

# RHEOLOGY BULLETIN



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# RHEOLOGY BULLETIN

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## THE SOCIETY OF RHEOLOGY

Dedicated to the Development of the Science of the  
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## EDITORIAL

### Streamlining Production and Distribution of Current Periodical Articles

A paper on the above subject by Z. Troy, Librarian of the Boyce Thompson Institute for Plant Research, appeared in the July-August issue of *Special Libraries*. The author points out a fact which must be obvious to every thinking person, namely that something must be done soon to control the flood of published material which threatens to engulf all our storage capacity and to spill from our crowded shelves in disorder and confusion. Most of us are now in a position of receiving a steady stream of journals in which only a small percentage of the written articles are pertinent to our present needs. The author suggests that all actual printing be handled by a central agency, which we might call "Scientific Publications, Inc." or "S.P.". It is the function of "S.P." not only to print the full article, properly edited of course, but also to issue a periodical index and abstract journal, issued both in its entirety and by subject sections. An individual would then subscribe for a certain classification and be billed at regular intervals just as we are now billed for the U. S. patents we subscribe for under certain classifications. The individual would also be in a position to order any article he wished from "S.P.", regardless of its classification, by paying the actual cost. This system has many analogies with the operation of the Office of the Superintendent of Documents and the Government Printing Office in Washington.

The *Rheology Bulletin* is primarily an abstract journal. Its function is conceived to be very much like that of a classified telephone directory, to let the reader know what is available in the field of his interest, and where it may be found. It is a signpost to help the weary traveller on his way, but more than this, it is a sign that a new science is growing to maturity.

The *Rheology Bulletin* is rendering a useful service, of a type which is in step with the times. Much thought is being given to ways and means of rendering it more effective. Dr. Huggins has a letter to the Editor in the present issue, which is worth studying. Professor Bingham has a plan for prompt publication of brief references to all the recent literature. This will be outlined more fully in the next issue, but it may be said now that Professor Bingham will make available to readers of the *Bulletin* his very complete Index, in continuation of the extensive *Rheology Index* which he published in the *Journal of Rheology* 2, 10-108 (1931).



## Our Abstract Service

The August issue carried a list of twenty two journals which our abstractors are now covering regularly for the Rheology Bulletin. The following journals may now be added to that list:

Journal of the American Ceramic Society  
Bulletin of the American Ceramic Society  
Journal of Chemical Education  
Journal of the Chemical Society of London  
Nature  
Paper Trade Journal  
Philosophical Magazine  
Review of Scientific Instruments  
Review of Modern Physics  
Transactions of the American Institute of  
Chemical Engineers

## Abstractors in this Issue

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

- T. Alfrey, Monsanto Chemical Co., St. Louis, Mo.
- E. C. Bingham, Dept. of Chemistry and Metallurgy, Lafayette College, Easton, Pa.
- A. Bondi, 1800 Baronne St., New Orleans 13, La.
- T. Boyd, Monsanto Chemical Co., Springfield, Mass.
- C. K. Bump, Monsanto Chemical Co., Springfield, Mass.
- Neill M. Brandt, Bausch and Lomb Optical Co., Rochester, N. Y.
- John D. Ferry, Dept. of Physical Chemistry, Harvard Medical School, Boston, Mass.
- A. Gemant, The Detroit Edison Co., 2000 2nd Ave., Detroit, Mich.
- R. H. Kelsey, Physics Research Division, The Firestone Tire and Rubber Co., Akron, Ohio
- T. S. Lawton, Monsanto Chemical Co., Springfield, Mass.
- R. M. Levy, Ecusta Paper Corporation, Pisgah Forest, N. C.
- H. Mark, Dept. of Chemistry, Polytechnic Institute, Brooklyn, N. Y.
- W. H. Markwood, Jr., 101 Lighthouse Road, Wilmington 274, Del.
- H. K. Nason, Monsanto Chemical Co., Springfield, Mass.
- W. W. Pendleton, Research Laboratories, Westinghouse Elec. & Mfg. Co., East Pittsburgh, Pa.
- D. Telfair, Monsanto Chemical Co., Springfield, Mass.



Samuel Zerfoss, Dept. of Ceramics, The Pennsylvania  
State College, State College, Pa.

. . . . .  
Minutes of the 1943 Annual Meeting of the  
Society of Rheology

The business meeting was called to order by President Mark at 4:00 P.M. at the Hotel Pennsylvania on October 29, 1943. It was announced that the registration of the meeting was 109, not including some students. Minutes of the 1942 meeting were accepted as read. Dr. Bingham presented the slate of present officers for re-nomination. It was moved and carried out that Dr. Bingham cast one vote for the election. The Secretary mentioned the need of some sort of membership certificate, and arrangements were made with Mr. Wakefield to have suitable cards printed for distribution by the Secretary.

The need for getting rheological material to the members, and ways and means of improving the Bulletin, particularly as regards abstracts, were discussed at length by President Mark, Professor Bingham and Mr. Wakefield. Professor Bingham discussed a system of numbering abstracts and the great desirability of having bibliofilms of scientific papers. It was the sense of the meeting that Dr. Bingham prepare an explanatory statement along these lines for the Bulletin. Dr. Huggins suggested the adding of Chemical Abstracts numbers to each of our abstracts. Dr. Hunter spoke in favor of the present method of preparing journals, an attempt to standardize nomenclature, a place to express opinions and also space for detailed announcements on definite ways in which the Bulletin might be expanded. Dr. Fischer agreed to work along these lines with Dr. Bingham. Dr. Hunter moved, and it was voted that all articles of rheological interest should at least be listed in the Bulletin as a matter of information for the membership.

On the motion of Dr. Hunter, The Society of Rheology appropriated One Hundred Dollars of its funds to the American Institute of Physics in behalf of its Building Fund. This motion was carried unanimously, and great interest was expressed in the plans for the new home at 57 East 55th St., New York City, for American physics and physicists.

President Mark announced with sorrow the recent death of one of our fellow members, Dr. Elmer O. Kraemer, and said a few words about his great importance as a man and scientist. Professor Bingham also spoke in tribute of Dr. Kraemer's achievements and of his splendid qualities and of his services to rheology and to the Society of Rheology of which he was one of the organizers. In honor of his memory, all present rose from their seats and stood for some time with



bowed heads to express our high esteem for Dr. Kraemer, and our sorrow at his passing away.

The technical program of the meeting was as printed in the August Rheology Bulletin, except that papers by Herschel and by Sack, Motz and Work, were not presented.

The Evanston Meeting of the American Physical Society,  
November 12 and 13, 1943

A symposium on "The Physics of Rubber and Other High Polymers" organized under the leadership of Warren F. Busse, was presented at the Evanston, Ill., meeting. A total of sixteen papers were given, as follows:

Present status of theory of elasticity of rubber,  
by H. M. James, Purdue University.

Stress-temperature relations in synthetic and  
natural rubbers, by L. A. Wood and F. L. Roth,  
National Bureau of Standards.

Some physical properties of natural and synthetic  
rubber, by W. B. Wiegand, Columbian Carbon Co.

Hysteretic and elastic properties of rubberlike  
materials under dynamic shear stresses, by  
J. H. Dillon, I. B. Prettyman, and G. L. Hall,  
Firestone Tire and Rubber Co.

Drift and relaxation of rubber, by M. Mooney,  
United States Rubber Co.

Light scattering in solutions, by P. Debye, Cor-  
nell University.

Physical methods of analysis of synthetic and  
natural rubber, by R. D. Barnes, American  
Cyanamid Co.

Some physical properties of commercial polymeriz-  
ed methyl methacrylate, by H. A. Robinson, Arm-  
strong Cork Co.

Rheological properties of natural and synthetic  
rubber, by R. H. Kelsey and J. H. Dillon, Fire-  
stone Tire and Rubber Co.

A new extrusion plastometer, by H. A. Schultz and  
R. C. Bryant, B. F. Goodrich Co.

Crystallization of long-chain compounds, by I. Fan-  
kuchen and H. Mark, Brooklyn Polytechnic Inst.

X-ray observations on the structure of rubber and  
the size and shape of rubber crystallites, by  
S. D. Gehman and J. E. Field, Goodyear Tire and  
Rubber Co.

Stress relaxation of natural and synthetic rubber  
stocks, by A. V. Tobolsky, I. B. Prettyman and  
J. H. Dillon, Firestone Tire and Rubber Co.

Hysteresis losses in high polymers, by H. S. Sack,  
Cornell University

Measurement of the surface area of carbon black  
by low temperature absorption, by P. H. Emmett,  
Johns Hopkins University.

Second-order transition in high polymers, by R. S.  
Spencer and R. F. Boyer, Dow Chemical Co.



## In Memoriam—Dr. Elmer O. Kraemer



ELMER O. KRAEMER

Dr. Elmer O. Kraemer of the Biochemical Research Foundation died suddenly while attending the 1943 Annual Meeting of the American Chemical Society at Pittsburgh. Overcome at luncheon on September 7th, he died at St. Joseph's Hospital, Pittsburgh, on the same day without regaining consciousness. Unheralded by any illness his sudden death, just after a short stay with his parents in Madison, Wisconsin, came as a severe and unexpected blow to his family, his fellow workers and to the world of science. We of the Biochemical Research Foundation mourn the loss of an admired and respected leader, a true friend and adviser whose willing help and wise counsel will be keenly missed.

Dr. Kraemer was born in Liberty, Wisconsin, on February 27, 1898. In 1918 he received his B.S. degree from the University of Wisconsin. He remained there as instructor working with the late Prof. Louis Kahlenberg for his Ph.D. degree. In 1921 he was awarded an American Scandinavian Fellowship and spent a year of research on colloid chemistry with Prof. The Svedberg at the University of



Uppsala, Sweden. He spent the latter part of 1922 and the early part of 1923 continuing colloid chemistry research with Herbert Freundlich at the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry in Berlin before returning to Wisconsin. Most of the year 1923 was spent in work on the kino-ultramicroscope, and for part of that year he was Assistant to Professor Svedberg who was at that time visiting lecturer in colloid chemistry at the University of Wisconsin. A year later, 1924, he was granted his Ph.D. degree at the University of Wisconsin where he remained as National Research Council Fellow doing research work on the optical properties of gelatin sols. In 1925 Dr. Kraemer was appointed Assistant Professor of Colloid Chemistry, and for two years he and his research students continued to study the properties of gelatin. His university connections were severed in 1927 when he joined the staff of the Experimental Station of the E. I. du Pont de Nemours Company at Wilmington, Delaware, as the leader of a group of research workers studying both fundamental and industrial colloid problems. For eleven years, until May 1938, he remained with the du Pont Company during which time he became well known for his profound knowledge of colloid chemistry, both fundamental and applied, and for the outstanding contributions to colloid science published by him and his collaborators.

It was during this time that he was instrumental in introducing into the du Pont Company's Research Laboratories the first oil-turbine high speed ultracentrifuge which was ever installed and operated outside Professor Svedberg's Institute at the University of Uppsala, and for many years Dr. Kraemer was responsible for the research carried on with the use of this highly specialized tool of the colloid chemist.

From the founding, in 1927, of the Cancer Research Fund of the Graduate School of Medicine, University of Pennsylvania (later to become the Biochemical Research Foundation of the Franklin Institute), Dr. Kraemer was assistant to Dr. Hamilton Bradshaw on its Advisory Council, and also visiting consultant on colloid chemistry, bringing his expert knowledge and broad scientific outlook to bear upon biochemical and cancer problems.

Dr. Kraemer resigned from his position with the du Pont Company in May 1938, and a few months later left with his wife and two sons to spend a further year on colloid research with Professor Svedberg at Uppsala, having been granted a fellowship by the Labor Foundation of Wilmington for this purpose. After having visited a number of the more important European research laboratories on behalf of the Biochemical Research Foundation he took up residence at Uppsala to continue the ultracentrifuge study of gelatin.



It was during this year that he collaborated with Dr. Svedberg, Dr. Pedersen and others in the writing of the book "The Ultracentrifuge" which appeared in both English and German editions just as the present war broke out.

This year spent in Sweden was undoubtedly one of the happiest of Dr. Kraemer's life. Having met the young American girl who was later to become his wife when she too was a graduate student at Uppsala University in 1921, the return to Uppsala with his wife and family had been keenly anticipated. Being back with his old professor, being in the laboratory where so much of modern colloid research methods have been developed and with the workers responsible for the developments, seeing his two sons settle down to the Swedish school system and do well both in school and in athletic activities, cycling with his family to old haunts, visiting the ancient places of Sweden all brought the greatest pleasure and much happiness to Dr. Kraemer.

Returning to Marshallton, Delaware, in the Fall of 1939 Dr. Kraemer took up full time duties with the Biochemical Research Foundation to supervise the physico-chemical research on biochemical colloidal systems. In addition to bringing his wealth of knowledge on scientific matters and placing them unstintingly at the service of his co-workers, his pronounced critical faculty and well-thought out opinions contributed enormously to the spirit in the Foundation's laboratory. His sincerity of purpose, his pleasant even-tempered disposition, his capacity for teaching others, his willingness to help others, to take pleasure in their successes and to sustain and cheer them when things just didn't go right, won for him the respect, admiration and friendship of all who were privileged to know him and work with him.

Because of his love of science and his sustained energy Dr. Kraemer sought much of his relaxation from research problems in editorial work, in writing, and in teaching. A clear, facile writer, he was the author of the section on Colloids in Taylor's "Treatise on Physical Chemistry" and was actively engaged in revising his section for the forthcoming enlarged edition of Taylor and Glasstone when death terminated his work. He was the author of two chapters on the chemistry of large molecules in the monograph published recently by Western Reserve University, Dr. Kraemer having been the authority chosen to deal with this subject in the series of lectures entitled "Frontiers in Chemistry" held there in 1942.

Dr. Kraemer was one of the founders of the Society of Rheology, and was an Assistant Editor of its publications up to the time of his departure for Sweden in 1938.



He was, at the time of his death, the editor of *Advances in Colloid Science*, one of the editors of the *Archives of Biochemistry*, a member of the editorial board for the *Monographs on High Polymeric Substances* and he was serving as consultant for a number of special Government committees concerned with the war effort.

Dr. Kraemer had been for many years actively interested in the University of Delaware and in 1940 had been appointed to the faculty as special lecturer in colloid chemistry. His special course in colloid chemistry attracted many, both students and graduate chemists in industry.

As is to be expected from so active a research worker, many publications in scientific journals stand to Dr. Kraemer's credit since his first paper in 1923 describing his work with Freundlich on the formation of manganese arsenate jellies. He enjoyed membership in many scientific societies and was frequently an active participant in important meetings taking particular delight in contributing to the specialized symposia on colloids and methods in colloid chemistry held at the New York Academy of Sciences. For his contributions to the world's scientific knowledge he was honored in 1938 by being listed among the 250 outstanding scientists by "American Men of Science." His work for the past five years had shown this honor to be well merited. It is singularly unfortunate that an untimely death has terminated his career.

#### NOTES FROM THE BIOCHEMICAL RESEARCH FOUNDATION

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E. O. Kraemer

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*Colloid Symposium Mono.* 2, 57-69 (1924)

E. O. Kraemer

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*J. Chem. Educ.* 1, 199-200 (1924)

E. O. Kraemer

Formation of Colloid Solutions by Electrical Pulverization in the High Frequency Alternating Current Arc  
*J. Am. Chem. Soc.* 46, 1980-91 (1924)

E. O. Kraemer and The Svedberg

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*J. Am. Chem. Soc.* 46, 2709-18 (1924)

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 J. Rheology 2, 292-306 (1931)  
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Van Nostrand, 2nd ed. 1931, vol. 2, pp. 1567-  
1721

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in "Annual Survey of American Chemistry", Chem.  
Cat. Co., 1931 vol. 6, chap. 5, pp. 70-102

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The Particle Size and Constitution of Colloidal Ferric  
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J. Phys. Chem. 36, 326-39 (1932)

J. B. Nichols, E. O. Kraemer and E. D. Bail-  
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The Particle Size and Constitution of Colloidal Ferric  
Oxide II. Dialysis and Aging

J. Phys. Chem. 36, 505-14 (1932)

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Viscosity and Molecular Weight of Polymeric Materials

J. Phys. Chem. 36, 3175-86 (1932)

E. O. Kraemer and F. J. Van Natta

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Molecular Weight of Linear Macromolecules by Ultra-  
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Molecular Weights of Cellulose

Nature 133, 370 (1934)

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J. Franklin Inst. 232, 193-7 (1941)  
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J. Franklin Inst. 232, 587-91 (1941)  
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J. Phys. Chem. 46, 177-82 (1942)

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Tech. Assoc. Papers 25, 706-11 (1942)

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J. Biol. Chem. 142-785-802 (1942)

L. E. Krejci, A. H. Stock, E. B. Sanigar,  
and E. O. Kraemer

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E. O. Kraemer, F. E. Bartell, and S. S. Kistler

**An Ultracentrifugal and Electrophoretic Investigation of an Ascitic Fluid from a Cancer Patient**

J. Franklin Inst. 235, 298-313 (1943)

E. B. Sanigar, L. E. Krejci, and E. O. Kraemer

**The Colloidal Behavior of Organic Macromolecular Materials**

in "Frontiers of Chemistry Series", Interscience Publishers, Inc., New York, 1943, vol. 1, pp. 73-94

E. O. Kraemer

**The Ultracentrifuge and Its Application to the Study of Organic Macromolecules**

in "Frontiers of Chemistry Series", Interscience Publishers, Inc., New York, 1943, vol. 1, pp. 95-124

E. O. Kraemer



## NEW BOOKS

### ELASTIC AND CREEP PROPERTIES OF FILAMENTOUS MATERIALS AND OTHER HIGH POLYMERS

By Herbert Leaderman, Sc. D.

Published 1943 by the Textile Foundation, Inc.,  
Industrial Building,  
National Bureau of Standards  
Washington 25, D. C.

The Textile Foundation was created in 1930 by the United States Congress. It is organized to engage in scientific and economic research for the textile industries and their allied branches.

"This book gives the results of an investigation on the elastic and creep properties of filamentous materials, carried out at the Massachusetts Institute of Technology under the auspices of the Textile Foundation. In general, when a longitudinal load is applied to a textile filament there occur both reversible and irreversible deformations which are themselves functions of time. The present study is concerned almost entirely with those creep phenomena which may be considered as of the nature of delayed elasticity. In order to make the problem amenable to analysis, irreversible deformations have been largely eliminated in the experimental work, and are considered only briefly in the course of the investigation.

Among textile substances, filamentous materials are preferable in many respects in connection with the study of mechanical behavior. First, these materials are reasonably uniform and can be tested in any desired length; the latter factor is of importance when very small deformations are to be measured. Furthermore, the structure can be modified by variation in fabrication technique or otherwise, and the resulting changes in mechanical behavior studied. The experimental data recorded herein are concerned with the creep and other properties of single filaments of silk, viscose and acetate rayons, and of nylon; the experimental investigation constitutes Part II of this work.

The phenomenon of delayed elasticity (or "primary creep"), together with the relationship between this phenomenon and the structures of high polymers, is discussed in Part I. Chapter I is concerned with the delayed-elastic behavior of materials in the light of some historically important work presented in the literature; in Chapter II the mechanical model analogy is developed in relation to the theories of Maxwell and Wiechert. The structure and mechanical



behavior of filamentous materials are very similar to those of other organic high polymers. For this reason, the discussion of creep behavior in Chapters I and II, and the presentation of the contemporary concepts of structure in Chapter III, are with reference to high polymers in general. The first three chapters of the book, forming Part I of this work, thus serve as an introduction to the experimental account presented in Part II.

In the course of this work an attempt has been made to distinguish and define clearly the various deformation and relaxation phenomena manifested by solid materials, and for this purpose a new terminology has been proposed. However, it is very difficult to evolve a completely satisfactory terminology, since the same phenomenon may manifest itself in markedly different ways according to the circumstances; for example, in polyvinyl chloride the property which is the chief subject of this work may be referred to as "creep", "delayed elasticity", or "high elasticity", depending upon the temperature and the plasticizer content."

The contents of the book are organized under the following headings:

#### Part I Creep and Structure

- Chapter I Primary Creep and the Superposition Principle
- Chapter II Mechanical Models and the Wiechert Theory
- Chapter III The Structure of High Polymers

#### Part II Elastic and Creep Properties of Filamentous Materials

- Chapter IV Experimental Investigation of the Creep Properties of Filamentous Materials
- Chapter V The Creep Properties of Silk and Rayon Filaments under Standard Conditions
- Chapter VI Creep Properties of Acetate Rayon: Temperature Effect
- Chapter VII The Creep Properties of Nylon

Dr. Leaderman is to be congratulated on doing a very thorough job. He has approached his problems in a fundamental way. His book is a significant contribution to the literature of rheology. It is worth very careful study, not only by textile workers, but also by all who are concerned with the phenomena of delayed elasticity.



## RHEOLOGY PROGRESS ABSTRACTS

### Apparatus and Methods

THE STRUCTURAL VISCOSITY OF MUCIN AND A NEW APPARATUS FOR ITS MEASUREMENT.—Petronio Zamboni, *Kolloid-Z.*, 102, 246-51 (1943).

The construction of a viscosimeter, which allows a discharge of liquid through a capillary at different pressures and which makes possible the exact measurement of small pressures, is described. This instrument is especially adapted to measurement of the change of discharge time with change of pressure on the so-called "fiber colloids" (Ostwald). If the pressure falls below a certain value, the discharge line appears greater than would be expected from the pressure drop. The phenomenon of structural viscosity is especially pronounced with mucin solutions. In ordinary viscometers, the discharge time increases with the displacement of its capillary in higher rates. In general, the special structural viscosity of string colloids appears especially noticeable. The anomalous behavior was destroyed by the presence of salts in concentrations of the same order magnitude as is necessary for the activation of mucin-dissolving enzymes.

T. BOYD

RECORDING PLASTOMETER FOR ORGANIC PLASTICS.—F. J. Biondi, *Brit. Plastics*, 14, (167), 687-8 (1943).

A parallel-plate plastometer, equipped with special heating devices for operation at high temperatures and with automatic recording of flow vs. time, is described. Typical curves, showing the effect of moisture content on the flow of a thermoplastic (not further identified), are given but the test temperature is not stated. Cf. *Bell Laboratories Record*, 21, (1), 18-19 (Sept., 1942).

H. K. NASON

MEASUREMENT OF ANOMALOUS VISCOSITY BY THE CAPILLARY TUBE METHOD.—A. C. Merrington, *Nature*, 152, 214 (1943).

Determination of anomalous viscosity by the capillary method depends upon the following familiar relationship,

$$P \propto \eta L/R^4 \quad (1)$$

Accordingly, for fixed values of P and L

$$\eta \propto R^4 \quad (2)$$



However, it has been observed that in certain cases proportion (2) is not valid. This anomaly has been referred to as the 'sigma' phenomenon. Various explanations of this effect have attributed it to a property of the material under study.<sup>1,2</sup>

In capillary methods  $P$  has usually been measured as the sum of the applied pressure and the hydrostatic head. Use of this pressure value in expression (1) is based on the assumption that any pressure drop within the instrument other than through the capillary is negligible compared to the latter because of the much larger dimensions of other parts of the instrument that may contain the subject material.

However, for materials whose viscosities are manyfold greater at low than at high rates of shear, the drop through the larger parts of an instrument, as defined by relation (1), may be an appreciable part of the total pressure, which is really

$$P_t = P_c + P_v \quad (3)$$

where  $P_c$  is the drop through the capillary and  $P_v$  the drop through other parts of the instrument downstream of the liquid surface. It is evident that in such cases the use of  $P_t$  instead of  $P_c$  for  $P$  in expression (1) would lead to erroneously high results for  $\eta$ .

The use of a modification of an instrument developed by Arveson<sup>3</sup>, whereby both  $P_v$  and  $P_c$  can be measured, has shown that the apparently anomalous viscosity-capillary size relationship, observed when  $P_t$  is substituted in proportion (1), disappears in at least some cases when equation (3) is taken into consideration.

The author does not claim that this is the entire explanation of the 'sigma' phenomenon in every case.

<sup>1</sup>Ambrose and Loomis, *Physics*, 4, 265 (1934).

<sup>2</sup>Dix and Scott Blair, *J. Applied Phys.*, 11, 9, 574 (1940).

<sup>3</sup>Arveson, *Ind. Eng. Chem.*, 24, 71 (1932).

W. H. MARKWOOD, JR.

A NOTE ON THE MOTION OF A MERCURY INDEX IN A CAPILLARY TUBE.—H. G. Green, *Phil. Mag.*, 24, 393 (1943).

Yarnold's investigation of the motion of mercury in-



dices in capillary tubes, assuming adherence to Poiseuille's law, indicated viscosities about six percent too high.

Poiseuille's law, however, dealing with unending, steady flow, has as primary assumptions the absence of radial flow and of slip at the glass surface. In the case of a finite index in which the whole of the fluid is transferred bodily, at least one of these conditions cannot hold.

Nevertheless, a re-examination of Yarnold's data wherein consideration is given to the pressure effect of the air in the lines and pressure cylinder (where pressure was presumably recorded) indicates that the flow of a finite index has the same characteristics as those of a continuous liquid.

W. H. MARKWOOD, JR.

FLOW PROPERTIES OF COATING CLAYS AT HIGH RATES OF SHEAR.—Kenneth A. Arnold, Paper Trade Journal, 117, (9), 28 (1943).

The author has developed a procedure for measuring the flow properties of paper coating clay slips at rates of shear in the range of  $8.0 \times 10^4$  reciprocal seconds, which is in the range of shear produced in high-speed coating machines. During the measurement, the slip is also subjected to pressures comparable to those in the actual coating nip. The procedure distinguishes between the Newtonian, dilatant, and thixotropic types of fluid flow, and indicates the behavior of slips possessing these types of flow in a roll nip. A method is presented for the quantitative determination of the degree of dilatancy and thixotropy of clay slips. This method does not destroy the structure of the clay system previous to the actual measurement of its flow properties.

A technique has been developed to insure reproducibility of the measurements of flow properties. The variables involved have also been investigated.

At high rates of shear, the nip viscosities of clay slips were found to be critically dependent upon clay concentration, especially at very high solids contents. The concentrations of three commercial paper coating clays required to produce slips of equal nip viscosity were found to differ widely. It was possible to prepare a fluid slip with a higher concentration of the clay possessing the smallest particle size and least hydration capacity. The third clay, which showed the largest particle size but the lowest degree of hydration, was found to be intermediate as to maximum possible concentration in a fluid slip.

Extremely dilatant slips were produced from the two



clays of lower hydration capacity, although one of these showed a small particle size. No degree of dilatancy could be attained in slips of the more highly hydrated clay, although it possessed the larger particle size.

With these clays, the range of dispersing agent required to give minimum viscosity to the slips was found to increase as the concentration of clay was increased. This was true with either dispersing agent--sodium pyrophosphate or sodium silicate. However, the amount of sodium silicate used as the dispersing agent is much more critical than that of sodium pyrophosphate.

In general, the flow properties of clay slips were found to change considerably with the amount of mechanical work to which they were subjected. On ball milling, the slips showed an initial decrease in viscosity over several hours of milling. The test for hydration of the clay particles indicated a gradual increase in this property during milling. Greater changes took place during milling in slips containing comparatively low percentages of the dispersing agent. In the preparation and application of coating clay colors, the mechanical work applied to the color should be carefully controlled in order to produce uniform coating.

The results of nip viscosity measurements showed very little correlation with low-shear viscosity measurements in the MacMichael viscometer. Furthermore, certain slips which showed weakly dilatant behavior at low rates of shear, according to Sheets, were actually thixotropic under high shear. Thus, it follows that viscosity measurements made at one rate of shear, or at relatively low rates of shear, have little significance as an index of the flow behavior at high rates of shear.

By a careful selection of the amount of work applied, the amount of dispersing agent used, and the concentration of the clay, it was possible to prepare slips from different clays which showed very similar flow properties.

R. M. LEVY

A VISCOMETRIC METHOD FOR DETERMINING FREE MENTHOL IN PEPPERMINT OIL.--L. J. Swift and M. H. Thornton, Ind. Eng. Chem., Anal. Ed., 15, 422-3 (1943).

American oil of peppermint is now generally purchased for its menthol content rather than for use as a flavoring agent and drug. A simple practical test for field and laboratory determination of the menthol content was developed from the theory that the viscosity of the oil is governed by the amount of menthol present. The theory was tested with oils whose compositions were adjusted by additions of



the pure major constituents menthol, menthone, and esters. The experimental work indicated that the viscosity of the oil was changed but slightly when the percentage of menthone was varied over its natural range while the esters had greater effect but still small enough to be of no practical consequence.

Viscosity-menthol percent curves were established at three temperatures. A variation in materials in the natural oil that were insoluble in a mixture of methanol and ethanol made correction factors necessary; these were determined for each of three levels of insoluble matter content.

The viscometric method of analysis offered advantages in the economy of equipment, time, sample volume and technical training required. It was found to apply to fresh as well as preserved oil for the determination of free menthol; the presence of resins caused unreliable high results.

NEILL M. BRANDT

THIXOTROPIC BEHAVIOR OF OILS.—Ruth N. Weltman, Ind. Eng. Chem., Anal. Ed., 15, 424-9 (1943).

Twenty-two oils covering a viscosity range of 1 to 800 poises were tested in a rotational type of viscosimeter capable of causing rates of shear as high as 1070 sec.<sup>-1</sup> (1450 rpm). Data taken during the increase and decrease of shear rate and plotted as a hysteresis loop indicated that above a certain "limiting rate of shear" oils usually classified as Newtonian liquids could be made to exhibit thixotropic characteristics. The relation between the reciprocal of the rate of shear and the viscosity in the Newtonian region was found to be linear. The product of the limiting rate of shear and the Newtonian viscosity was constant for all oils tested when the rate of shear was rapidly increased and decreased with no delay at the peak value. The curve of the top rates of shear, above the limiting rate, plotted against the viscosity at that rate was found to be similar to that obtained from top rates of shear vs. the plastic viscosity of true thixotropic liquids. Additional thixotropic behaviors noted were: above the limiting rate of shear the torque intercept increased with the shear rate and upon rest there was complete recovery of structure.

Evidence is presented against the assumption that the results might have been caused by conditions of slippage, turbulence or elevated temperature. It is suggested that, from the theoretical standpoint, at rest and toward the limiting rate of shear the molecules are of a random distribution while beyond the limit, the minimum directional force, they may start an alignment in the direction of shear.



The warning is given that higher viscosity oils and higher rates of shear when employed in standardizing viscosimeters may lead to unreliable results.

NEILL M. BRANDT

## Bituminous Materials

POWDERED MINERAL SUSPENSIONS IN BITUMENS AND RELATED SUBSTANCES, I.—H. Walther, Kolloid-Z., 103, 54-60 (1943).

The effect of adding various inert substances to bitumens and related materials is discussed in a series of four articles. The stabilizing actions of mineral powders on bitumens and related substances is considered. In general, certain mineral powders, as powdered asbestos, slate and chalk, stabilize bituminous materials by raising the softening point and lowering the breaking point. Flow is increased and the brittleness decreased at lower temperatures. The weather resistance is raised and the film-stability is improved by reduction of tear tendency. Grain size of the filler affects the physical properties.

T. BOYD

## Cellulose

THE DEPENDENCE OF THE VISCOSITIES OF CELLULOSE NITRATE SOLUTIONS UPON DEGREE OF NITRATION.—H. A. Wannow, Kolloid-Z. 102, 29-34 (1943).

Cellulose samples of two different polymerization degrees (295 and 525) were nitrated to various degrees from 10.5% to 13.8%. Phosphoric acid and phosphoric anhydride were used in the nitrating mixture in place of sulfuric acid to minimize chain degradation. Osmotic pressure measurements verified the fact that nitrated samples from a given cellulose possessed essentially the same polymerization-degree, even though containing different amounts of nitrogen. Viscosity measurements were made of dilute solutions of all samples in acetone. The intrinsic viscosity was found to be strongly dependent upon degree of nitration. The more highly nitrated samples possessed the higher intrinsic viscosities. Curves are included showing the quantitative increase of the viscosity constant  $K$  with % of nitrogen.

T. ALFREY



A SIMPLE METHOD FOR DETERMINING THE DEGREE OF POLYMERIZATION OF REGENERATED CELLULOSE AND FOR THE QUANTITATIVE SEPARATION OF COTTON AND WOOD CELLULOSE.—E. Schwartz and W. Zimmermann, *Melliand Textilber*, 22, 525 (1941); *Kolloid-Z.*, 103, 74 (1943). cf. *Melliand Textilber*, 23, 73 (1942).

It was found that artificial fibers from regenerated cellulose of DP less than 600 dissolve almost quantitatively in 10% NaOH at  $-5^{\circ}\text{C}$ . after swelling with water, and this is used as the basis of a method for determining DP of regenerated cellulose. In such solutions, the  $K_m$  value of  $7.0 \times 10^{-4}$  is used with Staudingers equation;  $N_{sp} = K_m \cdot c$ . DP ( $c = \text{g. cellulose per liter}$ ). Control of composition is easier, and sensitivity to atmospheric oxygen is less than when cuprammonium solutions are used.

Native cotton is less than 2% soluble in 10% NaOH at  $-5^{\circ}\text{C}$ ., but cotton strongly degraded by bleaching is more soluble (about 7%). Isolated hemp fiber is soluble up to 22.5%.

A method for the quantitative separation of cotton-wood cellulose mixtures and for the determination of the DP of the components was worked out. This can be used for the usual kinds of cotton, if they have not been overbleached or otherwise chemically degraded.

The dry solids content of the sample is first determined by oxidation with bichromate. The fabric is then treated with enough 10% NaOH to give a very dilute solution of the wood cellulose. The undissolved cotton, which is strongly swollen by the alkali solution, is filtered off and washed, taking care to keep water on the suction filter to protect the cotton from atmospheric oxygen. The cotton is then dried at  $60^{\circ}$ , dissolved in cuprammonium solution and its DP determined viscometrically ( $K_m = 5 \times 10^{-4}$ ). The solution of wood cellulose in NaOH is analyzed and its average DP is determined from viscosity measurements.

H. K. NASON

ASSOCIATION AND SOLVATION OF CELLULOSE DERIVATIVES IN ORGANIC SOLVENTS.—E. Steurer, *Z. Phys. Chem.*, A190, 1, 16 (1942).

In order to study the mutual forces between high polymer molecules in solution a combined osmotic and viscosimetric investigation is undertaken. Ethyl cellulose (51%  $\text{OC}_2\text{H}_5$ ) is studied at various concentrations in various liquids. In solvents with high dissociating activity, such as chloroform, dioxan, *m*-cresol and benzyl alcohol, ethyl cellulose is molecularly dispersed up to concentrations of about 1.5%. The reduced osmotic pressure is very nearly a



linear function of the concentration and leads to a molecular weight of about 50,000 for the unassociated molecules. In cyclohexane, benzene, toluene and m-xylene, however, a distinct tendency for molecular agglomeration can be observed above concentrations of 0.1%. It seems that in benzene on the average four molecules form a secondary particle of a molecular weight of about 200,000, in toluene three molecules are aggregated to particles of molecular weight around 150,000. This agglomeration can be broken up by extreme dilution, by addition of polar liquids such as alcohol or acetone or by increased temperature. The transition from the unassociated molecules of molecular weight around 50,000 to the higher agglomerates is continuous and reversible.

H. MARK

COMPARATIVE OSMOTIC AND VISCOSIMETRIC MEASUREMENTS WITH FRACTIONATED AND UNFRACTIONATED NITROCELLULOSE.—E. Husemann and G. V. Schultz, *Z. Phys. Chem.*, B52, 1 (1942)

Purified Egyptian cotton with a DP of about 2700 was used throughout the investigation. It was degraded in three different ways:

- (a) By homogeneous hydrolysis in concentrated phosphoric acid at 27°C.
- (b) By heterogeneous hydrolysis in 0.5 molar aqueous solution of potassium bisulfate at 60°C.
- (c) By homogeneous oxidation in copper ammonia solution.

The degraded samples are nitrated to 2.6 nitro groups per glucose unit (13.14% N), dissolved in acetone and fractionated from 2.6 solutions by stepwise addition of water. The fractions are then redissolved and their osmotic pressure and intrinsic viscosity are determined. The osmotic measurements are carried out by the static method, the molecular weights are computed with the aid of a semi-empirical equation, which takes care of the deviations from van't Hoff's Law. The investigated fractions showed osmotic molecular weights from 17,000 to about 400,000 (P from 150 to 1500).

The intrinsic viscosities were determined in Ostwald viscosimeters at room temperature in acetone.

Comparison between  $[\eta]$  and P leads to the belief that the Staudinger rule holds for both fractionated and unfractionated and unfractionated nitrocelluloses. The  $K_m$



constants are  $8.2 \times 10^{-4}$  and  $10.2 \times 10^{-4}$  respectively.

H. MARK

MOLECULAR DISTRIBUTION OF DEGRADED CELLULOSES ON THE BASIS OF OSMOTIC AND VISCOMETRIC MEASUREMENTS.—G. V. Schultz and E. Husemann, Z. Phys. Chem., B52, 23 (1943).

Purified Egyptian cotton with a DP of 2700 (MW about 450,000) was degraded:

- (a) By homogeneous hydrolysis with phosphoric acid and
- (b) By heterogeneous hydrolysis in an aqueous potassiumbisulfate solution.

The degraded samples were nitrated (about 13.14%), dissolved in acetone and fractionated precipitated through stepwise addition of water. Osmotic and viscometric measurements were carried out with the fractions. The heterogeneity H of the degraded samples are determined with the aid of the equation

$$H = \frac{P_{\eta}}{P_n} - 1 \quad (1)$$

$P_{\eta}$  is the viscosity average polymerization degree as obtained from the intrinsic viscosity  $[\eta]$ .  $P_n$  is the number average as determined from osmotic measurements or end group determinations.

In the course of the degradation H increases first and decreases later. This means that the material becomes first more heterogeneous, but in the later stages of the degradation assumes again a higher degree of homogeneity. The distribution curves of the various degradation products support this result and show that during the degradation fragments of  $P \sim 500$  are more frequent than one would expect from random splitting of glucosidic linkages in the chain. This fact is interpreted by the hypothesis that particularly reactive bonds are regularly distributed along the cellulose chains in distances of 500 glucose units.

H. MARK

### Concrete and Mortar

A NEW ASPECT OF CREEP IN CONCRETE AND ITS APPLICATION TO DESIGN.—Douglas McHenry, Preprint for 46th Annual Meeting, A.S.T.M. Pittsburgh, 1943.

The nature of creep and recovery are discussed, and a



principle is stated which governs the superposition of creep when the load varies with time. An equation is developed which defines creep as a function of stress, age of loading, and elapsed time after loading. This creep equation, combined with the superposition principle, provides a means for expressing the strain history when the stress history is known. The treatment indicates that problems of concrete design may be solved by the methods of conventional elasticity, provided the true loads or displacements are replaced by certain fictitious loads or displacements. Numerous laboratory tests which form the basis and the verification of the treatment are described.

#### AUTHOR'S ABSTRACT

### Elements

THE VISCOSITY OF SULFUR.—R. F. Bacon and R. Fanelli, J. Am. Chem. Soc., 65, 639-48 (1943).

The viscosity of carefully purified sulfur was determined over the range 150° to 325°C. in capillary viscometers. The viscosity is independent of the rate of heating and cooling and of the previous heat treatment of the sulfur.

Preheated sulfur containing organic impurities has low viscosities due to the formation of hydrogen persulfides; preheating has no effect on the values for pure sulfur. Curves showing the effect of hydrogen persulfide in lowering the viscosity of sulfur are given. Hydrogen sulfide, through reaction to form persulfides, greatly reduces the viscosity of sulfur. The lowering effect of ammonia is due to the formation of minute quantities of hydrogen sulfide and persulfides by reaction with the sulfur. It is believed that traces of these substances are responsible for much of the lack of concordance in the recorded physical data for sulfur. The effect of halogens on lowering the viscosity of sulfur is shown in detail.

Above 80°, the viscosity of sulfur shows a gradual drop to a minimum at about 157°. Above 160°, the viscosity increases rapidly to a maximum at about 187°, above which it falls off sharply. These changes are explained on the basis of changes in the make-up of the sulfur molecule. At temperatures near its melting point, the sulfur molecule is an 8-membered puckered ring. As the temperature is increased, this ring tends to rupture, and the decrease in viscosity up to 160° is taken as evidence for a simplification of the molecular structure. Above 160°, polymerization into longer chains take place, and this reaches a maximum at about 187°. At temperatures around 200°, a single molecule may contain as many as 12,000 atoms. Above



187°, the molecules tend to rupture with increasing temperature, and at the boiling point numerous short chains predominate.

The similarity between "elastic" sulfur, presumably consisting of chains containing many atoms, and rubber is pointed out.

H. K. NASON

## Gels

THE EFFECTS OF PRESSURE ON SOL-GEL EQUILIBRIA, WITH SPECIAL REFERENCE TO MYOSIN AND OTHER PROTOPLASMIC GELS.--  
D. A. Marsland and D. E. S. Brown, J. Cell. Comp. Physiol, 20, 295 (1942).

The apparent viscosities of solutions of myosin, methyl cellulose, and gelatin were measured under confining pressures up to 8000 lb/sq. in., by a falling sphere method. In this pressure range, the viscosities of the myosin (2 - 3%) and methyl cellulose (1.66%) solutions decreased by about a factor of 10, while that of the gelatin (4%) increased by a similar factor. These changes were reversible. Qualitatively, this represents shifting of a "sol-gel equilibrium" toward the sol or toward the gel, respectively. The times of fall followed the equation

$$\log_e (t/t_0) = K \cdot (p-p_0)$$

If the constant K is interpreted as  $\Delta V/RT$ , where  $\Delta V$  is a molar volume change associated with a gel-sol transition, the following values of  $\Delta V$  are obtained: Methyl cellulose, -80 cc.; myosin, -120 cc.; gelatin, +135 cc. After change of pressure, the equilibrium was reestablished far more rapidly for myosin than for the other substances. This is attributed to the operation of an enzyme system, and is discussed in relation to muscular contraction and protoplasmic reactions.

JOHN D. FERRY

## Glasses and Slags

CONCERNING THE RHEOLOGY OF ORGANIC GLASSES.--V. W. Scheele, M. Afeis and L. Lahaye, Kolloid-Z., 103, 1 (1943).

In a preliminary discussion, flow curves of organic glasses are classified under the following form types:



## A. Pure Flow

1. Pure viscous flow
2. Pure plastic flow

## B. Quasi Flow

3. Quasiviscous flow
4. Quasiplastic flow

These four types may be described in terms of the following four equations

$$v = \frac{1}{\eta} \cdot \tau$$

$$v = \frac{1}{\eta} \cdot (\tau - f)$$

$$v = \frac{1}{\eta_{\phi}} \cdot \tau^n$$

$$v = \frac{1}{\eta_{\phi}} \cdot (\tau - f)^n$$

The experimental results for four polyvinylacetates (of increasing degree of polymerization), are discussed. Low degrees of polymerization can best be described in terms of quasiviscous flow, whereas a true flow limit (quasi plastic flow) appears for higher degrees of polymerization.

The concept of "deformation power, as determined by the equation

$$\int_{v=0}^{v=v_1} \tau \cdot dv$$

is introduced. It is shown that flow characteristics may be described in terms of this quantity. Furthermore, when the log of the deformation power is plotted against the reciprocal of the temperature, a straight line results. The slope and intercept thus obtained may be used in describing the temperature dependence of the flow properties of a given material.

D. TELFAIR



## Lignin

THE NATURE OF LIGNOSULPHONIC ACIDS FRACTIONATED BY CHEMICAL AND PHYSICAL METHODS.--W. A. Schenck, Paper Trade J., 117, (14), 97 (1943).

The author, after a critical discussion of the sulphonation of lignin in the sulphite cooking process on the basis of Freundberg's structural formula for lignin, describes experiments which had as their goal the fractionation of lignosulphonic acids from two widely different cooks by chemical and physical methods. These fractions were further investigated in order to determine whether the lignin is sulphonated by the entrance of several sulphonic acid groups into the lignin molecule without degradation of the latter, or whether the lignin molecule is broken into smaller fragments each having one sulphonic acid group. The equipment and experimental conditions are described and typical examples of the fractioning conditions are presented. The results obtained so far indicate that a breakdown of the lignin molecule into smaller sulphonated fragments takes place.

R. M. LEVY

## Metals

DIFFUSION IN SOLID METALS.--W. Seith, Angew. Chemie (Die Chemie) 56, 21-4 (1943).

Gases or solids may diffuse into solid metals by both chemical and physical processes. In the case of the latter, the diffusing element may (1) penetrate between the atoms in the crystal lattice, (2) displace lattice members by a substitution process, or (3) enter faults in the crystal lattice or, by displacement, cause adjacent members of the lattice to enter such faults.

Rate constants for the diffusion of one element into another may be determined, and such data for the diffusion of carbon, nitrogen, silica, manganese and chromium into iron and of gold, platinum and nickel into copper at high temperatures (650-1400°C.) are given.

"Self" diffusion may be studied by measuring the rate of penetration of a radioactive isotope into a material; data of this type are given for lead at temperatures ranging from 110 to 320°C.



The diffusion constant varies with temperature according to the relation:

$$D = Ae^{-Q/RT}$$

Q represents the minimum energy required for displacement of an atom from its lattice position; for lead it is about 30,000 calories per gram atom. For cubic crystals, the ratio of Q to the melting point of the crystal is approximately a constant with an average value around 46.3.

Where the diffusing atom differs in size from that of the material into which it is diffusing, diffusion may be more rapid because of internal disturbance of the mixed crystal lattice.

Diffusion rate is also affected by the crystallographic orientation of the base material, by the type and amounts of other atoms present, and by exposure to an electric field.

H. K. NASON

## Petroleum Products

PSEUDOPLASTICITY OF LUBRICATING OILS AT LOW TEMPERATURES.--M. Jordachescu, Thesis No. 113, E.N.S.P. Strassbourg (France) 1935.

After reviewing the historical development of viscosity measurements and interpretations on Non-Newtonian liquids the author proceeds to describe the mechanical behavior of lubricating oils at subzero temperatures. He uses capillary viscosimeters with capillary radii between .8 and 2.0 mm, applies transpiration pressures up to 250 cm watercolumn. All the oils tested show yield values greater than zero at temperatures below their cloudpoint. He finds the yield value (a) to be a linear function of the capillary radius, (b) to increase with the time of exposure to such low temperatures, reaching a true equilibrium value sometimes only after many days, (c) to increase exponentially with falling temperature, (d) to be readily influenced by the thermal, mechanical, and refining history of the sample. He also finds that oils are strongly thixotropic at temperatures below their cloudpoint. Microscopic observation of small carbon particles which were suspended in the oil in a specially designed capillary system proved that the viscosimetrically determined yield values are fictitious, since movement of the oil under differential pressures of one tenth the yield value could be observed. This movement was, however, not steady, but "jerky" in the beginning, then changing to an accelerated motion until after several minutes of acceleration a steady flow set in. "Elasticity"



of various frozen oils was determined by means of a concentric cylinder system suspended from an extremely sensitive torsion wire device. Elasticity of such gelled oils was found to increase with falling temperatures, and to vary considerably for different oils depending upon their origin. To prove his hypothesis that all these phenomena are caused by "hindered" crystallization due to the multicomponent nature of lubricating oils the author prepared binary and ternary mixtures of various pure fatty acids, and measured the viscosity and yield value of the pure compounds as well as of the mixtures at temperatures near their respective melting points. He found no yield values for the pure compounds even when already starting to crystallize, small yield values for the binary mixtures, and considerable yield value for the ternary system.

A. BONDI

PHYSICAL PROPERTIES OF LUBRICATING OILS AT LOW TEMPERATURE.--A. Bondi, Petroleum Refiner, 22, 287 (1943).

This study is essentially a continuation of above abstracted thesis into the realm of practical application. In addition to measurements of mechanical properties the heats of solidification of various lubricating oils were determined in order to estimate the amount of actually crystallizing material. The latter was found to range in most cases between 2 and 10% of the oil. Viscosity measurements were made at considerably higher pressure differentials and rates of shear than those of Jordachescu. Most measurements were performed at a shearing stress of approximately  $4 \text{ kg cm}^{-1} \text{ sec}^{-2}$ , which is the order of magnitude of starting torque determining shearing stresses in automotive equipment. Determinations were continued well below the pour points of most of the oils under study. Various methods of refining and compounding have been evaluated from the point of view of winter performance of lubricating oils. The surprising discovery has been made that admixture of small percentages of certain surface active agents or certain solvents reduces the low temperature viscosity of lubricating oils by between 1 and 4 powers of ten! Finally new testing standards for the characterization of low temperature performance of lubricating oils have been suggested.

AUTHOR'S ABSTRACT

VISCOSIMETRY AND NEW GRAPHICAL VISCOSITY CLASSIFICATIONS.--C. M. Larson and W. C. Schwaderer, Oil and Gas. J., 42, (10), 49 (1943).

This article discusses the present status of viscosimetry and viscosity classifications in the petroleum in-



dustry as applied to automotive lubricants. Graphs are presented for the determination of the Viscosity Index (a conventional and rather arbitrary classification index for the temperature coefficient of the viscosity of lubricating oils). On closer study the presented curves reveal very soon the arbitrariness and limitations of the Viscosity Index system by their peculiar curvature, which cannot be based on any law of nature but only on the "standard equations" which define the temperature coefficients of the viscosities of the two series of oils having zero and hundred viscosity index, and which have been standardized by the A.S.T.M.

A. BONDI

THE OVERALL PLATE EFFICIENCY OF HYDROCARBON FRACTIONATING COLUMNS AS A FUNCTION OF VISCOSITY.—H. G. Drickamer and J. R. Bradford, *Nat. Petroleum News, Tech. Ed.*, 32, R-378 (1943).

Plotting the results of overall plate efficiency calculations on 34 commercial fractionating columns and 30 cases out of the literature vs. the logarithm of the "Feed stock molan average viscosity" at average column temperature in centipoises resulted in a straight line. The slope of this line indicates a dependence of the plate efficiency on liquid phase viscosity to the minus .62 power. This result is in agreement with the empirically derived figures in other mass transfer equations where mass transfer coefficients have been found to vary inversely as the liquid phase viscosity to the .58 to .67 power. Theoretical considerations would require dependence of the efficiency of diffusional operations on viscosity to the 1.0 power.

A. BONDI

### High Polymers

INTERMOLECULAR FORCES AND CHAIN CONFIGURATION IN LINEAR POLYMERS—THE EFFECT OF N-METHYLATION ON THE X-RAY STRUCTURES AND PROPERTIES OF LINEAR POLYAMIDES.—W. O. Baker and C. S. Fuller, *J. Am. Chem. Soc.*, 65, 1120-1130 (1943).

A series of nine N-methylated polyamides, with methyl substitution varying in polydecamethylene sebacamide from 0 to 55 mole per cent., has been studied as a representative group of linear polymers showing physical properties ranging from hard brittleness to rubberiness. Young's modulus, moisture sorption and relative solubility were chosen as properties representing the gross solids, while the corresponding fine structure was studied by X-ray diffraction from oriented and unoriented sections.



The elastic modulus and hardness decrease rapidly with increasing N-methylation, as the hydrogen bonding and other polar forces decline. Relative solubility increases. Moisture sorption also increases, since the disorder introduced by the N-methylation leaves polar groups uncoordinated, and hence free to sorb water. This is in spite of the somewhat hydrophobic character of the methyl group, which replaces bonding hydrogen.

The interchain spacings are not appreciably changed by the methyl substitution, but at higher amounts of substitution one of the principal spacings (3.76 Å.) becomes diffuse. However, the spacings between the dipole layers, related to the identity period along the chain, are more than 25% shorter in the crystal form characteristic of the lower ranges of N-methylation than in the normal extended form. The chains appear to be restricted by partial folding along the fiber axis. This retracted form can be converted to an extended one by stretching in which the fiber period lengthens (as from 20.5 to 26. Å.) and the structure changes also. This behavior is reminiscent of fibrous proteins, as are many other properties of these polymers.

Similar retraction phenomena have been introduced in normally extended, unsubstituted polyamides by allowing plasticizers, such as cresol, to penetrate into the polar layers. The resulting structural changes demonstrate polar association of the plasticizer, often considered as a mechanism for plasticizer action.

A possible explanation of chain twisting is that it results from a compromise of the packing tendencies of the paraffin sections and polar sections of the chain. In general, it may reflect competing packing tendencies.

The chain retraction and extension observed may be the first stages of rubbery elasticity.

H. K. NASON

VISCOMETRIC ESTIMATION OF PARTICLE DIMENSIONS. II. MICELLAR CHANGES INVOLVED IN THE HEAT-BODYING OF TUNG OIL.—J. P. Hollihan and D. R. Briggs, *J. Phys. Chem.*, **47**, 30-9 (1943).

relative viscosities of tung oil, bodied for 0, 39, 61, 101 and 139 min. (gelation occurred at longer times) at 209°C. in a stream of nitrogen, were determined at concentrations of 0.949-4.000 g. per 100 cc. in carbon tetrachloride. Apparent molecular weights, calculated from the Staudinger equation, varied from 790 for untreated oil to 1570 for the sample bodied 139 minutes. A progressive



increase in degree of asymmetry of the oil micelles with time of bodying is indicated, and the data seem to be satisfactorily represented by the exponential form of the Einstein equation for spherical particles. Relative molecular weights, length-diameter ratios calculated by Simha's equation (for rod-like ellipsoids of revolution), partial specific volumes, and specific viscosities are shown as a function of bodying time. Inflections in the curves are taken as evidence that the bodying reaction takes place in successive stages.

H. K. NASON

POLYMERIZATION OF STYRENE IN THE PRESENCE OF 3,4,5-TRIBROMOBENZOYL PEROXIDE.--C. C. Price and B. E. Tate, *J. Am. Chem. Soc.*, 65, 517-20 (1943).

The average number of end groups per polymer molecule, calculated from viscometric data by the Kemp-Peters equation, agrees satisfactorily with the average calculated from cryoscopic data for samples of polystyrene prepared in the presence of anisol, p-bromobenzoyl peroxide and chloroacetyl peroxide.

H. K. NASON

VISCOSIMETRIC DETERMINATION AND SHAPE CHARACTERISTICS OF POLYAMIDES IN SOLUTION.--A. Matthes, *J. Prakt. Chem.*, 162, 245 (1943).

The polymers of  $\epsilon$ -aminocaproic acid are investigated. Solvents are concentrated sulfuric acid and 40% sulfuric acid. The number average molecular weight is determined by counting the amino groups at the ends of the chains with the van Slyke method. The average polymerization degrees ( $P$ ) investigated range from 3.5 to 43.5. Viscosity measurements are carried out in concentrated and in 40% sulfuric acid at room temperature. The Staudinger rule is invalid in both cases. The intrinsic viscosity  $[\eta]$  is connected with the polymerization degree by an equation of the form

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

The numerical values for  $K$  and  $a$  are 0.0281 and 0.668 in concentrated  $H_2SO_4$ , and 0.0268 and 0.510 for 40% sulfuric acid. Extrapolation of expression (1) in the range of higher degrees of polymerization (200-400) leads to the belief that the  $PD$  for commercial Perlon L (poly-aminocaproic acid) is around 300.

The kinetics of the depolymerization (hydrolysis) of the polymer in 40% sulfuric acid is investigated and it is



found that the reaction is of the first order in respect to the number of hydrolysible bonds.

The  $[\eta]$  -P relationship of a series of other polymers, such as polyvinylchloride, polyvinylacetate, polyvinylalcohol, polyacrylic methylester, polymethacrylic methylester, polymethylacrylonitril and polystyrene in various solvents is discussed; they all deviate from the Staudinger rule and obey equations of the form (1). The exponent  $a$  in these equations is a means to characterize the average shape of the dissolved molecules. If  $a = 0$ , one has rigid spheres; if  $a = 0.5$ , one has statistically curled up chain molecules and if  $a = 2$ , one has rigid rods.

H. MARK

## Rubber

THE PHYSICAL STATES OF RUBBER IN RELATION TO ITS MOLECULAR STRUCTURE.—L. R. G. Treloar, Chem. & Ind., 62, 326 (1943).

Rubbers and plastics may exist in several or all of the following states: (1) glassy, (2) rubberlike or highly elastic, (3) crystalline, (4) viscous liquid. While some plastics may only exist in two states, rubbers exist in all four states and are, therefore, used to explain the dependence of physical properties on molecular structure and arrangement for other plastics.

The rubber molecule is thought to be a long chain of rotatable sections, which is crumpled together in the non-stretched case. The elastic state, according to Guth and Mark, is characterized by a stretched long chain molecule's returning completely to its crumpled state of rest because of the thermal fluctuations present. From this theory two thermodynamic deductions are made: (1) the tension in a rubber sample held at a fixed extension is proportional to the absolute temperature, (2) the heat liberated by stretching is equal to the work done -Joule effect.

The three conditions for elasticity are: (1) long chain molecules possessing freely rotating links, (2) weak secondary forces between molecules, (3) three-dimensional network of interlocking between molecular chains.

At low temperatures, rubber becomes hard and brittle like glass but retains the same molecular structure as in the elastic state. This is known as the glassy state. The brittleness is traced to the loss of the power of free rotation and molecular mobility. The temperature of transition to the glassy state depends on the magnitude of the



intermolecular forces which may be lowered by plasticizers.

In the crystalline state the molecular arrangement becomes more or less regular. Rubbers never completely crystallize in that they always contain an important proportion of amorphous sections. A lone molecule passes alternately through amorphous and crystalline regions. Crystallization requires bulk movement of molecular segments to a lattice structure and always requires time. Since orientation is produced by stretching, the latter reduces the crystallization time. There is a minimum crystallization temperature, for rubber-like materials, below which very little crystallization occurs. Unstretched crystalline rubber is hard and inextensible but tough and flexible due to the intimate mixing of amorphous and crystalline parts. When prestretched, crystalline rubber has the added desirable characteristic of fibrosity due to orientation of the molecules. Stretching has been shown by Hook to have produced crystallization in rubbers.

At high temperatures rubbers tend to show the irreversible flow of viscous fluids but have high viscosity and superimposed elastic effects. Flow is greatly reduced by vulcanization of rubber because of the crosslinks produced. Flow is seen to increase with stress up to the point where crystallization starts and thereafter decreases to low amounts. The conclusion is that crystallization produces an effect analogous to the cross linkage produced by vulcanization.

W. W. PENDLETON

THE EFFECT OF PETROLEUM SOLVENTS ON THE COLD RESISTANCE OF SYNTHETIC VULCANIZATES.--Ross E. Morris, Robert R. James, Emil H. Berger and Theodore A. Werkenthin, India Rubber World 108, No. 6 (1943).

Oil resistant synthetic rubbers often have added to them certain ester type of softeners in order to improve their cold resistance. Gasoline and other light petroleum products are absorbed to some extent, and extract the softeners. The effect of the presence of these solvents is investigated. The apparatus of Selker, Winspear and Kemp, with some modification, is used to determine the brittle point of the vulcanizates after 30 days immersion in various solvents. It is concluded that the cold resistance of the synthetic rubber is improved by this immersion treatment.

R. H. KELSEY



THEORY OF THE ELASTIC PROPERTIES OF RUBBER.—Hubert M. James and Eugene Guth, *J. Chem. Phys.*, 11, 10, 455 (1943).

A simplified model of bulk rubber is proposed, which considers the material as a fluid, having through it a network of flexible chains. A statistical analysis of chains of independent links is given, and applied to stress-strain computations. The thermo-elastic properties of rubber are predicted, and the similarity of the behavior of rubber and an ideal gas is explained. The shape of the rubber stress strain curve is shown to be a result of the "internal pressure" of the fluid, and the limited extensibility of the chains. The general theory is said to be applicable to other physical properties of stretched rubber.

R. H. KELSEY

### Liquids and Solutions

THE VISCOSITY-CONCENTRATION RELATION IN COLLOIDAL ORGANIC SOLUTIONS.—H. Eilers, *Kolloid-Z.*, 102, 154-69 (1943).

The relation between viscosity and concentration given by the author and van Dijck (in a previous paper) for emulsions of high viscosity materials meeting the conditions for the viscosity behavior for infinitely dilute and for closely packed masses of spheres, was applied to solutions of high molecular weight compounds in organic solvents. It was necessary in doing this to modify the equation since for many of these solutions the "voluminosity" of the particles is a function of the concentration.

Over a very great range of concentrations, a linear relation was found between the voluminosity of these particles and the rheological concentration, i.e. the product of the voluminosity and the concentration in parts by volume, so that the viscosity behavior can be described by

$$\eta_r = \left( 1 + \frac{2.5 v_{c_v} C_v}{2(1-1.35) v_{c_v} C_v} \right)^2 = \left( 1 + \frac{2.5 (Q_{c_v} + 1) \cdot C_v}{2(1-1.35)(Q_{c_v} + 1) C_v} \right)^2$$

$$= \left( \frac{1 - 0.1 v_{c_v} C_v}{1 - 1.35 v_{c_v} C_v} \right)^2 = \left( \frac{1 - 0.1 (Q_{c_v} + 1) \cdot C_v}{1 - 1.35 \cdot (Q_{c_v} + 1) \cdot C_v} \right)^2$$



in which

$$V_{c_v} = \frac{bV_0}{C_v(V_0-1) + b} \quad \text{or} \quad Q_{c_v} = Q_0 \cdot \frac{b-C_v}{Q_0C_v + b}$$

$V_0$  = Voluminosity at infinite dilution

$Q_0$  = the rheological swelling =  $V_0-1$

$b$  = the length cut by the  $V$  line from the abscissa through  $Q_0 = 0(V_0=1)$

For a rheological concentration  $V_{c_v} C_v$  greater than about 0.65, deviations occur in many cases, probably caused by the fact that the micelles of the dissolved material do not meet the conditions set up for the equation; spherical shape, not deformable, and uniform size.

In the solutions of polystyrene in tetralin formerly studied by Staudinger, the rheological swelling  $Q_0 = V_0-1$ , that is the rheologically determined increase in volume over the unit volume of the material in dry state, is proportional to the molecular weight  $M$ , between 600 and 600,000.

$$Q_0 = KM$$

This relation proves correct also for other groups of polymeric substances such as solutions of acetyl glucoses, from cellobiose octa acetate, up to and including Staudinger and Daumiller's soluble eu colloidal cellulose triacetate.

Many synthetic resins, such as phenol formaldehyde resin, have a practically constant value for  $V_{c_v}$ ; and the value for  $b$  is also very large.

The quantity,  $b$ , which expresses the resistance towards decrease of the rheological swelling with increasing concentration, is, in the case of many groups of solutions, independent of the molecular weight of the polymers (poly-oxy decanoic acid in  $C_2H_2Cl_4$ , nitrocellulose in butyl acetate, cellulose acetate in *m*-cresol); in other cases  $b$  increases with increasing molecular weight (rubber in chlorobenzene, balata in tetralin, polyethylene oxides in dioxan) while for polystyrene in tetralin, this quantity decreases with increasing molecular weight.

In the case of low molecular weight rubber hydrocarbons (rubber decomposed by long plasticizing, hemicolloidal balata) the  $V_{c_v} C_v - V_{c_v}$  lines show a break. They follow a horizontal line at first, and then change over to an inclined line which fits into the group of lines obtained with the



higher molecular weight products. The viscosity behavior of these products in very dilute solution probably does not provide a true means for measuring the molecular weight. But a better value is obtained by extrapolating the value for the voluminosity obtained at higher concentrations.

C. K. BUMP

MOLECULAR SURFACE ENERGY OF SULFUR DIOXIDE ADDITION COMPOUNDS. II.--J. R. Bright and J. J. Jasper, J. Am. Chem. Soc., 65, 1262 (1943).

Viscosity measurements were made on the addition compound of sulfur dioxide with triethylamine over the temperature range 0 to 30°. A modified Poiseuille viscosimeter was used, and the system was closed to the atmosphere. Poiseuille's kinetic energy correction was negligible since a long capillary tube with a small radius was used.

Over the temperature range investigated, the temperature viscosity relationship is expressed by the equation

$$\log \eta = 1240 T^{-1} - 3.51171$$

The average deviation of the data from this curve was found to be 0.6%.

T. S. LAWTON

SOLUTION VISCOSITIES OF THE AMYLOSE COMPONENTS OF STARCH.--J. F. Foster and R. M. Hixon, J. Am. Chem. Soc., 65, 618-22 (1943).

Ethylene diamine solutions of amyloses (the unbranched components) from corn, potato, tapioca and lily bulb starches, a "crystalline amylose" from corn, and a synthetic starch, were studied in capillary viscometers at 30°. The results leave little doubt that the amyloses are essentially linear polymers.

The viscosity limits fall in an inverse order to the potentials at which the amyloses take up iodine from solution, confirming the postulate that this potential is a function of the molecular weight of the amylose. Synthetic starch is anomalous both with respect to its iodine titration curve and the viscosity-concentration relationship of its solutions. The former anomaly can be best explained on the basis of heterogeneity. The latter indicates increased polymer-polymer interaction which cannot be explained by heterogeneity but may be due to the presence of polar groups in the molecule, perhaps phosphate groups.

H. K. NASON



OSMOTIC PRESSURES OF POLYVINYL CHLORIDE SOLUTIONS BY A DYNAMIC METHOD.--R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, 47, 59-70 (1943).

Reliable osmotic pressure data for four samples of polyvinyl chloride were obtained, using an improved osmometer and an elegant dynamic technic developed by the authors. Molecular weight values calculated from these data agree reasonably well with the values calculated from viscosity data in cyclohexanone solution using Staudinger's equation and the authors' value of  $7 \times 10^{-5}$  for the constant.

H. K. NASON

## Starch

AMIOCA - A NEW INDUSTRIAL STARCH.--C. G. Caldwell, *Paper Trade J.*, 117, No. 16, 27 (1943).

Amioca, the starch produced from a new variety of corn, popularly known as "waxy maize" is characterized by its lack of amylose. It competes with tapioca and other related starches but differs from them in that it retains the fluidity and non-jelling character of the original starch. This is in strong contrast to both potato and tapioca starches whose acid conversion products tend to be unstable and gel up because of the presence of shortened amylose molecules.

This starch is reported to gelatinize sharply starting at 70°C. and proceeding over a range of only 8°. This is in contrast to ordinary cornstarch which begins to gelatinize at 64°C. and continues over a range of 30° or more. The hot viscosity of dilute pastes prepared from this product has been reported greater than that of tapioca at temperatures of 75 to 90°C.

Considerable impetus has been given to the development of Amioca because of the curtailment of importations of tapioca starch from the Far East.

R. M. LEVY

## Theory

SOME ASPECTS OF RHEOLOGY.--E. Heymann, (*Univ. of Melbourne*) *Australian J. Sci.*, 5, 168 (1943).

Ideal elastic deformation is observed with crystalline ionic compounds (salts) and of covalent lattices in which the covalent bonds extend through the entire crystal



(diamond, carborundum). Steep potential troughs result in high rigidity. With covalent compounds, where all valencies are satisfied within the molecule, and only weak van der Waals and dipole forces exist there, the incidence of plastic flow occurs at low shearing stresses (most organic compounds of low molecular weight). Yield values at still lower shearing forces, even vanishing, are found in systems whose structural units are of colloidal dimensions, (resins, asphalt, rubber, jellies, paint clays, etc.). The potential troughs must be very shallow. Attractive and repellent forces are often shielded by solvation jackets and small mechanical forces (such as by shaking) which are capable of upsetting the equilibrium and causing the system to flow, (thixotropy). Elongated particles, giant molecules with fringes, chains of small particles or long-chain molecules forming a felt-like loose network, must be considered in the explanation of plastic and jelly-like systems, possessing a yield value, particularly where the particles bear no electrical charges (asphalt, artificial resins). Interlocking of structural elements may be due to covalencies, van der Waals forces, or mechanical entanglement. Plasticity is generally found in systems containing large structural elements, from colloidal molecules to the size of microscopic crystals.

A liquid owes its viscosity to the intermolecular forces (van der Waals, dipole, hydrogen bond). The structure is not very different from that of a solid, but there are continuous fluctuations with particles slipping from one configuration to another. Configurations will be favored which relax occurring stresses. However, only molecules which during collisions with others have received energy in excess of the average will be able to leave existing configurations (activated molecules) and relieve the stress. Whatever the mechanism in detail, a probability function is always involved, and the viscosity may therefore be expected to be proportional to  $e^{E/RT}$ .

Among solutions, those of high molecular compounds are of particular interest. Theoretical analysis leads to the conclusion that the viscosity steeply increases with the ratio of length to thickness of the particles, but the statistical shape of a chain molecule in solution is not that of a rigid rod. The chain will have a zig-zag form and curling may occur. The length is not proportional to  $n$  (no. of C atoms) but rather to  $\sqrt{n}$ . Eirich has shown that flexible threads increase the viscosity less than rigid rods. Staudinger proposed that the increase of viscosity should be proportional to the molecular weight of the solute. If this were correct, it would have the same importance as Avogadro's hypothesis; but it does not accord with the above theoretical consideration nor with



independent experimental measurement. It holds best for chains of medium length but caution is necessary for m.w. 100,000. The problem is complicated by interaction between chains, change of the kinetic units by cluster formation and also by immobilization of solvent between the chains.

Dilute solutions of chain molecules behave as Newtonian liquids. On increase of concentration, however, deviations are observed. The apparent viscosity decreases with the shearing stress, due probably to the orientation of the chains in the direction of flow. This is supported by the occurrence of birefringence (stream double refraction).

There is another group of systems which show non-Newtonian flow. They are colloidal solutions which at low temperatures and high concentrations show a tendency toward jelly formation ( $\text{Fe}_2\text{O}_3$ -sol, soap, agar, rubber). They have elongated molecules and tend to form clusters but the structure may be destroyed by shaking (thixotropy). They show elasticity in addition to viscosity (visco-elastic), the viscosity being merely apparent. These systems are transitional between the Newtonian and plastic.

EUGENE C. BINGHAM

OVERALL PLATE EFFICIENCY OF COMMERCIAL HYDROCARBON FRACTIONATING COLUMNS AS A FUNCTION OF VISCOSITY.—H. G. Drickamer and J. R. Bradford, Trans. Am. Inst. Chem. Eng., 39, 319 (1943).

For any group of columns having similar tray design and operated near maximum capacity, the overall tray efficiency is primarily a function of the physical properties of the material being fractionated.

In this investigation, viscosity was selected as the determining physical property for several reasons:

First, the Stokes-Einstein equation for molecular diffusivity

$$D = KT/6\pi r\mu$$

is an inverse function of viscosity.

Second, the mass transfer equation of Chilton and Colburn

$$K = (G_m/M_m) / (\rho k_d/\mu)$$

denotes turbulent mass transfer as an inverse function of viscosity.



Third, the von Karman equation for film thickness

$$y = (\text{constant})\mu/G(f/2)$$

indicates film thickness is directly related to viscosity.

Fourth, the equation of liquid mass transfer coefficient

$$K_{1a} = 3.4/(\mu)^{.58}$$

developed by Sherwood and Walter also indicates an inverse relationship between mass transfer rate and viscosity.

Since a preliminary correlation between  $K_{1a}$  and tray efficiency was quite successful, an inverse relationship between tray efficiency and viscosity was postulated.

The following relationship was found to exist,

$$E = 0.17 - 0.616 \log (\Sigma M\mu)$$

wherein

$E$  = plate efficiency (ratio of theoretical to actual plates).

$\Sigma M\mu$  = "molar average viscosity".

The latter is the sum of the products of the mol fraction of each component and its viscosity at the average column temperature.

This work is the result of a study of test data on 54 petroleum refinery fractionating columns varying between four and seven and a half feet in diameter.

W. H. MARKWOOD, JR.

VISCOSITY, MOLECULAR FORM, AND SOLVATION.--H. Fromm, Kolloid-Z., 102, 86-90 (1943).

This paper constitutes a proposal for a standardized and rationalized (German) nomenclature in the rheology of colloidal solutions. It is argued that the limiting value of  $\left(\frac{\eta_{sp}}{c}\right)$  is not a measure of viscosity, but rather of the rate of increase of viscosity with concentration. The word "Zahigung", or "viscosation", rather than the familiar "Zahigkeit", is suggested as the basic part of any expression relating to such a quantity.



It is pointed out that the concentration of a colloidal solution may be expressed in terms of (1) volume fraction of solute, (2) volume fraction of solute plus solvated hull, or (3) weight of solute per unit volume of solution. Other methods of specification are mentioned, but not discussed in detail.

When the concentration is expressed in terms of the volume fraction (1), the limiting value of  $\left(\frac{\eta_{sp}}{c}\right)$  is given the name "Zahigungshauptzahl". When  $c$  is the volume fraction, including any solvated hull, (2),  $\lim_{c \rightarrow 0} \left[\left(\frac{\eta_{sp}}{c}\right)_c\right]$  is given the term "Gestaltbeiwert de Zahigung". Finally, when the third specification of concentration is used, the word "Zahigungswert" is used.

In all of the above cases it is assumed that the shear stress,  $\tau$ , as well as the concentration has been extrapolated to the limit zero. A fourth term, "Gestaltfaktor der Zahigung" is suggested to refer to the rate of increase of relative viscosity with concentration, without the limitation of small  $\tau$ . Here the second specification of concentration is used. The "Gestaltfaktor der Zahigung", unlike the other three quantities, is not a specific property of the solute, but is also a function of the shear stress.

The following symbols are suggested for the above terms:

- (1) "Zahigungshauptzahl" -  $Z_v$
- (2) "Gestaltbeiwert der Zahigung" -  $k_0$
- (3) "Zahigungswert" -  $Z$ .
- (4) "Gestaltfaktor der Zahigung" -  $k$ .

TURNER ALFREY

THE VISCOSITY FUNCTION. IV. NON-IDEAL SYSTEMS.---  
E. P. Irany, J. Am. Chem. Soc., 65, 1392 (1943).

The systems sulfuric acid-ether, the aqueous and formamide mixtures of dioxane, the lower alcohols, and fatty acids are discussed with emphasis on the viscosity characteristics. Prevailing methods of interpretation of the observed data result in erroneous conclusions on association, dissociation, compound formation, etc., and the author proposes complete revision of the field of graphical analysis. Misinterpretation of observed data has been due to arbitrary premises inherent in the usual



methods of graphical analysis.

The non-ideal systems mentioned have been the subject of much investigation, and the viscosity data have been given contrary treatment. The author has treated these data by means of functional scales which were developed by him in earlier papers, and this method of treatment has proven to be very reliable. This method yields reasonable and harmonious results, and does not show the contradictions and deviations obtained in the customary methods of graphical analysis. Also, this method reveals the small differences which are not apparent by other methods.

T. S. LAWTON

FLUIDITY OF MIXTURES WHICH OBEY BACHINSKII'S LAW.—

F. Kottler, J. Phys. Chem., 47, 277-93 (1943).

A modified form of Bachinskii's law, based on molal units and mole fractions was set up and ideal mixtures were defined by sets of three equations. These laws of mixture were tested by data for the following pairs: benzene and bromobenzene, benzene and chlorobenzene, benzene and iodobenzene, benzene and carbon tetrachloride, benzene and benzyl benzoate, and carbon bisulfide and methyl iodide. It is concluded that all obey Bachinskii's law and that, except for the last mixture, all fluidity vs. mole fraction curves are sagging. The first four cases have been classified as almost ideal, and it is concluded that the ideal curves are not straight lines, but sag below such lines. Deviations from linearity become too small for detection in the cases of pairs whose constants do not differ appreciably. The sagging of the fluidity curves increases and that of the viscosity curves decreases with increasing temperature. Sagging should therefore be judged from a series of curves taken at different temperatures rather than from a single curve.

H. K. NASON

BREAKDOWN OF THIXOTROPIC STRUCTURE AS A FUNCTION OF

TIME.—Ruth N. Weltmann, J. Applied Phys., 14, 343 (1943).

By means of a rotational viscometer, the thixotropic breakdown of oils and suspensions of pigments is determined at several rates of shear. The product of the rate of breakdown of thixotropic structure and the time of agitation is found to be a characteristic constant for each material, independent of the rate of shear. The time necessary to bring the thixotropic structure to its minimum is found to be independent of the rate of shear. Experimental curves and data are given. The findings are stated to apply to oils at rates of shear in which they



behave like thixotropic plastics.

R. H. KELSEY

VISCOSITY AND MOLECULAR WEIGHT. I. THE NITRATE OF WOOD CARBOHYDRATES.--S. Coppick, Paper Trade J., 117, No. 7, 25 (1943).

This paper reviews the relationship between the viscosity of solutions of cellulose and its nitrated derivatives with the degree of polymerization and molecular weight.

Viscosity functions are given for the nitrate of the carbohydrate material in wood, and these functions are compared with those for nitrated cotton. The author shows that Staudinger's reduced viscosity function is inaccurate as an expression for molecular weight determinations. He also shows that Kraemer's intrinsic viscosity is a much more reliable function for degree of polymerization measurements on very high molecular weight materials.

The author uses the viscosity-concentration equations proposed by Farrow and Neale and Fickentcher to permit rapid determination of the intrinsic viscosity at infinite dilution. By the use of these equations only one viscosity measurement at a conveniently high concentration (0.3%) is necessary to determine the molecular weight. These formulas give values which vary by only 5% from those given by the most accurate infinite dilution measurements of the intrinsic viscosity.

The modified Farrow and Neale equation used in this work is the same as that proposed by Straus and Levy in the form:

$$\frac{1}{C} + 0.5 = S \left[ \frac{1}{\ln N_r} \right]$$

where C = concentration (grams per 100 ml.)

S = slope of the line

$N_r$  = relative viscosity

The intrinsic (N) is obtained by writing the equation as:

$$S = \frac{\ln N_r}{C} (1 + 0.5c)$$

so that at infinite dilution

$$(N) = \left[ \frac{\ln N_r}{C} \right]_{C \rightarrow 0} = S$$



The Fickentcher equation used is:

$$\frac{\ln N_r}{C} = \frac{75K^2}{1 + 1.5 KC} + K$$

where K is a parameter defined as the "Eigenviskositat" or viscosity coefficient.

This equation apparently holds for a great number of polymers including cellulose and its derivatives. From a single viscosity measurement at a conveniently high concentration the value of the viscosity coefficient may be calculated. The limit of the above expression as the concentration approaches zero is given by

$$(N) = \lim_{C \rightarrow 0} \left[ \frac{\ln N_r}{C} \right] = 75K^2 + K$$

The carbohydrate in wood is shown to have a much greater molecular magnitude than the literature assumes, and approaches that of raw cotton.

R. M. LEVY

EXTERNAL FRICTION OF SOLIDS.--Andrew Gemant, J. Applied Phys., 14, 456 (1943).

The theory of external friction does not present a complete and unified picture that would explain all of the experimental observations in this field. The basic mechanism, as suggested by Coulomb, refers to the microscopic protuberances of sliding surfaces which have to be lifted over each other, a process that, in its final balance, can be considered as conducive to the generation of heat. This process, however, is certainly overlapped by a number of complicating effects. Among such effects are: elastic distortion and plastic flow of protuberances, molecular attraction forces acting between molecules of adjacent surfaces, microscopic welds produced between protuberances, and abrasion.

For the interpretation of experimental facts, it is customary to express the friction force as the product of the normal pressure and a factor, the so-called coefficient of friction  $\mu$ . The latter varies for different combinations of materials from around 0.2 to 1.5. It is independent of the normal pressure and the area of contact.

It is customary to differentiate between the static and dynamic value of the coefficient  $\mu$ . The static



value is related to the so-called angle of repose and can be determined by means of it. The dynamic coefficient is usually (but not always) lower than the static value. It is usually constant for small and medium velocities, but decreases as the velocity of sliding becomes larger.

There is very little knowledge of the effect of temperature upon the friction coefficient, but in a few cases a decrease was observable as the softening point of one of the two materials was approached.

If one of the two bodies moves with a constant speed, and the other is supported elastically, a periodicity is observed in the latter's motion, an effect called stick-slip motion. This process may develop into self-excited vibrations that have practical significance in a number of cases.

Depending upon the nature of the sliding surfaces, some other effects may become noticeable: the softer material might leave traces upon the harder, as a result of abrasion of its protuberances. The abraded layer may act as a lubricant in the further progress of sliding.

Impurities, such as adsorbed moisture, may influence the friction process considerably.

In case friction is accompanied by contact electrification, the friction forces will also be altered.

AUTHOR'S ABSTRACT

THE VARIATION OF VISCOSITY OF LIQUIDS WITH TEMPERATURE.--  
M. K. Srinivasan and B. Prasad, Phil. Mag. (7) 33, 258-71 (1942).

Seven equations expressing the relation of viscosity to temperature were examined and tested with data on organic liquids and fused metals. The simple equation of Andrade (Nature, March 1, 1940 and April 12, 1930),

$\eta = Ae^{\frac{b}{T}}$  was found to be as precise as his modified equation  $\eta \cdot v^{\frac{1}{3}} = A e^{\frac{cv}{T}}$  (where A, b and c are constants and v is the specific volume). These equations are based on the assumption that the transfer of momentum in liquids takes place by molecules of adjacent layers coming in close contact for some time rather than by transfer of material particles. The equation holds for associated liquids providing the association is not a function of temperature.

Silverman's equation,  $\eta = kv/T \cdot e^{\frac{Q}{RT} - CT}$  where k, Q and



c are constants (Trans. Farad. Soc., 29, 285, 1933), requiring a knowledge of the density, gave good results for unassociated liquids and some metals. This equation assumed that some structure in the liquid was breaking up and

being reformed again. Madge's equation  $\eta = \frac{Ae^{BT}}{T - b}$  where

A, b, and B are constants (J. Phys. Chem., 34, 1599, (1930)) treated liquids as a case of an elastic solid when the material breaks down under stress rather than a matter of diffusion as in gases. The equations of Madge, Andrade and Silverman were shown to apply fairly well to unassociated organic and metal liquids over wide ranges of temperature.

S. ZERFOSS

ON THE RELATION BETWEEN VISCOSITY AND DENSITY OF LIQUIDS AND LIQUID MIXTURES.—M. K. Srinivasan, Phil. Mag. (7) 32, 253-8 (1941).

An equation relating viscosity to density is discussed;  $\log \eta = \alpha + \frac{B}{\rho_0 - \rho}$  where  $\alpha$ , B,  $\rho_0$  are constants. The

equation holds fairly well for associated and unassociated liquids over wide ranges of temperature. It holds for certain associated liquids, such as tertiary alcohols, even though the association changes with temperature. It does not hold for water. If one assumes that the density changes linearly with temperature over short ranges, the equation is similar to that of Andrade and fits the data equally well. The equation was tested with data for octane, other organic liquids and for gallium.

S. ZERFOSS

VISCOSITY-TEMPERATURE FUNCTIONS OF LIQUIDS.—A. H. Nissan, Phil. Mag. (7) 33, (215) 441-456 (1941).

The viscosity-temperature relationship for various liquids can be expressed as a simple polynomial series provided the temperature term is properly chosen. The temperature term used in the series was  $T/T_B$  where T is the absolute temperature of the measurement and  $T_B$  is the boiling point of the liquid measured. The equation proposed would have the form

$$\log \eta = K + K_1 \cdot (T/T_B) + K_2(T/T_B)^2 + K_3(T/T_B)^3 \dots$$

The equation was tested for liquids of organic and inorganic composition showing various degrees of association. Procedure is given for determining the number of terms necessary in the equation. Numerous graphs are shown.

S. ZERFOSS



THE VISCOSITY-TEMPERATURE FUNCTION OF LIQUIDS.—E. P. Irany, Phil. Mag. (7) 33, (224) 685-688 (1942).

The graphical method employed by Nissan for making the  $\eta$ -T curves linear was discussed. Irany claims priority on the method and discusses several applications.

S. ZERFOSS

### LETTERS TO THE EDITOR

Sir: At the occasion of the last World Petroleum Congress in Paris 1937 an international committee has been formed to study methods for the determination and formulation of the temperature coefficient of viscosity. Due to well known conditions in the intervening years activities of this committee have surely been entirely impossible. The need for finding a way to properly describe the temperature coefficient of the viscosity of liquids is today greater than it has ever been before (since present modes of expression (Viscosity Indices) have been found pitifully inadequate). It appears to the writer, that it might well behove our society to set up a commission to study this problem and submit its findings and proposals to the ASTM, API, CRC, the U. S. Bureau of Standards and the various procurement and engineering divisions of the armed forces.

It must be admitted that the present status of our knowledge of the viscosity function is not too encouraging. But in view of the inadequacy of the present systems of characterization a concerted effort of a number of competent men would be well warranted and is prone to succeed in finding a satisfactory means of expressing the temperature coefficient of viscosity in engineering instead of storekeeper units.

Very truly yours,

A. BONDI

River Petroleum Corp.  
Chem. Operations Div.  
Belle Chasse, La.

Sir: In connection with E. C. Bingham's recent appeal for the standardization of viscosity measurements we would like to direct attention to an effect which is usually neglected. This is the possibility of the existence of considerable temperature gradients within the liquid to be tested, when highly viscous materials are subjected to high rates of shear. Due to the low heat transfer coefficient in such systems the heat of friction cannot be



dissipated as fast as created and a substantial temperature gradient is set up in the system. The writer observed quite frequently in recent rheological literature the possibility of such an effect to have been overlooked and the experimental results therefore - at least partially - misinterpreted. Quantitative experimental and theoretical treatment of this subject exists so far only in the field of lubricating technology but not yet for the methodology of viscosity measurements. In view of the considerable amount of work being done at present on the determination of the viscosity of asphalts and other highly viscous materials information about the possible influence of this effect would be of great value.

Very truly yours,

A. BONDI

River Petroleum Corp.  
Chem. Operations Div.  
Belle Chasse, La.

Sir: During the discussion, at the New York Meeting, of a possible journal devoted solely to rheology, it occurred to me that a publication plan very seriously considered a few years ago for the x-ray and electron diffraction field might be even more applicable to the field of rheology. Briefly, this plan, as applied to rheology, is as follows:

Papers of interest to rheologists would continue to be published in various journals, as at present. As soon as possible after the publication of each paper of this sort, the Society of Rheology, or some other organization (such as the American Institute of Physics) working with it, would purchase from the publisher a certain number of reprints, without covers. Periodically (bimonthly?) these would be sorted, trimmed to a uniform size if possible, bound in covers similar to the covers of any ordinary scientific journal, and mailed to each member of the Society and to other subscribers. On the covers would be printed a title (e. g., "Rheology Papers"), a table of contents (listing title, author and journal reference for each paper), information regarding the Society, and a statement that permission for distributing the papers in this way had been obtained from the copyright owners.

It seems to me that most papers which are of interest to rheologists are of even more interest to people in other fields--different fields for different papers--and that publication should preferably be in the field of major interest in each case. The system outlined here would permit that and still would give rheologists a more complete collection of the papers in their field than if the Society



again published a separate journal of original papers.

I believe that it would be advantageous if this reprint collection and distribution scheme could be made international, as regards both the sources of the papers and their destinations. If sufficient funds were made available, translations of articles in foreign languages might be made and included in the collection (Cf. "Rubber Chemistry and Technology.")

Although it would seem to be inadvisable to start any project of this sort in the near future, there is certainly nothing to be lost in discussing now plans for action after the war.

MAURICE L. HUGGINS

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