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VISCO-ELASTIC BEHAVIOUR

A MEETING of the British Society of Rheology was held during April 29-30 in the Physics Department of King's College, Newcastle upon Tyne. About seventy members and visitors, including some from abroad, met to hear and discuss papers, under the chairmanship of Dr. L. R. G. Treloar, president of the Society.

The flow properties of a system consisting of a mixture of methylmethacrylate and pitch in tar oil were discussed by L. J. Wood and G. Phillips (Coal Tar Research Association). Measurements of viscosity and elastic modulus in the system, and also in one having no polymer added to it, have been made. Both the specific viscosity, defined as the viscosity divided by the retardation time, and the elastic recovery are practically independent of temperature, but markedly dependent on stress. The equilibrium rate of shear and the stress are related by a power law; the apparent viscosity increases as the stress is raised. The elastic recovery can be expressed as $1/e = 1/e_m + b/S$, where e is the elastic recovery, S the stress, b the gradient, and e_m the intercept of the reciprocal recovery/reciprocal stress plot. With increasing polymer concentration from 0 to 2 per cent the value of e_m increases steadily and that of b decreases slightly. Results to date suggest, however, that above this concentration e_m and b remain practically constant.

Dr. A. S. Lodge (Rayon Research Association) outlined a theory of the stresses and birefringence set up in flowing polymer solutions. The deformation of networks is considered to account for most of the viscous stresses observed, and flow birefringence is due to anisotropy of networks. The theory is developed from one which Treloar applied to the rubber-like state and compared with the results of experiments by Signer and by Schmidli.

Dr. K. Weissenberg (Colloid Science Department, Cambridge) demonstrated some interesting experiments, illustrating recent advances in the goniometry of flow, particularly those involving the three-dimensional case of pure shear. For quantitative experiments the material under investigation is contained between two rubber sheets, or within a rubber tube, and the displacements and forces across three

mutually perpendicular planes are measured. The conventional technique of testing produced motions of 'simple' laminar shear, and in these the geometry is very complicated because there is a shear-dependent angular deviation between the main axes of the stresses, the strains and their various derivatives in time. The new method of testing resolves this complexity, as it produces motions of pure irrotational shear in which the main axes of all the stresses and strains and time derivatives remain always parallel to one another. The tube formation by rolling of a cylinder has now been established as a phenomenon of great generality which may be regarded as counter-part to the well-known normal pressure phenomenon occurring in elastic and visco-elastic solids and liquids (such as the climbing up of a material on a rotating stirring rod).

Drs. H. Kolsky and F. C. Roesler (Imperial Chemical Industries, Ltd., Welwyn) showed how relaxation spectra may be derived from mechanical measurements on solids. In attempting to correlate the mechanical behaviour of materials with the microscopic processes which cause them, it is desirable to obtain what is termed a 'relaxation-time spectrum' of the material. This treatment postulates that the mechanical behaviour of the solid corresponds to the summation of an infinite number of relaxing elements each with its own time of relaxation, and the spectrum describes the relative strength of these elements. Thus peaks in the relaxation-time spectrum would correspond to the presence of a large number of mechanisms which have characteristic times of values around the peak, and in many cases, especially with metals, it has been possible to correlate these peaks with specific processes taking place in the material.

A number of methods have been developed for the determination of relaxation-time spectra from experimental data and for the conversion of results of one type of measurement into another. The basis of this method is the Fourier analysis of the experimental curve on a logarithmic plot into its separate components. Each component is then multiplied by an appropriate eigen value, and a new curve is thus synthesized. These methods have been tried on a number of published experimental results, and have proved to be extremely effective in dealing with these problems. Recently a numerical iteration method, which avoids the necessity for an explicit Fourier analysis, has also been developed; and while this is not of such wide application as the other approach, in the cases where it may be used it is generally more convenient and may be shown to be

equivalent to the more detailed method which employs Fourier analysis.

J. E. Caffyn and L. Goodfellow (Physics Department, Durham) described the mechanical and electrical properties of sodium chloride and made a survey of the effect of mechanical deformation on the electrical conductivity. Apparatus to enable transient electrical phenomena in sodium chloride to be investigated and its application to the study of the changes in electrical properties (particularly conductivity) of ionic crystals were described. Typical results were given for several of the alkali halides, and their variations among different crystals were discussed. A new electrical phenomenon associated with the plastic deformation of the alkali halides and its dependence on temperature was mentioned. Its significance for the earlier measurements was discussed.

Dr. R. Roscoe (Physics Department, Newcastle) spoke of the interpretation of mechanical relaxation in solids. It follows from Boltzmann's principle of superposition that the mechanical behaviour of any material which shows linear visco-elastic effects can be represented in terms of a spectrum of relaxation times or, alternatively, as a spectrum of retardation times. The question arises as to which of these two spectra can be more directly interpreted in terms of the molecular relaxation processes which are ultimately responsible for the visco-elastic effects. It is shown that, when these processes consist in the breaking of linkages in a solid structure, the spectrum of relaxation times for the molecular processes is identical with the retardation time spectrum, provided there is only weak interaction between the individual relaxation processes.

P. J. Kirby (James A. Jobling and Co., Ltd., Sunderland) described results of experiments on 'Pyrex' glass from which the relaxation spectrum over a range of temperature up to the annealing range can be derived. A migration of alkali ions in the vitreous network gives rise to another relaxation process—in electrical conductivity—and the half-maximum widths of the relaxation spectra are compared with those relating to the visco-elastic effects of the entire network. The distribution of relaxation periods suggests a distribution of the activation energies governing the process. A measure is thereby obtained of the associated distribution of potential barrier heights in the vitreous network. The migration of a network-modifying ion is subject to a wider range of irregularity of activation energy than the general visco-elastic deformation of the network-forming ions.

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Drs. A. W. Pryor and E. G. Richardson (Physics Department, Newcastle) have carried out experiments using ferrite transducers of 50 and 100 kc./s. excited magnetostrictively to send torsional waves down long rods made of metal or glass. By varying the temperature in a container surrounding the rod, and measuring the attenuation and phase-shift of transmitted pulses, the elastic modulus and viscosity of the material of the rod or of a liquid under shear in the container were measured. The absorption is less in solutions of rubber in benzene than in pure solvent. The fact that the absorption in these highly viscous solutions is many times less than those calculated from the classical formula—by substituting the known shear viscosities—can be explained by assuming that the high viscosities are by-passed by associated elasticities (that is, these liquids behave at high frequencies more or less as solids).

THE BRITISH SOCIETY OF RHEOLOGY

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PROPOSED MEETINGS FOR 1955-56

At a recent committee meeting following the Annual General Meeting at Exeter, various topics were suggested as suitable for future meetings of the Society. Members of the Society and other interested persons or organisations are asked to express views on the suitability of these topics and to inform the Secretary if they wish to submit a paper on one of the subjects. A list of four proposed subjects is given below:-

Rheology of Protein Systems	(Jan. 1956)
Rheological Measurements and Automation	(Apr. 1956)
Extrusion and Rolling Processes	(Jun. 1956)
Rheology of Textiles	(Sep. 1956)

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THE BRITISH SOCIETY OF RHEOLOGY

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JAPAN: THIRD RHEOLOGY SYMPOSIUM

The Third Rheology Symposium was held in Kyoto (the Institute of Fundamental Physics, Kyoto University) from 18th to 19th November, 1953, under the joint auspices of the Chemical Society of Japan, the Physical Society of Japan and the Highpolymer Society of Japan.

Two lectures were invited and seventeen original papers were read. Most of the original contributions treated the important problems on rheology of dilute and concentrated solutions of high polymers, solid high polymers and textile fibres. Because of the want of time, the invited lectures were confined only to the following two subjects: "Textile Industry and Rheology" by Dr. M. Horio (Kyoto Univ.) and "Phenomenological and Molecular Aspects of Rheological Behaviours" by Dr. H. Takenaka (Fuji Photo Film Co.). On the basis of his many achievements, Dr. Horio explained the relationship between the rheological behaviour and fine structures of cellulose and synthetic fibres, and molecular interpretation of the rheological properties of these materials. His lecture gave many suggestions to the audience concerning the approach to rheological studies. Dr. Takenaka reviewed various methods for researching rheological problems in detail, mentioning the recent progress in the field of rheology.

Two hundred or more research workers having an interest in rheology attended the meeting from various provinces. The chairs were taken by Drs. I. Sakurada (Kyoto Univ.), J. Furukawa (Kyoto Univ.), R. Goto (Kyoto Univ.), Y. Sawaragi (Kyoto Univ.), and S. Oka (Kobayashi Institute of Physical Research).

Abstracts of the papers are included in this Bulletin.

SUMMARIES OF THE PAPERS
read at the Third Rheology Symposium

**Non-Newtonian Viscosities in Dilute Aqueous Solutions of Sodium
Carboxymethylcellulose**

HIROSHI FUJITA AND TERUTAKE HOMMA

(Department of Fisheries Faculty of Agriculture, Kyoto University)

The reduced viscosity vs. concentration relation was measured for sodium chloride solutions of sodium carboxy methyl cellulose (Na-CMC of $\overline{DP}=400$ and $\overline{DE}=0.7$) in a range of low concentrations (0.003 to 0.09 g./110 ml.), and the data obtained were analyzed according to the procedure of Pals and Hermans. The results confirmed in many aspects the findings which had previously been made in the literature, and supplied values of the necessary molecular quantities for our own sample. They indicated that our Na-CMC molecule was relatively uncoiled even in solutions of high ionic strength. The Huggins slope constant was found to increase approximately linearly with increasing reciprocal of the ionic strength of the solution.

Next, the shear dependence of the reduced viscosity in dilute solutions of this polyelectrolyte was investigated by the use of a viscometric apparatus which was especially designed for accurate measurements at low shear-rates. The shear-rate region investigated was from about 50 to 1000 sec^{-1} . The measurements were made on salt-free solutions and on solutions of constant ionic strength; in both cases only the regions of sufficiently low concentrations were treated. In the salt free solutions the η_{sp}/C vs. q (q is shear-rate) curves showed an upward curvature rather than a quadratic dependence at the limit of shear rate. In this case, the initial slope of each curve increased markedly with increasing dilution. The plots of η_{sp}/C vs. q for solutions of constant ionic strength (ca. 0.0015 moles/l.) were approximately represented by straight lines within the concentration range investigated. The slope of the straight lines decreased regularly with increasing dilution. There was some evidence observed that these plots have a horizontal initial tangent but this was never conclusive due to the paucity and inaccuracy of experimental data at shear-rates smaller than 100 sec^{-1} . The intrinsic viscosity obtained from η_{sp}/C vs. C curves at constant shear-rates for the isoionic system was independent of q . From these findings it was realized how markedly the viscous behaviour in dilute solutions of the polyelectrolyte studied was influenced by the addition of small amounts of neutral salt, not only in viscosity value itself but also in its shear-rate dependence. Our data and results herein presented were concerned only with a sample of one (average) molecular weight and one degree of etherification. More data, therefore, are needed on samples of varying degrees of polymerization and etherification before a more definite understanding of the problem herein treated is possible.

Dynamic Properties of Concentrated High Polymer Solutions. II

H. HIRAI AND S. ONOGI

(Department of Textile Chemistry, Faculty of Engineering, Kyoto University)

The dynamic viscosity η^1 and the dynamic rigidity G^1 of aqueous solutions (12 per cent weight) of polyvinyl alcohol of various average molecular weight were measured by means of the electromagnetic transducer method at various temperatures, and the results were presented at the last symposium. Since it was found, however, that the inertia of the sample solution affected considerably the observed values of G^1 at higher frequencies than 150 cps, the values were corrected by employing Markovitz's equation.

The dynamic behaviours of the solutions in frequency range of about 35-400 cps

can well be represented by the simple four-elements model of Maxwell or Voigt type with suitable parameters. From the experimental results, these parameters could be determined mathematically, and it was found that a similar equation to that of melt viscosity given by Flory was held between the average molecular weight of solute polymer, temperature and η'_3 , which was equal to $\eta''_2 + \eta''_3$. The dynamic behaviours could also be represented by the generalized Maxwell or Voigt model, and the distribution of relaxation times and pure viscosity η_v of each solution at various temperatures could be determined from the experimental results.

The ripening process of viscose was also studied by measuring G^1 and η^1 at various temperatures. In the early stages of ripening, η^1 decreased slowly and G^1 increased gradually with the course of time, while η_v was kept constant. These characteristics however, increased considerably in the intermediate stage and greatly in the last stage. Thus, η^1 had a minimum value at about a Hottenroth value of 10. On the other hand, the falling ball viscosity don't take a minimum but increased continuously in the same manners as G^1 during the ripening. The dependence of G^1 and η^1 upon the frequency was found to be greater in the later stage of the ripening.

The Internal Timescale of High Polymers, II

SIGE HARU ONOGI

(Department of Textile Chemistry, Faculty of Engineering, Kyoto University)

As mentioned previously, the dynamic viscosity η and the imaginary part of the complex dynamic compliance J'' of many high polymers measured in ordinary frequency range, which appears to be remote from the range of the anomalous dispersion of the complex dynamic modulus, conform to the following equations, respectively:

$$(\eta - \eta_2 - \eta_3) / \omega^2 \tau_2^2 + (\eta - \eta_3) = 0,$$

and

$$\eta_2 (1/J''\omega - \eta_3) / \omega^2 \tau_2^2 (\eta_2 + \eta_3) + [1/J''\omega - \eta_2 \eta_3 / (\eta_2 + \eta_3)] = 0,$$

where, η_2 , η_3 and τ_2 are constants, and ω is angular frequency.

Both the internal timescales, τ_2 in these equations, depend solely upon the experimental timescale and are independent either of the nature of materials to be tested or of the environmental conditions. The values of τ_2 obtained from the data in the frequency range of the order of 10 - 10^2 cps are not of the order of seconds, as was erroneously reported by the previous authors, but of 10^{-3} second. The internal timescale of the order of seconds can only be obtained in much lower frequency range of 10^{-2} - 10^{-1} cps. Thus, it is difficult to correlate the parameters of mechanical models simply with molecular mechanisms.

The relationship between the so-called distribution of relaxation time and applicability of the above equations was also mentioned.

Rheology of Concentrated Solution of Linear Polymer

MISAZO YAMAMOTO AND HIROSHI INAGAKI

(Department of Chemistry, Faculty of Science, and Department of Textile Chemistry, Faculty of Engineering, Kyoto University)

Concentrated solutions and melts of high polymers have particular rheological properties such as viscoelasticity, structural viscosity and spinnability. In order to explain these particular behaviours, a three-dimensional network of infinite polymer molecules with a random distribution of crosslinks was assumed, and treated statistically. This network differs from the usual one for rubberlike materials in that its crosslinks are not necessarily restricted to chemical crosslinks but may be of a more transient type such as hydrogen bonds or the entanglements in the physical sense. It was assumed that these crosslinks can break under a shearing stress, and that the probability of the

breaking depends upon the number of segments and the end to end separation of the chain molecules.

The results of the calculation satisfactorily explain, at least qualitatively, the experimental results, especially those of structural viscosity. The relation between the structural viscosity and the spinnability was discussed in connection with the "strength" of the crosslinks.

On the Thermo-Reversible Sol-Gel Transition

K. YOKOKURA AND Y. KOBATAKE

(Department of Applied Chemistry, Tokyo Institute of Technology)

The gel point in the temperature variation of the thermo-reversible sol has been placed at the temperature where elasticity appears. But the recent development of the dynamic measurements characterizes the elastic modulus by the measurement methods and it must be recognized that all the gel points are dependent on their measuring conditions. However, it may be proper in the molecular theory to define it as follows: the gel point is the temperature where the theoretically infinite cluster is formed with restriction in the degree of kinetic freedom, because the elastic modulus in the low frequency measuring will be the result of the rubberlike network that is characteristic of the gel.

The cluster formation like this was indicated theoretically by Flory-Stockmeyer. And we will attempt the following treatment, in relation to the temperature variation of the so-called static elastic modulus, for the network elasticity is the proper resultant of this formation.

In the first place, the extent of reaction in Flory's paper (1941) is written in terms of variables, temperature and others. Owing to this particular definition, however, there is some discrepancy between both the extents of reaction, and then the elastic modulus cannot be freed from this influence. Subsequently, we will split the gel in two portions, and introduce the number of the network junctions obtained from the extent of reaction in the gel portion and the segment number belonging to this portion into Flory's formula of the rubberlike elasticity. Consequently, the temperature derivative of the elastic modulus near the gel point is negative by the decrease of the junctions. We will try to find, though a primitive method, to what extent the elasticity in gel can be explained from the viewpoint that the rubberlike elasticity is predominant in comparison with the crystallike elasticity over the melting point of the solvent.

Rheological Properties of Some Polymerised Oils

TSURUTARO NAKAGAWA

(Department of Chemistry, Faculty of Science, Tokyo University)

Such drying oils as tung oil and linseed oil, when heated, gradually get polymerized and become elasto-viscous; they are thread-forming and spring back elastically when the stirring is stopped. The rheological properties of these oils seem to be in some relation to the manufacture and use of paints and printing inks. The four sample oils which are listed below were made of linseed oil by heating it to polymerization and subjected to the test.

- No. 0: the most highly polymerized, sticky, viscoelastic matter,
- No. 1 } moderately polymerized, thread-forming, highly viscous liquid,
- No. 2 }
- No. 3: simply viscous, less thread-forming liquid.

The dynamic viscosity and dynamic elasticity of these oils were measured by the top-drive coaxial rotational oscillation rheometer. The amplitude ratio and phase difference were observed by the photographic method. Experimental condition was changed in the following range.

Temperature: 20°C, 30°C, 40°C, 50°C, 60°C.

Period of oscillation: 10~200 seconds.

Rigorous analysis of this rheometer taking account of the inertia of the liquid, which was formulated by S. Oka, is compared with the simple method which has since been used by the author, and it is concluded that, in such low frequencies as was shown above, the difference between the two methods is negligible.

The amplitude dependence of the dynamic visco-elasticity was negligible, and so the rheological property of these oils is linear.

The frequency dependence was tested. Oils No. 3 and No. 2 behave as simple Newtonian liquid; no elasticity is observed in the frequency range used and the viscosity has no frequency dependence. Oil No. 1 shows a slight elasticity which increases rapidly in a high frequency range; the viscosity also shows dispersion and decreases gradually in a high frequency range. Oil No. 0 is typically visco-elastic; viscosity ($10^2 \sim 10^3$ poises) and elasticity ($10^1 - 10^2$ dynes/cm²) show marked dispersion in the similar manner as in No. 1.

The temperature dependence of viscosity conforms to Andrade formula

$$\eta = A \exp (B/T);$$

the apparent activation energy is about 15 kals.

Weissenberg effect of these elastic liquids was evaluated in arbitrary units. When a rod (1 cm dia.) is rotated in a constant speed (2—3 rotation per second) in an elastic liquid, then the liquid climbs up to the rod to an equilibrium height H..

No. 0 (the most elastic)	—	—	—	H: 10 cm
No. 1	—	—	—	H: 5 cm
No. 2	—	—	—	H: 1 cm
No. 3 (Newtonian)	—	—	—	H: 0 cm

In water glass, which is a very viscous fluid, none climbs up. This substance, in fact, is purely viscous and exhibits no elasticity in our rheometer test.

Rheological Behaviour of Nitroglycerine-Nitrocellulose Gel

TEIZO OKAWA

(Nobeoka Factory, Asahi Chem. Ind. Co., Ltd.)

Viscoelastic properties of Nitroglycerine (Nitroglycerine only and the mixture containing 30% Nitroglycol)—Nitrocellulose (N% = 12) Gels have been measured by the phase difference method using the concentric cylinder rheometer, the inner cylinder rotating with the sinusoidal torsional displacement.

Effects of the rotating period (or frequency), temperature, concentration and the degree of polymerization of the nitrocellulose upon the viscoelasticity were studied. The nature of the gel-elasticity has also been discussed.

On the Viscoelastic Properties and Skiing Quality of Ski Wax

GUNJI SHINODA AND MASAKI SHIMBO

(Faculty of Engineering, Osaka University)

There are many kinds of ski waxes according to their skiing condition (*i.e.*, atmospheric temperature, snow temperature and the kind of snow crystal) and their purposes (*i.e.*, for downhill only or for cross-country racing).

Many racers conventionally judge their efficiency according to the hardness felt upon the nail of thumb or their adhesive tendency to the sole of the ski.

To make such methods of measurement more precise quantitatively, we make a small hardness tester, a sort of penetrometer, and intend to clarify their complicated viscoelastic properties. The tester is a cone of 90° at the top, and has constant weight. We measure the depth of its penetration, and also measure the length of time of their penetration and observe the influence of temperature on them.

Next, we construct a miniature ski (model ski) of reduced weight, width and length, the reduction made according to the usual model experimental law, and coat them with the above mentioned ski waxes. We measure their kinetic and static frictions.

From these measurements, we can conclude that there exists a fairly regular relation between the viscoelasticity (or penetration) and frictions as shown above. We also wish to show some relation between the ski wax and the organic crystals instead of the snow crystals.

The Second Order Transition Temperature of High Polymer System

NISHIO HIRAI

(Faculty of Science, Okayama University)

Recently P. J. Flory and K. Ueberreiter considered the second order transition temperature as a isofree volume state at which the free volume of the high polymer system is of a certain constant value. From this view point, the relations between the second order transition temperature T_2 and the thermal expansion coefficient β_2 and T_2 and melting temperature T^1 are considered. The author evaluated the empirical formula of Boyer and Spencer that the product of β_2 and T_2 is constant about 5% for various substances.

The author postulates that the melting point T^1 indicates another iso-free volume state and induces the relation : $T_2/T^1=0.7$.

This is the empirical rule which was found recently by R. G. Beaman, *J. Polymer Sci.*, **9**, 470 (1952); N. Hirai, *J. Chem. Soc. Japan*, **74**, 445 (1953); and E. Junckel, *Kolloid Z.*, **130**, 64 (1953), independently.

The volume fractions and T_2 's of plasticizer and polymer are v_1 and v_2 , T_{21} and T_{22} , respectively, then the T_2 of the system is represented as follows :

$$T_2 = v_1 T_{21} + v_2 T_{22} - \Theta v_1 v_2$$

$$1.3 \cdot R \cdot \Theta = w_{12}$$

where w_{12} is the interaction energy between plasticizer and polymer. This formula can be applied not only to polymer-plasticizer system but to the copolymer system and self-plasticidation.

Meaning of Frozen State of High Polymers

JUNJI FURUKAWA

(Department of Industrial Chemistry, Faculty of Engineering, Kyoto University)

Boyer and Spencer interpreted the frozen state or the second-order transition point through the use of concept of iso-viscous or iso-elastic state, about which, however, no complete explanation was given. The author has suggested the cross-linking theory, by which viscoelastic behaviour of linear high polymers was theoretically elucidated. In the equirebrium state with respect to cross-linkage, the following equation is given.

$$v \exp \left\{ (S/vkTA^1)^2 (v v_0/2\rho) \right\} = K(N_0 - v) \quad (1)$$

where S is stress per cross sectional area A^1 , v_0 is the volume of the segment, ρ is density, N_0 is the number of segments per cc and K is equilibrium constant of cross-linkage. This equation gives the negative value of (dv/dt) but in the following temperature it follows that $dv/dt=0$:

$$T_f = \frac{1}{vkh} \left(\frac{S}{A^1} \right)^2 \frac{v_0}{2\rho} \quad (2)$$

$$\text{or } \frac{h}{2} = kT(\lambda^2/2\rho n) = -kT \ln \frac{N_0 - v}{v} \quad (3)$$

where λ is elongation of the chain and n is the number of segments per chain. In the equation (3) the first term denotes the half formation heat of cross-linking, the second a thermal free energy of segment, and the third a mixing energy of linked and unlinked segments, in other words, the free energy necessary for the migration of the linking. T_f should mean the ideal fusing point. Below T_f , the concentration of v decreases with cooling, but assuming the limit value of λ , which is equivalent to the value at ultimate

elongation of the chain, (dv/dt) becomes zero again in another point T_m , i.e.,

$$\lambda = cn/n^{\frac{1}{2}} = c/(\nu v)^{\frac{1}{2}}, \quad (4) \quad c = \text{const.}$$

$$T_m = h\rho/kc^2 \quad (5)$$

Below the temperature T_m , it follows that

$$kT(\lambda^2/2\rho n) > -kT \ln \frac{N_0 - v}{v}$$

From this equation, it is understood that below the freezing point the migration energy of linking is larger than the vibrational energy of the segment and such a condition results in the fixing of linking and ideal elastic state.

The effects of the solvent, molecular weight of polymer and applied stress are also discussed.

Viscoelastic Behaviours of Polyvinyl Acetate Films

RYEUM SEUNG KEUN

(Chemical Institute of Kyoto University)

Viscoelastic properties, such as dynamic modulus, viscosity and mechanical loss tangent, of polyvinyl acetate films were measured by means of the vibrating reed method over a frequency range from 20 to 80 cps at 5-40°C. The polymer sample (PVAC₀) was obtained by polymerizing the monomer in emulsion with emulsifier "Monogen" and its DP was determined by viscosity measurements as 6380. This polymer sample was changed into polyvinyl alcohol of DP 960 by saponifying it with NaOH. Polyvinyl alcohol thus obtained was acetylated again into acetate (PVAC₁) in pyridin-acetic anhydride. Its DP was found by viscosity measurements to be 930. PVAC₀ has more branchings and linkages than PVAC₁, and hence the former can be considered to be heterogeneous while the latter, homogeneous.

(1) *Temperature and Frequency Dependences of the Dynamic Modulus.*

The dynamic modulus of each sample increases with decreasing temperature and approaches a limiting value of $3.8 \cdot 10^{10}$ dynes/cm² at temperatures below 20°C. In a transition region, however, it decreases with increasing temperature. The decrement of the modulus of PVAC₀ is larger than that of PVAC₁, and the difference between the observed values of modulus of PVAC₀ on heating and cooling can hardly be observed at temperatures below 20°C. The dynamic modulus measured at constant temperatures is almost independent of the frequency.

(2) *Effects of the Frequency and Temperature on the Dynamic Viscosity.*

Dynamic viscosity η increases with increasing temperature until about 30.3°C, but at higher temperature it decreases with increasing temperature. The values of η measured at constant temperature are approximately proportional to the reciprocal of the frequency.

(3) *Temperature and Frequency Dependences of the Loss Tangent.*

Loss tangent $\tan \delta$ measured at constant frequency increases at first with increasing temperature, and after reaching the maximum at about 30.3°C becomes smaller again. Thus, polyvinyl acetate has its transition point at about 30.3°C. On the other hand, when the measurements were carried out at constant temperature, maxima of $\tan \delta$ could be found in a frequency range of 40-50 cps.

(4) *Values of the Reduced Factor.*

Values of the reduced factor (at 25°C) obtained from the observed values of the modulus according to Ferry do not agree with those obtained from the viscosity, showing that an anomalous dispersion of the complex dynamic modulus occurs in the transition region.

Studies of High Polymers by Ultrasonic III

YO MAEDA

(Central Research Laboratory, Hitachi Co. Ltd.)

Elastic moduli and losses of natural and synthetic rubbers were measured by pulsed ultrasonic waves of frequency 2.67 MC over the temperature range from -60°C to 90°C . It was found for all samples that the modulus decreases with increasing temperature and the maximum of loss factor occurs at some temperature in this range. The temperatures at which the peaks of $\tan \delta$ occur are -13°C and -12°C for natural and GR-S rubbers, 30°C and 14°C for Hycar OR-15 and GR-1 respectively. Attenuation 87 db/cm for GR-I is the greatest and 39 db/cm for GR-S is the smallest.

Plotting the complex compliance in complex plane, we obtain the so-called Cole-Cole's circular arc. From the above data, the parameter α , which measures the distribution of relaxation times, are 0.48 the smallest for natural rubber and 0.59-0.66 for the others. We notice that these values of α are all smaller than the previously reported values 0.72-0.78 for polyvinyl chloride.

Measurements of activation energies and comparison to dielectric properties are at present being attempted.

On the Hysteresis and the Non-Linear Vibration Characteristics of Textile Materials

TOMONOBU MANABE

(Synthetic Laboratory, Nippon Rayon Co., Ltd.)

Vibration characteristics of high polymer materials observed by many researchers are non-linear, so if a differential equation which represents the vibration characteristics is found and the relations between the constants in the differential equation and the constants considered as material constants are clarified, these constants become very effective means to obtain the information about the materials and specify their physical properties. From this point of view, a non-linear differential equation is assumed and the relations between these constants are clarified and the method of measuring these constants is proposed and the relation between the energy dissipated during vibration and those constants is described.

Study on the Frequency Dependence of Internal Friction of Several Textile Fibres, III

Measurements of the propagation constants of longitudinal waves along the several textile fibres over ranges of frequency from audio to super-sonic

K. FUJINO, H. KAWAI, T. HORINO AND K. MIYAMOTO

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The propagation constants of longitudinal waves along the several textile fibres (viscose rayon, Bemberg rayon, acetate rayon raw silk, degummed silk and Amilan-synthetic polycapramide fibre) were measured under constant static tension by means of the longitudinal wave resonance method (mainly at lower frequency experiments) and of the longitudinal wave propagation method (mainly at higher frequency experiments) over ranges of frequency from 2 Kc to 200 Kc and of relative humidity from 5% to 90% at constant temperature, 20°C .

Although the principles of both the experimental methods are quite the same as mentioned by A. W. Nolle in 1947, the apparatus employed by us is of a vertical type and is very different from that of the horizontal type which has been used by S. Silverman et al. since 1944. Because the conventional apparatus of the horizontal type has a defect that the contact condition between the sample strip and the wave detector is hardly kept constant during the observations and consequently the accuracy of measurements of attenuation constant is very low.

Generally speaking of any sample, the propagation wave velocity increases slightly with increasing frequency and decreases with increasing moisture contents in the sample strip, but the frequency dependence of propagation wave velocity is not affected so much by the changing moisture contents, with the exception of a few special cases of Amilan at relatively lower humidity.

The attenuation constant, on the other hand, increases with increasing moisture contents and decreases remarkably with decreasing frequency. The logarithm of the attenuation constant bears a straight-line relation between those of frequency. This straight-line inclines about 45 degrees against frequency axis, and furthermore the slope of this line decreases slightly with increasing moisture contents in the sample strip.

Using these propagation constants, the dynamic modulus of elasticity and mechanical loss tangent were evaluated and their frequency dependences were examined.

It is concluded from our experimental results that for any textile fibre no anomalous dispersion can be found in the frequency range covered, though for various gum strips such anomalous dispersion were found by Witte, Mrowca, Ivey, Guth et al. (1949) in the same frequency range. Furthermore, according to the model theory of the continuous distribution of retardation times, the shape of the so-called "retardation spectrum" of any textile fibre seems to be smooth in this frequency range and very different from that for gum strips.

On the Dynamical Behaviour of the Rubber Vibration Absorber Under the Test of Constant Rate of Loading

YOSHIKAZU SAWARAGI AND NARINOBU SUGAI
(Faculty of Engineering, Kyoto University)

On the Dynamical Behaviours of the Natural Rubber Stocks in the Vibration Test

YOSHIKAZU SAWARAGI AND HIDEKATSU TOKUMARU
(Faculty of Engineering, Kyoto University)

Interpretation of Mechanical Behaviours of Viscose Rayon by a Classical Mechanical Model

ICHIRO SAKURADA

(Department of Textile Chemistry, Faculty of Engineering, Kyoto University)

On the basis of a consideration that crystalline regions in a fibre affect neither the ultimate strength, elongation nor the modulus of elasticity of the fibre while amorphous regions do affect, the chain molecules or masses of them in the amorphous regions were assumed to be equivalent to springs and dashpot in a mechanical model. Thus, when a cellulosic fibre is subjected to hydrolysis with mineral acid, parameters of the mechanical model must be altered, since hydrolytic reaction must occur mainly in the amorphous regions and parts of chain molecules in these regions must be ruptured.

SUMMARIES OF PAPERS

read at meetings of the Society

A theory of stress and birefringence in a flowing polymer solution

A. S. LODGE

(British Rayon Research Association, Heald Green Laboratories, Wythenshawe, Manchester)

It is assumed that in a concentrated solution, the polymer molecules form a loose network structure whose junctions arise from secondary forces and entanglements and continually break and form. When the solution flows, the network deforms, and the consequent change in configurational entropy gives rise to a stress which is calculated in terms of flow history by means of Green and Tobolsky's extension of the kinetic theory of rubberlike elasticity. A similar theory is used to calculate flow birefringence which arises from network deformation when the chain links are optically anisotropic. Hydrodynamic resistance and form birefringence are neglected.

The proposed mechanism seems capable of giving viscosities of the observed magnitude. The viscosity is independent of shear rate. The theory gives a "Weissenberg effect" associated with a tensile stress in the direction of the streamlines in stationary shear flow, as observed in rubber and other solutions. It is predicted that, on cessation of a shear flow, this tensile stress will relax more slowly than the tangential component of stress unless all junctions have the same mean lifetime, in which case both stress components relax together.

For any flow history at constant temperature, the stress and refractive index ellipsoids are coaxial, and their anisotropies are proportional. This leads to a constant stress-optical coefficient $2 \Delta n / \Delta p = \Delta n \sin 2\chi / \tau$ (where Δn denotes a difference of principle refractive indices, Δp the difference of the corresponding principle stresses, χ the extinction angle, τ the shear stress) different from the "Maxwell constant" $\Delta n / \tau$ except at low shear rates when $\chi = 45^\circ$. Published data on moderately concentrated polystyrene solutions yield values of this stress-optical coefficient which are constant over appreciable ranges of shear rate, polymer concentration and chain length distribution and which give a value for the optical anisotropy of an equivalent random link which agrees with that obtained from measurements on pure polystyrene in the rubberlike state at 110°C .

Paper read 29th April, 1955.

Relaxation Processes in Glass

P. L. KIRBY

(Research Laboratories, J. A. Jobling and Co. Ltd., Sunderland)

Reversible delayed elastic deformation in glass and internal friction effects are attributed to the same complex relaxation process and the wide range of relaxation periods involved is described by a distribution function. The approximate form of this relaxation spectrum is obtained from the analysis of experimental measurements. Results for the relaxation spectra of "Pyrex" glass at several temperatures up to the annealing range are given. Annealing increases the width of the distribution function.

The migration of alkali ions in the vitreous network gives rise to another relaxation process and the half-maximum widths of the relaxation spectra are compared with those relating to the viscoelastic effects of the entire network. The distribution of relaxation periods suggests a distribution of the activation energies governing the process. A measure is thereby obtained of the associated distribution of potential barrier heights in the vitreous network. The migration of a network-modifying ion is subject to a wider range of irregularity of activation energy than the general viscoelastic deformation of the network-forming ions.

Paper read 30th April, 1955.

Propagation of ultrasonic shear waves in viscoelastic substances

E. W. PRYOR and E. G. RICHARDSON

(King's College, Newcastle)

Using ferrite transducers of 50 and 100 kc/s excited by magnetostriction means, torsional waves have been sent down long rods made of metal or glass.

By varying the temperature in a furnace surrounding the rod, and measuring the attenuation and phase shift of transmitted pulses the elastic modulus and viscosity of the material of the rod were measured.

At room temperatures the rod was jacketed by a liquid in to which the rod transmitted shear waves. From the additional attenuation, the absorption coefficient in the liquid was derived.

A study of solutions of rubber in benzene and of gum arabic in water at various concentrations in this respect was made. The absorption was less than in pure solvent. The fact that the absorption in these highly viscous solutions is many times less than those calculated from the classical formula by substituting the known shear viscosities can be explained by assuming that the high viscosities are by-passed by associated elasticities (*i.e.*, that these liquids behave, at high frequencies more or less as solids).

Paper read 30th April. 1955,

The Diamond Tool Industry in 1954

This is the 10th successive report in this series on the Diamond Tool Industry. It is divided into 18 sections, for instance, scientific aspects, hardness and micro-hardness, surface finish testing, fine boring and turning, truing of grinding wheels, etc. In each of these sections it is referred to outstanding work published during 1954 and in some instances also to publications in 1953. The publication of 12 pp. contains about 200 references. The literature referred to in this report can be obtained on loan, in England only, on application to: The Industrial Diamond Information Bureau, St. Andrew's House, 32-34 Holborn Viaduct, London, E.C.1.

RHEOLOGY ABSTRACTS

3160. Viscous flow in melts of "rigid anisotropic" molecules.

A. A. K. AL-MAHDI AND A. R. UBBELHODE. *Trans. Faraday Soc.*, 1955, **51**, 361.

3161. The behaviour of casting slips with organic peptisators.

H. L. ANDSAGER. *Trans. 2nd Int. ceram. Congr.*, p. 187, 1950.

Reference is made to the article by C. W. Parmelee and C. G. Harman (*Trans. Brit. Ceram. Soc.*, **30**, 30A, 1931) reporting that the use of organic bases prevented attack on plaster moulds. Their investigations comprised casting a number of plaster of Paris bars, subjecting them to the influence of slips with different electrolytes for 3 hr., drying them, then repeating the process a different number of times for each of the different bars. The strength of the bars was then tested. Prompted by Parmelee's and Harman's work, the author attempted to introduce piperidine as electrolyte in casting slip, basing it on a body of the following composition (%): Zettlitz kaolin, 25; English kaolin, 25; quartz, 28; feldspar, 22. During grinding, 0.2% BaCO₃ was added to remove sulphate. The relation between the concentration of piperidine and the viscosity of the porcelain slip after 24 hr. storing is shown. When NaOH is used, the viscosity decreases more than by using piperidine; it was not possible to show a similar curve to that for piperidine by using NaOH as electrolyte, even with slips with a much greater solids content. The opinions of other authors are quoted on the occurrence of 2 minima. As far as the properties of piperidine as a base as well as a protective colloid for kaolin are concerned, in the minimum interval only slight changes in the viscosity occur by doubling the amount of electrolyte, and the system on the whole shows comparatively little sensitivity to neutral salts which do not react with OH⁻. The effects of KCl, K₂SO₄, Ca(NO₃)₂, and BaCl₂ on a kaolin slip containing 0.008 mol. piperidine per litre of water, are shown. The viscosity, measured with a rotation viscosimeter, was 145 centipoises in the water slip and 31 centipoises in the piperidine slip. It is concluded that piperidine is unsuitable for the production of porcelain slips; it may, however, be of importance in engobe slips when it is necessary to lower the viscosity for spraying. B.C.R.A.

3162. Rheological properties of certain joint-sealing compounds for concrete canal linings.

E. R. BALLANTYNE. *Australia Commonwealth Scientific & Industrial Research Organization, Division of Building Research Technical Paper No. 2, Melbourne*, 1954.

The rational design of extrusion equipment for the placement of jointing or caulking compounds in buildings and civil engineering structures requires a knowledge of the flow properties of these materials. The flow properties of five proprietary bituminous jointing compounds, and of four modifications of one of these, were measured at various temperatures by extrusion through tubes of different lengths and diameters, and were found to approximate to the behaviour of a Bingham body. The pressures required to extrude the materials under some of the conditions likely to be met in the Kiewa hydro-electric project in Victoria are tabulated. A.

3163. Theory of elasticity and consolidation for a porous anisotropic solid.

M. A. BIOT. *J. Appl. Phys.*, 1955, **26**, 182.

A consolidation theory for the settlement under loading of a porous deformable elastic solid containing a viscous fluid is developed for the general case where there is anisotropy. S.T.

3164. The dissipation of frictional heat.

H. BLOK. *App. Sci. Rev.* 1955, 5A (2—3), 151.

3165. Sedimentation potential and velocity of solid spherical particles.

F. BOOTH. *J. Chem. Phys.*, 1954, 22, 1956.

The electrical effects accompanying the steady fall of solid charged spherical particles under gravity in an electrolyte are examined theoretically. For a single particle falling in an infinite electrolyte, it is shown that, owing to fluid flow round the particle, the double layer field is modified. The effect in the double layer region is complicated, but outside this region a field is set up of the same form as that which would arise from a dipole fixed at the centre of the particle with its axis vertical. A general expression is given for this dipole field in the case of non-conducting particles. The calculations extend previous work in that no restriction on the relative dimensions of the particle size and double-layer thickness is imposed. It is shown that the interaction between the charge on the particle and the modified field alters the sedimentation velocity of the particle. The calculations show that in practical cases the effect might, in favourable circumstances, reduce the velocity by a few per cent.

The analysis is extended to suspensions containing a large number of particles uniformly distributed. A.

3166. Sedimentation velocity and diffusion of a solvated substance.

PING-YAO CHENG. *J. Chem. Phys.*, 1955, 23, 191.

Based on the contention that the driving force for the motion of a species relative to the mass flow in a particular direction is the negative gradient of total potential of that species in that direction, equations for both the sedimentation velocity and the diffusion of a solvated substance are derived. They are reduced to the usual expressions for a nonsolvated substance. The partial specific volume term on the equations of sedimentation velocity is shown to have theoretical justification. The advantages of expressing the sedimentation velocity in terms of solvated species are discussed. It is also shown that for the diffusion of a solvated species the "thermodynamic factor" calculated in the usual way is always greater than the gradient of chemical potential of the solvated species, except at zero-concentration, by a previously neglected term arising from solvation. The effect of solvation on diffusion coefficient and on the relation between the frictional coefficients in the sedimentation and diffusion are also discussed in the light of this theory. A.

3167. The viscosity of pseudo-plastic fluids.

JU CHIN CHU, K. C. BURRIDGE AND F. BROWN. *Chem. Eng. Sci.*, 1954, 3 (6), 229.

A modified Ostwald viscometer was used to determine the apparent viscosities of sodium carboxy-methyl cellulose, polyvinyl alcohol and sodium polymethacrylate. A.A.M.

3168. Stresses exerted by water held in wet webs of paper-making fibres.

G. N. CHRISTENSEN AND W. W. BARKAS. *Trans. Faraday Soc.*, 1955, 51, 130.

3169. On the break-down of thixotropic materials.

SVEN-ERIC DAHLGREN. *Trans. Chalmers University of Technology, Gothenburg, Sweden*, 1955, No. 159.

3170. Rheology of moist cement pastes, or cement slurries.

R. DELLYES. *Rev. Mater. Constr.*, 1954, (465), 193-213.

The report discusses the rheological properties of plastic fluids of the Bingham type and their application to the production and transport of raw cement slurries in the cement industry. The theory of viscous or Newtonian fluids is first developed, and a general differential equation for rectilinear permanent viscous flow is evolved which, with circular cylindrical flow, gives the Poiseuille formula. Similarly, the general differential equation for permanent rectilinear plastic flow is developed, and several examples are studied, particularly flow in a circular conduit for which a generalized Poiseuille formula is arrived at. The method of obtaining an approximate solution for the problem of flow in a pipe is presented. The use of the coaxial, adjustable-velocity viscosimeter for determining the rheological coefficients of plastic fluids, is justified, whilst the theory of this apparatus, its construction and calibration are dealt with. Examples of viscosity curves obtained experimentally are shown and interpreted. Some test results are reported for cement slurry when studying the variation of rheological coefficients with water content, addition of fluidizing agents, or other factors affecting flow. B.S.A.

3171. Application of the Galaskin method to problems in hydrodynamic stability.

R. C. DI PRIMA. *Quart. Appl. Maths.*, 1955, 13, 55.

A theoretical treatment of stability is applied to the cases of flow between co-axial rotating cylinders and flow over concave surfaces. R.R.

3172. Some fundamental experiments on high temperature creep.

J. E. DORN. *J. Mech. Phys. Solids.*, 1955, 3, 85.

The high temperature creep strain of thermally stable alloys appears to be a function of a temperature (T), compensated time (t), namely $t \exp(\Delta H/RT)$, and the stress, ΔH being the activation energy for creep. E.W.J.M.

3173. On the representation of rheological results with special reference to creep and relaxation.

P. FELTHAM. *Brit. J. Appl. Phys.*, 1955, 6, 26-31.

The remarkable qualitative similarity in the response of solids of widely different structures to applied stresses, particularly in creep and relaxation, is ascribed to relaxation centres all of which, in a given solid, have approximately the same heat of activation, but, on account of variations in their geometry such as shape and size, have different entropies of activation. A normal distribution of entropies of activation is shown to lead to a log-normal spectrum of relaxation times of the type originally proposed by Wiechert on heuristic grounds. Boltzmann's superposition principle and the relation between creep and relaxation derived by Zener are used to show that this distribution yields a form of stress relaxation curve common to many solids, as well as Andrade's $t^{1/4}$ -creep law. Experimental data, given in the literature, on the creep and relaxation in pure polycrystalline aluminium, rubber, polymethylmethacrylate and ceramics are shown to be in good agreement with the theory. The significance of Nutting's law of deformation is discussed. A.

3174. Extensions of the Rouse theory of viscoelastic properties to undiluted linear polymers.

J. D. FERRY, R. F. LANDEL AND M. L. WILLIAMS. *J. Appl. Phys.*, 1955, 26, 359.

The Rouse theory for viscoelastic properties of very dilute solutions is modified for application to undiluted linear polymers. With the effective segment mobility expressed in terms of steady-flow viscosity, the theory is applied to polymers of rather low molecular

weight essentially without further change. In high molecular weight polymers, it is assumed that for modes of motion with relaxation times above a critical value the effective segment mobility drops abruptly, in accordance with the effect of entanglement coupling on steady flow viscosity as described by Bueche. Properties in both the transition region between glasslike and rubberlike consistency and the rubberlike or plateau region are predicted semiquantitatively with no arbitrary parameters. In an alternative application to the transition region, the average effective friction coefficient per monomer unit can be calculated for both linear and lightly cross-linked systems. A.

3175. Rheological properties of coal during carbonization.

D. FITZGERALD. *Nature*, 1955, **175**, 515.

The strain-retardation and stress-relaxation phenomena were observed using a modified Gieseler apparatus. E.W.J.M.

3176. Determination of a viscosity scale in the region of the working zone.

J. HERBERT. *Verres et Réfr.*, 1954, **8**, 74.

The author shows that, for a given glass, the curve representing the variation of $\log 10^{13}/\eta$ (η being the coefficient of viscosity of the glass), as a function of the temperature logarithm, is composed of two straight lines. One of these lines corresponds to low temperatures in the plastic zone, the other to higher temperatures in the fluid zone. These two straight lines meet at a point corresponding to a temperature T_2 , for which $10^{13}/\eta$ has a value of *c.* 7.5, almost independent of the glass composition (except for glasses rich in B_2O_3 and Na_2O). After having indicated the practical method of determining this point, the author supports his results by a consideration of the structure of the vitreous network. B.C.R.A.

3177. Determination of compressive strength of concrete by using its sonic properties.

C. E. KESLER AND Y. HIGUCHI. *American Society for Testing Materials Proceedings*, 1953, **53**, 1044-51; *discussion*, 1052.

In predicting the quality of concrete by sonic methods, the prediction is usually based on the initial modulus of elasticity; however, considering concrete as viscoelastic, an analysis of a rheological model of concrete clearly shows that a property in addition to the initial modulus of elasticity must be considered. The one property, other than modulus of elasticity, that promises to be of greatest help in predicting the strength of concrete is the coefficient of viscosity. While this property may be an excellent one to use, it cannot be determined readily from sonic tests of concrete; but logarithmic decrement, which is related to the coefficient of viscosity, can be easily obtained from sonic tests. To establish whether or not there exists a relationship between the modulus of elasticity and damping capacity of concrete and the compressive strength of concrete, some 300 standard 6 by 12 in. cylinders were tested. From the test data a set of curves is obtained from which the strength of concrete, made of aggregates used in this investigation, can be predicted. The accuracy of the prediction is generally within an error of 5 per cent. This accuracy can be obtained without knowledge of the age, mix or moisture content of the concrete. The results clearly show why the use of the modulus of elasticity alone is not sufficient to predict accurately the strength of concrete. A.

3178. Intrinsic viscosity of flexible macromolecules: corrected tables.

J. G. KIRKWOOD, R. W. ZWANZIG AND R. J. PLOCK, *J. Chem. Phys.*, 1955, **23**, 213.

The corrections apply to a table given in a previous paper. (*J. Chem. Phys.*, 1948, **16**, 565.) S.T.

3179. Self-diffusion coefficient and viscosity in liquids.

J. C. M. LI AND P. CHANG. *J. Chem. Phys.*, 1955, **23**, 518.

The relation between self-diffusion coefficient and viscosity is examined in terms of the early hydrodynamic theory and Eyring's kinetic theory. They differ by a factor of about 6. A detailed consideration of the kinetic theory shows that this factor should have been included in Eyring's derivation of viscosity if a proper meaning is given to the relative velocity involved. A.

3180. Rotations, orientations and collisions of suspended particles in velocity gradients.

R. ST. J. MANLEY, A. P. ARLOV AND S. G. MASON. *Nature*, 1955, **175**, 682.

A study of the behaviour of rods, glass spheres and bubbles in a liquid subject to a velocity gradient undergoing rotational and translational movements. E.W.J.M.

3181. Modifications of structural-mechanical properties of flour doughs by mechanical working.

B. A. NIKOLAEV AND L. S. BEGANSKAYA. *Kolloidnyi Zh.*, 1954, **16**, (6), 455.

Describes a complicated apparatus for compressing cylinders of dough. Deformation and recovery curves are shown and effects of working and resting on Young's modulus, viscosity and their ratio are given. Results confirm much earlier work. G.W.S.B.

3182. A molecular approach to the problem of viscoelasticity.

A. H. NISSAN. *Nature*, 1955, **175**, 424.

The stress-strain behaviour of paper is considered as a problem of chemical kinetics. During deformation the energy input goes to raise the hydrogen bond potential, the bonds between fibres being almost entirely made up of hydrogen bridges between cellulose and hemicellulosic components. The following equation is derived, using the Morse function: $f = E\sigma - K\sigma^2 + \dots$ where f is the stress, σ the strain. $E = 2a^2U_0$ and $K = 3a^3U_0$. U_0 is in units of energy per unit volume. a , can be evaluated rheologically as $2K/3E$ or spectroscopically from the infra red absorption of cellulose. E.W.J.M.

3183. The plastic collapse of cylindrical shells under axially symmetrical loading.

E. T. ONAT. *Quart. Appl. Maths.*, 1955, **13**, 63.

3184. The propagation of sound in solutions of rubber and perspex.

A. W. PRYOR. *Acustica (Zurich)* 1954, **4**, 658.

The ultrasonic attenuation in the frequency range 4—18 Mc/s of rubber in benzene (1, 5 & 10 g/100cc) and of perspex in pyridine (3g/100 cc) and the dynamic shear resistance at 50 Kc/s of a rubber solution (10 g/100 cc) were measured. The ultrasonic absorption of the solutions was found to be less than that of the solvents. The elastic relaxation is found to agree with the usual model of a spring in series with a dash-pot, both in parallel with a dash-pot. The high shear viscosity appears to be relaxed even at 50 Kc/s. L.G.

3185. Velocity and absorption of ultrasonics in liquid sulfur.

A. W. PRYOR AND E. G. RICHARDSON. *J. Phys. Chem.*, 1955, **59**, 14.

In order to derive some of the visco-elastic properties of liquid sulfur, particularly in the transition region where polymerization takes place, measurements of ultrasonic velocity and attenuation over the range of temperature 100 to 250° have been made. Comparison is made between the "ultrasonic viscosity" deduced from such measurements and those derived in a conventional viscometer. A model is suggested to account for the acoustic behaviour of sulfur above 160°. A.

3186. Mechanism of the disruption of liquid jets.

E. G. RICHARDSON. *Appl. Sci. Res.*, **A4**, 374-380.

By means of a technique of micro-flash illumination, photographs are obtained of a water jet issuing from a straight nozzle. Three regimes of flow can be distinguished, each of which results in a special type of break-up into drops. The sinuous type and the type called "atomization" are discussed in the light of theory. A.

3187. On anomalies of the onset of turbulence in colloidal solutions.

I. I. ROGACHEV. *Kolloidnyi Zh.*, 1954, **16**, (6) 464.

Phenomenon is described in terms of modifications in the flow-profile in anomalous systems. G.W.S.B.

3188. Experiments on the creep of concrete under two-dimensional stressing.

A. D. ROSS. *Mag. Concr. Res.*, 1954, **6**, (16), 3-10.

The tests were designed to investigate the creep of concrete specimens under (a) two compressive principal stresses, and (b) one compressive and one tensile principal stress. The equipment for producing the stresses and the gauges for measuring the strains are described. Results are presented which suggest that creeps develop in the principal directions with magnitudes generally of the same order as the corresponding creeps under simple stress. Poisson's ratio for creep strains appears to be negligible. A.

3189. A new optically-recording apparatus for the measurements of the "viscosity temperature" of glass.

W. ROTHE. *Silikat Tech.*, 1954, **5**, 296.

With glass 4 regions of viscosity are distinguished: (1) the de-stressing region, in which the viscosity has a value of about 10^{13} poise; (2) the working region in the blow lamp, with a viscosity of 10^5 - 10^9 poise; (3) the lower liquid region, corresponding to the glass-working region in the tank and therefore also called the "gathering viscosity", corresponding to 10^3 poise; this is the order of the viscosity both for manual and machine working; and (4) the upper fluid region during melting or refining, about 10 poise. Of these, stage (2) is of particular importance. Since the viscosity depends essentially only on the temperature and the glass composition, this so-called "viscosity-temperature" is a characteristic of any glass. A full description is given of a new apparatus for measuring the "viscosity-temperature". B.C.R.A.

3190. Dislocation model of liquids.

J. ROTHSTEIN. *J. Chem. Phys.*, 1955, **23**, 218.

A liquid model which combines the advantages of hole and crystallite theories of liquids is suggested. S.T.

3191. Viscosity anomaly of supercooled liquids.

G. W. SEARS. *J. Chem. Phys.*, 1955, **23**, 604.

The anomaly is explained by assuming that thermodynamically stable rods of the solid phase exist in the supercooled liquid. S.T.

3192. Laminar flow in channels with porous walls at high suction Reynolds' numbers.

J. R. SELLARS. *J. Appl. Phys.*, 1955, **26**, 489.

The problem of laminar flow at high Reynold's numbers in channels with porous walls is considered by an iteration process as an extension of the simpler problem of laminar flow at low Reynold's numbers. S.T.

3193. Influence of particle shape on viscosity of clay suspensions.

J. SELSING. *Trans. 2nd Int. ceram. Congr.*, p. 21, 1950.

Viscosity measurements in dilute suspensions of clay and kaolin will reveal differences in particle shape, and thereby indicate whether more careful investigation will pay. Viscosity measurements will indicate the amount of very small particles in a shorter time than sedimentation methods, and hereby they afford a quick and objective estimation of the plasticity. Viscosity measurements are very inexpensive and are easily executed.

B.C.R.A.

3194. The plastic indentation of a layer by a flat punch.

R. T. SHIELD. *Quart. Appl. Maths.*, 1955, **13**, 27.

3195. On some interrelationships in butter-churning processes.

V. N. SHUVALOV AND I. N. NLODAVETS. *Kolloidnyi Zh.*, 1954, **16**, (5), 396.

A further description and extension of earlier work. (See Abstr. 2328.) G.W.S.B.

3196. Elastic constants of AgBr at 28°C.

D. S. TANNHAUSER AND A. W. LAWSON. *J. Chem. Phys.*, 1954, **22**, 2092.

The elastic constants of AgBr single crystals have been obtained by an ultrasonic pulse method.

S.T.

3197. Temperature dependent creep in zinc crystals.

D. O. THOMPSON. *J. Appl. Phys.*, 1955, **26**, 281.

Tensile creep measurements obtained with seven single crystals of zinc of 99.99% purity can be described by the empirical formula $\mu = bt^m$ where μ is the shear strain, t the time after the completion of the application of stress, m a temperature dependent parameter the form of which is given, and b is another parameter which though temperature independent is not stress independent.

S.T.

3198. Continuous automatic control of consistence of Portland cement slurry.

E. V. TKACHEV. *Tsement*, 1953, **19** (2), 8-14; *Silikattech.*, 1954, **5**, 177-8.

Cement slips are typical non-Newtonian systems in their flow characteristics, slightly thixotropic as clay-limestone-water mixes, and have a Bingham yield value, combined with a hysteresis of the flow curve. In practice, the apparent viscosity is sufficient to control the flow and consistency of the slurry in certain empirical limits. The toleration in which these limits are given can be determined by two photocell systems, connected to electronic controlling circuits to regulate the feeding rate from the slip container into the burning zone of the cement furnace. The optical equipment is very simple: the flow parabola of the slip jet is projected on the margins of the photocells, and every deviation from the normal parabola is immediately indicated by a partial screening of the photocells. The whole mechanism works entirely automatic and is highly reliable.

B.S.A.

3199. Creep of zinc crystals.

E. P. T. TYNDALL, R. A. ARTMAN, C. A. WERT AND R. EISNER. *J. Appl. Phys.*, 1955, **26**, 286.

The plastic extension of zinc crystals in the region just beyond the elastic limit is found to obey the empirical law, $\mu = bt^m$ in which μ is the resolved shear strain, t is the time, m is a constant with a value close to 0.5 for initially unstrained crystals and b is dependent on the resolved shear stress. Application of a theory due to Koehler shows that b should be related to stress (σ) in such a way that a plot of $\ln(mb\sigma^2/\Delta\sigma)$ against $1/\sigma$ should be a straight line of slope $-cG$. In this, $\Delta\sigma$ is the stress increment from one creep

curve to the next, G is the shear modulus, and c is the concentration of anchor points which determines the lengths of segments of dislocation lines which generate according to the Frank-Read mechanism. The experiments are in fair agreement with this theory and values of c obtained are roughly equal to the concentrations of metallic impurities. The small amount of dissolved gases appears to play no significant part in the creep process. A.

3200. On the flow of thick greases.

D. S. VELIKOVSKII. *Kolloidnyi Zh.*, 1954, 16 (6) 406.

At high rates of shear in a capillary tube, greases show Bingham ("Shvedov") behaviour. At low stresses, there is a true yield-value, followed by an inflected (Ostwald) curve; but the "Laminarast" extrapolates to a small intercept on the stress axis. Wall-stress is plotted *vs* shear rate. (Assuming correct interpretation of undefined symbols.) G.W.S.B.

3201. Conference on structural-mechanical properties of colloidal systems and macro-molecular compounds. (Report)

M. P. VOLAROVICH. *Kolloidnyi Zh.*, 1954, 16 (6), 475.

Held at Inst. of Phys. Chem., Acad. Sci., (U.S.S.R.), (Dec. '52—Jan. '53).

Many well-known rheologists attended: Rebinder, Trapeznikov, Vinogradov, Tolstoi, etc. G.W.S.B.

3202. Plastic deformation of ceramic-oxide single crystals.

J. B. WACHTMAN AND L. H. MAXWELL. *J. Amer. ceram. Soc.*, 1954, 37, 291.

It was found that plastic deformation takes place in periclase above 1,100°C., in rutile above 600°C., and in sapphire above 900°C. The mechanism is slip; in sapphire (0001) is the slip plane and (1120) is the slip direction. All creep curves for sapphire in tension show the same qualitative features. Each consists of 3 stages: a stage of increasing creep rate (sometimes called an incubation period), a stage of large but decreasing creep rate (sometimes called first-stage creep), and a stage of small and nearly constant creep rate (sometimes called second-stage creep). The so-called third-stage creep, characteristic of metal, has not been noted. Plastic deformation increases the electrical resistivity of sapphire at constant temperature. B.C.R.A.