

ΠΑΥΤΑ



ΣΕΙ

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BIBLIOGRAPHY OF BOOKS ON VISCOSITY, VISCOMETRY AND RHEOLOGY

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THIS bibliography contains in chronological order books, pamphlets, and periodicals which deal with general principles or with more than one type of material. The books include, as a rule, a bibliography of articles dealing with subjects of limited scope. The only article recorded here is that of Poiseuille (1) which was later translated into English (20) and appeared in book form.

Symposia are recorded under the year of publication. The language of the publication is indicated where the title is translated.

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- (21) Philippoff, W., *Die Viskosität der Kolloide*. Steinkopff, Dresden, 1942.
- (22) *Symposium on the Viscosity of Liquids and Colloidal Solutions* (Russian). Vol. I, Soviet Academy of Sciences, 1941.
- (23) Reiner, Markus, *Ten Lectures on Theoretical Rheology*. Rubin Mass, Jerusalem; Norman, New York, 1943.
- (24) *Symposium on the Viscosity of Liquids and Colloidal Solutions* (Russian). Vol. II, Soviet Academy of Sciences, 1944.
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SOCIETY OF RHEOLOGY

1945 FALL MEETING

THE 1945 annual meeting of the Society of Rheology was held October 26th and 27th at the Hotel Pennsylvania, New York City. Abstracts of the papers presented at the meeting are given below.

ANNUAL MEETING ABSTRACTS

ANOMALIES OF FLOW.

EUGENE C. BINGHAM.

Anomalies of flow have been the *bêtes noires* of rheology, nevertheless are intriguing to the investigator. Changing the rate of shear, the pressure, the temperature, the composition or the concentration has offered opportunities to discover not only regularities, and therefore natural laws, but also inconsistencies which have led on to new researches.

The field of colloidal solutions yielded many perplexities; yet when these anomalies are cleared away it promises to be more fertile than those more easily tilled. It has been shown that the fluidities of many protein solutions are linear, but gelatin, egg albumin, pseudoglobulin, euglobulin, sodium caseinogenate, and glycogen seemed to form a goodly number of exceptions. By starting with the pure solvent, the fluidity is now found to be linear in each case until the drops of the emulsoid interfere with each other. Another linear curve appears when the deformation of the drops of the disperse phase enters. This explanation of this type of anomaly of flow is at once apparent when plotting fluidities, yet it could be made only with difficulty, if at all, in plotting viscosities.

THE RATE PROCESS THEORY OF FLOW, APPLIED TO VISCOUS LIQUIDS.

A. BONDI.

The magnification of the effects of chemical constitution on viscosity and its pressure and temperature functions in the case of more viscous fluids makes it advantageous to calculate their characteristic parameters. The connection between energies, entropy, and volume increase of activation and spatial configuration as well as hydrogen bonds, etc., thus becomes very clearly discernible. These relations are illustrated by numerous examples. An interpretation is presented of the energy of hole formation, ΔH^h , in terms of the Lennard-Jones theory of the liquid state and of the energy and entropy of activation for motion into the hole in terms of activation of internal vibrations.

THE EFFECT OF PLASTICIZERS ON THE VISCOELASTIC PROPERTIES OF VINYL RESINS.

CAPT. WILLIAM AIKEN, TURNER ALFREY, JR., ARTHUR JANSSEN, and H. MARK.

Tensile creep studies were made on plasticized vinyl resins, the following conditions being widely varied: nature of resin; nature of plasticizer; concentration of plasticizer; and temperature. The present paper is primarily concerned with the properties of vinyl chloride resins plasticized with tricresyl phosphate (TCP), trioctyl phosphate (TOP), and dioctyl phthalate (DOP).

1. Creep curves for TCP and TOP formulations are different in shape. The "5-second stiffness" of a plasticized formulation thus gives an incomplete picture of its flexibility. A TOP sample and a TCP sample with the same 5-second stiffness are actually quite different both in their very quick response and their long-time response to stresses. In a test lasting only 0.1 second, the TOP sample may be several times as flexible as the TCP; in a test of long duration, the TCP sample will creep more than the TOP. This indicates that increases in the quick flexibility of a resin are not necessarily accompanied by too great an increase in long-time creep. It also indicates the desirability of carrying out complete creep (or relaxation) studies in the evaluation of a series of plasticizers.

2. The effects of temperature observed in this study are entirely consistent with those previously reported by Clash and Berg, which can be summarized in the statement: "at high temperatures TOP plasticized samples are stiffer than TCP samples; at low temperatures TCP plasticized samples are stiffer." This statement, however, should be amplified to the following: "At high temperatures and/or long times of stress application TOP samples are stiffer than TCP samples; at low temperatures and/or short times TCP samples are stiffer."

3. Dioctyl phthalate is intermediate in character between tricresyl phosphate and trioctyl phosphate. This is again in agreement with the results of Clash and Berg.

4. Mixtures of tricresyl phosphate and trioctyl phosphate show behavior which is "intermediate" between the behaviors of the individual plasticizers. In certain ranges of temperature and time scale, however, the mixture imparts greater flexibility to the film than either individual plasticizer.

5. In the range of stresses studied, the plasticized films obey the Boltzmann Superposition Principle; recovery curves are identical with creep curves.

6. With a fixed plasticizer, the stiffness of a plasticized vinyl chloride-vinyl acetate resin increases both with increase in molecular weight and with increase in vinyl chloride content.

STRESS-STRAIN CURVES OF VISCOELASTIC MATERIALS.

TURNER ALFREY, JR.

The stress-strain curve of a material which exhibits stress relaxation and creep has a much less simple significance than that of an ideal elastic material. It is well known, for example, that such curves are dependent upon the rate of testing. In this paper stress-strain curves at constant rate of loading and at constant rate of elongation are analyzed for viscoelastic materials which obey the Boltzmann Superposition Principle.

1. The stress-strain curve at constant rate of elongation can be calculated from the distribution of relaxation times. For a viscoelastic material the curve will exhibit a curvature which persists to zero stress, which makes it impossible to determine any well-defined "initial slope."

2. The stress-strain curve at constant rate of loading can be calculated from the distribution of retardation times. Here also curvature, as well as higher derivatives, persists to zero stress.

3. If the stress-strain curve is known for one rate of loading or rate of elongation, curves for other rates can be calculated by a simple procedure.

4. In each case, there is a close correlation between curvature of the stress-strain curve and the sensitivity to testing speed.

5. Stress-strain curves at constant rate of elongation are more sharply curved than those at constant rate of loading. If rates are adjusted to make the early parts of the curves coincide, the curve of constant rate of elongation will fall below the other at higher stresses.

6. Experimental results are presented which bear out these theoretical predictions.

DILUTE SOLUTION VISCOSITY OF HETEROGENEOUS HIGH POLYMERS.

R. S. SPENCER and R. F. BOYER.

The effect of heterogeneity on the dilute solution viscosity-concentration relationship for a high polymer is shown, both theoretically and experimentally, to consist of an increasing of the slope of the reduced viscosity-concentration line. A heterogeneity coefficient is defined as the ratio of the slope of the reduced viscosity-concentration line to the slope of the same line for a corresponding homogeneous polymer having an identical intrinsic viscosity. Expressions are derived for the heterogeneity coefficient for the general case and for several special cases, namely, mixtures of two similar polymer fractions, Schulz's molecular weight distribution, and a normal number distribution. It is shown that the constants in the intrinsic viscosity-molecular weight relationship may be calculated from the heterogeneity coefficient and other constants of a polymer mixture, provided the form of the distribution function of the mixture is known. These viscosity constants are calculated for a sample of polystyrene in toluene and fair agreement obtained with the observed values.

NEW DEVELOPMENTS IN EMPIRICAL FLOW METHODS FOR PLASTICS.

ROBERT BURNS.

An informal discussion of the present trend of thought in the utilization of empirical flow methods. Engineering motives underlying certain recent changes are explained, including revisions of Deformation Under Load ASTM:D621 (parallel plates at elevated service temperatures), Heat Distortion Temperature ASTM:D648 (centrally loaded simple beam), Flow Properties of Thermoplastic Molding Materials ASTM:D569 (single capillary), Rockwell Hardness ASTM:D785 (ball indentation) and other standard tests, as well as a few which are not standard. The need is emphasized for an improved understanding of fundamentals, leading eventually to fewer but better tests.

THEORY AND APPLICATION OF THE PARALLEL PLATE PLASTOMETER.

G. J. DIENES and H. F. KLEMM.

A method has been established for the measurement of the viscosity of high polymers at low rates of shear in the range 10^4 to 10^9 poises using a parallel plate plastometer. This is based on a mathematical criterion for separating the viscous portion of the deformation from the "elastic" and "delayed elastic" components. Experimentally, the plate separation is measured at a given temperature as a function of time. The theory furnishes a relation, which is also the criterion for predominantly viscous deformation, between viscosity, plate separation, applied load, and time. This relation, a modified form of Stefan's equation, is used for calculating the viscosity from the experimentally observed quantities. The method has been applied to polyethylene and vinyl chloride-acetate resin compounds. The viscosity-temperature behavior of these materials is shown to be simple over the temperature range studied, that is, log viscosity varies linearly with the reciprocal of the absolute temperature. Data are presented which show that polyethylene resins and polyethylene resin-paraffin wax mixtures follow Flory's relation, that is, log viscosity varies linearly with the square root of the weight average molecular weight. Accordingly, the parallel plate plastometer offers promising possibilities for the empirical determination of the weight average molecular weight of these materials. Data are also presented on plasticized vinyl chloride-acetate resin systems which point to a close parallel between the effects of increasing temperature and increasing plasticizer concentration.

VISCOSITY OF CELLULOSE ACETATE SOLUTIONS.

W. BADGLEY and H. MARK.

An investigation has been made to determine the nature of the relationship of molecular weight to intrinsic viscosity for the systems cellulose acetate-acetone and cellulose acetate-methyl cellulose. Measurements have been made on representative fractions resulting from a careful fractionation of the commercial acetate. The molecular weight range studied extended from 31,000 to 360,000. The results indicate that the Staudinger equation and its more recent modification are inadequate to describe the molecular weight-intrinsic viscosity relation over the entire molecular weight range. An empirical expression of the form:

$$[\eta] = KM^a - K'M^{2a}$$

is suggested to represent the data fairly well.

Some evidence concerning the homogeneity of the fractions has been obtained from a consideration of number average and weight average molecular weights, the latter being obtained from light scattering measurements. Calculation of axial ratios from the recently developed theory of Simha indicates that the molecules curl up considerably as the molecular weight increases.

THE VISCOSITY OF THREE BURMA OILS AT HIGH PRESSURES.

R. B. DOW, F. S. VEITH, and C. E. FINK.

The present study concludes the measurements that were undertaken a few years ago on the viscosity-pressure-temperature characteristics of

several foreign lubricating oils over a pressure range of 50,000 p.s.i. The earlier studies on Russian and Rumanian oils (*J. Inst. Pet.*, 27, 301, 1941) showed that the pressure coefficient of viscosity:

$$a = 1/P[\log \eta/\log \eta_0 - 1]$$

at 100°F. was in the range between 4.10 and 5.11×10^{-5} 1/p.s.i. The pressure coefficients for the three Burma oils at the same temperature are 5.09, 4.65, and 4.31×10^{-5} , respectively. At a pressure of 10,000 p.s.i. the mean temperature coefficient of viscosity between 100° and 130°F. was between 1970 and 2710×10^{-5} 1/°F., as against 1810, 2340, and 2580×10^{-5} for the Burma oils under the same conditions. Although the behavior of the Russian, Rumanian, and Burma oils appears to be similar under pressure, inspection data taken at atmospheric pressure reveal that the paraffinic, naphthenic, and aromatic percentages are substantially different.

USE OF THE ANILINE POINT IN PREDICTING THE PRESSURE COEFFICIENT OF VISCOSITY OF HYDROCARBON OILS

R. B. DOW and C. E. FINK.

Although the aniline point (ASTM D611-41T Tentative Method) shows little or no correlation with the coefficient of viscosity of oils at atmospheric pressure, it can be used to predict the pressure coefficient of viscosity over a pressure range up to 20,000 or 30,000 p.s.i. From viscosity-pressure-temperature data published previously for lubricating oils, it has been possible to compute the pressure coefficient of viscosity (*cf.* preceding abstract) for 24 oils where a linear relationship exists between viscosity and pressure over a range of 20,000 p.s.i. or higher. A graphic plot of these coefficients at 100°F. versus aniline points in °C. shows that the coefficient increases as the aniline point decreases, in a way that can be represented by a second degree curve. A plot of aniline function (RI 3721, U. S. Bur. Mines, p. 7, 1943) against pressure coefficient of viscosity shows a similar relationship but the correlation is poorer. In extending the analysis to pure hydrocarbons, the viscosity of which has been measured under pressure by Bridgman and Dow, it was found that no satisfactory correlation exists between the aniline point and the pressure coefficient of viscosity at various pressures at 30°C. While the aniline function for these liquids also appears to be unrelated to the pressure coefficient at 7110 p.s.i., at higher pressures (28,440 to 56,880 p.s.i.) it shows, for the normal paraffins, a good correlation, increasing with the pressure coefficient. The difference in behavior of the aniline function for pure, normal hydrocarbons and lubricating oils is not readily explained, but it would appear that the aniline function is of more fundamental importance than the aniline point in regard to considerations of structure of liquid hydrocarbons.

STRAIN HARDENING UNDER COMBINED STRESSES.

W. PRAGER.

Experimental investigations of the strain hardening of metals under combined stresses are usually restricted to cases in which (1) the directions of the principal stresses remain fixed with respect to the material, and (2) the ratios of the magnitudes of the principal stresses are not varied during any one test. If an isotropic material is tested in this manner, the principal axes of stress and strain must coincide, and it is to be expected that the ratios of the principal

strains will remain constant during each test. Moreover, if the material has identical stress-strain diagrams in pure tension and in pure compression, a reversal of the signs of all strains may generally be expected to correspond to a reversal of the signs of all stresses. The paper is concerned with incompressible plastic materials which possess all these properties and are tested in the manner defined above. The most general type of stress-strain relation which can arise under these circumstances is established, and various special cases of this relation are discussed.

AN INTERPRETATION OF SOME USEFUL PROPERTIES OF TEXTILES IN TERMS OF A MOLECULAR MODEL. (MECHANICAL PROPERTIES OF TEXTILES. II.)

GEORGE HALSEY and HENRY EYRING.

Various commercially important properties of textiles, such as "toughness," "resiliency," and "elasticity," are expressed in terms of the results of standard tests as interpreted in terms of the molecular model presented in an earlier paper. The stress-strain curves of common textile materials are fitted by this method under varying conditions, and show its adequacy.

The rate of loading as a factor in the results of tests is discussed, and prediction of high rate experiments is presented.

A VISCOMETER FOR MEASUREMENTS DURING THIXOTROPIC RECOVERY; RESULTS WITH A COMPOUNDED LATEX.

M. MOONEY.

A viscometer is described for measuring the viscosity of a liquid immediately after an abrupt reduction of the shearing stress to a very low value. A hollow cylinder on a torsion suspension is immersed in the liquid contained in a narrow annular channel. The inner wall of the channel is rotatable with respect to the outer wall, and by this rotation the liquid is stirred or sheared. After the stirring is stopped, the viscosity is measured by photographically recording the rotation of the hollow cylinder, driven by a nearly constant torque applied through the torsion suspension.

Measurements were made on a commercial compounded latex containing 47.5% total solids. Immediately after stirring, the latex is a Newtonian liquid with a viscosity of 0.05 poise. Thereafter, the viscosity increases at an initial rate and to an ultimate value, both of which decrease as the shearing stress for measuring the viscosity is increased. The steady viscosity is attained approximately in 10 seconds. The observed extremes, in steady viscosity, were 11 and 0.5 poises, corresponding to the shearing stresses of 1.3 and 10.7 dynes per cm.²

The experimental data are fitted approximately by theoretical curves based on these assumptions: All aggregates of solid particles are broken up by the stirring. During subsequent thixotropic recovery, loose aggregates are formed which contain considerable trapped water. The rate of aggregation follows Smoluchowski's theory of slow coagulation; but both the coagulation rate constant and the per cent volume of water in the coagulates vary with the applied shearing stress. The relative viscosity of the suspension of aggregates follows an empirical law based on Eilers' data on aqueous suspensions of bitumen spheres.

RHEOLOGY PROGRESS ABSTRACTS

APPARATUS AND METHODS

FACTORS AFFECTING RESULTS OBTAINED WITH THE MOONEY VISCOMETER.

ROLLA H. TAYLOR, *India Rubber World*, **112**, 5, 582 (1945).

Errors in the measurement of the viscosity of synthetic rubbers resulting from improper operation of the Mooney viscometer are discussed. Cleanliness is said to be an important factor; suitable cleaning methods are described, as well as methods of keeping rubber out of the bearings of the instrument. Calibration is discussed; it is stated that, although calibration may be made at any point on the instrument, calibration will not compensate for rubber in rotor bearings. In discussing the effect of dimensions on readings from instrument to instrument, it is pointed out that, if dimensions are taken into account, viscosities obtained agree very well with calculated values. Proper adjustment of platens, die closures, and plungers is described, as well as the preparation of test pieces. It is asserted that, if proper precautions are taken, readings on a large number of instruments will agree within one point, whereas, under improper handling, readings may vary more than twelve points.

R. H. KELSEY

A HIGH TEMPERATURE, HIGH PRESSURE RHEOMETER FOR PLASTICS.

H. K. NASON, *J. Applied Phys.*, **16**, 338 (1945).

The need for a high-temperature, high-pressure instrument for evaluating the flow properties of thermoplastic materials is discussed. Inadequacy of existing plastometers for such application and the similarity of the problem to that of rubber are pointed out. A new rheometer, of the Bingham type (gas-actuated extruder) designed to be operated in a high-temperature oil bath was found to be suitable. Shearing stresses and rates of shear may be calculated in absolute units, but this refinement is said to yield no additional information over the extrusion rate-pressure data. The limitations of the instrument are its slowness, the necessity of cleaning before each test, and its impracticality for thermosetting materials. Data are given for several plastic materials.

R. H. KELSEY

A RAPID OPTICAL METHOD FOR ESTIMATING THE SPECIFIC SURFACE OF POWDERS.

E. SHARRATT, E. H. S. VAN SOMEREN, and E. C. ROLLASON, *J. Soc. Chem. Ind.*, **64**, 73-5 (1945).

A method of estimating surface areas from an observation of the optical density of their dilute suspensions has been examined. This is a very rapid method adapted to routine testing, and does not involve a knowledge of the specific gravity of the powder under test. The method gives satisfactory results directly with opaque powders lying within the 2.5-150 μ range principally. Transparent powders give low results, but the method is of some value as a means of comparison. It is also of value as a rapid means of estimating

the dispersing powder of different deflocculants for a given powder. 11 references.

B.I.P.C.

AN AUTOMATIC HEAT DISTORTION RECORDER FOR PLASTICS.

GEORGE A. HEIRHOLZER and R. F. BOYER, *ASTM Bull.*, No. 134, 37-41 (1945).

An instrument in use at the Dow Chemical Co., Midland, Michigan, is described. It is automatic and plots the deformation-temperature behavior in approximately the same time now required for giving only one point on the deformation curve with the A.S.T.M. instrument. Typical results obtained are illustrated and hints on operation are given.

B.I.P.C.

PORTLAND CEMENT DISPERSION BY ADSORPTION OF CALCIUM LIGNOSULFONATE.

FRED M. ERNSBERGER and WESLEY G. FRANCE, *Ind. Eng. Chem.*, 37, 598-600 (1945).

The results of turbidity tests on Portland cements suspended in an aqueous medium, with and without addition of calcium lignosulfonate, as obtained with the Wagner turbidimeter, show that the addition agent disperses the suspended cement particles. In the tests reported, the degree of increase in turbidity for two types of Portland cement in an aqueous medium is shown to be a function of the amount of adsorbed dispersing agent. It may be concluded that the mechanism of dispersion involves the positive adsorption of lignosulfonate anions by the cement particles. The determination of an adsorption isotherm for calcium lignosulfonate and Portland cement suspended in water is described; data are given for a typical cement.

B.I.P.C.

A FLOW-CURVE RECORDER FOR A ROTATIONAL VISCOMETER.

RUTH N. WELTMANN, *Rev. Sci. Instruments*, 16, 184-91 (1945).

In the study of thixotropic substances and of materials of non-Newtonian behavior, it is important to obtain complete flow curves (rate of shear *vs.* shearing stress) which are taken in accordance with a standardized procedure. The time interval for any given increase or decrease in rate of shear should remain constant. A recorder which draws complete flow curves has been developed as an attachment for a Couette type of viscometer. The deflection of the bob, which is proportional to the shearing stress, is plotted against the speed (r.p.m.) of the cup, which is proportional to the rate of shear. For precise measurements, the bob suspension spring must not be subjected to any friction load; therefore, the recorder uses sparks generated by a high voltage to puncture the recording paper. The sparking electrode is moved by the bob deflection spring while the paper is moved perpendicularly to the electrode motion by the transmission handle, the position of which controls the cup speed. A number of measurements made with the recorder are shown. The recorded flow curves permit immediate interpretation and calculation (without any replotting) of the plastic viscosity, the yield value, and the thixotropic behavior of the tested materials. Also, a method is proposed for determining the plastic viscosity and the yield value at initial agitation, which are identified as "the initial thixotropic viscosity" and "the initial thixotropic yield value."

B.I.P.C.

THE DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTION IN HIGH POLYMERS BY MEANS OF SOLUBILITY LIMITS.

D. R. MOREY and J. W. TAMBLYN, *J. Applied Phys.*, **16**, 419-24 (1945).

By means of polymer fractions of known molecular weight, dissolved in solutions of known compositions, it is possible to determine the solubility law which relates the point of solution saturation to the molecular weight and concentration of the dissolved polymer. Having established such a calibration, it is possible to determine the molecular-weight distribution in a heterogenous sample of the polymer by suitable operation on a curve relating the mass of polymer precipitated to the amount of precipitant added to the solution. Optical means, making use of scattering from the precipitate, are used to obtain this latter curve. The method is applied to cellulose acetate butyrate and is shown to give results in agreement with gravimetrically obtained distribution curves. 11 references.

B.I.P.C.

A BIBLIOGRAPHY OF ELECTRON MICROSCOPY. III.

CLAIRE MARTON and S. SASS, *J. Applied Phys.*, **16**, 373-8 (1945).

The compilers bring their previous bibliography up to date as far as is possible under present conditions; the material is again arranged in eight groups. A table from Ruska's bibliography (*cf.* B.I.P.C., **15**, 95) has been translated and included; this table gives a summary of the types of electron microscopes developed in Germany, the application of each type, and the number of papers about each type published up to the end of 1943. For purposes of comparison, a similar table has been prepared showing the number of papers published in countries exclusive of Germany during the same period.

B.I.P.C.

MICROSCOPIC STUDIES OF LYOGELS; ULTRA-ILLUMINATION BY INCIDENT LIGHT.

ERNST A. HAUSER and D. S. LE BEAU, *Ind. Eng. Chem.*, **37**, 786-9 (1945).

A new technique employing the Ultropak microscope—*cf.* *Z. wiss. Mikroskop.*, **48**, 450 (1931)—is described which permits the microscopic examination of lyogels, particularly of natural and synthetic rubber, with ultra-illumination by incident light. The morphology of the original lyogel and that of its fractions, separated by solvent extraction, can be studied, as well as the changes it undergoes when subjected to chemical reactions or physical forces. The Ultropak differs from the standard type of dark-field optics by making use of ultra-illumination with indirect light. This means circular illumination of the preparation from above; it causes a dark-field effect, but the light does not pass through the magnifying lens system before it is reflected by the specimen through it into the observer's eye or onto the photographic film. Results so far obtained by this technique in the study of natural and synthetic rubbers, soap, and other lyogels are discussed. Several microphotographs are reproduced as examples of the applicability and versatility of this simple technique for studying the morphology of lyogels. 19 references.

B.I.P.C.

VISCOSITY-MOLECULAR WEIGHT RELATIONS FOR CELLULOSE ACETATE BUTYRATE.

J. W. TAMBLYN, D. R. MOREY, and R. H. WAGNER, *Ind. Eng. Chem.*, **37**, 573-7 (1945).

The relations between the molecular weights of fairly homogeneous fractions of cellulose acetate butyrate and the viscosity function $\ln \eta_r/c$ (determined in acetone and acetic acid) are given for the two cases: (a) the limiting value as $c \rightarrow 0$, known as intrinsic viscosity; (b) the value at $c = 0.25$ g. per 100 cc. The establishment of a relation using the latter viscosity figure permits the determination of the viscosity-average molecular weight without recourse to extrapolation to zero concentration. Upon degrading samples of heterogeneous (unfractionated) cellulose acetate butyrate by heat, ball milling, and ultraviolet light, it was found that $\ln \eta_r/c$ values and the number-average molecular weights (from osmotic pressure) are also related by equations similar in form to those obtained on fractions. A means is thus at hand for obtaining the more useful number average of heterogeneous cellulose acetate butyrate from a single viscosity measurement. It is pointed out that the establishment of a simple relation between the quantities for any polymer depends on the kinetics of the polymerization or degradation process and its effect on distribution curves. 14 references.

B.I.P.C.

CLAYS

SHRINKAGE OF EXTRUDED STEATITE TUBES.

H. H. HAUSNER and ANGELA F. NAPORAN, *Bull. Am. Ceram Soc.*, **24**, 246-50 (1945).

Extruded steatite tubes shrink in a peculiar way. Sometimes the inside diameter shrinks more than the outside and in some cases the outside shrinks more than the inside. Very rarely do both diameters shrink in the same manner. The shrinkage of tubes was studied to determine whether there are laws governing the shrinkage of extruded materials. The writers conclude that the pressure distribution during the extrusion process plays a major role in the shrinkage of tubes and some pressure distribution will essentially affect their shrinkage.

J. A. PASK

BALL CLAY INVESTIGATION: SYMPOSIUM III, 46TH ANNUAL MEETING, APRIL 1944.

RALSTON RUSSELL, JR., CHAIRMAN, *Bull. Am. Ceram Soc.*, **24**, 122-38 (1945).

The symposium is part of the attempt among A.C.S. members to standardize tests applied to ball clays, a very commonly used raw material in the ceramic industry. One of the chief attributes of this type of clay is its very high plasticity. The section of the symposium on "Variations in Plastic character" by A. S. Watts may be of interest to the readers of *Rheology Bulletin*. Watts' discussion of the factors affecting plasticity is comprehensive.

J. A. PASK

FUNDAMENTAL PROPERTIES OF RAW CLAYS INFLUENCING THEIR USE.

C. G. HARMAN and C. W. PARMELEE, *J. Am. Ceram Soc.*, **28**, 110-18 (1945).

A number of different types of clays were experimented with. It was found that the cation-adsorption capacity and the nature of the adsorbed cation are closely related to the heat of wetting, pH, and equilibrium moisture. Permeability, drying rates, and dry strengths (for single-base clays) are closely correlated and are dependent on pore structure and pore volume, as well as on base-exchange capacity. Large weak ions, when present, bring about a dense, stable pore structure, which imparts difficult drying characteristics, high dry strength, and low permeability. Small strong ions, such as hydrogen, induce the reverse effects. The properties of clays may be defined as functions of ion-sorption capacity, nature of the adsorbed cation, and packaging, provided that the water content and soluble salts are controlled.

J. A. PASK

FIBERS

FIBROUS (FORMS) FROM GLOBULAR PROTEINS.

F. R. SENTI, M. J. COPLEY, and G. C. NUTTING, *J. Phys. Chem.*, **49**, 192-211 (1945).

By means of heat, water, and mechanical shear, several globular proteins have been converted into a fibrous form giving an x-ray diffraction pattern nearly identical with that of β -keratin of stretched hair and wool. Among the proteins thus converted are lactoglobulin, ovalbumin, casein, zein, peanut, protein, soybean protein, gliadin, hemoglobin, serum albumin, edestin, and tobacco-seed globulin. The process is most effective when applied to native, typically heat-denaturable proteins. Under similar but milder conditions, most of the proteins give a second type of fiber pattern, characterized by the appearance of the 4.6 Å. "backbone" reflection on the meridian and the 10 Å. "side-chain" reflection on the equator. When a protein is heated in the presence of water, the diffraction pattern sharpens and new lines appear, indicating ordering of chains analogous to that occurring in the annealing of cellulose ester and polyamides. Relative dimensions of the crystallites giving the fiber patterns are deduced from the sequence in which the x-ray reflections are when a protein filament is stretched. Comparative data on birefringence, x-ray diffraction, and swelling anisotropy as measures of molecular orientation are presented. Tensile strength is increased by conversion of the globular protein to the oriented fibrous form. Wet strength after treatment with boiling water and dimensional stability of oriented ovalbumin filaments are improved by acetylation and hardening with formaldehyde or quinone. 31 references.

B.I.P.C.

NEWER FIBRES.

PAUL LAROSE, *Can. Chem. Process Inds.*, **29**, 476-9 (1945).

The main requirements of a textile fiber are fiber length, a certain minimum strength to withstand stresses, softness and suppleness, elasticity, resistance to creasing, ready recovery from distortion, and resistance to repeated stresses. The natural fibers possess these properties in varying degree; many of them have failings which can be overcome in the artificially produced fibers. The artificial fibers thus have the advantage that they can be controlled

within limits at will. The author discusses the extent to which the molecular structure of fibers is important in determining their suitability for use in textiles, considering the protein-derived types (Lanital, Aralac, or Ardil), as well as nylon, Vinyon, Fortisan, and glass. A molecular weight of 10,000 or more of the raw material is necessary if the fiber made from it is to have strength, insolubility, and general resistance to chemicals. The tenacity of the fiber increases with the degree of polymerization up to a certain degree, after which further polymerization is of little benefit. A high molecular weight alone is not sufficient for strength; the macromolecules must be in chain form if flexibility and elasticity are desired and the number of cross linkages or the "netting" index must be low to produce a good textile fiber—*e.g.*, the building units must have a few side chains with groupings that exert a strong attraction on neighboring units. The mobility of the chain depends on the strength of the bonds holding the chains together, such as van der Waals' forces, polar forces, and hydrogen bonds. The effect of the structure on the melting point is similar to that affecting strength. Melting the substance results in a reduction in the attraction between chains, thereby lowering the melting point. Water absorptivity and dyeing reactions are mainly controlled by the chemical nature of the substance; however, some structural features must also be taken into consideration. Oriented fibers do not take up dyes as readily as unoriented ones. If a fiber has not been uniformly drawn, it will show dark and light spots from the variation in dye affinity. Water solubility is largely controlled by the polar groups present. When solubility is too great, as with protein fibers, they must be stabilized by some kind of treatment, such as with formaldehyde. Glass fibers, being of inorganic origin, do not exhibit the forces coming into play in organic fibers. Their main advantages are high tenacity and strength, and high resistance to heat and chemical reagents. Their extensibility and flexibility are very low; it is not possible to make a knot in glass yarn. In conclusion, brief reference is made to the fact that some important fiber properties do not depend on either chemical or physical structure, but on dimensions and configurations, such as diameter and shape of fiber, or whether made from a continuous filament or with staple fibers. B.I.P.C.

FOAMS

FOAM DRAINAGE.

GILBERT D. MILES, LEO SHEDLOVSKY, and JOHN ROSS, *J. Phys. Chem.*, **49**, 93–107 (1945).

The flow characteristics have been studied of liquid in foams of relatively uniform bubble size and uniform liquid concentration without concomitant foam breakdown. The rates of drainage of liquid from these foams have been measured and shown to approach an approximate simplified equation corresponding to liquid flow in a vertical capillary. The rates of flow of liquid through these foams have been measured as a function of the liquid held in the foam. An empirical equation in accord with these data is given. The rates of flow of liquid through foams decrease with increase in both surface and bulk viscosities as well as for smaller bubble sizes. Differences in flow characteristics through stable foams are more pronounced at certain temperatures. Attempts to evaluate foam stability from foam drainage rates which have been reported in the literature are not considered generally valid. B.I.P.C.

LITERATURE RESEARCH AS A CHEMICAL TOOL.

S. J. COOK, *Can. Chem. Process Inds.*, **29**, 526, 535. (1945).

The essential purpose of the present paper is to emphasize the benefit of adequate training in the use of scientific literature and to suggest a plan whereby this training may be secured. It would be of mutual advantage to science departments and library schools, if a special course in the use of scientific library materials could be given to science students by library school instructors in cooperation with professors of the science departments concerned. The course should be obligatory and introduced in the third or fourth year of the undergraduate program.

B.I.P.C.

ALGIN—A MARINE COLLOID OF MANY USES.

ANON., *Chemurgic Digest*, **4**, 233, 235-6 (1945).

Algin is a dried, purified, mucilaginous substance extracted from kelp—a white to cream-colored, amorphous, odorless, and tasteless powder. Chemically, it is stated to be the sodium salt of polymerized uronic acid, manuronic acid in particular. Its solubility in water is limited by the viscosity of the resulting solution; the viscosity curve will rise very rapidly with the increase in the percentage of algin used. The raw material from which algin is derived includes the algae of the genus *Laminaria* found on the northwestern seaboard of the United States, where the kelp is cut by dragging or by hand. It undergoes a curing treatment in a near-by station to prevent fermentation while it awaits further processing. The stabilized kelp is brought to the processing plant in Maine where the algin is extracted, purified, and dried under vacuum. The present uses of the material are manifold; its remarkable characteristics as a colloidal stabilizer, emulsion stabilizer, dispersing agent, and thickening agent have resulted in its adoption in widely diversified fields, such as the drug, pharmaceutical, cosmetic, textile finishing, textile printing, rubber, cold water paints, agricultural, food, ice cream, confection, and paper industries.

B.I.P.C.

INK**THE RELATIONSHIP BETWEEN THE RHEOLOGICAL PROPERTIES AND WORKING PROPERTIES OF PRINTING INKS.**

R. BUCHADAHL and J. E. THIMM, *J. Applied Phys.*, **16**, 344-50 (1945).

It is shown that the working properties of a printing ink—*i.e.*, its performance during the printing operation—can be interpreted in terms of the rheological properties as measured in a rotational viscometer. The instrument used in this investigation is a viscometer of the Stormer type. Data are presented to show that it is necessary to distinguish between time-dependent and time-independent flow phenomena. Various theories suggested to explain the time-independent flow phenomena are discussed briefly. The flow of a printing ink over the main mechanical elements of a typographic printing press is analyzed and correlated with simple flow phenomena which can be measured in a rotational viscometer. 11 references.

B.I.P.C.

VISCOSITY REDUCTION BY PAINT THINNERS.

E. H. MCARDLE, *Am. Paint J.*, **29**, 27 (1945).

The viscosity changes in paints caused by addition of thinners are due to "friction" of the large vehicle molecules rather than to "friction" between the molecule of thinner, or between thinner and vehicle. A large "surface" of the dissolved vehicle molecule means a large viscosity contribution. Length and concentration of the dissolved molecules increase, of course, equally the viscosity of the paint. For a given vehicle solids and a single thinner the viscosity, η , and volume concentration, C_v , satisfy the equation:

$$\frac{\log \eta}{C_v} = \text{const.}$$

or

$$\log \eta_r \times \frac{\text{moles thinner}}{\text{moles solids}} = \text{const.}$$

where η_r means the relative viscosity of the dissolved solids alone. The viscosity factor, ηf , of a vehicle solids is a modification of E. O. Kraemer's intrinsic viscosity and defined as:

$$\eta f = (\log \eta_r \times \text{moles thinner}) C_v = K$$

Experiments were made with the following thinners: toluol, xylol, pseudo-cumene, methylnaphthalene, Solvesso No. 1, naphtha, *n*-heptane, paraffinic lacquer diluent, paraffinic mineral spirits. Ester gum, linseed oil, butyl phenol resin, phthalic alkyd, and cellulose nitrate and natural rubber in various solvents were used for the paints. A good thinner should show a maximum reduction of paint viscosity and should have a high dispersive power. Both requirements are filled by toluol. Cellulose nitrate and natural rubber behave differently from the resins used in most paints. The viscosities of the solutions were determined in Gardner-Holdt tubes; a Ubbelohde viscometer was used for the thinners. The effectiveness of the various thinner types is compiled in several tables.

BRUNO ROBERTS

PETROLEUM PRODUCTS

SEPARABILITY CHARACTERISTICS OF LUBRICATING GREASES.

T. G. ROEHNER and R. C. ROBINSON, *Insl. Spokesman*, **9**, No. 2 (1945).

Practical experience with certain lubricating greases indicated that the pressure exerted in an ordinary grease cup tends to separate a grease into oil and soap due to a "filtering effect." The authors subjected a series of greases to a pressure differential of 7.5 p.s.i. across a fritted glass filter (5-10 μ pores). The amount of oil separated per unit time (in this apparatus) predicted the behavior of the same greases in the actual grease cup very well. The rate of separation of oil from grease in this tester decreases with time as the layer closest to the glass filter plate exhausts its oil content more rapidly than the bulk of the sample. The initial rate of separation is proportional to the

inverse of the viscosity of the oil from which the grease had been compounded, while in the later stages of separation the influence of oil viscosity becomes less pronounced. Increasing of soap content decreases rate of separation. Temperature increase increases the rate of separation, but not in proportion to the decrease in oil viscosity (probably due to change of oil/soap interaction with increasing temperature). Separability characteristics depend strongly on the soap type employed and are also very sensitive to variations in the method of grease preparation, the number of variables being nearly inexhaustible.

A. BONDI

NOTES ON THE OPERATION AND APPLICATIONS OF THE S.O.D. PRESSURE VISCOSIMETER.

J. C. ZIMMER and J. B. PATBERG, *Inst. Spokesman*, **9**, No. 4-5 (1945).

Additional data and applications of the previously (*Rheol. Bull.*, **15**, No. 2, 1944) described instrument are presented. The use of a hydraulic fluid of 20 to 25 stokes is recommended to minimize slippage in the constant volume pump. The error due to laminar flow of very viscous greases in the cylinder and—more important—the error due to convergence of flow lines at the entrance to the capillary may be very large, especially when short capillaries are used. (This point was also made in the discussion of the Monsanto viscometer for plastics by H. K. Nason at the Fall Meeting of the Society in New York 1944-Rev.) Viscosities measured in the $L/D = 12$ capillary were more than 25% higher than when measured with capillary of $L/D = 40$ (the standard model). Application of the data obtained to various practical problems, such as prediction of resistance to flow in grease dispensing equipment, low temperature starting torque data of transmission oils, is also discussed.

A. BONDI

PLASTICS

IMPACT STRENGTH OF PLASTIC MATERIALS AT VARIOUS TEMPERATURES.

D. A. SHINN, *Modern Plastics*, **22**, 145-52, 184, 186 (1945).

In the present investigation, Izod and Charpy impact data were determined for several types of unfilled thermoplastic and filled and unfilled thermosetting plastic sheets and molded materials, as well as resin-impregnated compressed laminated wood panels, especially to show the effect on the impact properties of temperature variations within the range of -67° to 158° F., which is that encountered in the normal operation of aircraft. Additional data were obtained relative to notched and unnotched specimens, edgewise and flatwise tests, directional effects, laminated specimen tests, as well as the effect of moisture content. In general, an increase in temperature increases the impact energy absorption, but some materials exhibit practically no change caused by temperature variation. There is no definite relation between the Izod and Charpy tests but, in general, a material giving good values as measured by the Izod test would be rated approximately the same by the Charpy test, both in the relative amounts of impact absorbed, and in the notch sensitivity when expressed as the ratio of notched to unnotched impact values. No relationship was established between the impact strength and either the

tensile or flexural properties. Comparisons are made between the impact energy and the energy absorbed during a bend test, but the data have no direct correlation because of the differences in the effects of paper, cloth, and wood fillers on the impact properties. Illustrations and numerous tables and diagrams are included. B.I.P.C.

FLEXURAL PROPERTIES OF PLASTICS.

W. A. ZINZOW, *ASTM Bull.*, No. 134, 31-7 (1945).

A summary of the test results obtained by five different laboratories cooperating with Committee D-20 is given. The purpose was to determine the effect of the loading of the edge radii, the rate of crosshead motion, and the effect of the span-depth ratio on the flexural properties. These data were needed for the preparation of A.S.T.M. Tentative Method of Flexural Test of Plastics (D 790-44 T). Tabulated data and diagrams are included. B.I.P.C.

POLYMERS

POLYTHENE, PHYSICAL AND CHEMICAL PROPERTIES.

FREDERCK C. HAHN, MAURICE L. MACHT, and DAVID A. FLETCHER, *Ind. Eng. Chem.*, 37, 526-33 (1945).

The hydrocarbon resin, polythene, recently became available commercially from domestic sources. The low electrical losses, together with its high resistance to moisture and chemicals and toughness over a wide range of temperatures, have led to wide usage, particularly in the electrical field; these properties indicate other potential applications. As a means for protecting metal surfaces from corrosion and applying polythene coatings in general, the process of flame spraying the powdered material is described. The low moisture permeability and good water resistance of polythene indicate its suitability for the coating of cloth, paper, wood, brick, and concrete, for the fabrication of containers (milk and other liquids), and for packaging in general. For the latter purposes, the plastic can be applied either as sheeting or as an impregnant for paper. 22 references. B.I.P.C.

PROTEINS

ARTIFICIAL PROTEIN FIBRES: THEIR CONCEPTION AND PREPARATION.

W. T. ASTBURY, *Nature*, 155, 501-3 (1945).

The author discusses the scientific principles underlying the development of Ardil from the protein of peanuts, which was an outcome of x-ray and related studies of the molecular structure of biological tissues. The x-ray study of keratin gave the explanation of the α - and β -forms and laid the foundation for the concept of the polypeptide grid; the next advance came from an x-ray comparison of a number of protein preparations before and after wetting, and further through a study of denaturation (a thoroughgoing irreversible phenomenon) by heat. The α -form revealed the existence of folded polypeptide chains which, on denaturation by chemicals (unfolding of the chains), could be

drawn parallel, resulting in artificial fibers with an oriented β -photograph. Decisive orientation effects were first obtained with denatured preparations of edestin, seed globulins, and excelsin, also with egg white; the first fibers were spun from strong urea solutions. The commercial production of Ardil from arachin, the peanut globulin, was developed by chemists of Imperial Chemical Industries Ltd., on the basis of these purely fundamental studies. Brief reference is made to American investigations with egg albumin and chicken feather keratin. 12 references.

B. I. P. C.

THEORY

A UNIVERSAL VISCOSITY CORRELATION.

O. A. UYEHARA and K. M. WATSON, *Natl. Petroleum News*, Tech. Sect., **36**, (Oct., 1944).

The authors derive several equations to calculate the dynamic viscosity at the critical temperature from other physical properties. All are based on the Kammerlingh-Onnes equation

$$\eta_{\text{crit}}(T_c/M^3P_c^4)^{1/6} = k$$

where $k = 3.5$, a universal constant. On this basis, a chart is constructed of the "reduced viscosity" vs. reduced temperature and pressure. From this generalized chart, the viscosities of most substances in both the liquid and the vapor state (preferably the latter) can be estimated with an average deviation of less than 20%. By the use of Watson's pseudocritical concept, this correlation can also be applied to mixtures. Substances to which the theorem of corresponding states cannot be applied are, of course, outside the range of this type of correlation.

A. BONDI

THE EFFECT OF SOLVENT TYPE ON THE VISCOSITY OF VERY DILUTE SOLUTIONS OF LONG CHAIN POLYMERS.

ELIZABETH M. FRITH, *Trans. Faraday Soc.*, **41**, 17-27 (1945).

A semiquantitative discussion is given of the viscosity relationships of polymers in various solvents. Quasithermodynamic reasoning, based on modern statistical theories, show how the slope of the ordinary viscosity concentration curve is related to the interaction energy between solvent and polymer. It is shown how small differences in interaction energy appreciably alter the slope. These differences are traced back to slight kinking of the long molecular chains in agreement with the qualitative views of Mark. Retention of solvent effect on viscosity at zero concentration is demonstrated but not proved; it is inferred that more extensive coiling of the chains is necessary than the slight kinking which affects the slope.

B. I. P. C.

IMPACT TESTING OF PLASTICS; RELATION TO STRUCTURE AND COMPOSITION.

D. R. MOREY, *Ind. Eng. Chem.*, **37**, 255-63 (1945).

Several factors play a part in rapid mechanical deformations; they may be studied by the use of mechanical models whose mathematical characteristics simulate the behavior of real materials. A correspondence may be

drawn between the model elements and structural features such as primary and secondary bonds. The question of materials being characterized by a continuous range of bonds differing in time constants is examined. It is shown that the concept of bond breakage and re-formation as a function of thermal energy fluctuations can explain the known inverse roles of velocity and temperature in many mechanical phenomena. The value of a dispersion of bond properties in making materials resistant to impact fracture is pointed out. The effect of notches or cracks upon the stress distribution is illustrated, and it is shown how these play a part in determining the relative behavior of different materials. The propagation of shock waves in the material subjected to an impact blow is discussed, together with the question of their dissipation by a dispersion of certain bond qualities. It is pointed out how such well-known factors of impact resistance as plasticizer and moisture content, temperature, molding conditions, etc., enter into the phenomena of fracture propagation, bond dispersion, stress concentration, and shock wave dissipation. A number of workers, particularly in the metals industry, have been developing, in recent years, experimental methods for obtaining complete stress-strain curves during a short time of impact loading. These methods are illustrated in this article, and are compared as to their ability to yield information about the general stress-strain-time-temperature behavior of a material. 28 references.

B.I.P.C.

THE INFLUENCE OF MOLECULAR FLEXIBILITY ON THE INTRINSIC VISCOSITY, SEDIMENTATION, AND DIFFUSION OF HIGH POLYMERS.

ROBERT SIMHA, *J. Chem. Phys.*, **13**, 188-95 (1945).

Expressions for the mean square separation of chain ends and modifications of the formula for an ideal coil are discussed. On the basis of these and the hydrodynamic theory of intrinsic viscosity, an interpretation of the modified Staudinger rule is offered. It relates the exponent of the molecular weight to a flexibility parameter of the chain in a given solvent, varying between zero and one. Recent data on polystyrene and on cellulose nitrate are analyzed in greater detail. By means of the frictional ratio, the sedimentation and the diffusion constants are connected with the degree of polymerization in terms of the flexibility parameter. The limiting dependence of sedimentation and diffusion rate upon molecular weight for a straight chain and an ideal coil is also found in this manner. A comparison shows satisfactory agreement between values for the flexibility parameter found from intrinsic viscosity and those determined from sedimentation or diffusion rates, for certain cellulose esters and starch derivatives. Effects of solvent and of inhomogeneity in respect to molecular weight are discussed briefly.

B.I.P.C.

ORIENTATION AND RUPTURE OF LINEAR MACROMOLECULES IN DILUTE SOLUTIONS UNDER THE INFLUENCE OF VISCOUS FLOW.

J. FRENKEL, *Acta Physicochim. U.R.S.S.*, **29**, 51 (1944).

Combination of the Kuhn-Boeder theory of flow orientation with Boltzmann's formula leads to a very convenient form of the law of flow orientation—as simultaneously developed by Bondi, *Rheol. Bull.*, **15**, No. 3 (1944)—

which is then generalized to include also polymeric molecules. The theory also predicts the existence of a critical velocity gradient at which the molecule tends to be disrupted (into two equal halves) if the extending force becomes equal to the bond strength. The theory is applied to explain depolymerization by ultrasonics.

A. BONDI

ABSTRACTORS IN THIS ISSUE

A. BONDI

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B. ROBERTS

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BINGHAM RHEOLOGY

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