

RHEOLOGY BULLETIN



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EDITORIAL

A BRIEF SURVEY OF MEMBERSHIP OF THE SOCIETY OF RHEOLOGY

Introduction

The natal day¹ of the Society of Rheology was December 19, 1929 when the first meeting for organization was held at the National Bureau of Standards. From the beginning the position of the Society among other scientific societies has been unique in that the membership includes many distinguished scientists and engineers who are also active in other societies more closely related to their professions, or which represent the branches of science in which they took their academic degrees. Granting that all members of the Society are interested in the practice of "science of the deformation and flow of matter" and are therefore entitled to be called rheologists within the limits of their various degrees of interest, objectively it must be admitted that this basis of definition does not serve the practical purpose of identifying the majority of the membership. Since the beginning of the war, the membership of all scientific and engineering societies has been scrutinized for many purposes, especially by the federal government which has been seeking trained personnel on one hand, and on the other, critically examining the professional qualifications of members who on the basis of training and experience would be judged as being better able to serve their country in the laboratory rather than in the armed forces. What can be said about the average (hypothetical) member of the Society of Rheology, what is his professional background, where does he live, how stable a member is he? To answer these questions and to give members some information about their colleagues, the Secretary has attempted a preliminary survey which it is hoped will indicate some statistical trends that may be significant for the future.

Numerical Changes of Membership

Suppose that the numerical trend be examined on the basis of the membership for the following years.

1932	204	1940	115
1933	119	1941	136
1936	78	1942	161
1938	118	1943	171
1939	123	1944	168 (April 19)

The rapid rate of decline from 1932 to 1936 was undoubtedly due to the increase of membership dues from \$3.00 to \$6.00, although the difficulties of publication were contributory.

During this transition period the Journal of Rheology was discontinued and the Rheology Leaflet, later to become the Bulletin, was started as the only publication of the Society.

¹Prof. E. C. Bingham in, "The History of the Society of Rheology", to appear soon in the Bulletin.

A plot of the above figures shows that the rate of membership increase is decreasing slowly with the result that a membership of 200 will not be reached at the present rate until about 1947. Even to maintain this rate the membership this year must reach 180. The rate of increase during 1940-42 was such as to promise a roster of 200 by the end of this year. While 12 new members should be the minimum to be added this year, with additional effort on the part of the Society it should be possible to obtain the necessary 32 to reach the goal of 200 members that was predicted by the 1940-42 rate. This should be a challenge to every member of the Society.

On March 31 it was reported that 37 domestic members had been dropped from the mailing list of the Bulletin for non-payment of dues. This is nearly 21% of the 1943 roster, 5 more members than the goal that should be reached this year! This alarming drop raises the question of turnover of membership in the Society. A survey of the 1941 roster showed that 28% of the present membership was active at that time, but that 43% of the present membership has been added since. Is such a rapid turnover beneficial to the future of the Society? It probably represents a tendency for specialization in the Society. This exists in all societies and, in a certain sense, is inevitable as progress opens up new fields. But, in view of the greater need for dissemination of fundamental rheological principles and applications, it appears that the Society has a definite responsibility in several fields which up to now in this country have had little or no attention. One immediately thinks of the great dairy industry which in Britain has been brought into rheology through the efforts of the British Rheologists' Club. The medical sciences are just beginning to obtain recognition in the Society, although many physiologists and pathologists are interested in rheology. The fields embracing plasticity of metals, rubber, and ceramics have been neglected although they have several representatives in the Society. Then there is the outstanding scarcity of petroleum technologists, who in the past few years have contributed advances in viscometry. To participate actively in several fields immediately raises the question of organization and finance, particularly publication, which the Society is not in a position to face at present. With the problem of publication before the Society there should be considered ways and means of broadening the interests and activities of the Society, since the two problems are related. If the Society were to emphasize

fundamentals which are applicable to all fields, rather than specialization in certain fields of limited interest, which is subject to constant change, it is to be supposed that the Society could become the common meeting ground for many groups which at first sight might appear to be quite far apart as regards interests and practice. It is not too much to hope at the present time that the Society can formulate plans for a post-war expansion that would bring in several thousand members once the ways and means are ready.

Geographical Distribution of Membership

The present membership is distributed principally among the following states:

New York	25%	Massachusetts	6%
New Jersey	14%	California	4%
Pennsylvania	13%	Maryland (D.C.)	4%
Ohio	10%	Delaware	4%

Over 50% of the membership is concentrated over a relatively small area the center of which is close to New York City. Considering extremes, one member is found in each of the following states: Texas, Wyoming, Rhode Island and Oregon. Three percent of the membership are subjects of the British Empire which has one member in Australia.

Returning to the 37 members who became inactive last year, the greatest losses were:

New Jersey	27%	New England	13%
New York	19%	Pennsylvania	10%

The states having the greatest percentages of members also have the greatest percentages of loss, with the exception of the New England States. It would appear that in these states should the most intensive drives be made for members. The loss in New Jersey is serious, but also significant is the loss in New England.

Professional Distribution of Membership

The procedure for determining professional or vocational distribution is complicated by the fact that a person educated as a chemist, for example, may be doing work of an engineer or physicist. The criterion adopted was to label a member according to one or more of the following sources of information: membership in a national, professional society, major field of study as given in American Men of Science, type of vocation, or major interest as indicated by research papers. It has been possible to classify most members with some degree of accuracy. Of 163 members considered, only 25 remained unclassified for lack

of information. The membership is divided into 7 major fields of activity:

chemistry	47.5%	administrative	5.0%
physics	14.0	rheology	3.0
teaching	13.0	ceramics	3.0
engineering	11.0	unclassified	15.0

The sum exceeds 100% as a member may be counted in two or more classifications. This is particularly true of teaching and administration as most of the members in these fields are chemists or physicists by training. The 3% engaged in rheology were so classified since they are recognized by virtue of their vocation or major research activity over a long period of time. These men also completed their formal education in chemistry or physics.

Professional Standards of Membership

The Society has no specified standards for admission to membership, due to the fact that since its inception it has been composed of specialists who would normally be highly acceptable to other scientific societies. Eligibility for membership is determined by a Membership Committee, appointed by the President of the Society, which acts on applications received and transmitted by the Secretary. Membership is on a common basis as the Society does not elect Fellows. It appears desirable that formal recognition of research and achievement in rheology by the election of Fellows should be considered in the near future, much like the system now in operation in many of the leading scientific and engineering societies.

The 6th edition of the American Men of Science (1938) contains biographical sketches of 43% of the present membership. This figure will be increased when the present edition is examined. While the academic background and experience of only a few of the members are known completely, a survey shows that 33% state that they have received the doctorate in science, engineering, or mathematics. In the limited time available for this survey it has been impossible to prepare statistics on the number of other societies to which the members belong, as is also the case for special honors, advanced studies, and publication of research. It would be to the interest of the Society if more complete professional and vocational information of its membership were available.

Summary

To conclude this preliminary survey it may be said that the average (hypothetical) rheologist of the Society is a chemist by profession but with associations in physics

and engineering. Residing in the East, within a few hundred miles of New York City, he is engaged primarily in industry but has interests in teaching, perhaps to the extent of doing part-time teaching. He is listed in American Men of Science on the basis of advanced study which has led to his Ph.D., or the equivalent. Unfortunately, he has been a member of the Society of Rheology only during the past 3 to 5 years with the result that he is not entirely clear as to his interests in rheology, although he enjoys the symposia of the Society if they are close to his own field of interest. Sometimes he becomes neglectful to the point of not paying his annual dues.

R. B. DOW

THE 1944 FALL MEETING

The regular annual Meeting of the Society of Rheology is scheduled for November 17 and 18 at the Hotel Pennsylvania in New York City. Dr. W. F. Fair, Jr. Chairman of the Program Committee is arranging a good program. He will be very glad to review contributions from members of the society or others who are working in related fields. Abstracts, about 200 words in length should be sent to Dr. Fair as soon as possible and the final copy of the paper should be in his hands by October 1st.

IN MEMORIAM---WINSLOW HOBART HERSCHEL

Mr. Winslow H. Herschel was born in Boston, Mass. on August 28, 1873. He was graduated from Harvard University, receiving his A. B. degree there in 1896, and spent three semesters at Polytechnikum, Zurich, Switzerland. Later he engaged in general work as a civil and mechanical engineer and taught for two years at the University of Maine, Orono, Maine. From 1911 to 1913 he was employed as an inspector in the Purchasing Department of the Isthmian Canal Commission, Pittsburgh, Pa.

Mr. Herschel joined the staff of the National Bureau of Standards as an assistant physicist during December 1913. He worked on lubricants, developing specifications and standards of quality, and became chief of the lubricants section in 1920. He specialized in measurements of viscosity and published several papers in this field. During 1933 he was transferred to the Bureau's Clay and Silicate Products Division, and at the time of his retirement was an associate materials engineer in that division. He died on March 8, 1944.

Mr. Herschel was very much devoted to the interests of the Rheology Society and was Vice-President during the years 1929-31.

NEW BOOKS

The review of "A Survey of General and Applied Rheology" by Dr. G. W. Scott Blair, Rheology Bulletin Vol. XV No. 1, Page 19 failed to mention the publisher. The book is published by Pitman Publishing Corp., 2 West 45th St., New York 19, N. Y. The price is \$4.00.

Abstractors in this Issue

The following Good Friends have cooperated in making this May 1944 Rheology Bulletin a success. Their addresses have been published in other issues.

Neill M. Brandt
A. Bondi
J. D. Ferry
R. H. Kelsey
R. M. Levy
H. Mark
J. A. Pask
W. W. Pendleton
R. Simha
S. Zerfoss

RHEOLOGY PROGRESS ABSTRACTS

Theory

The first nine of the following abstracts should have appeared in Vol. XV No. 1 but were omitted on account of the space limitation mentioned on Page 4 of that issue.

VISCOSITY AT THE BOILING POINT.-- THE RHEOCHOR.--J. N. Friend and W. D. Hargreaves, Phil. Mag. 34, 643 (1943).

An expression that would correlate the composition and structure of a liquid with its viscosity has long been sought. Such a function should preferably be additive and independent of temperature. A property similar to Sugden's parachor, $M \cdot \Theta^{1/4} / D$ would fulfill these requirements ($M = M.W.$; $\Theta =$ surface tension; $D =$ density).

Sharma has shown that $\log \Theta$ is proportional to $\log \eta$ in certain cases, and Silverman and Roseveare have expressed such a relationship by

$$\Theta^{\frac{1}{4}} = A/\eta + B$$

wherein A and B are constants depending upon the liquid.

One of the authors of the present paper earlier expressed the following relation for nonassociated liquids:

$$k = \Theta/\eta^{\frac{1}{2}}$$

But again, k may vary with temperature because of liquid structure changes. However, over temperature ranges in which k is constant, $\eta^{\frac{1}{2}}$ may replace $\Theta^{\frac{1}{4}}$ in the parachor to yield what has been termed the "rheochor".

At temperatures near the boiling point, vapor densities become appreciable in relation to liquid densities. The authors have made the observation that replacement of D in the rheochor with $D + 2d$ (D = vapor density) gives constant values for the rheochor, R, over considerable ranges of temperature, that is:

$$R = M \eta^{\frac{1}{6}} / (D + 2d) \quad (\text{empirical})$$

That such an expression is valid for nonassociated substances is supported by data on 20 substances.

Furthermore, it is shown that for monomerics R is a definite fraction of the molar critical volume and is changed only slightly by pressures up to 6000 p.s.i.

Since R is additive, analogous isomers should yield similar values. Evidences supporting this fact are given.

Atomic, group and structural rheochors at the boiling point are also reported.

W. H. MARKWOOD, JR.

LAMINAR FLOW OF OIL.- COAL SUSPENSIONS.--Gradishar, Faith and Hedrick, Trans. Am. Inst. Chem. Eng. 39, 201 (1943).

This paper presents appreciable experimental data to indicate that friction losses in pipe due to laminar flow of suspensions of 200 mesh coal in fuel oil can be predicted from the viscosity and density of the oil used to prepare the suspension, the concentration of coal in the suspension, the concentration at which plastic flow begins and the velocity of flow:

$$\frac{H}{L} = \frac{V \mu_o}{D^2 \rho_o} \cdot \left(\frac{K_o}{K_o - C_v} \right)$$

wherein:

H = Difference in static head between two points in a pipe, ft.

L = Distance along H, feet

V = Mean velocity of flow, ft./sec.

μ_o = Viscosity of oil, lb./ft. sec.

D = Diameter of pipe, feet

ρ_o = Density of oil

K_o = Volume concentration of solids at which flow becomes plastic

C_v = Volume concentration being studied

However, the method employed to determine viscosity, and the use and definition of such terms as "zero fluidity" restrict the data to specialized use. The Saybolt Universal Viscosimeter was used for this work and "zero fluidity" was reached when the concentration became high enough to plug the viscometer and prevent flow through the orifice. This concentration was also defined as the one at which flow changed from viscous to plastic. Such definitions and assumptions are open to question.

Nevertheless, the interesting relationships developed, of which the above is one, are based on theoretical considerations and should prove useful if exploited by somewhat more elegant and generally applicable experimental techniques.

W. H. MARKWOOD, JR.

TECHNICAL APPLICATIONS OF EXTERNAL FRICTION OF SOLIDS.—
Andrew Gemant, J. Applied Phys. 14, 510 (1943).

From among the standard mechanical devices utilizing friction, belts, clutches, and brakes are dealt with. The principle of the device is first explained, followed by a description of the various more frequently used types. The significance of the friction surfaces in terms of the power transmitted is shown, and figures for the friction coefficients of representative materials are given in the form of tables and graphs.

Next the Lanchester type of vibration damper is explained in a manner similar to the previous one.

The following section deals with self-excited vibrations, as caused by friction. One possibility is that the friction acts as a particular kind of driving force, maintaining a vibrational motion. Examples are the whirl of rotating shafts and the so called shaft whipping. Another possibility is the maintenance of natural vibrations by means of a unidirectional motion, a process occurring in many every day examples.

The last paragraph deals with grinding and crushing. In these processes the total work spent against the frictional forces is partly utilized for the subdivision of parts into smaller particles. This is an exception to the general rule according to which frictional work reappears only as heat energy. An outline of the theories for grinding and crushing is presented although they are both rather imperfect. Much work remains to be done along these lines.

AUTHOR'S ABSTRACT

THE VITREOUS STATE: SOME SEMIQUANTITATIVE CONSIDERATIONS.--Maurice L. Huggins, J. Phys. Chem. 47, 502 (1943).

From the structural point of view, the vitreous state may be defined as a state in which the arrangement of the component atoms or molecules possess a permanence similar to that in the crystalline state and a randomness similar to that characteristic of liquids. In general, a substance tends to be a solid if interatomic bonds, strong enough to successfully resist breaking by thermal collisions, form a three-dimensional network. If a regular network structure has a considerably lower energy than any irregular structure, the solid tends to be crystalline. If, however, different arrangements have practically equal energy, it tends to be amorphous.

The above considerations are elaborated upon by considering the equilibrium dependence of the arrangement upon (1) the difference (ΔE) of the energy of the system before and after a small internal structural rearrangement, (2) the magnitude E of the energy hump passed over or the "activation energy," (3) the thermal energy, and (4) the number of subsystems of nearly the same energy. Non-equilibrium behavior is also considered. The rate of change of structural units from one state to another is shown to also depend upon the above four quantities.

Curves are given which illustrate the effects of changing the above variables.

The behavior of a silicate glass is discussed in the light of the above considerations.

D. TELFAIR

NOMOGRAPH FOR APPARENT VISCOSITY OF SULFITE STOCK.--
D. S. Davis, Ind. Eng. Chem., Ind. Ed. 35, 1128 (1943).

A nomograph, for determining the viscosity of sulfite stock is given for convenient solution of the equation:

$$\log \mu = \log 0.095 DC^3 - 0.05U$$

where

μ = apparent viscosity (lb./ft. sec.)

D = internal diameter of pipe (ft.)

C = moisture-free consistency (%)

U = average linear velocity (ft./sec.)

The apparent viscosity μ , from the nomograph, is used in determining apparent Reynolds number from which head losses are calculated from the standard friction factor plot.

N. M. BRANDT

GRAPHICAL ANALYSIS OF TRANSIENT PHENOMENA IN INDUSTRIAL PROCESSES.--K. J. De Juhasz, Instruments 16, 466-472 (1943).

The interrelations among liquid level, rate of influx and rate of efflux for a storage vessel are determined by graphical analysis. It is assumed that a constant rate of influx and efflux exists during a small finite time element, whereby the level is changed by a small finite amount which can be graphically determined. The new level determines a new rate of influx and efflux, which again is assumed to be valid for the next time interval, for which the new change of level is determined. Thus, step by step, the entire duration of the phenomenon can be covered in a number of steps. The procedure is applied to nine examples of flow processes, such as suddenly and gradually changing rates of influx and efflux.

AUTHOR'S SUMMARY

THE IMPORTANCE OF THE FORM OF MACROMOLECULES TO THEIR PHYSICAL PROPERTIES.--H. Staudinger, V.D.C. Bezirksverband Hessen-Nassau, June 24, 1943, Angew. Chem. 56, 251 (1943).

The importance of the form of the macromolecules to the physical properties of macromolecular materials is illustrated by the examples of cellulose, starches and glycogen, polysaccharides with fiber-forming and branched spherical molecules.

The form of the molecule can be determined by viscosity measurements, since materials with spherical molecules follow a different viscosity-rule than do materials with linear molecules. For the former, viscosity number ($Z\eta$) for a homologous polymer series is constant (example glycogen), as required by the Einstein law. With linear polymers, however, the $Z\eta$ -value increases in proportion to the number of chain members (n), i.e., with the degree of polymerization. For polymer-analogous linear-molecular materials, $K_m \cdot R$ is therefor constant; for these, the viscosity law for linear polymers is identical in form with that for spherical particles, as can be demonstrated by experiment.

For a series of important macromolecular products, which appear to be formed of fiber-molecules, for all polyvinyl derivatives (polyvinyl chloride, polystyrene, polymethacrylic esters), and for rubber this viscosity law does not apply. The following relation, from W. Kuhn, R. Houwink and H. Matthes, exists:

$$Z = K_m \cdot n^x$$

It has been proven that unbranched polyesters obey the viscosity rule for fiber molecules, while with those polyesters, for which the viscosity-number varies as a function of chain length as expressed by the formula of Kuhn, branching exists in the molecule and is greater with increasing chain length. It is, therefore, probable that the elongated macromolecules of all synthetic plastics are branched; this applies also for the macromolecules of rubber and gutta percha, for whose branching additional proof exists. On the basis of this result the elasticity of rubber is to be treated on entirely new principles.

H. K. NASON

VISCOSITY AND CONSTITUTION.—G. V. Schulz, Die Chemie 56, 207 (1943).

The viscosities of gases, liquids, and solutions are reviewed.

T. ALFREY

MODEL EXPERIMENTS ON FIBER MOLECULES.—H. A. Stuart. Die Chemie 56, 207 (1943).

In order to study the relation between molecular structure and macroscopic physical properties of high polymers, mixtures of glass chains (to represent polymer molecules) with glass beads (to represent a low molecular weight solvent) were shaken in a shaking machine, and the molecular configurations and modes of packing were observed. The adhesive forces between the chains and beads were varied in magnitude (to represent solvation in the analogous molecular case).

In the case of "free molecules in an indifferent solvent", the chains are curled according to the laws of statistics. "Solvation" causes a reduction in the amount of curling. The limiting case of a fully extended molecule is not observed in nature; this would result in a quadratic dependence of intrinsic viscosity upon molecular weight.

In concentrated systems, the chains tend to become parallelized, so that finally a state is reached where a conglomerate of bundles of parallel chains are observed, along with other less ordered regions.

T. ALFREY

EXPLORING STRESS-STRAIN RELATIONS OF ISOTROPIC PLASTIC SOLIDS.—W. Prager, J. Applied Phys. 15, 1 (1944).

It is pointed out that it is not possible to measure stress-strain relationships at any point in a test specimen, but only certain resultants over the entire specimen. Reliable stress strain relations may be determined only if fairly uniform stress and strain distributions are established in the specimen. The use of a thin-walled tube in torsion and tension is suggested as a means of obtaining uniform distribution. A graphical representation of the state of stress and strain is described. The theories of St. Venant, Levy and Mises, Prandtl and Reuss and of Hencky and Nadai are discussed.

R. H. KELSEY

ON VISCOSITIES AT THE BOILING POINT.--J. Newton Friend and W. D. Hargreaves, Phil. Mag. 35, 57-64 (1944).

Viscosity temperature data are given for the aromatic amines and for cyclohexane and certain of its derivatives. The purpose of the research was to evaluate the rheochor of the amino group and to find its effect on the 6- carbon ring formation. The rheochor was stated as $M (10^3 \eta)^{\frac{1}{3}} (D + 2d)$ where M is the molecular weight and D and d are respectively the density of the liquid and vapor. The following atomic group and structural rheochors were evaluated at the B.P.: C-12.8; (H attached to C)-5.5; OH(Hydroxy 1)-20; O(etheric)-10; Cl-27.3; Br-35.8; I-47.6; NO₂-38.9; C₆H₅ (attached to alkyl)-100.7; (co-ordinate bond)-0.4.

S. ZERFOSS

THERMODYNAMIC ANALYSIS OF THE DEFORMATION OF THE ELASTIC TISSUE FROM THE POINT OF VIEW OF THE STATISTICAL THEORY OF RUBBER ELASTICITY.--E. Wohlisch, H. Weitnauer, W. Grüning and R. Rohrbach, Kolloid-Z. 104, 14 (1943).

The object of this investigation is the elastic tissue in the ligamentum nuchae of the ox, consisting merely of elastin. The reversible deformation and the dependence of elastic tension upon temperature were determined in a dynamometer. A pplication of thermodynamics then yields the variation of heat content, internal energy and entropy with change in length of the sample. Graphical integration gives latent heat and energy of deformation. Up to elongations of 122 % ΔS decreases with increasing degree of deformation. At higher elongations it increases again. An analogous minimum results for ΔU at 87 %. These results are quantitatively similar to those obtained for the muscle tissue where, however, the inversion point for the entropy had previously been found to be at about 43 % elongation. (cf. E. Wohlisch and W. Gruning, Pflugers Arch. 246, 469 (1942). At the inversion point, the heat evolved is calculated to 0.107 cal/g. On the basis of the composition of the tissue the specific heat is estimated to about 0.65 cal/g. This is in agreement with preliminary results obtained for the heat change by direct measurement. From the minimum of the energy curve the heat of crystallization of elastin is estimated to about 0.18cal/g.

ROBERT SIMHA

MECHANISM OF SOLVENT ACTION.--Arthur K. Doolittle, Ind. Eng. Chem. 36, 239-44 (1944).

The purpose of the present paper is to offer a mechanical picture of the action of solvents on macromolecular

substances, such as nitrocellulose, Vinylite resins, etc., in order to afford a better understanding of the solution process, and especially of the reverse of the process, film formation, which is of great industrial importance. Two principal equilibria are simultaneously operative in the solution of resinous substances—solvation-desolvation and aggregation-disaggregation. The rate of desolvation is substantially fixed at constant temperature, but the rate of solvation is a function principally of solvent concentration. The threshold concentration required to initiate the solution process diminished to a constant minimum value as a homologous series of solvents is ascended. This minimum value, called "class threshold concentration," is independent of the diluent and, therefore, serves as an absolute comparison of different classes of solvents for a given resinous substance. The aggregation-disaggregation equilibrium of the solute macro-molecules depends on the solvation-desolvation equilibrium, since disaggregation results when the "active centers" are solvated. In fluid solutions the extent of aggregation of the solute macromolecules increases linearly with decrease in solvent concentration but, as the latter approaches the threshold value, desolvation permits aggregation at multiple points of contact. The result is either gelation or precipitation. In film formation, the high viscosity, resulting from aggregation by means of gradual two- and three-dimensional growth as the resin desolvates during evaporation of the solvent, obstructs the tendency of the macromolecules to unite with one another at the maximum number of points of contact. A rather extended structure results. Plasticization prevents complete desolvation of the resin and, therefore, diminishes the opportunity of the macromolecules to unite with one another at multiple points of contact. In this manner a less rigid structure is provided.

B. I. P. C.

Apparatus and Methods

APPARATUS FOR MEASURING THE CONSISTENCY OF PLASTIC SUSPENSIONS.--(Miss) F. G. van Selms and H. R. Kruyt, *Rec. trav. chim.* 62, 398 (1943); THE INFLUENCE OF TRACES OF WATER ON THE PLASTICITY OF STARCH AND QUARTZ SUSPENSIONS IN ORGANIC MEDIA.--H. R. Kruyt and F. G. van Selms, *ibid.*, 407; THE INFLUENCE OF A THIRD PHASE ON THE RHEOLOGY OF SUSPENSIONS.--H. R. Kruyt and F. G. van Selms, *ibid.*, 415.

A measure of the yield value of a suspension is obtained by determining the velocities with which a steel ball rolls through a tube filled with the material and tilted at different angles. The angle corresponding to zero velocity

is found by extrapolation, and the yield value is taken as proportional to the sine of this angle. The diameters of the ball and the tube are 8.0 and 9.6 mm., respectively.

Suspensions of starch in a mixture of carbon tetrachloride and paraffin (with the same density as that of the particles, to avoid settling) showed yield values which increased markedly with the water content of the starch, up to 14%. With starches of higher water contents, homogeneous suspensions could not be obtained.

Suspensions of quartz powder in a mixture of tetrabromethane and tetrachlorethane (with the same density as that of the particles) also showed yield values which increased markedly with the water content of the quartz, up to about 2%. From 2% to 12% water content, the yield value was constant; above 12%, it decreased somewhat. Suspensions of quartz particles fractionated into different size ranges all gave similar curves for yield value as a function of water content, levelling off above 2% water. The maximum yield values attained were inversely proportional to the average particle sizes (3 to 12 μ).

Suspensions of glass beads in a similar mixture of organic liquids showed the same phenomenon, with the yield value increasing to a maximum value at a water content of about 1%, this value being inversely proportional to the particle size (15 to 30 μ).

The results are interpreted in terms of the cohesion of particles by the flowing together of aqueous films which are supposed to be adsorbed on their hydrophilic surfaces. In order to separate two particles joined in this way, the area of the interface between water and surrounding organic liquid must be increased. By calculating this area, it is possible to predict the shape of the experimental curves for yield value, and also the inverse proportionality to particle size.

As a further confirmation of the hypothesis, it is shown that a suspension of a hydrophobic powder (coal) in water has no yield value if the powder is dry, but develops a high yield value when first moistened with a small amount of liquid (xylene) which is adsorbed on the powder and is immiscible with the dispersion medium.

JOHN D. FERRY

SURVEY OF THE LITERATURE ON PLASTICITY, VISCOSITY AND ALLIED PROPERTIES.--Paul G. Herold and W. J. Smothers, Bull. Am. Ceram. Soc. 23, 184-188 (1944).

A search of the literature and a grouping of the methods used in various industries for measuring plasticity, consistency, and viscosity show that most of the industries have standardized on the measurement of viscosity. Industries such as the ceramic, paint, rubber, and cellulose industries are still attacking the problem of plasticity. Characteristic apparatus used in each industry for measuring rheological properties is described.

85 references.

AUTHOR'S ABSTRACT

Cellulose

CUPRIETHYLENE DIAMINE AS A SOLVENT FOR PRECISE DETERMINATION OF CELLULOSE VISCOSITY.--R. S. Hatch, Ind. Eng. Chem., Anal. Ed. 16, 104-7 (1944).

A modification of the tentative A.C.S. method for the precise determination of cellulose viscosity was developed using a different method of manipulation and cupriethylene diamine as the solvent. The cupriethylene diamine solvent was found to eliminate the use of such extreme caution in avoiding degrading effects of minute quantities of oxygen as was necessary with the solvent cupraminonium hydroxide. With reasonable rapidity of procedure, commercial nitrogen, containing about .05% oxygen, could be used without appreciable effect, and, in addition the cupriethylene diamine solvent, 0.5 molar in copper, was the more efficient dispersing agent. Details concerning equipment, its calibration, procedure and calculations are given in a concise and comprehensible manner. There are two figures, one comparing results by the A.C.S. method and the modified method, and the other showing the relation between "observed seconds" and viscosity in centipoises.

NEILL M. BRANDT

A RAPID CUPRIETHYLENEDIAMINE VISCOSITY METHOD FOR CONTROL WORK.--R. M. Levy, P. Muffat and W. D. Harrison, Paper Trade J. 118, No. 6, 29-31 (1944).

A procedure has been developed for the rapid determination of the disperse viscosity of cellulose. The solvent used is the relatively stable aqueous cupriethylenediamine. The procedure consists of first subjecting the moist pulp

lap to a wet disintegrating process in a disintegrator resembling a continuous beater. The relative advantages of using a moist pulp sample for routine pulp and paper mill viscosity control can be readily appreciated if bleached pulp is being dumped from a conventional type of bleaching engine with a definite narrow range viscosity specification. The rapid method of control as presented was found to be very satisfactory for such purposes. Drying previous to determining the viscosity presents many experimental difficulties, and usually these procedures are expensive as well as tedious, especially if solvents such as acetone are used.

The present method is well adapted to "mass production" control where many samples are handled daily. The entire test, including all operations in duplicate, can be carried out by unskilled workers in approximately twenty minutes with a degree of reproducibility of one per cent or better.

R. M. LEVY

THE NATURE OF THE CUPRIETHYLENEDIAMINE CELLULOSE SOLVENT.--R. M. Levy and P. Muffat, Paper Trade J. 118, No. 5 32-36 (1944).

A comprehensive study of the nature of the cupriamine cellulose solvents is presented, with particular reference to cupriethylenediamine. A study of the factors involved in the various complex reactions of this solvent with cellulose is given, together with a complete summary of previous work on this subject. It is hoped that such a study will materially aid in the future progress of cellulose viscometry. The nature of the solvent as well as the mechanism of reaction of these complex bases is discussed in the light of the experimental results obtained. The investigation of these various copper complexes included light absorption studies, electrometric titrations, and the preparation of some of the solid compounds. An attempt was made to bring theory and experimental observations into agreement and a number of facts are presented that have been apparently overlooked in the past.

R. M. LEVY

DISINTEGRATION AND DEGRADATION OF HIGH MOLECULAR SUBSTANCES IN THE OSCILLATING MILL.--Erwin Steurer, Chem. Tech. 16, No. 1, 1-3 (1943) (In German).

A review is given of the various publications of recent years on the physical and chemical changes which high polymers, such as polystyrene and cellulose, undergo during milling in the oscillating mill (model Vibratom developed by the I.-G. Farbenindustrie). Electron microscopic observation of wood pulp reveals, as the smallest structural units,

so called basic fibrils of average diameter of 150 A. and varying length, the latter depending upon the time of treatment. Fibrils located in the less attacked fiber bundles measure about 2500 A., whereas those in more loosened portions measure 400 A. The last mentioned value is in agreement with the viscosimetrically determined chain length. The lattice structure which is revealed in the x-ray diagram of the cellulose fiber disappears on milling. However, after treatment of the structureless material with water, the diagram of the cellulose hydrate modification is obtained. Observed increases in the heat of solution and the heat of wetting indicate that the latent energy of the milled material has increased. Other physical changes comprise increases in absorptivity, reactivity toward hydrochloric acid, solubility, and swelling ability. The rapid drop in viscosity is indicative in chemical degradation. This is shown by all materials investigated, such as wood pulp, ramie, cotton, methyl- and ethylcellulose, and cellulose acetate, as well as polyvinyl alcohol, polyvinyl acetate, and polystyrene. In all cases, the viscosities, after the initial drop, tend to approach a constant value. The smallest D.P. thus far determined on milled cellulose preparations and derived from osmotic pressure measurements was 44 as compared with an original D.P. of 1780 (Molecular weight 290,000). Degradation to a still lower D.P. appears possible. Neither oxidation, nor heat, nor hydrolysis seems to be responsible for the degrading effect. The fact that the heat of activation of the milling reaction is practically zero, seems to indicate that the degradation consists in the activation and cleavage of the molecules by mechanical action alone. This effect may be compared with the photochemical degradation of cellulose. 18 references.

B. I. P. C.

MACROMOLECULAR COMPOUNDS. (299) THE FIBRILLAR STRUCTURE OF NATURAL AND SYNTHETIC CELLULOSE FIBERS.-- Magda Staudinger, J. prakt. Chem. 160, No. 5-7, 203-16 (1942) (In German).

In contrast to polyoxymethylenes and polyethylene oxide, the D.P. has no influence upon the physical structure of ramie and cotton fibers as revealed by microscopic observation. However, upon mechanical treatment, the structure of such fibers changes, and the fibrillar arrangement is shown more distinctly. Characteristic of the structure of the more degraded cellulose fibers is their separation in the transverse direction into shorter segments which appear after mechanical treatment, particularly after subjecting the fibers to swelling treatments of various kinds. Cotton fibers which had been degraded to a D.P. below 200 failed to show the ballooning phenomenon in such swelling agents.

Synthetic cellulose fibers (such as viscose and cuprammonium rayon) show, in addition to the fibrillar arrangement, a certain amount of granulation (ultramicroscopic observation) in their interior portions which is coarser for the fibers of a high D.P. Considering the fact that cellulose fibers reveal fibrils whatever the treatment and the resolving power of the microscopic device, it is postulated that the finest fibrils are separated by the macromolecules themselves. It is further argued that micelles as such do not exist because any micellar structure should be revealed under the electron microscope. Thus, the micelles, the existence of which is derived from x-ray analysis, must be looked upon as being a state of the solid undisturbed matter, rather than as fundamental structural units. This state is changed and destroyed by mechanical treatment and swelling, and only fibrils remain.

B. I. P. C.

THE MECHANISM OF FLOW OF PAPER STOCK IN PIPES.--John L. Gray and J. A. Van den Akker, Paper Trade J. 118, 17, 29-34 (1944).

Previous work on surface friction of papermaking stock against solid surfaces has been extended to higher velocities and higher consistencies through the use of larger-scale equipment. Two regimes of flow exist--viz., one in which "plug flow" always occurs, and another in which either "instantaneous plug flow" or "equilibrium" flow takes place. For a given pulp the differentiation between these two regimes depends upon the consistency of the pulp; above a critical consistency, and at velocities above a critical value, freshly mixed stock displays the instantaneous type of flow for a period of time depending upon the properties of the stock and the stock and the velocity; after this period of time the flow spontaneously transforms to the equilibrium class of flow which is characterized by a much lower surface friction and associated with a visually different type of motion of the stock. Data relating to the phenomenon are presented, and a theory of the flow of stock in pipes is presented. The implications of this theory with regard to test measurements of friction head loss and the ultimate paper mill use of such test data are discussed.

R. M. LEVY

VISCOSITY MEASUREMENTS WITH VISCOSE SOLUTIONS.--
M. Takei, Kolloid-Z. 106, 30 (1944).

It has been shown that the relative viscosity η_r of polymer solutions as function of concentration c can be reasonably expressed by

$$\eta_r = 1 + \frac{ac}{8} \quad (1)$$

$$\frac{1}{a} = bc + \frac{1}{k} \quad (2)$$

The two parameters b and k represent somehow the size, shape and solvation of the dissolved particles and can be used for an empirical characterization of the system under consideration.

Cellulose xanthate solutions were prepared from alkali cellulose of various degrees of ageing with various amounts of carbon bisulfide and caustic soda respectively, and were ripened for various periods. Then, their relative viscosities were measured at concentrations of 3, 7, 11 and 15% by weight and the values of b and k were computed.

The results indicate:

- (1) With increasing ageing of the alkali cellulose, the solvation of the dispersed xanthate decreases gradually; chemical degradation of the cellulose chain takes place.
- (2) Ripening does not affect noticeably the degree of polymerization of the cellulose; however, the solvation of the dispersed xanthate decreases at high degrees of ripening (low index).
- (3) This latter decrease is more pronounced at low CS₂ concentration and vanishes gradually if sufficient CS₂ (up to 45%) is used.

The results are discussed and it seems that one gets reasonable agreement of all experimental facts by assuming that the original crystallites of the cellulose are highly swollen and penetrated by alkali, but are not completely dispersed in solutions of technical concentrations (7--8% cellulose by weight). Xanthation takes place preferentially in the fringes of these crystallites, where the protruding chains are in a somewhat disordered arrangement.

H. MARK

Clays

CATAPHORESIS OF PURIFIED, FRACTIONATED KAOLINITE PARTICLES.--W. L. Coughanour and J. L. Utter, *J. Am. Ceram. Soc.* 27, 4, 116-20 (1944).

The cataphoretic velocity of three purified, monodisperse fractions of Florida kaolin were determined by the ultramicroscope method. The effect of particle size, kaolinite concentration, and electrolyte concentration on the migration velocity of the particles were observed. Calculations of zeta potential, charge density, and total charge were made for the various systems. It was shown that the zeta potential decreases with increasing particle size and increasing clay concentration. The plots of migration velocity versus electrolyte concentration follow the usual form for such curves, rising rapidly with the first electrolyte additions and flattening out as equilibrium is reached.

J. A. PASK

CASTING CHARACTERISTICS OF CLAYS: I, IMPROVED METHODS FOR DETERMINATION.--R. Russell, Jr. and W. C. Mohr, *J. Am. Ceram. Soc.* 27, 4, 97-113 (1944).

The investigation covered the development of reliable laboratory tests to indicate the relative properties of different clays with the primary consideration of their casting behavior. Methods were given for the determination of casting rate, permeability, water retention, fluidity, thixotropy, organic content, shrinkage, and dry strength. Samples of fast- and slow-casting kaolins and ball clays were used to indicate the utility of the methods employed; results were also given for two composite bodies. In developing the test procedures using the Buchner funnel (vacuum), the effect of the following factors were determined: mixing procedure, ratio of clay to flint, feldspar vs. flint as the nonplastic, electrolyte content, quantity of slip used, specific gravity of slip, slip temperature, aging and vacuum pressure. The optimum procedure for testing clays was then evolved.

J. A. PASK

FUNDAMENTAL STUDY OF CLAY; V. NATURE OF WATER FILM IN PLASTIC CLAY.--F. H. Norton and A. L. Johnson, *J. Am. Ceram. Soc.* 27, 77-80 (1944); cf. *B.I.P.C.* 13:9.

Using a pure monodisperse system of kaolinite particles of known diameter and thickness, it has been possible to calculate with a fair degree of precision the thickness of the water film separating the particles and the variation in thickness of this film for different pressures. The

particles average 0.32 micron in diameter and 0.04 micron in thickness; the water-film thickness averages 0.005 micron or about 60 molecular layers; under conditions of permeable pressing, the thickness of the film varies inversely with the pressure to 600 lbs. per sq. inch, above which distortion of the particles occurs. It has also been possible to calculate with considerable certainty the force acting between two clay particles; it was found to vary between 0.12 and 0.0006 dyne.

B. I. P. C.

FUNDAMENTAL STUDY OF CLAY: VI, FLOW PROPERTIES OF KAOLINITE-WATER SUSPENSIONS.—F. H. Norton, A. L. Johnson and W. G. Lawrence, *J. Am. Ceram. Soc.* 27, 5, 149-64 (1944).

The flow properties of six monodisperse kaolinite fractions (average diameters from 0.28 to 10.0 microns) were studied over a large range of concentration. Also, a general discussion of the flow of suspensions is presented. The author sets up an equation relating viscosity to concentration which holds over a very wide range. The viscosity of a suspension is obtained from the sum of three quantities, namely, those contributed by (1) the liquid, (2) the individual particle, and (3) the collisions of the particles:

$$\eta_s = \eta_l(1 - C) + K_1 C + K_2 C^n$$

where C is proportional to number of particles, K_1 and K_2 depend on size of particles (or groups), shape, and surface activity, and n depends on surface activity but not on mean particle size. This relation was shown to apply to all concentrations up to the point where the particles pack close enough for dilatency to start. The first and second terms dominate at low values of C and the third one is most important at high values.

Thixotropy is found to be due to the sum of two quantities, namely, the contribution of (1) the individual particle and (2) the interference of the particles. The yield point in the kaolinite fractions was found to be proportional to the cube of the concentration. With these relations, the author deems it possible to calculate the viscosity of a casting slip for any change in specific gravity.

J. A. PASK

Glass

SURFACE TENSION AND PERSISTENCE OF CORDS IN GLASS.--
Mellen A. Knight, J. Am. Ceram. Soc. 27, 5, 143-5 (1944).

The action of surface tension in molten glasses is discussed in relation to cord persistence. The author concludes that the only stable form for cords under the influence of interfacial tensions alone is a spherical one. Other factors, such as high viscosities, vary diffusion rates, and mechanical and thermal stirring cause the irregular shapes found in practice. Further studies may show that various other physical properties of molten glasses have greater influences than has surface tension.

J. A. PASK

VISCOSITY OF RECENT CONTAINER GLASS.--Howard A. Robinson and Charles A. Peterson, J. Am. Ceram. Soc. 27, 5, 129-38 (1944).

The paper describes in detail furnaces and equipment to measure the viscosity of glass over the entire range of technical interest. Three different pieces of apparatus have been used to cover the range. The first is a concentric cylinder apparatus to measure viscosities between 100 and 3 million poise. A fiber viscometer was used for the region between 10^{10} and 10^{16} poise. In the region between 10^6 and 10^{10} poise, the empirical softening point furnace can be used to measure that temperature at which viscosity is equal to 4.5×10^7 poise.

The concentric cylinder viscometer's calibration was found to check with that of Lillie's and was not a function of the viscosity. Complete viscosity data as a function of temperature are given for sixteen commercial container glasses. It was shown that the Fulcher equation, $\log \eta = -A + \frac{B}{T - T_0}$, fits the data obtained to within 0.5% for the glasses measured.

J. A. PASK

Metals

THE PROBLEM OF REDUCTION OF VIBRATIONS BY USE OF MATERIALS OF HIGH DAMPING CAPACITY.--Andrew Gemant, J. Applied Phys. 15, 33 (1944).

Dangerous mechanical vibrations in machinery parts that might lead to fatigue and fracture can be reduced to harmless amplitudes by using materials of high internal friction.

This method was suggested by Allen, Kroon and A. L. Kimball.

It appears that such a method is not always practical, because materials of high damping often have low mechanical strength. These two opposite requirements have to be reconciled in some manner.

One way out of this difficulty, as suggested here, may be the use of a material that has low overall damping, (hence, possibly high mechanical strength) but a damping characteristic that rises to high values when certain conditions present in the particular machinery part in question, are fulfilled. One of these conditions may be a high stress, another may be a particular frequency. Both of these conditions are pertinent for dangerous resonant vibrations, and if the damping rises to high values when one of these two conditions prevails, then the material will fulfill its purpose.

It is known that alloys can be made that have a high damping only at high stresses. This particular problem will be dealt with in another publication. On the other hand, damping is known to exhibit peaks occasionally at certain frequencies according to a mechanism discussed by Zener.

A few practical cases are dealt with next, and it is shown how the vibrations can be reduced to reasonably low values by using materials that have one of the two characteristics specified above. Such cases are turbine blade vibrations, both with continuous and partial admission of steam, and crankshaft vibrations in Diesel engines. Another highly important field, not covered in this paper, is airplane designing in which the method would be used to prevent dangerous wing and propeller vibrations that might lead to fracture. Not only alloys, but plastics too, can be used, utilizing the same principle of specifically variable damping.

AUTHOR'S ABSTRACT

EFFECT OF STRAIN RATE UPON PLASTIC FLOW OF STEEL---

C. Zener and J. H. Hollomon, J. Applied Phys. 15, 1, (1944).

A method is described by which the relation between stress and strain in the plastic region is measured, and the dependence of this relation upon the rate of strain may be determined. The equivalence of strain-rate and temperature are demonstrated, and isothermal and adiabatic stress-strain relations are discussed. It is shown that the rate of strain and the temperature are related through a single parameter, so that the behavior of steels at high rates of strain may be determined by tests at moderate rates.

R. H. KELSEY

Petroleum Products

FLOW CHARACTERISTICS OF LUBRICATING GREASES.—A. Beer-bower, L. W. Sproule, J. B. Patberg, and J. C. Zimmer, Paper read at National Lubricating Grease Institute Convention (1942).

In order to characterize the rheological properties of lubricating greases in units of physical and engineering significance the authors developed a rugged, yet quite precise, capillary viscosimeter, which permits flow measurements over a wide range of shear rates (between 10 and 10,000 sec.⁻¹). It consists of a suitable and interchangeable stainless steel capillary through which grease is forced from a cylinder by displacement with a hydraulic fluid delivered from a constant volume displacement Zenith gear pump, which in turn is driven by a 1/3 HP induction motor through a geared constant speed reducer. The grease cylinder and attached capillary are suspended in a constant temperature air bath. Since the displacement of the pump is known for every given speed, the pressure on the hydraulic fluid line is the dependent variable from which to compute the shearing stress and the apparent viscosity of the grease. A set of 8 capillaries of widely varying standardized dimensions is supplied with the instrument. Apparent (plastic) viscosity vs. rate of shear curves are presented covering a wide range of representative greases at temperatures between -40°F. and + 77°F. and rates of shear up to 10,000 sec.⁻¹. At 77°F. the apparent viscosity of most greases approaches a constant value near a rate of shear of 10,000 sec.⁻¹. This constant viscosity is of the same order of magnitude as the viscosity of the base oil without the soap. The effect of the various soaps on this limiting viscosity is, however, still very noticeable. The apparent viscosity of most greases at low rates of shear is between 2 and 5 powers of ten higher than the viscosity of the base oil. It appears possible to correlate grease consumption under various operating conditions as well as "pumpability" with the apparent viscosity at the appropriate rate of shear at the operating temperature. The heretofore used "consistency" measurements, such as penetration and SLL Mobility readings did (of course) not permit such correlation.

A. BONDI

REPORT ON GREASE DROPPING POINT METHODS.—J. C. Zimmer, The Institute Spokesman, 7, 12 (1944), 8, 1 (1944).

In continuation of above studies on the applicability of the new grease viscosimeter (the SOD Pressure Viscosimeter) the author shows that the various grease melting and dropping points, which are still in common usage, are

entirely meaningless as a characterization of the flow behaviour at elevated temperatures. At a constant rate of shear the viscosity of a number of representative greases was determined over a temperature range of from 70 to 350°F. and the data presented on graphs. The majority of these curves present the rather unusual picture of minima and very pronounced maxima on a viscosity vs. temperature curve. These phenomena are of course due to the well known phase transitions in mineral oil/soap systems. It is nevertheless quite astounding to find materials which have a 15 times higher viscosity at 280°F. than at 220°F. (a Ca-Base Grease). The general trend of the curves is about as follows (with rising temperature on a log viscosity vs. linear temperature scale). The viscosity drops in a curve which is concave to the temperature ordinate until (in most cases) it reaches a minimum at the first transition point, increases then more or less steeply to a very well defined maximum which in the case of Al and Ba soaps extends as a long plateau of practically unchanged viscosity over an interval of about 90°F. and then drops off rapidly to very low values. Na-base greases show as many as three such minima and maxima in their viscosity-temperature curve between 70 and 350°F. Future study will reveal whether other greases possess in reality also more than one transition point, only of less clear cut appearance. The available data are still not numerous enough to permit any generalized interpretation. Also, so great a number of composition variables remained undisclosed that the presented data have at best but phenomenological value. The technical importance of an exact understanding of the rheology of lubricating greases is, however, bound to bring forth considerable further activity along these lines which have hitherto been unexplored.

A. BONDI

High Polymers

THE THERMOPLASTIC FLOW OF POLYSTYRENE.--N. M. Foote,
Ind. & Eng. Chem. 36, 244 (1944).

Despite the failure of the Newtonian equation at high viscosities, apparent viscosities from flow data were used because they permitted a correlation of results with the de Guzman equation:

$$\eta = A e^{B/T}$$

where

η = viscosity
A, B = constants
T = absolute temperature

Two types of test methods were used, i.e. the rate of compression of a small disk in a parallel-plate plastometer and the length of flow in capillary tubes.

Parallel-Plate Compression

The Stefan equation for apparent viscosity was used:

$$\eta = \frac{2\pi}{3} \cdot \frac{F h^5}{v^2 \left[-\frac{dh}{dt} \right]} \cdot \left(\frac{2.54}{1000} \right)^4$$

where

η = viscosity, poises
V = volume of test piece, cc
F = force of compression, dynes
h = height, mils
 $-\frac{dh}{dt}$ = rate of decrease in height, mils/sec.

A nomogram for handling the Stefan equation was presented.

Capillary Flow Test

A three capillary split mold was used with 0.24, 0.16, and 0.08 cm diameters. Measurement of three different lengths of flow was possible for each pressure and temperature. The following equation was used to calculate apparent viscosity.

$$\eta = \frac{t P R^2}{4 L^2}$$

where

η = viscosity, poises
t = time, seconds
P = pressure, dynes/sq. cm.
R = radius, cm.
L = length, inches

A nomogram for handling this equation was also given.

Discussion

Departures from linearity in the plot of $\log \eta$ vs.

reciprocal absolute temperature were found, indicating changes in material or in type of flow.

Capillary tests on polystyrene were subject to many unexplainable discrepancies, even in the lengths of travel in the same test. Different viscosities were found at the same temperature when different loads were applied. The advantage of the capillary test was stated in the fact that a comparison of flow at approximately equal work input over a range of temperature was available.

An explanation of the lowered apparent viscosity in tests involving more work or higher rates of shear may be in the non-equilibrium distributions of the total energy supplied so that some molecules involved in the flow are at "effectively higher temperatures". Along with this explanation are various theories such as "yield value", "structural viscosity", "sigma phenomena" elastic extension, statistical probability of flow, and compressibility of the material.

For low rates of shear, the author finds that polystyrene shows an activation energy of 40 kg-cal. At 21 pounds per square inch the relation is:

$$\ln \eta = \frac{40,000}{RT} - 30$$

where

η = apparent viscosity in poises
 R = gas constant in calories
 T = absolute temperature

W. W. PENDLETON

DEPENDENCE OF VISCOSITY UPON CONCENTRATION AND ITS SIGNIFICANCE FOR THE SHAPE OF DISSOLVED HIGHPOLYMER MOLECULES.--H. L. Bredee and J. de Booy, Kolloid-Z. 99, 171 (1942).

The relation of the viscosity of a highpolymer solution to the concentration, C , can be expressed over a fairly wide range of concentration by the empirical formula:

$$V_0 C = V_0' C (1 + V_0' C)^{\alpha - 1}$$

This expression, which is supported by a fairly large experimental material, contains two constants: one is the voluminosity of the material at infinite dilution (V_0) which expresses the degree of solvation of the polymer; the other (α) expresses the deviation of the average particle

from the spherical shape. The voluminosity is connected with size and shape of the dispersed molecules in extremely dilute solution; the shape factor, α , on the other hand, refers to the behavior of the system at somewhat higher concentrations.

The increase of viscosity at higher concentration depends upon various contributions, namely:

1. The intermolecular forces between the dissolved particles.
2. The interaction between the dissolved particles and the solvent.
3. An eventual electrical interaction between the particles of the solute, and
4. Interaction of hydrodynamic character.

In order to support the different influences, it seems advisable to carry out viscosity measurements in the higher concentration range in various solvents and at various temperatures. In this article, a number of such measurements is discussed and it is attempted to connect their results with the chemical nature of the polymer.

The expressions of Takei and Erbring, Eilers and Hermans on the dependence of viscosity upon concentration are discussed.

H. MARK

THE RHEOLOGICAL BEHAVIOR OF POLYVINYLCHLORIDE PASTES.--
H. Saechtling, *Kunststoffe* 33, 127 (1943).

Polyvinylchloride is finely powdered and intimately mixed with certain plasticizers, such as phthalates and phosphates. Eventually also fillers can be added.

As long as the system is kept cool, one obtains thick pastes which can easily be brought upon fabrics, paper or other bases. Upon heating to about 150°C, the pastes undergo a ripening process, which converts them into a tough and flexible film which adheres strongly to the underlying material.

The rheological properties of these pastes have been studied with the aid of flow curves taken in a band viscometer. This instrument allows the determination of the viscosity as a function of the composition of the paste, of temperature and of the shearing force. It also permits the discovery of the presence of a yield value if there

is any.

It was found that most pastes show a definite yield value and a distinct dependence of the viscosity upon the shearing force in the sense that at higher shearing forces the viscosity decreases. The same thing is true for increasing temperature and increasing amount of plasticizer. The investigated pastes contained 50 to 70% polyvinylchloride and from 30 to 50% plasticizer, and exhibited viscosities between about 100 and 4000 poises. The "heated" values were between .05 and .5 lbs. per square inch.

H. MARK

THE RELATIONSHIP BETWEEN VISCOSITY AND PARTICLE SIZE, PARTICULARLY IN HIGH POLYMER SOLUTIONS.--Wo. Ostwald, Kolloid-Z. 106, 1 (1944).

All available experimental evidence points to the fact that the intrinsic viscosity of solutions, particularly of highpolymer solutions, is a rather complicated function of the size and shape of the dispersed particles.

These particles may be single macromolecules or aggregates of them, depending upon the nature of the polymer and the solvent, the concentration of the solution, the temperature, etc. The most general relationship seems to be an S-S-shaped curve, which has been observed with polymethacrylic esters in acetone and chloroform, with cellulose acetates in acetone and with a number of other systems of relatively polar character. More homopolar systems, such as rubber, polystyrene, polyvinyl derivatives in toluene, benzene, dioxane or tetrahydrofuran, lead to somewhat simpler S-shaped curves between intrinsic viscosity and molecular weight or to curves which are definitely concave towards the abscissae.

The linear Staudinger equation holds only with very limited accuracy over a limited range of molecular weights and is definitely disproved as a general relationship by the present state of experimental evidence. The S- or S-S-shape of the viscosity-molecular weight curves is not surprising if one considers the complicated character of the systems under consideration, particularly the irregular shape of the dissolved particles and their tendency for solvation.

H. MARK

Rubber

VISCOSITY AND STRUCTURE OF PURE HYDROCARBONS.--Henry R. Kierstead and John Turkevich, J. Chem. Phys. 12, 1 (1944).

The authors discuss Arrhenius' equation $\Phi = A \exp(-E/kT)$ for fluidity Φ , and calculate A and E for 44 pure hydrocarbons from published data. The equation is said to hold with fair accuracy, but that errors in temperature measurement introduce large deviations in the calculated values. The effects of structure on A and E are described, particularly the effects of chain length, branching, unsaturation and side chains.

R. H. KELSEY

SYMPOSIUM ON THE THEORY OF LONG-RANGE ELASTICITY

American Chemical Society Meeting

April 3-6, 1944

I - INTRODUCTION. M. L. Huggins, Eastman Kodak Company, Rochester, New York.

Equations derived from theory were presented for the calculation of Young's modulus of elasticity of rubber-like materials.

II - STATISTICAL THERMODYNAMICS OF RUBBER. Frederick T. Wall, University of Illinois, Urbana, Illinois.

"A statistical theory of rubber elasticity is developed on the basis of the following postulates. First, it is assumed that free rubber molecules are flexible long chains capable of assuming many shapes without change in energy and subject to a Gaussian distribution of length components. Secondly, it is supposed that the macroscopic dimensions of a piece of rubber are proportional to the corresponding root mean square length components of the molecules. Finally, it is assumed that the volume of rubber does not change as it is stretched.

"The theoretical calculations are carried out by first determining the most probable distribution of molecular lengths compatible with a given macroscopic condition. After that the probability that an assembly of molecules have a given distribution is evaluated. The entropy of deformation is then obtained from those probabilities after which a theoretical equation of state is readily derived.

"For a simple stretch the equation of state obtained is

$$f = \frac{NkT}{l_0} (\alpha - 1/\alpha^2)$$

where f is the force of elongation, N the number of independent molecular segments, l_0 the length of the unstretched rubber, $\alpha (l/l_0)$ the ratio of the actual length to the unstretched length, k equals Boltzmann's constant, and T the absolute temperature. For rubber subject to pure shear of amount γ it is found that the shearing moment is given by

$$\tau = NkT\gamma$$

thus showing that rubber should obey Hooke's law with respect to shear."

AUTHOR'S ABSTRACT

III - MOLECULAR WEIGHT IN THE NETWORK THEORY OF RUBBER.

Hubert M. James, Radiation Laboratory, Massachusetts, Institute of Technology, Cambridge, Massachusetts.

"The essential physical ideas in the theory of rubber, considered as a coherent network of flexible molecules, will be emphasized, and the relation of this theory to others which provide no picture of the structure of rubber will be pointed out. The question of the molecular weight in soft vulcanized rubber -- in the network theory, the mean molecular weight of chain segments between junctions in the network -- will be discussed. An expression for the forces exerted by a network of arbitrary structure will be given. The relation between the magnitude of these forces and the mean molecular weight of the segments, on which estimates of molecular weight are based, depends on the distribution of mean fractional extensions of the segments in the unstretched state of the network. In making estimates of molecular weight it is commonly assumed, in effect, that the distribution of segment extensions is that which would be produced by thermal agitation of the isolated segments. Consideration of a simple example indicates that this distribution is not to be expected; reliable estimates of molecular weights should be based instead on a theory of network formation."

AUTHOR'S ABSTRACT

IV - NETWORK STRUCTURE AND PHYSICAL PROPERTIES OF VULCANIZED RUBBER. Paul J. Flory, Goodyear Research Laboratory, Akron, Ohio.

"The basic structural element of the network structure produced by vulcanization, or cross-linking of rubber molecules, is the chain between cross-linkages. The reaction of the network to deformation may be analyzed by considering the constraints imposed upon four chains which meet at a cross-linkage. These constraints arise from the displacements of the four 'nearest neighbor' cross-linkages, which, in turn, are a consequence of the deformation. The results for extension of rubber are identical with those of Wall and Treloar by other methods.

"Swelling of rubber in solvents is accompanied by two opposing entropy effects: (1) increase in entropy due to mixing of rubber chains and solvent, and (2) decrease in entropy due to deformation (expansion) of the network. Equations can be derived which represent the dependence of equilibrium swelling on number of cross-linkages, effect of swelling on elastic modulus, and effect of extension on equilibrium swelling. Inverse proportionality between the modulus of elasticity (unswollen) and the five-thirds power of the equilibrium volume swelling ratio is predicted.

"The ends of the original rubber molecules produce network 'defects' in the vulcanizate. This effect of finite molecular weight on physical properties can be introduced into the various equations.

"A number of the predictions of theory are supported by experiment."

AUTHOR'S ABSTRACT

STRESS-STRAIN DATA FOR VULCANIZED RUBBER UNDER VARIOUS TYPES OF DEFORMATION.--L. R. G. Treloar, Trans. Farad. Soc. 40, 59 (1944).

Four types of strain were considered, namely: 2-dimensional extension of a sheet, simple elongation, simple shear, elongation and shear normally to the direction of elongation. The two types of rubber considered were a sample containing 8 % S and a latex rubber. For extensions not exceeding 300-400 %, the statistical theory is in general agreement with the experimental findings for the first sample. Discrepancies are found in the cases of shear and elongation. The data for latex rubber are in less good agreement with the theoretical predictions. Hysteresis effects indicate that here the assumption of

an ideal elastic network is less appropriate, probably because of the more pronounced tendency for crystallization.

ROBERT SIMHA

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Eugene C. Bingham

Arranged Alphabetically by Authors

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LETTERS TO THE EDITOR

Absolute Viscosity of Water

The following is a part of a preliminary report by J. R. Coe, Jr., and T. B. Godfrey, of the National Bureau of Standards, which will be published in full in Journal of Applied Physics.

Sir: "Absolute viscosity of water at 20°C: 1.002 centipoise".

Viscosity of water relative to its viscosity at 20°C,
, including for comparison, values obtained by others:

Temp. °C	<u>Compilers' Values</u>		
	Bingham	Dorsey	Cragoe
	1918 (1)	1929 (2)	1943 (3)
-9.30	2.571	---	2.528
-8.48	2.479	---	2.445
-7.23	2.350	---	2.326
-6.20	2.252	---	2.234
-4.70	2.121	---	2.110
-2.10	1.922	---	1.919
0	1.7832	1.7784	1.7829
5	1.5112	1.5056	1.5140
10	1.3012	1.2984	1.3035
15	1.1347	1.1348	1.1358
20	1.0000	1.0000	1.0000
25	.8893	0.8872	0.8885
30	.7967	.7933	.7959
40	.6527	.6480	.6518
50	.5457	.5445	.5460
60	.4665	.4658	.4659

Experimenters' Values

Temp.	Hosking	White & Twining	Geddes	Coe & Godfrey	Swindells
0C	1909 (4)	1913 (5)	1933 (6)	1941 (7)	1942 (8)
-9.30	---	2.531			
-8.48	---	2.440			
-7.23	---	2.324			
-6.20	---	2.234			
-4.70	---	2.106			
-2.10	---	1.916			
0	1.7821	---			
5	1.5129	---			
10	1.3027	---			
15	1.1352	---			
20	1.000	(1.0000)	1.0000	1.0000	1.0000
25	0.8873	(0.8885)	0.8885	0.8885	0.8885
30	.7952	---	.7947	.7960	---
40	.6531	---	.6519	.6518	.6513
50	.5467	---	---	---	.5456
60	.4662	---	.4660	---	.4657

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J. R. COE, JR.
T. B. GODFREY

Comments on data by Coe and Godfrey

Sir: Many capillary viscometers of the Ostwald type, with a constant head of liquid, are calibrated with water using accepted values of viscosity at various temperatures. Measurements of the viscosity of other liquids can be obtained from data on the density of the liquid and the time of flow which can be measured with very high precision as Grinnel Jones has done using an electric eye. For such purposes, accurate relative values for water are very important. The very precise measurements of Coe and Godfrey are probably of the most practical value from this standpoint.

Respectfully,

LYMAN J. BRIGGS, Director
NATIONAL BUREAU OF STANDARDS

APPLICATION

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

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

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

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

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