to be a time phenomenon, caused by the ratio of the time of observation and the time which is necessary for the polymer to assume its equilibrium volume by diffusion of macromolecules and their segments.

The rate of attainment of equilibrium depends upon:

- (a) the nature of the polymer, such as molecular weight, amount of branching, amount of cross-linking, etc.
- (b) the previous history of the sample.
- (c) the temperature.

The rate curves, as measured experimentally, show that under certain conditions the attainment of equilibrium is a second order process, while under others it appears to be a zero order reaction. It is attempted to suggest for the interpretation of the observed facts a mechanism which involves competition of nucleus formation and particle growth, and which seems to be capable of representing quantitatively the experimental results.

RIGIDITIES AND THE KINETICS OF SETTING OF GELATIN GELS

John D. Ferry

The rigidities of gels of Eastman purified de-ashed gelatin were measured by following the propagation of transverse vibrations. The gelatin was dissolved at 37°, adjusted to a pH of about 5.5, brought to 15°, and maintained at that temperature thereafter. The rigidity was measured at intervals during the setting of the gel.

Over a frequency range of 100 to 1250 cycles/sec., there was no dispersion of rigidity. Over a concentration range of 17.7 to 61.9 g/l, the final rigidity attained was proportional to the square of the concentration. Using this relationship, the rigidities measured during the process of setting may be expressed in terms of concentration of a "gel form" of gelatin. The increase in concentration of this "gel form" follows the course of a bimolecular reaction, with a rate constant of $0.12 \text{ (g/l)}^{-1} \text{ hr}^{-1}$.

The results will be discussed with reference to the optical rotation measurements of Smith (J. Am. Chem. Soc., 41, 135 (1919)) and the molecular structure of gelatin.

SECOND ORDER TRANSITIONS IN HIGH POLYMERS

R. F. Boyer and R. S. Spencer

This paper has three principal sections: The first part lists coefficients of expansion and transition temperatures for several materials such as polyethylene; Styraloy 22; Nylon; and Saran in its amorphous, crystalline, and oriented states.

The second part deals with volume expansion measurements as an analytical tool in studying high polymeric compositions. Three types of binary systems were investigated: (1) a mixture of incompatible polymers where the dispersion is of microscopic order; (2) a mixture of two incompatible polymers molecularly dispersed; and (3) polymer plus compatible plasticizer. A quantitative determination of composition is possible for case (1), but the other two systems are more complex because of interaction of the components.

The third part of the paper concerns an interpretation of second order transition effects. It is shown that the product of the transition temperature ($\circ K$) by the cubical expansion coefficient above the transition temperature is constant (approx. 0.15) for such widely different polymers as rubber and polystyrene with transition temperatures at -68° and $+82^{\circ}C$. respectively.

The transition effect is believed to be a problem in the viscous flow of long chain molecules. Data on the anisotropy of linear expansion coefficients for the oriented Saran exemplifies this point. The divergence between brittle temperature and transition temperature for low molecular weights, and their identity for high molecular weights, is considered as one aspect of the viscous flow theory.

A NEW THEORETICAL TREATMENT OF RUBBERLIKE ELASTICITY

Maurice L. Huggins

Considering long-range elasticity as involving many rearrangements of small groups of atoms, the limiting magnitude of the elastic modulus and the shape of the stress vs. strain curve may be considered as functions of the temperature and the changes of entropy, energy and atomic positions in these individual rearrangements. Equations for these functions are deduced and represented graphically. They are also correlated with experimental data and interpreted in terms of the structure of rubber and other substances having rubberlike properties.

THE EFFECT OF THIXOTROPY ON PLASTICITY MEASUREMENTS

Henry Green and Ruth N. Weltmann

Many industrial mixtures, such as colloidal suspensions, printing inks, paints, etc. are thixotropic. Since thixotropy means a breakdown of structure (decrease in consistency) upon agitation and a rebuilding of structure upon subsequent rest, the consistency measurement, the values of viscosity and yield value, will depend on the degree of agitation the sample experiences.

Therefore, the plasticity measurement by itself does not have any physical significance; but only obtains such if the state of thixotropic breakdown is known and can be accurately designated.

This has been achieved by obtaining thixotropic levels, stable thixotropic conditions, during speed decrease, which can be designated properly by their respective top speeds. Also, three thixotropy constants, describing the degree of thixotropy present in a material, have been developed.

Two of these constants evaluate the plastic viscosity change and the third one the yield value change resulting from a breakdown of thixotropic structure by agitation obtained either over a period of time or by successive increasing speeds.

Practical examples show how to calculate the plastic viscosity and yield value for any desired thixotropic state, if measured under a known thixotropic condition. For these calculations the three above mentioned thixotropy constants are required.

ELASTIC PROPERTIES OF SOME HIGH POLYMERS AT DIFFERENT FREQUENCIES

H. S. Sack, in collaboration with
J. Motz and R. N. Work

An apparatus has been designed to determine the elastic modulus and the damping (internal friction) of plastic and similar materials by a vibrational method. The resonance curves of lateral, torsional or longitudinal vibrations of the material in question are measured in a frequency range of 100 c.p.s. to 2000 c.p.s. and at temperatures between -20°C and 100°C . The amplitude of vibration is very small and for purposes of comparison static measurements with very small leads have been made on the same samples. With a few exceptions the dynamic value of Young's modulus is higher than the static value. The damping (given by the log. decrement) is in many cases independent of frequency. The

variations with temperature show characteristic differences between polyvinyl chlorides and natural and synthetic rubber.

----- RHEOLOGICAL REVIEW -----

SOME RHEOLOGICAL PROPERTIES OF MATTER
UNDER HYDROSTATIC PRESSURE

R. B. Dow
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Although scientists have been investigating a variety of problems at high hydrostatic pressures since the 17th century, it was not until early in the present century that pressures of the order of 10,000 atmos. were generated and measured under laboratory conditions. Canton¹ in 1762 found that water is compressible but it was not until 1881 that the viscosity of water was shown by Roentgen² to decrease by about 1% between 5° and 11°C. when subjected to a pressure of 20 atmos. The first important contribution on gases was the classical work of Amagat³ who determined the compressibility over a pressure range of 3,000 atmos., and a temperature range of 200°C., the pressures being higher than any that had been used previously. Flow phenomena in solids under pressure were discussed by Hallock⁴ in 1888 but the first significant study in this country was that of Barus⁵ who investigated a variety of geological problems in the laboratory during the period 1889-1892. His experiments with marine glue called attention to the relatively enormous increase of viscosity with increase of pressure. Bridgman's famous investigations date from 1906 to the present time. Several of his papers will be referred to subsequently. Many systematic studies have become known through the efforts of Tammann (1893) in Germany, the Geophysical Laboratory (1911) of this country, Cohen of Utrecht (1910), and Michels of Amsterdam (1923). During the past twenty-five years a number of papers have appeared on rheological properties under pressure from all parts of the world, the trend being toward higher pressures as advances in metallurgy and engineering techniques permitted the generation and maintenance of pressure under extreme conditions. In this brief survey it will be possible only to mention briefly some of the more significant results that have been obtained with gases, liquids, and solids under high pressure.

Viscosity of vapors and gases under pressure, fluid but not hydrostatic, has not been investigated extensively. Phillips⁶ found that the viscosity of CO₂ increases with density through the critical region, behaving much as the p-v isothermals. For a critical density of 0.464 gm/cm³ (73.0 atmos.), the critical viscosity is 0.321×10^{-3} c.g.s. units. Naldrett

and Maass⁷ made careful studies of the same substance in the critical region by use of an oscillating-disc viscometer to find interesting time lags. Michels and Gibson⁸ showed that between 100 and 1000 atmos. the viscosity of N_2 at $75^\circ C.$ increases by over 150%. Over a range of 300 atmos., H_2 showed only an 8% increase at $25^\circ C.$ Smith and Brown⁹ used the rolling-ball method to measure the viscosity of ethane and propane over a pressure range of 340 atmos. at temperatures ranging from $15^\circ-200^\circ C.$ Comings and Egly¹⁰ have described an interesting method of correlating viscosity with critical temperature and pressure that seems to hold well at high pressures. It should aid in predicting the viscosity under pressure when experimental data are not to be had.

The compressibility of $H_2, O_2, N_2,$ and air over a range of 3000 atmos. and $200^\circ C.$ was measured by Amagat³ who showed unusual technical skill in obtaining data of high accuracy. Bridgman¹¹, investigating at pressures up to 15,000 atmos. at ordinary temperatures, found further evidence of departure from the perfect gas law, e.g., at 15,000 atmos. the volume of N_2 is 16 times greater than it would be if the law were valid. For H_2 it is 9 times greater, and for He 6 times greater. He established beyond question the compressibility of atoms and molecules, thus substantiating Richard's earlier hypothesis of the effect. A significant experimental result was the observation of the diffusion of H_2 through steel at high pressure, an effect that could be studied further with profit. Benedict¹² has accurately determined the equation of state of N_2 over a wide range of temperature and pressure, from -175° to $200^\circ C.$ and up to 6000 atmos. Michels and Michels¹³ found an equation of state for CO_2 over a range of 3000 atmos. and 150 C. Bartlett¹⁴ and Verschoyle¹⁵ have studied the compressibility of gaseous mixtures of H_2 and $N_2,$ and N_2 and CH_4 over a range of $200^\circ C.,$ the first working at pressures up to 1000 atmos. and the latter over a range of a few hundred atmos. Recent interest was shown in the hydrocarbon vapors of propane, butane, isobutane, etc. by the occasional appearance of papers describing compressions over a relatively low pressure range.

Turning to liquids, it is apparent that more extensive studies have been made of rheological properties under pressure. Surface tension measurements are important since they provide a means of determining the difference of effective volume of a molecule in the interior and at the surface of a liquid. Lynde¹⁶ observed that the relative tensions decreased with pressure for the liquid pairs: water-mercury, mercury-ether, water-ether, chloroform-water, and carbon disulphide-water. Halpern at Harvard has been experimenting with the use of penetrating radiation to determine photographically meniscus level in a tube enclosed in a pressure vessel, but his work has not been published to date.

Bridgman¹⁷ was the first to examine the viscosity of pure liquids over a wide experimental range, followed by Dow¹⁸ who investigated a series of liquid mixtures composed of the same liquids under similar pressure conditions. The pressure effect on viscosity is in general very large, the coefficient varying from a 10-fold increase under 12,000 atmos. for methyl alcohol to over 10^7 increase for eugenol over the same range (extrapolated). Water, while showing an initial decrease with pressure at low temperature, e.g., 0°, 10°C., behaves normally as other liquids at higher pressures. The viscosity of lubricants under these conditions has been studied by Hersey¹⁹, Hyde²⁰, Dow²¹, and others. It has been shown for oils that the temperature effect on viscosity over a pressure range of 1500 atmos. can be represented accurately on the A.S.T.M. Viscosity-Temperature Chart D341-37T²². The following types of viscometers have been used at high pressures: Capillary, falling-weight, freely-falling (Stokes), and rolling-ball (slanted tube). Norton, Knott, and Muenger's application of Hersey's capillary tube method to study flow properties of lubricants under pressure is interesting since they demonstrated that time of application of pressure, magnitude of pressure, and temperature determine the consistency of an oil near apparent solidification. Under these conditions, however, solidification is not of the usual type of freezing with definite change of volume²⁴.

Of the theories proposed to account for the pressure effect on viscosity those of Andrade²⁵ and Eyring²⁶ are the most successful. The latter has considered both unimolecular and bimolecular processes in relation to his theory of reaction rates. The activation energy of flow is taken as an arbitrary fraction of the energy of vaporization, and the free volume is evaluated in terms of velocity of sound in gas and in liquid. The theory represents the viscosity of ether well over the experimental pressure range, but gives values less than those observed if unimolecular flow is considered and greater than those observed if bimolecular flow is chosen. For the more complex liquids there is poorer agreement between theory and experiment, but this picture provides a clear, simple mechanism of flow properties that offers much promise for future development as more complete physical and chemical properties of the liquid state are obtained.

The p-v-t relations for liquids have been exhaustively studied by Bridgman²⁷ over a period of many years. Similar relations for oils have been summarized by Dow and Fink²⁸. Glycerine under 12,000 atmos. loses 13.4% of its original volume, while more compressible liquids like pentane and ether lose more than 30% under the same conditions. Mercury decreases only about 4% under these circumstances, while oils appear to fall about half-way between the most and least compressible of liquids. Water is relatively incompressible, so much so, that one would not follow Jules Verne to use it to absorb blast pressures as described in his trip to the moon.

Mention should be made of a broad field that has many possibilities for rheologists, that of pressure effects on reaction velocity in solution. Many contributions have come from Cohen²⁹, Bassett³⁰, Gibson³¹, Perrin³², and their associates but the experimental results need further clarifying and classifying, as well as confirmation in many cases. Bridgman and Conant³³ did similar work with organic and biological compounds which was further studied by Dow and associates³⁴. The saponification of ethyl acetate increases with pressure until at 1500 atmos. the reaction proceeds 37% faster than at 1 atmos. The inversion of cane sugar in solution, on the other hand, decreases by about 25% over the same pressure range. The process of denaturation, probably a fundamental reaction of metabolism, is greatly accelerated by pressure. Many other interesting facts are to be found in the literature which can not be discussed at present.

Few of the rheological properties of solids have been studied under high pressure, although many of the physical and chemical properties under this condition are of indirect interest. Plastic flow of rocks has been investigated by Griggs³⁵ and Goranson³⁶. Griggs shows that pressure alone does not produce flow in quartz and that limestone, when loaded to 1400 atmos., shows such a low creep rate that deformation would be negligible even if continued at the same rate for millions of years. Alabaster, however, has a flow with the logarithm of velocity of deformation proportional to the stress, so that as the stress is increased, the rate of flow increases exponentially, quite unlike ordinary viscosity. Goranson has suggested a phase mechanism to account for permanent deformation of solids under uni-directional stress as well as hydrostatic pressure. Bridgman³⁷ has been able to push his geophysical studies to pressures of 50,000 atmos. with the result that two new phase transitions have been found in quartz at 14,000 and 17,000 atmos., and also that the abnormal compressibility of quartz becomes normal at about 35,000 atmos.

Bridgman³⁸ combined high hydrostatic pressure (50,000 atmos.) with high shearing force (10,000 kg/cm²) to observe flow in metals and other substances. Generally speaking, shearing force increases with pressure until surface slip changes to internal slip which is reflected by a change of direction of the stress-pressure curve. The stress continues to be a function of pressure in the region of plastic flow, an experimental fact that does not appear to have been generally recognized previously.

Dane and Birch³⁹ have shown the effect of pressure on the viscosity of boric anhydride glass by making use of the Hersey capillary viscometer at pressures up to 2000 atmos. The ratio of viscosity at 1000 atmos. to that at 1 atmos. is 1.58 at 516°C. and 4.48 at 359°C.

Further advances in rheological techniques will undoubtedly appear as the ranges of temperature and pressure are in-

creased. In 1940 Bridgman⁴⁰ announced the attainment of pressures of 250,000 atmos., followed a few months later by a similar announcement by Goranson and Johnson⁴¹. Ultra-high pressures are obtained in a cascade arrangement where the highest pressure is generated in a chamber which is also surrounded externally by hydrostatic pressure to increase its mechanical strength. At these pressures rheology cannot be ignored - - - it is practically impossible to prevent flow.

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----- CONTRIBUTED PAPERS -----

THE VISCOSITY FUNCTION

Ernest P. Irany

The viscosity of a liquid is a unique function of its state. Many attempts have been made to define quantitative relationships between viscosity and volume, temperature and pressure, respectively, (the "viscosity functions") but our concepts of the liquid state and the constitution of liquids are not precise enough to make theoretical deductions more than speculative. The question as to what should define a truly "ideal" liquid cannot be answered with certainty and even if we assume that a given liquid or a mixture of liquids should approach closely to the requirements of ideality, none of them can cover more than a very limited range of measurable viscosities.

The first step towards a still remote rigorous solution of the problem of viscosity - and, incidentally, a precise concept of the liquid state - must be based on

I. proof that a unique and general viscosity law exists which is not subject to individual factors;

II. the quantitative determination of viscosity functions relative to volume (ideal mixtures), temperature and pressure which are additive throughout the whole range of liquid viscosities.

If these two postulates can be validated it is possible to define a fictitious "ideal liquid" which satisfies the basic law without limitation by discontinuities of state or by instability of substance and which could serve as a model of liquid constitution in a complete sequence of conceivable conditions.

As an illustration, a viscosity function $\Theta(\eta)$ may be defined as additive in terms of temperature,

$$\Theta(\eta) = aT + b$$

where a and b are fixed individual material constants. Graphically, this would mean that in a diagram using temperatures as abscissas and the function of viscosity as ordinates, the viscosity-temperature relation of every liquid would appear as a straight line, only the position of which would be determined by the material constants a and b .

The so far hypothetical function has been proposed in various simple mathematical forms, for example

$$\Theta(\eta) = \log \eta, \quad \Theta(\eta) = 1/\eta$$

but none of these terms can rate more than a rather crude approximation within the relatively narrow ranges of viscosities which single liquids can cover. If extended over larger sections, these functions fail. The same applies to various formulations of the viscosity-pressure function and those relating to the viscosities of liquid mixtures.

The writer has sought a different approach to the problem: he assumed a diagram in which the viscosity function of a liquid appears linear against proportionate units of e.g., temperature. The measured viscosities thus provide fixed points of a scale which may be completed by interpolation, and which represents graphically the function $\Theta(\eta)$.

By showing that other liquids - in fact, all those examined, with only a few obvious exceptions - yield the identical Θ scale or that they all plot as straight lines in that scale, proof is given that a fundamental viscosity-temperature function exists. The same method was successfully applied to the viscosity-volume (mixture) function yielding another generally valid viscosity scale Φ and to the viscosity-pressure function embodied in a third viscosity scale, Π . (1,3) Together, these three scales establish the existence of a unique and general viscosity law which, in this graphical form, can be stated independent of material factors. (Postulate I).

The great number of data used and carefully examined in this work and the degree of accuracy achieved are evidence for a correct guess of the normal or near-ideal character of the liquids relied upon as standards. Nevertheless, a rigor-

ous attitude towards the problem would demand an a-priori definition of ideality and a decision on what liquids would come nearest to it. It must be admitted that no such absolute definition can be given beyond assuming that the series of liquid aliphatic hydrocarbons are the most logical choice, except, perhaps, the liquefied rare gases. The hydrocarbons cover over-lapping viscosity sections by means of which it was possible to determine the three functional scales with a very high degree of accuracy through the whole range of practical viscometry. For evidence that other types of compounds are in perfect accord with the results obtained, the original papers ought to be consulted. Thus, postulate II appears to be satisfied.

Considering the extent to which the polarity of small molecules is influenced by their structure it is difficult to account for purely constitutional factors in a complex property such as liquid viscosity. Only among the high-molecular members of polymer-homologous series, polar character and solvation effects become constant enough to be eliminated from comparison. Applied to series of macro-molecular substances, the graphical principle of the functional viscosity scale has been further substantiated by the remarkable regularities it has revealed. (2)

With regard to the viscosity of liquid mixtures and solutions, the significance of the Φ scale has been firmly established. It is very important that the statement of composition in terms of component volumes be mandatory.

An enormous amount of literature is devoted to the interpretation of viscosity phenomena in liquid mixtures. It is curious to note that the premises on which these observations are based, are in most cases not even questioned. Absolute viscosity as well as a variety of assumed functions of viscosity are used in every possible combination with weight, volume or molar composition; it is clear that many conclusions, though derived from good experimental data are entirely wrong. The whole field is in need of critical revision. (4)

The writer claims that his functional Φ , Θ and \mathcal{J} scales of viscosity are the best possible approximation to the unique viscosity functions which undoubtedly exist. They not only lead to more concordant and reliable conclusions than the confused and arbitrary methods now in use but they also reveal fine distinctions which cannot be found by other means.

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Research Laboratories, Shawinigan Chemicals, Ltd.,
Shawinigan Falls, Quebec, Canada,
August 5, 1943.

----- RHEOLOGY PROGRESS ABSTRACTS -----

APPARATUS AND METHODS

AUTOGRAPHIC LOAD-ELONGATION APPARATUS FOR FIBERS.--
Arnold M. Sookne and Henry A. Rutherford, *J. Res. Nat. Bur. Standards*, 31, 25 (1943) (RP 1546).

An automatic, self-recording apparatus for determining the load-elongation characteristics of single fibers is described. It can be used for making either a continuous load-elongation record at constant rate of elongation or a point-by-point record at constant rate of loading; and can also furnish relaxation curves. The construction is based on a chainomatic balance, combined with the automatic electronic balance device of Muller and Garman (*Ind. Eng. Chem., Anal. Ed.*, 10, 436 (1938)).

JOHN D. FERRY

METHOD OF TESTING ELASTICITY OF SYNTHETIC RUBBERS AT LOW TEMPERATURES.--George D. Kish, *Oil and Gas J.*, 42, 4, 43, (1943).

In order to determine the degree of embrittlement of elastomers at low temperature the author developed a simple device, the "Elastensometer". It consists of a calibrated spring which transmits the force necessary to produce a measurable deflection of the free supported specimen. This force is indicated on a scale and expressed in pounds. The working parts, the base of the instrument, are sufficiently small to fit into a 300 cc beaker. The test is conducted while the base of the instrument is immersed in a cup of alcohol. The temperature is gradually lowered by addition of dry ice. The specimen, .290" in diameter by 1.5" long, is deflected .050" in the center. The force necessary to produce this deflection is plotted vs. temperature. At a certain temperature called "the critical limit", a sudden change of curvature can be observed. Since the force indicated by the instrument is directly proportional to the modulus of elasticity the change of curve indicates a sudden rapid increase of the modulus of elasticity with falling temperature. From the figures presented it may be inferred that the "critical limit" is the temperature at which dE/dT change by approximately one order of magnitude. The absolute value of E for one of the elastomers studied was approximately 9000 psi. at the critical temperature of -40°F . and 36,000 psi. at -68°F .

A. BONDI

THE PENETROMETER METHOD FOR DETERMINING THE FLOW PROPERTIES OF HIGH VISCOSITY FLUIDS.--

It has been called to my attention by Dr. A. Nadai, consulting engineer of our Laboratories, that equations (48) and (50) of my paper "The Penetrometer Method for Determining the Flow Properties of High Viscosity Fluids", published in the April issue of the "Journal of Applied Physics", are dimensionally in error. These equations were quoted from a British paper by W. Lethersich ("Journal of the Society of Chemical Industry", 61, 101, 1942.). No derivation was given by Lethersich for these equations. They were used by the writer to show the insignificant elastic forces as compared to the viscous forces acting when a needle of the dimensions of the A.S.T.M. penetrometer needle is pushed into a material such as asphalt. Each equation is wrong by a linear dimension and, since the ratio is taken, a fortuitous agreement with experimental results was possible.

The use of these erroneous equations in no way impares the validity of the penetrometer equations or the method for determining viscosity by the penetrometer.

Since my paper is being studied by the A.S.T.M. at the present time, it is important that this error be noted by those concerned.

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ASPHALTS AND BITUMENS

VISCOSITY OF COAL-TAR RESIDUES.--W. F. Fair, Jr. and E. W. Volkmann, An. Ed. Ind. & Eng. Chem., 15, 240-2 (1943).

The viscosities at 25°C. were determined with the falling coaxial cylinder viscometer for 23 samples of coal tar residues. A.S.T.M. penetrometer tests at 100 grams, 5 seconds, 25°C. were obtained on each sample and the viscosity calculated from the penetration data by Saal's equation --

$$\eta = \frac{5.9 \times 10^9}{(\text{penetration})^{1.93}}$$

The viscosity values calculated from penetration data by this equation are in fair agreement with the viscosity data obtained in the falling cylinder viscometer for those pitches with a penetration of more than 50 decimillimeters. "The greatest deviation is 21% and the average deviation is 6.7%."

For pitches with penetration readings less than 50 decimillimeters there is wide divergence between the values

calculated by the Saal formula and those obtained with the falling cylinder viscometer. This divergence is considered to be caused by some factor not considered in the equation and not by the appearance of anomalous flow properties. The shape of the penetrometer needle is probably responsible for the failure of the formula at readings below 50 decimillimeters.

R. N. TRAXLER

THE VISCOSITY OF PITCHES.—W. F. Fair, Jr. and E. W. Volkmann, *An. Ed. Ind. & Eng. Chem.*, 15, 235-9 (1943).

Rheological data on six pitches having Ring and Ball softening points of 52.2 to 57.0°C. were obtained by means of the falling coaxial cylinder viscometer. Absolute viscosities at 25°C. determined on most of the materials at 5 or 6 different rates of shear and shearing stresses indicated that the pitches were Newtonian (truly viscous) liquids at that low temperature. The temperature susceptibility of each pitch was calculated from the absolute viscosity value at 25°C. (converted to kinematic viscosity at 25°C.) and an assumed viscosity of 10,000 stokes at the Ring and Ball temperature. Viscosity data on the pitches also were obtained at various temperatures using the falling cylinder and capillary tube viscometers. Plotting log log viscosity versus log temperature gave curves that showed a break near the softening point. This break in the curve is caused by changes in the susceptibility of the material at its softening point, and not to instrumental differences.

Measurements at 25°C. on seven high boiling pitch distillates were made in the falling coaxial cylinder viscometer. The complete rheological data which are given indicate that the flow properties of these pitch distillates depend on the treatment prior to making the measurement, the shearing stress used, and intermediate fluctuations of temperature.

R. N. TRAXLER

CELLULOSE

MECHANICAL PROPERTIES OF CELLULOSE ACETATE AS RELATED TO MOLECULAR CHAIN LENGTH.—Arnold Sookne and Milton Harris, *J. Res. Nat. Bur. Standards*, 30, 1 (1943) (RP 1513).

Films were made from fractions of cellulose acetate varying in degree of polymerization. The weight average degree of polymerization, \overline{DP}_w , expressed as number of glucose residues per chain and determined viscosimetrically (Sookne *et al.*, *Ibid.*, 29, 123 (1942)), ranged from 30 to 380. The tensile strengths, bursting strengths, ultimate elongations,

and folding endurances were determined. These quantities increased rapidly from \overline{DP}_w 30 (at which no coherent film was formed) to \overline{DP}_w 150, above which further improvement was slight.

Films were also made from mixtures of the fractions in various proportions. When the mechanical properties of mixtures of a given pair of fractions are plotted against \overline{DP}_w , curves are obtained which have the same shape as the corresponding curves for the original fractions, but lie below them. For a given value of \overline{DP}_w , therefore, the most nearly homogeneous material has the highest tensile strength, etc. Furthermore, mixtures containing fractions of low \overline{DP}_w have lower tensile strengths than those which do not.

When the number-average degree of polymerization (\overline{DP}_n) of each mixture is calculated, it is found that the tensile strengths of all the mixtures plotted against \overline{DP}_n fall on the same curve, which also coincides with that for the original fractions; and similarly for the other mechanical properties.

It is suggested that the number-average degree of polymerization (or molecular weight) of a polymer is a more significant quantity than the weight average for correlation with mechanical properties.

JOHN D. FERRY

CERAMIC MINERALS

EFFECT OF HIGH PRESSURE EXTRUSION ON THE ADSORPTION CAPACITY OF FLORIDIN.—R. C. Amero and R. G. Capell, Petr. Refiner, 22, 23, (1943).

In the course of a study of the effect of high pressure extrusion on the properties of Floridin (a gray blue siliceous clay used as adsorbent in the oil industry), viscosity measurements of 4% suspensions of hydrated extruded and unextruded Floridin were made. The effect of extrusion was to increase the viscosity of the suspension in distilled water by more than 50%, in 3% NaCl by approximately 35%, in 26.4% NaCl by approximately 10%. These suspensions showed a slight increase of viscosity in prolonged standing.

A. BONDI

A STUDY OF SOME ALIPHATIC AMINES ON THE VISCOSITY OF CLAY BODIES.—Murray A. Schwartz, Theses, N. Y. State College of Ceramics, May 1943.

Since organic deflocculants offer certain advantages over inorganic deflocculants the effects of some aliphatic amines on the viscosities of water slips prepared with a

hotel china body and a talc semi-vitreous dinner ware body were studied. Viscosity tests were made with a Brookfield Synchro-Lectric Viscosimeter. The results are given below.

Hotel China Body Slips

(Viscosity in Centipoises)

	Molecular Weight	Solubility	Per cent deflocculant				
			0.00	0.02	0.04	0.08	0.16
Monoethyl-amine	45.08	S	3120	2520	1200	219	24
Diethylamine	73.14	S	3120	2960	1608	130	20
Triethylamine	101.19	P.S.	3120	3828	3480	1768	79
Mono-n-Butyl-amine	73.14	S	3120	1920	1696	112	25
Mono-Isobutyl-amine	73.1	S	3120	2160	1260	242	33
Mono-sec-Butyl-amine	73.1	S	3120	1280	456	127	20
Mono-n-Propyl-amine	59.1	S	3120	1380	492	70	20
Monoamyline	87.16	S	3120	2800	1600	448	76
Di-n-Propyl-amine	101.2	P.S.	3120	3000	1720	336	30
Sodium carbonate plus sodium silicate			3120	2620	1396	360	51

Talc Semi-Vitreous Dinner Ware Slip

(Viscosity in Centipoises)

	Per cent deflocculant		
	0.00	0.05	0.20
Sodium carbonate plus sodium silicate	2360	1494	386.8
Monoethylamine	2380	89	27.0

Mono-n-Propylamine and Mono-sec-Butylamine evidently proved to be the most powerful deflocculants for hotel china bodies. In general those amines with a high molecular weight and poor

solubility were the poorest deflocculants. Monoethylamine proved very effective as a deflocculant for the talc semi-vitreous dinner ware slip which could not be effectively deflocculated with a mixture of one part sodium carbonate and one part of sodium silicate.

AUTHOR'S ABSTRACT

GASES

VISCOSITIES OF THE METHANE-PROPANE SYSTEM.--L. B. Bicher, Jr. and D. L. Katz, Ind. Eng. Chem., Ind. Ed., 35, 754-61, (1943).

The viscosities of methane, propane, and four of their binary mixtures (20, 40, 60 and 80 mole percent methane) were experimentally determined at pressures from 400 to 5000 pounds per square inch and temperatures from 77° to 437°F. The instrument, a rolling-ball inclined tube viscometer, produced results with an average error of 3.2 percent. It is brought out that the experimental values of viscosity correlate with those calculated from molecular weight, temperature, and pressure. This correlation allows calculation of the viscosity of any light paraffin hydrocarbon or mixture within about 3.5 percent. The apparatus and technique used are described and typical calculations from experimental data are presented.

NEILL M. BRANDT

THE DYNAMIC VISCOSITY OF NITROGEN.--W. L. Sibbitt, G. A. Hawkins and H. L. Solberg, Trans. A.S.M.E., 65, 401-05, (1943).

A nickel capillary 118 feet long, in the form of a 2 foot mean diameter coil, was used in this investigation, and data are reported covering a considerable number of tests on nitrogen at pressures up to 1020 psi. and 923°F. The nitrogen gas used for this work was taken from standard cylinders and passed through a calcium chloride drier, before being discharged into a heater ahead of the capillary tube. Upon emission from the capillary tube, the nitrogen was cooled by direct contact with a saturated sodium-chloride spray. The cooled gas was then collected over a saturated sodium-chloride solution in a 4-1 burette. This system (diagram) proved very accurate and effective for this work.

The calculation of the dynamic viscosity was effected by the use of Poiseuille's Law modified for application to curved capillaries as follows:

$$\eta = \frac{c_1 \Phi \cdot \Delta p}{Wv} \quad (1)$$

where η = viscosity
 Δp = pressure differential
 W = weight rate of flow
 v = specific volume of fluid
 $C_1 = \frac{\pi D^4}{128 \cdot L}$
 D = diameter of capillary
 L = length of capillary
 Φ = factor for curved capillary

Φ , as quoted from another source, was taken as

$$\Phi = 1 - \left[1 - \left(\frac{k_0}{k} \right)^x \right]^{\frac{1}{x}} \quad (2)$$

where x = a constant

$$k = R \left(\frac{D}{d} \right)^{\frac{1}{2}}$$

R = Reynold's Number

D = inside diameter of capillary

d = diameter of coil

The factor Φ was determined from calibration tests using water, and the relationship between Φ and the Reynold's Number R , based on a large number of tests, is given for this equipment.

The dynamic viscosity of nitrogen gas as a function of temperature and pressure is given in the form of curves, and the agreement of these results with the data of other investigators is discussed. The final result is an empirical equation describing the results to within 1.6 per cent maximum deviation, this equation being

$$\eta = (A + E) + [BT + CT^2 + DT^3] \quad (3)$$

where $E = (p - 14.7) + [aT + bT^2 + cT^3]$

$$A = -8.80 \times 10^{-3}$$

$$B = 7.00 \times 10^{-5}$$

$$C = - 4.67 \times 10^{-8}$$

$$D = 1.283 \times 10^{-11}$$

$$a = 8.08 \times 10^{-9}$$

$$b = - 1.20 \times 10^{-11}$$

$$c = 4.76 \times 10^{-15}$$

T = absolute temperature, R

p = pressure, p.s.i.

Bibliography and readers' comments are appended.

L. E. WELCH

GLASSES AND SLAGS

THE VISCOSITY AND WORKING CHARACTERISTICS OF GLASSES.

Part I. - The Viscosity of Some Commercial Glasses at Temperatures Between Approximately 500° and 1400°.—James Boow and W. E. S. Turner, *J. Soc. Glass Tech.*, 26, 117, 215-240, (1942).

As the preliminary to systematic review of the relationship between the viscosity of mass of glass (or, more strictly, between the viscosity at different points of the mass) undergoing manipulation by hand or machine and the temperature ranges between which the various stages of manipulation can be satisfactorily carried out, the viscosities of 24 glasses, three of them synthesised from pure materials and 21 of different types employed commercially, have been determined by two precision methods, the Margules method for temperatures from approximately 750° to 1400°, and by a fibre extension method for temperatures from approximately 500° to 800°. From the results, combined with such trustworthy data as have been obtained by other workers, factors have been derived for the oxides SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, and PbO by which, within prescribed limits of composition, the viscosities of glasses containing them can be calculated.

AUTHOR'S ABSTRACT

PETROLEUM PRODUCTS

THE VISCOSITIES OF PURE HYDROCARBONS AND LUBRICATING OILS AT VARIOUS TEMPERATURES.—M. R. Cannon and J. M. Geist, *Am. Phys. Soc.*, Penn. State Meeting, June 18, 1943.

Viscosity data were obtained for fifty-five hydrocarbons in the gasoline range at 0°C, 20°C, and 40°C. The measure-

ments were made with modified Ostwald viscometers with water baths for temperature control. The viscosity-temperature behavior of the hydrocarbons followed the equation $\eta = Ae + B/RT$. With this equation, the viscosities of the hydrocarbons may be calculated between 0°C and 40°C with a deviation of less than one percent. Some trends in the viscosity behavior of the measured hydrocarbons were noted. Among the octanes, the more compact molecules had the highest viscosity-temperature coefficients. For the hydrocarbons which had approximately the same viscosities at 40°C, the alkylcyclopentanes had the lowest viscosity-temperature coefficients. They were followed by the alkylbenzenes, the alkylcyclohexanes, and the paraffins in that order. Vapor baths with automatic pressure regulation, which may be used for temperature control between 100°F and 500°F, were constructed. However liquid baths were preferred up to 210°F. The viscosities of three lubricating oils were determined at 100°F and 210°F using water baths, and at 300°F, 400°F, 450°F, and 500°F using the vapor baths. Their viscosity-temperature behavior did not follow the above equation. The measured viscosities of the lubricating oils were compared with values read from A. S. T. M. Viscosity-Temperature Charts. Above 300°F the chart values were always higher than the measured viscosities, by as much as ten percent at 500°F.

AUTHOR'S ABSTRACT

LOW TEMPERATURE CHARACTERISTICS OF GREASES.--Thomas A. Maxwell, Petr. Refiner, 22, 17, (1943), Nat. Petr. News Ref. Tech. Ed., 35, R-42, (1943).

The author determined the flow resistance of Na, Li, Ca, Al, Pb, and Ba greases in the temperature range from -67°F to -150°F. As measuring device served the grease torque test machine according to Army/Navy Specs. AN-G-3, 5/30/1943, using an 8 ball bearing No. 204 packed with 5 g of grease and submerged in an air bath, cooled by liquid Nitrogen. The time in seconds required for one revolution of the test bearing at a torque of 2000 g cm is used as numerical value of the flow resistance of the substance under study. Plotting secs. per revolution at the test temperature vs. viscosity at 100°F of the oil in which the soap is suspended, it becomes apparent that the viscosity of the oil is of greater consequence for the low temperature characteristic of greases than the nature of the soap base. The author unfortunately did not measure the low temperature viscosity of the oil base in order to confirm this finding quantitatively, but since the pour points of the oils were given as -60 to -65°F glassy solidification and therefore validity of the Walther-Ubbelohde formula for the Viscosity-Temperature function can be assumed even below the pour point temperature. The reviewer estimated the ratio of the viscosities at -67°F of the two oils of highest viscosity to be approximately 20, while the ratio of the flow resistances of the various greases

based on these two oils vary between 28 and 35. The low viscosity greases could not be evaluated in this manner because of the lack of precision of the testing device in the low viscosity region. From the figures given above it appears that the authors conclusions, although based on insufficient data are essentially correct but somewhat underestimate the still quite marked effect of the nature of the soap base on the low temperature "viscosity" of greases.

A. BONDI

POUR POINT STABILITY OF TREATED OILS UNDER WINTER STORAGE CONDITIONS.—Caleb E. Hodges and A. Bruce Boehm, *Oil and Gas J.*, 42, 7, 103, (1943).

The temperature at which paraffin wax containing oils will stop flowing under the influence of gravitational force is called the pour point. This point can be lowered considerably by the addition of surface active hydrocarbons (condensation products of chlorinated paraffin and naphthalene, traded under the name "Paraflow"). These are adsorbed on the surface of the freshly formed wax crystals and thereby prevent the formation of stable gel-structures. If the temperature of the once frozen sample is raised sufficiently to have part of the paraflow redissolve in the oil but not sufficiently high to melt the wax crystals on recooling oil will have been adsorbed strongly on the crystal surfaces and will not be displaced by the paraflow. The latter is only a comparatively weak surface active agent and therefore preferentially adsorbed only on freshly formed surfaces. In consequence a gel is formed on recooling and the pour point raised. The article discusses how this can be avoided by blending of oils of widely varying molecular weights and composition and by adding only certain optimum percentages of the surface active agent.

A. BONDI

RESINS

REVERSIBLE HARDENING OF SHELLAC IN STORAGE.—L. McCulloch, *Ind. Eng. Chem., Ind. Ed.*, 35, 825-26, (1943).

After briefly reviewing the characteristics of shellac, experimental work on the reversible gelation of shellac is described. The effects of moisture and temperature on the hardening rate were studied. The data obtained from the investigation lead to the conclusion that water accelerates polymerization at room temperatures, has but little effect from 40°C. to 70°C. and retards it as the temperature approaches 150°C. Between 150°C. and 165°C. the presence of water causes a reversal of gelation.

NEILL M. BRANDT

RHEOMETRY OF ORGANIC GLASSES.—W. Scheele, M. Alfreis and L. Lahaye, *Kolloid-Z.* 103, 1, (1943).

Four samples of polyvinyl acetate of different average polymerization degree were investigated at various temperatures and shearing stresses in a consistometer of Hoesppler.

The first sample, having the lowest molecular weight, was studied between 35° and 60°C with shearing stresses between 1 and 50 kg per square cm. Its flow curves, which are reproduced in a figure, show that this material behaves as a Newtonian liquid under the conditions of the experiment. The second sample, having a higher polymerization degree, was studied between 45° and 80°C and shearing stresses between 1 and 50 kg per square cm and showed Newtonian behavior only at the high temperature end of this range. Samples three and four, having very high molecular weights, were investigated between 40° and 90° and 50° and 110°C respectively, and showed Newtonian behavior at higher, non-Newtonian at lower temperatures.

If one plots the log of the total work of deformation against the reciprocal absolute temperature, one gets straight lines, which indicate the existence of an activation energy for the flow of these materials. This activation energy was found to be different for the four different samples.

H. M.

MECHANICAL BEHAVIOR OF VISCO-ELASTIC MATERIALS.—H. Umstaetter, *Kolloid-Z.* 103, 7, (1943).

The author discusses the Staudinger equation, for which he first attempts to give a "thermodynamical" derivation. This shows the limited range of the validity of the Staudinger equation and it is emphasized that great caution has to be taken if one wants to apply this relation. It is only permissible to use it for one poly-homologous series and even in this case, the K_m constant may not maintain a constant value.

The collisions of rigid and flexible macromolecules are analyzed and the importance of Kuhn's micro- and macro-Brownian movement is discussed. It is then shown that the knowledge of the complete flow curve and the influence of temperature on the flow curve is of great help in obtaining indications as to the size and shape of the dissolved macromolecules.

H. M.

RUBBER

THE MECHANICAL PROPERTIES OF POLYMERIC MATERIALS.--

Arthur Tobolsky and Henry Eyring, *J. Chem. Phys.*, 11, 125-34, (1943).

The authors present a molecular model of the rubber-like materials in terms of which their elastic viscous properties can be interpreted. This interpretation is applied to stress relaxation at constant elongation and to creep under constant stress. The extrusion of rubber through a tube is discussed. The authors state that while some data on extrusion can be interpreted on the basis of the simple model presented, other data indicate that more than one type of flow mechanism is operating. A description of the mechanism of rubber in vibration is given. The breaking of cotton and rayon threads under load is discussed, and the free energy of activation is calculated.

R. H. KELSEY

AN IMPROVED PROCEDURE FOR TESTING WITH THE PUSEY AND JONES PLASTOMETER.--Ross E. Morris and Richard Harmon, *Rubber Age (N.Y.)* 53, 2, 131-35, (1943).

The authors think that the present procedure for measuring the hardness of rubber is faulty in that it makes no provision for neutralizing the friction in the instrument. A vibrating mounting platform is suggested, and a new procedure is proposed. Data are presented, comparing the results obtained with the new procedure with those obtained by the A.S.T.M. method.

R. H. KELSEY

A METHOD OF TESTING THE ELASTICITY OF SYNTHETIC RUBBERS AT LOW TEMPERATURES.--George E. Kish, *Rubber Age (N.Y.)* 53, 2, 139-40, (1943).

A method and an instrument are described for determining the elastic behavior of synthetic rubber at low temperature. The instrument, a bending-beam type is arranged so that the specimen may be immersed in a dry ice and alcohol mixture. Data are given showing the critical points at which the elastic modulus of rubberlike materials begins to increase rapidly. It is said that the test can be carried out in 30 minutes, including preparation of the specimen.

R. H. KELSEY

In a rather extensive article natural rubber is compared to copolymers made from butadiene and styrene, butadiene and acrylonitrile, and those known as Butyl rubber, all chosen by the Government for relief of the present rubber shortage. While the variety of properties covered is rather broad, the points of greatest interest to the Rheologist are those concerning the correlation of X-ray diffraction with stress-strain curves and the use of viscosity measurements as a means of calculating average molecular weight.

In the correlation of X-ray diffraction with stress-strain curves, the effect of carbon black filler upon both natural and Butyl rubbers was studied. Tensile strength is related to crystallization which occurs on elongation. With Butyl rubber the tensile strength develops through its own crystallization.

Any added carbon contributes but little and may actually interfere with the alignment of the crystallites thus counteracting a higher tensile strength. In natural rubber, where crystallization proceeds gradually with elongation, the carbon particles supply anchor points between crystallites promoting greater tensile strength.

Viscosity measurements by means of an Ostwald capillary viscosimeter were made on solutions of the benzene soluble part of butadiene-styrene polymers. The determinations were made at 25°C. upon a solution of 0.1 to 0.3 gram per 100 cc. The plot of the log of relative viscosity with concentration proved to be linear. This relationship permits the calculation of average molecular weight if a constant has been determined by comparison with osmotic pressures or freezing point determination. These values being missing in this case, intrinsic viscosity (η) was reported.

$$(\eta) = \frac{\log_e \eta_R}{C}$$

where (η) = intrinsic viscosity
 η_R = relative viscosity
C = concentration (unit moles per liter).

The average molecular weight was calculated arbitrarily using the Kemp and Peters constant in the Staudinger equation:

$$\text{mol. wt.} = \frac{\log_{10} \eta_R}{C} \times 0.75 \times 10^4$$

While the equation does not hold rigidly for synthetic rubbers, it does serve to give relative molecular weights. The values obtained were about half those determined by the ultracentrifuge. However, since the relation as expressed is for linear molecules, the values for branched chains such as these are expected to be low.

A complete determination involving successive extractions of the sample by the solvent blends requires about a week. A rapid method was developed after it had been observed that the molecular weight calculated from the amount and viscosities of the fractions agreed well with that calculated from the viscosity of the solution of the entire sample. This shorter method required less than 24 hours. Each separate fraction was removed from a different sample and the viscosity-molecular weight calculation carried on from that point. It was found that these results of the "simultaneous" fractionation agreed well with those of the original "successive" fractions.

Tests of solubility and viscosity of synthetic rubbers require a knowledge of the history of the sample since these properties are generally lowered by milling.

NEILL M. BRANDT

THEORY

ON ANOMALIES OF ELASTICITY AND FLOW AND THEIR INTERPRETATION.--Robert Simha, *J. Phys. Chem.*, 47, 348-63, (1943).

A very clear and concise presentation of the fundamental definitions pertaining to the elasticity and plasticity of matter is given. The extension of these fundamental concepts to the evaluation of the properties of complex materials such as inorganic glasses and high polymers is outlined in detail.

The mechanism of relaxation and relaxation time occurring in these more complex materials is extensively discussed with a view to the interpretation of such phenomena in terms of molecular structure. It is shown that fluid-like solutions of high polymeric materials are characterized by Maxwell's postulations as to the existence of a single relaxation time, but the behavior of more solid-like media such as silk threads, synthetic high polymers and glass fibres is more accurately described by a relaxation spectrum or series of different relaxation times. The mathematical theory underlying a quantitative method for the determination of such a relaxation spectrum from creep test data is outlined, but the execution of such computations is accomplished only with extreme numerical effort, especially if there are several relaxation times contingent with a given material.

The analogy between the mechanical and electrical behavior of these complex materials is cited and discussed. An explanation of the Boltzmann memory function in terms of relaxation and elasticity is also included. A very valuable bibliography of correlated research and speculation by other investigators is appended to this dissertation.

L. E. WELCH

THE STRUCTURE AND CONSTITUTION OF GLASS.--Eric Preston, J. Soc. Glass Tech., 26, 114, 83-107, (1942).

The structure and constitution of glass are discussed from various angles. In the section on viscosity, a general review is given. Neglecting density changes and other factors, a plot of viscosities of the soda-silica glasses at a single temperature, 1200°, with the square of the number of tetrahedral units required to give a particle of minimum size satisfying all the requirements of ratios of S_1 , O and Na atoms yields approximately a linear line. The minimum found (by the author) in the soda-silica viscosity-composition curves may be associated with the establishment of relatively small size units as the average particle, or perhaps infinite sheets, whilst the absence of the minimum (results of Lillie) might indicate that extensive networks still existed in the melts, causing the viscosity to be considerably greater than in the former case.

K. H. SUN

INTERNAL FRICTION IN SOLIDS.--A. Gemant, J. Appl. Phys., 14, 204, (1943).

This paper gives a general account on energy losses (internal friction) in solids that are subjected to vibrations. First, the quantitative relations are established, by means of which these losses can be expressed either as the so-called logarithmic decrement δ or the so-called equivalent viscosity η' . It is essential to differentiate between these terms and realize their meaning, in order to avoid misinterpretation of results.

There are several methods available for the measurement of δ , such as the revolving rod method used by Kimball, decay of free vibrations, and the sharpness of resonance in case of forced vibrations. These methods and some results obtained by means of them are described. A few fundamental, although approximate, empirical relations can be deduced from these results, such that the decrement generally varies slightly with the frequency, that it usually increases with the temperature, and so on.

The possible mechanisms of internal friction are next

discussed. One is a thermal mechanism, investigated by Zener in a quantitative manner, and occurring chiefly at flexural vibrations, with inhomogeneous materials, and at small amplitudes. Frequency maxima of δ are characteristic for this process. The other fundamental cause of friction is a plastic flow of the material. It is shown how the decrement can be calculated if the plastic flow resistance for sufficiently small time intervals after application of a steady stress is known. The agreement between computed and experimental values of δ for lead is satisfactory. The fact that plastic flow resistance generally decreases with increasing stress can be used as a basis for explaining the empirical fact that δ usually varies only slightly with the frequency.

AUTHOR'S ABSTRACT

TECHNICAL APPLICATIONS OF THE INTERNAL FRICTION OF SOLIDS.--A. Gemant, J. Appl. Phys., 14, 258, (1943).

First, applications of solid friction in the field of mechanical engineering are discussed. Damping of crankshaft vibrations is partly external, for instance through the viscous damping of a propeller, partly internal, namely, that caused by solid friction of the crankshaft material. This latter effect is relatively small, but may be increased artificially (to be discussed in another paper to be published shortly by the author). The whirl of rotating shafts is a case opposite to the previous one in the sense that internal friction excites the whirling motion (so-called self-excited vibration).

A second application of solid friction is in metallurgy. This is a new and promising field. By using the resonance method of determining δ , and following its changes with changes in pretreatment, temperature, etc., or during corrosion, a simple, nondestructive, and fairly sensitive test is carried out, which will improve in usefulness if it is learned how to interpret its results better than is possible today.

Damping in rubber, particularly in automobile tires, is a process of primary importance, since the heat developed during rotation increases the temperature and promotes the deterioration of rubber. To keep δ within reasonable limits is one of the chief purposes of rubber technology. Synthetic rubber, although surpassing natural rubber in many respects, show higher values of δ . Hence, there is considerable room for improvement in this respect, and an understanding of the mechanism of friction will certainly help in achieving this aim.

Dielectric losses in solids are due, partly at least,

to rotation of dipoles in a medium opposing rotation. While in gases and liquids it is the viscosity that plays a role in determining the so-called time constant of the dipoles, in solids it is internal friction that takes this role. In using data for the equivalent viscosity η' , as can be derived from damping measurements, the order of magnitude of the dielectric dissipation factor and of the frequency at which it goes through a maximum can be successfully computed.

AUTHOR'S ABSTRACT

THE VISCOSITY OF DILUTE SOLUTIONS OF LONG-CHAIN MOLECULES. V. Dependence on the Solvent.--Maurice L. Huggins, *J. Applied Phys.*, 14, 246-48, (1943).

Staudinger's relation between η_{sp}/c and the molecular weight of a chain molecule solute should theoretically apply only if the chain molecules are kinked in a purely random way. With actual solutions, one would expect the kinked chains to be more or less tightly coiled than for purely random kinking, depending on whether the average cohesive energy density between like units (solvent molecules and solute sub-molecules) is greater or less than that between unlike units. The tighter the coiling, the less is the specific viscosity, for a given solute molecule chain length. This cohesive energy density difference is closely related to μ_1 , the constant, characteristic of a given solute-solvent system, which enters into the equations recently derived by the author for the activities of the components and for related quantities, such as osmotic pressures, solubilities, and precipitabilities. From this relationship, it has been shown that the η_{sp}/c values for solutions of a given polymer in different solvents should, in general, be symbatic with the proportion of a poor solvent which is required to produce precipitation of a solid phase. Data from the literature on polystyrene and polybutene solutions are in agreement with this conclusion.

AUTHOR'S ABSTRACT

PERMEABILITY IN RELATION TO VISCOSITY AND STRUCTURE OF RUBBER. THE VISCOSITY OF PURE LIQUIDS. I. Non-polymerized fluids. II. Polymerized ionic melts.--R. M. Barrer, *Trans. Farad. Soc.*, 38, 322, (1942); *ibidem*, 39, 48, 59, (1943).

A "zone" theory of viscous flow (η) and diffusion^(D) is developed from the following assumptions. The energy of activation E_A is distributed over a zone of degrees of freedom within the medium. Its size is determined by the ratio E_A/T . A further cooperation may be required between rotational and vibrational molecular motions before an elementary act of flow or diffusion can occur. On the basis of the classical kinetic theory the following equation is

deduced for the fluidity:

$$\phi = \frac{1}{\eta} = (kT)^{-1} \exp\left(-\frac{E}{RT}\right) \sum_{f=1}^n \frac{\rho_f \lambda, b}{2d\tau_0} \left(\frac{E}{RT}\right)^{f-1} \cdot \frac{1}{(f-1)!}$$

f denotes the number of degrees of freedom in the activated zone, $E = E_A + fRT$ is the total energy of activated degrees of freedom, λ , and d are of the order of molecular distances, τ_0 is the mean period of libration within the activated zone, b has the dimension of a volume, ρ_f is a "synchronization" factor in agreement with the above assumption and characteristic for the particular degree of freedom f , and n may be understood as the maximum number of degrees of freedom of the "zones." This theory leads to the following main results:

If we write $\eta = \eta_0 \exp\left(\frac{E_A}{RT}\right)$ and $D = D_0 \exp\left(-\frac{E_A}{RT}\right)$, then a

relation should exist between $\log \eta_0$ and E_A and $\log D_0$ and E_A for any series of liquids at constant T . The slopes of such plots should be determined essentially by the temperature and be independent of the nature of the medium. $\log \eta_0$ is a function of the size of the activated zone. In the language of the transition state theory these results indicate a relation between the energy and entropy of activation at a constant temperature into which furthermore the cooperation factors ρ_f enter.

An extensive discussion of data on polar, polar, hydroxyl- and hydrogenbonded liquids, of liquid metals and ionic liquids is presented and the properties of the parameters η_0 and E_A examined, particularly in regard to homologous series. Satisfactory connection with the theory is established. Corresponding limiting values of f (if one dominant term is taken in the above expression) are: 3-7, 3-37, 1-3, 4-8. For glasses values between 2 and 21 are computed. Analogous data for the energy in the activated degrees of freedom and estimations of the zone volume are given.

ROBERT SIMHA

VISCOSITY OF PURE LIQUIDS. I. Non-Polymerised Fluids.--
R. M. Barrer, Trans. Farad. Soc., 39, 48-59, (1943).

The Arrhenius equation ($\eta = \eta_0 e^{-E_A/RT}$) has been used in a study of the viscosity of many pure liquids of all kinds. In some E_A varies with temperature, in others it is nearly independent of temperature. Variations of E_A with the nature of the liquid; and of E_A and $-\log \eta_0$ with chain length in some homologous series are discussed in terms of current views on the liquid state.

Consistent functional relations are found between $-\log \eta_0$

and E_A . These appear as straight lines of slopes and intercepts on the $-\log \eta_0$ axis increasing as temperature decreases. The same consistent behavior is noted when $-\log \eta_0$ is plotted E_A/T . These relations are independent of the nature of the liquid for liquid permanent gases, non-polar liquids, polar liquids, hydrogen and hydroxyl bonded liquids, non-polymerised ionic melts and liquid metals. The data approximate to the general viscosity function

$$\eta = 3.71 \times 10^{-3} e^{-0.23E_A/RT} \text{ poises.}$$

The zone theory of viscous flow gives a satisfactory interpretation of, or predicts, the various properties observed.

AUTHOR'S ABSTRACT

THE VISCOSITY OF PURE LIQUIDS. II. Polymerised Ionic Melts.--R. M. Barrer, *Trans. Farad. Soc.*, 39, 59-67, (1943).

The Arrhenius energy of activation, E_A , for polymerised ionic melts may be very large and frequently depends on temperature. A relation was found between $-\log \eta_0$ and E_A/T which obeys the equation.

$$-\text{Log } \eta_0 = 0.115 E_A/T \cdot (1 + 0.00152 E_A/T)$$

Over the range $8.6 < E_A/T < 100$ the relation is virtually a linear one, but the straight line has a different slope and intercept from that for molecular and non-polymerised fluids. Reasons based on the zone theory are given for the relative position and slope of these lines.

The linear form of the $-\log \eta_0$ vs. E_A/T curve was derived, and similarly it was shown that the zone theory could reasonably cover the observed range of values of η_0 of from 2.14×10^{-1} to 1.6×10^{-43} poises.

In many flow systems it was possible to estimate the number of degrees of freedom involved in each zone, and the total energy per activated degree of freedom necessary for flow to occur, as well as the zone volume. This calculation was carried out for typical glasses, liquid metals, simple ionic melts, non-polar and polar or hydroxyl bonded fluids.

The range of the Arrhenius energy of activation was compared for many kinds of rate processes.

AUTHOR'S ABSTRACT

The meaning of the softening point T_s as measured in the various empirical tests, in which essentially the temperature is determined at which a given deformation D_{test} is produced by a fixed stress, is discussed. For this purpose the total deformation of the viscous-elastic material is resolved into its well known three parts. The first one, the ordinary, negligibly small elastic strain, can be neglected. The remaining two are expressed in terms of the viscous flow energy E_{vis} and the mean orientation or relaxation time:

$$D(t, T) = At \exp(-E_{vis}/RT) + \frac{D_{HE}(\infty)(1 - e^{-t/\tau})}{D_{HE}}$$

with $\tau = B \exp. (U/RT)$ and $D_{HE}(\infty)$ proportional to the molecular weight according to the kinetic theory of rubber-like elasticity. Assuming for E_{vis} a value of 20 kcal mole⁻¹ and for U values found by Alexandrov and Lazurkin (Acta Physicochim. U.R.S.S., 12, 647, (1940)), $D - T$ curves are plotted. Two cases must then be considered in connection with the above-mentioned tests. First, $D_{test} < D_{HE}(\infty)$. If furthermore $D_{HE} > D_{vis}$ for the time t considered, then elastic properties are essentially measured. The molded product will contain residual elastic deformations unless the molding temperature is made sufficiently high. It is pointed out that the above conditions hold probably for the Martens type tests, the A.S.T.M. heat distortion test and the Bureau of Standards softening point test. Since the elastic transition temperature (the point at which highly elastic deformation develops) is found to be independent of molecular size, T_s in such cases will also be independent.

In the second case $D_{test} > D_{HE}(\infty)$. This applies to the modified Kraemer-Sarnow and Rossi-Peakes tests. They reproduce accordingly true flow properties. As a consequence, T_s values found in this manner increase with molecular size.

If D_{HE} can be neglected, then softening points are approximately isoviscous points. Using the relation between weight average molecular weight M_w and melt viscosity, found by Flory (J. Am. Chem. Soc., 62, 1057, (1940)) for linear polyesters, a $M_w - T_s$ relation is derived and satisfactorily compared with data on eight polyvinyl acetates with molecular weights between 3400 and 46000, as found by means of the Staudinger method. Deviations found for acetylated acetates are explained by assuming that $D_{HE}(\infty)$ cannot be neglected, and that T_s is sufficiently large such that $t/\tau \gg 1$. The curvature of the $\frac{1}{T_s}$ vs. $\sqrt{M_w}$ plot is a

measure of the relative magnitude of elastic deformation present.

Finally, the temperature dependence of the flow (dD/dt) curve is discussed and the curvature of the "apparent viscosity" - $\frac{1}{T}$ plots interpreted in terms of the two energies present in the expression for D , namely E_{vis} and U . Various data found in the literature are critically examined on the basis of these concepts.

ROBERT SIMHA

BREAKDOWN OF THIXOTROPIC STRUCTURE AS FUNCTION OF TIME.--Ruth N. Weltman, J. Applied Phys. 14, 343-50, (1943).

This paper analyses the rates of breakdown of thixotropic structure occurring while the thixotropic material is agitated at a constant rate of shear for a prolonged period of time.

Plastic viscosities are measured on a rotational viscometer subsequent to various time intervals of agitation at various constant rates of shear. While the yield value remains essentially constant for each rate of shear, being independent of the elapsed time of agitation on the plastic viscosity decreases with increasing time of agitation until an equilibrium plastic viscosity is reached. A longer application of agitation at the same rate of shear does not have any effect on the plastic viscosity; further thixotropic breakdown can only be obtained by increasing the applied rate of shear of agitation.

The plastic viscosity was found to be proportional to the logarithm of time of agitation up to the equilibrium point. The proportionality constant and also the time necessary to obtain the equilibrium plastic viscosity are shown to be independent of the rate of shear applied to agitate the material. Therefore, the proportionality constant depends only on the rate of thixotropic breakdown in the material during the time of agitation. It is called "the time coefficient of thixotropic breakdown" and is defined as the product of rate in breakdown of thixotropic structure and time of agitation at any rate of shear. Its dimensions are the same as the dimensions of viscosity, namely dynes sec/cm². The experiments were conducted on pigment suspensions and oils. Representative data are given for two oils and five pigment suspensions.

AUTHOR'S ABSTRACT

The author uses as a measurement of thixotropy the ratio between liquid volume and solid volume of a suspension, that gives a thixotropic system whose time of solidification upon rest is one minute.

He found that clay particles suspended in various liquids show different degrees of thixotropy. According to logical deductions he finds that particles suspended in polar liquids are less thixotropic than if suspended in non-polar liquids.

In order to obtain relative values for the liquid-solid interfacial tension the author conducts measurements of grinding hardness on quartz in various liquids. The grinding hardness is defined as the loss in area per square centimeter of the quartz crystals during grinding if ground with carborundum under a definite pressure for a definite time. It is arbitrarily chosen to be equal to 100 in distilled water. The interesting fact is that the value of thixotropy obtained from clay particles suspended in various liquids increases in the same order that the grinding hardness of quartz does for the same liquids.

A thixotropic material, if a gel, is in a state of order, where the forces between the particles are orientated to a certain degree and the liquid is contained rigidly between the particles. Upon motion the orientation of the particles is lost and heat motion sets in changing the material from a gel system to a liquid one.

According to the author the degree of thixotropy increases with the distance the particles are separated when the thixotropic material is in a gel-like state. This distance depends on the force of attraction and repulsion. If the material is in a gel-like state the particles are at a fixed distance, at an equilibrium position, when the sum of both potentials (attraction and repulsion) is a minimum.

Calculations of the potentials are made for suspensions containing disk-like and spherical particles. The distance between the particles, at a minimum potential, when the thixotropic material is a gel, was found to be larger for suspensions, containing disk-like particles than for such containing spherical particles, if the particles were of equal diameter. Calculations also showed that the liquid volume contained between disk-like particles is larger than the one contained between spherical particles, even if the distance between the particles was assumed to be equal.

According to the above, materials containing spherical

particles are less thixotropic than those containing disk or needle shaped particles, if suspended in the same liquid. That statement agrees with experiments performed by other investigators.

RUTH N. WELTMANN

APPLICATION

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