RHEOLOGY BULLETIN

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SOCIETY OF RHEOLOGY

RHEOLOGY BULLETIN

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EDITORIAL

The Role of the Rheologist

Our friends the British have to be thoughtful and wise in their use of paper, restricting it to essential functions only   The Paper Control authorities have advised the Rheologists' Club that a limited use of paper is permissible provided the information circulated is felt to be necessary to the national interests. This action places a serious responsibility on those concerned with matters of publication of technical material as well as material of other kinds.   It forces your Editor to give thought to the role of the rheologist in these times of stress.   Our membership represents many industries directly involved in the war effort, petroleum and paper products, resins and rubber, proteins and plastics, ceramics and cements, to mention only a few. Our membership plays a real role in the technical guidance of these industries.   Our Bulletin is designed to serve the membership by being a medium of exchange of information of mutual interest.   It is primarily a cooperative enterprise of the members, and if Dr. A. in Alabama or Mr. M. in Michigan has gained something of value from its perusal he should feel the urge and obligation to send in an abstract or two for the general good. This takes times, of course, and it is to the credit of our members that they are all extra busy these days, but if the Bulletin is worth doing at all it is worth doing well.   The Editor regrets to announce that several letters have been received from regular contributors asking to be excused from further activity, for the time being.   This is the Society's problem, and it is a serious one.

For the benefit of new readers, it may be stated that the Bulletin does not appear monthly, and that back numbers of the current volume are the only ones forwarded free of charge to new members.

The 1942 Fall Meeting

The Society of Rheology will meet at the Hotel Pennsylvania on October 30th and 31st.   As was the case last year the meeting will be held concurrently with that of the Optical Society of America.   The program committee under the Chairmanship of Dr. W. F. Fair, Jr., has already lined up a number of interesting papers.   Full details will be announced in the next issue of the Bulletin.

The 1942 Colloid Symposium

About 1C0 members attended the Colloid Symposium which was held in June at Boulder, Colorado.   According to an announcement in the News Edition of the American Chemical Society the various papers will appear this fall in the Journal of Physical Chemistry.

AMERICAN CHEMICAL SOCIETY

Division of Physical and Inorganic Chemistry
Symposium on "Flow Under Abnormal Conditions"

R. Simha—Brooklyn Polytechnic Institute
"Anomalies of Flow and Their Theoretical Interpretation"—40 Min.
N. W. Taylor—The Pennsylvania State College
"Anomalous Flow in Glasses"—40 Min.
Wm. D. Harkins—University of Chicago
"Viscosity Studies in Two-Dimensional Systems"—40 Min.
E. O. Kraemer—Franklin Institute
"Abnormal Flow Properties of Organic High Polymers"
—40 Min.

This symposium will be presented at the Buffalo, N. Y., Meeting, on Tuesday, Sept. 8, 1942. Abstracts of these papers are printed by the Division of Physical and Inorganic Chemistry, and will be available at the meeting, or by writing to Prof. Oscar K. Rice, Dept. of Chemistry, University of North Carolina, Chapel Hill, N. C. The program was arranged by Professor H. Mark of the Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

Seminar on "Elasticity and Plasticity" at the Polytechnic Institute of Brooklyn

Review by H. L. Bender

A very interesting Saturday morning seminar has been held on alternate Saturdays this past winter at the Polytechnic Institute of Brooklyn. Fourteen meetings were held and were devoted to the fundamental study of "Elasticity and Plasticity" of crystalline solids, of normal liquids and of polymers. Lectures were held and discussions headed by H. Mark, R. Simha, H. Ellickson, T. Alfrey, F. Seitz, R. Fuoss, R. Speiser, S. Primakoff, H. Eyring, J. Press, H. L. Bender, and M. Harris. The main credit for instituting the series should go to Dr. Mark.

The following outline of the lecture notes indicates their possible interest to the questions of plasticity and flow. These seminar meetings are expected to continue next winter.

The first two lectures were by H. Mark. They covered the solid crystalline state as to structure and as to the internal reasons for external structure and strength values. He first detailed the facts of visual observation of crystals and crystal growth. Then consideration was given to the elementary cell data from X-ray measurements. Slides of the X-ray pictures were given and fine details of the images caused by superposition of reflections from atoms, molecules and particles were carefully explained. The separation of fundamental lines from secondary radiation effects was detailed with emphasis on the three dimensional crystal lattice distance which make up the unit cell or

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smallest separating distances. References were made to data and explanations in the book "The Modern Theory of Solids" by F. Seitz.

The second lecture by Dr. Mark went quite fully into the data and conclusions of intensity measurements of the X-ray reflections. Crystals were classified by the force holding the atoms in the lattice as to ionic, atomic metallic and molecular forces of both positive and negative types. The particles thus balance in a three dimensional space. Between such balancing atoms there will be variations of distances and of intensity of force considered as electronic. Positions of low electronic intensity were considered as actual holes in the structure. The conclusion was given that an ion or atom is held within a definite bonding region by at least six forces. The main Coulomb forces were considered as corrected by repulsive forces, dipole forces and zero point forces to get the final picture of a crystal solid where the crystal parts are held in place to resist movement in any direction.

Dr. Ellickson then treated the general theory of elasticity and plasticity from the viewpoint of the strength of solids. Time elements were given as essential for plasticity but eliminated for elasticity formulas. The elasticity position which a given force will induce was calculated in detail for gases and for solids. It was shown that under most favorable conditions at least three constants are needed to define the motion of a material and under unfavorable conditions the number of constants needed approach 36. The differences in the three main constants are used to express a difference in the proportion of the different forces which hold the solid together. The case of ionic overlap in metals was used to explain how some forces get so far from the average as to greatly affect the measured strength values of solids. Many of these forces holding solids are measured by sending waves through the solid and measuring the velocity in different directions.

Dr. Simha covered the response of the crystal atoms to outside forces. Diatomic molecules were first considered as under constant vibration. For gases, this vibration path extends over the whole volume, for solids paths are around a fixed position, with short vibrations. Then outside applied forces affect these vibrations. It is evident also that internal forces such as crystallizing forces also greatly affect the space covered by these atomic and molecular vibrations. Gaseous molecules are smaller than solid molecules but they move over greater total volume space. For mathematical reasons the vibrations were expressed as waves. Detailed wave calculations were shown for solid molecular particles. From the vibrations of diatomic molecules the force equations and wave lengths were derived for waves periodic in time and in space. As a demonstration experiment the presence of standing waves in a series of gas flames was demonstrated. Here the number and position of flame nodes changed

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with every change in noise vibration impressed on the flowing gas stream.

Data was given to show that energy waves transported through different materials gave different values of velocity as a result of the difference in atomic holding forces. Change in size of the holding force, as by change in temperatures will change the size of the vibration space but not change the solid volume until a transition force or temperature is reached.

Dr. Alfrey lectured on the thermodynamics of crystal structures. He summed up the knowledge of the heat capacity of crystals. The low temperature failure to follow the law of Dulong and Petit was stressed. The curves of specific heat often show short humps at transition points and this was explained in detail. The shape of the crystals was related to a minimum free energy content. He gave details of mechanical models which had been constructed to explain crystal elasticity and plastic flow. Such models provide a mechanism to explain the facts that for polymers the experimental curves change with stress and with time. Short range Van der Waals forces and valence bond forces seem well established. The fact that high polymer forces continue over long range means that some additional mechanism is needed. The high polymer data is, at present, explained by the curled molecular model. Such molecules on extension open side attractive forces something like a zipper process.

Dr. Mark restated this in another way as being similar to internal bond severance, that is, like an intense gasification. Contraction is then internal condensation. The picture becomes more complicated on consideration that the molecules freed from curling can then crystalize. Stretching thus can induce crystallization at local spots. The net result for stretched rubber is a free energy increase and also a decrease in entropy or in motion.

Dr. Seitz gave a very excellent address on the plasticity of solids. This was a qualitative survey showing some unknown factors and pointing to some well marked directions for future progress. The properties of single crystals were first surveyed. Slides of such crystals stressed were shown. Slips developed along parallel bonds but not every slip plane lets go. The spacing for developed slip planes for silver crystal is one micron. Liquids and plastics flow along three directions and in planes of size less than 1 micron. The value of a shear resistance to slip is very dependent upon the purity of the specimen and for silver, an amount of impurity of one part per 100,000 greatly raises the shearing stress. Cold working increases the strength thus in the same direction as effects of impurities. The measured value for slip is 10^7 dynes per square centimeter while the calculated value is 10^{10} dynes. The difference is considered as the effect of impurities in the crystal lattice. The known types of imperfections were surveyed. The effect of cold working of a

metal was shown to result in a stored energy as high as 1.2 cal. per gram for iron. Tests for location of this stored energy gave a summation of the energy as mostly stored on the atomic scale. All crystals in general show a cold work and an annealing effect. The effect of cold work is considered as dislocations. Two like dislocations are considered to repel each other and thus to attract and neutralize unlike dislocation regions. Thus a maximum of cold work energy is a maximum for such dislocations. The dislocation spots are about 1000 atoms apart. All such energy is stored as hardened spots which will anneal and for some metals the annealing temperature is at room temperature; for instance Zn completely regains its annealed value in 24 hours at 25°C.

Dr. Fuoss gave a fine address on the electrical properties of solids. Conductors have low resistance and do not store charges. Insulators are any solid which will store a charge for a time element. Non-polar materials conduct by electronic response whereas polar materials conduct by both electronic and by dipolar movements. Electronic density and free space are both involved in conductance, thus metallic alloys so constructed as to reduce free space will have high resistance. For instance, Mg_2Pb is not a good conductor as a solid. Impurities added to metal scatter the electron stream and thus increase resistance in direct proportion to the added impurity. In the same way heat disturbance will increase resistance. Some inorganic insulators will expand and contract with impressed AC voltage so here storage of electrons seems to have a physical meaning. Such a property of quartz crystals is used to turn electric cycles into motion.

The polar insulators are electrically unsymmetrical and are vibrated by applied electric cycles. The swing of such a molecule will depend upon both the viscosity of the mass and the size of the molecule and such an electrical cycle can be used as a measure of viscosity if the size is established. The time factor of electrical relaxation may be used to describe the polar system. By such means, the rotation of solid molecules may be located as a dielectric constant change. Camphor which solidifies at 175° continues to rotate down to —40°C. Even in the solid state here each round molecule can still turn within its own lattice space. Addition of a large side branch, as by adding bromine, causes rotation to stop at or nearer the point of solidification.

Measured on an electrical system the polymer molecules behave much like high viscosity liquids. The curve for polar polymer molecules behaves like a group of simpler molecules all of which are not alike. Most but not all of them show some evidence of a crystallization change at some point. So far, methyl methacrylate shows no crystallization. For rubber the dielectric constant reaches a peak at 12% sulphur content. This is explained by saying that beyond 12% sulphur cross bonds cut rotation effects. From the electrical measurements ALL polymers may be considered as cross bonded but some have

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more and stronger comparative cross bonds. Waxes are considered cross bonded as with weaker Van der Waals forces. Enough unsaturated cross bonds are considered to give rubbers. A rubber having projections between the bonds will become brittle at lower temperature. Thus styrene polymers are rubbery at high temperatures but brittle at room temperatures.

The strongest bonds are valence type such as sulphur in rubber or carbon in diamond. A diamond which is valence bonded in all directions is called a valence crystal but may well be considered as a kind of ultimate polymer form.

Dr. Speiser reported on the viscosity and hydrodynamics of liquids.

The contrast between the temperature-viscosity effects of water and air was shown. To define the properties of a liquid requires measures of pressure, viscosity and inertia. Viscosity is concerned with how much work causes movement and how much is lost in the process. It is a division of force between flow and heat or other losses. Thus the Reynolds number is a measure of such loss. There is then a dynamic condition and a geometric condition which limit viscosity measurements. Hydrodynamics do not apply to conditions where particles are large compared to the size of flow tubes such as blood in capillaries. The volume elements must be large in comparison to molecular size and must be small on the scale of the measurement tubes. Under these assumptions the formulas such as Stokes law were examined.

Dr. Primakoff gave a very clear picture of the present atomic theory of liquids but warned that no entirely satisfactory theory will yet interpret the properties of liquids as referred to their individual atoms or molecules. Since gases and solids have both been explained as assemblies of atoms, then present tendencies make liquids as either condensed gases or as expanded solids or as mixtures of gases and solids. Under either picture it becomes hard to understand what the individual molecule or particle is doing in the liquid structure. Gas particles are not bound to any position and solid particles are each sharply bound to one limited position. In liquids the particles seem bound to some position but that position itself is free to move within the boundaries of the liquid mass as if it were a large unwieldly gas molecule. Liquids of one class appear near to gases and liquids of another class appear almost like solids so the structural picture of a liquid may well be a transition state.

From X-ray pictures, some normal liquids seem to have building blocks the same as for the gas. For associated liquids the molecules seem distorted into some multiple type of units with some kind of bonding power. Liquid sulphur is thus called associated and viscosity increases with temperature increase which is contrary to liquid expectations. Within the liquid range there is often a more or less continuous change of X-ray picture from the type of solids to the type of gases.

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The states of solid, liquid and gas are increasing energy states. In a solid there are various levels but closely alike. The heat of fusion is pictured as a jump of empty energy spaces vacant until the lower liquid level is attained. Then the liquid may have various energy levels somewhat less alike than are the comparative levels in the solid. The heat of vaporization is a jump of empty energy spaces to the gas level. Here again in gases various nearly-alike energy levels occur. The best liquid theory so far is that of Lennard-Jones.

Dr. Mark then applied liquid data to high polymer liquids with long particles showing the changes in X-ray pictures of hydrocarbons as the carbon chain increased. A magnification of the spectra shows that carbon chains of 22 carbons, 23 carbons and 24 carbons can be detected.

Dr. Eyring gave an interesting lecture on viscosity and flow processes. Force added to a system increases movement but this increase is only a fraction of the movement already present. Thus the rate process was considered as the increased chance that a particle will be in position to pass over an energy barrier. Flow which starts long before breakage may be by big blocks or by individual molecules. Somewhere around every ten millionth time a vibration will result in a flow procedure. The melting of a solid does not change the free energy much since the entropy and heat seem to compensate each other. However, the liquid gain of 1/7th more volume about doubles the equilibrium change of flow. The comparative flow of large and small molecules show that the large molecules can themselves move directionally. Thus their internal motion can be neglected only for very dilute conditions. This can be summed up by saying that all carbon chains longer than ten carbons have, in concentrated solutions, some similar elements of motion. Thus again long molecules can only be differentiated in dilute solutions, as far as flow, or in melted condition at some arbitrary set temperature for comparative flow effects.

Dr. Press gave a summation of experimental data on mechanics of elasticity and flow. Such properties as water absorption of viscose changed greatly with stretching data. The elongation of water-swollen fiber changes with the applied load. The stress-strain curves were considered best to represent the summation of polymer properties. For polymers two main properties are of interest: (1) molar cohesion; and (2) rotation or motion of segment or of a single molecule. Cellulose has high molar cohesion but difficult rotation. Rubber has an ease of rotation as shown by stress-strain curve. The extra holes or space in amorphous films, as compared to crystalline materials, is of great technical value for flow effects. The act of stretching reduces such extra space and condenses part of the material to crystal sections which is likened to a liquid with fixed structural spots. Any one polymer chain is considered large enough to pass through both crystal and amorphous segments. If lubricated by heat or by solvents, all such crystal sections will re-

arrange to amorphous conditions. Too many or too large side chains may make crystallization impossible for a polymer. Crystallization of polymers is a slow process and rapid cooling may freeze in the disorder. In such a case, solvents will act as flow inducers to aid crystallization. The magnitude of the load is an important factor in polymer crystallization also due to the time factor of the crystallization process. The same explanation is made for samples loaded and dried then placed in solvents to give spontaneous elongations as much as 100%.

Dr. Bender gave a summation of odd data in the polymer field, for instance, where molecular weight methods gave values beyond infinity, where pressure gave permanent or temporary solids and where crystal growth could be hindered to give glassy solids. The theory of three dimensional melting, plasticization and solution was detailed. Plastic flow followed the pattern of dimensional melting and dimensional solvation. This theory leads to an occasional reversal of the explanations now made on the polymer crystallization scale, for instance, that of a solvated cellulose acetate mixture placed under tension. This causes elongation in one direction and contraction and compression in the right angle direction. Such a rod dried under tension contracts and compresses more. Now if such a solvent can be found as will melt the material in one direction only, then the compression can adjust itself to zero by a plastic flow effect of the solid material resulting in a large elongation. Such movement may sometimes result in partial crystallization as a secondary effect. Solvation is a trifunctional effect and a completely miscible solvent must be trifunctional whether the three functional effects come from one solvent or in the extreme case require a mixture of three solvents. For some cases three separate single functional solvents are known whose admixture is needed to attain solution. From the standpoint of viscosity, monofunctional or difunctional solvents give higher viscosities and trifunctional solvents give lower viscosities to solutions.

The series ended with a splendid paper by Harris on wool as a polymer and covering a chemical viewpoint of fibers. The shock and tensile strength of fibers have been greatly increased by the orientation and crystallization effects of stretching threads, but flexibility or elasticity decreases as the crystallinity increases.

Wool, the most elastic of the natural fibers, is a poly-copolymer of mixed amino acids R-CH-NH-COOH where the different R's project to the sides of the polypeptide chains.

The elastic mass is made up of chains, a large part of which are in disorder. With 50% of the actual material as side chains, there is little chance for close packing of the main stems. One seventh of the material is cystine, where the NH and COOH groups are tied up in polypeptide chains thus leaving the sulphur to act as cross bonds. Thus the molecular size of wool may well be the entire fiber with disulfide bonding playing an important

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part. The sulphur groups were reduced and split. Measure of stress strain curves showed that such linkage breakage allowed the fiber to stretch with less applied force, and to elongate more with the same load. When cross-linkage was restored by oxidation, then the strength was recovered. Reduced wool could be coupled with large groups to cause high heat loss on loading.

The act of growth extrusion of wool and the spinning motion of silk cause profound changes. These materials are liquids which, if disturbed, harden to a denatured or molecular rearrangement. Drawing also effects the result. The change is from a high concentration having a low viscosity to the same concentration but a high viscosity and expressed as a gel effect of motion. The rate of the motion changes the resulting strength by changing the orientation.

The entire series was considered a very successful session on polymer chemistry by all those who attended and the sessions for next year will repay consideration.

Activities of the British Rheologists' Club

Circular No. 4 (April 1942) of the British Rheologists' Club, issued by the Institute of Physics, The University, Reading, Berks, England, contains 17 abstracts dealing with rheological subjects, being serial numbers 89 to 105 inclusive. Titles, authors, and journal references are as follows:

89. Soil classification and its bearing on soil stabilization. A.H.D. Markwick. J. Inst. Petroleum **27**, 313 (1941).

90. Use of bitumen in soil stabilization. H. Gardener. J. Inst. Petroleum **27**, 329 (1941).

91. Action of alkalis on starches. G. B. Jambuserwala. J. Text. Inst. **32**, T 201 (1941).

92. The Tackmeter, an instrument for analyzing and measuring tack. H. Green. Ind. Eng. Chem., Anal. Ed. **13**, 632 (1941).

93. General law of friction for liquids and its application to the calculation of the resistance to motion of disperse systems under isothermal and non-isothermal conditions. A. Skryabin. Colloid J. (U. S. S. R.) **5**, 363 (1939).

94. Contribution to the problem of the flow of milk through pasteurizers. W. Sell. Milchwirtschlafl. Forsch. **21**, 42 (1941).

95. Chocolate coating. Factors affecting viscosity and coverage value of chocolate coating for ice cream products. J. H. Erb. Ice Cream Trade J. **37**, 18 (1941).

96. Consistency tests for lubricating greases. H. Levin and C. J. Schlagel. Ind. Eng. Chem., Anal. Ed. **13**, 295. (1941).

97. Plasticity of phenol-formaldehyde resins and moulding

powders. L. M. Debing and S. H. Silberkraus. Ind. Eng. Chem. **33**, 972. (1941).

98. Stress-strain characteristics of plastic clay masses. R. Russell, Jr. and C. F. Hanks, Jr. J. Am. Ceram. Soc. **25**, 16 (1942).

99. Working-range flow properties of thermoplastics. F. E. Wiley. Ind. Eng. Chem. **33**, 1377 (1941).

100. Reversible aggregations of colloidal particles. 1. Centrifugal experiments on thixotropic iron oxide sols. W. Heller. J. Phys. Chem. **45**, 1203 (1941).

101. A stress-strain curve for the atomic lattice of mild steel, and the physical significance of the yield point of a metal. S. L. Smith and W. A. Wood. Proc. Roy. Soc. **A 179**, 450 (1942).

102. New method of determining the viscosity of viscous liquids at increasing temperatures. K. Gohde. Chem. Fabrik **13**, 9 (1940).

103. New recording viscometers. Anon. Editorial. Instruments **15**, 34 (1942).

104. Viscosity of glass. S. R. Scholes. Modern Glass Practice, Industrial Publications Inc., Chicago, 1941. pp. 119-123.

105. Soil Mechanics. D. P. Krynine. McGraw-Hill Book Co., New York and London, 1941. pp. 27-48.

RHEOLOGY PROGRESS ABSTRACTS

Bituminous Materials

A recent paper of general interest to tar and asphalt technologists is one by Traxler, Romberg, and Schweyer.[1] Continuing the previous excellent work of Traxler and co-workers in this field, this publication describes a rotary viscometer suitable for studying the rheological properties of asphalts over a wide range of consistencies:

As contrasted with previously suggested types of rotating cylinder viscometers which usually measure consistency under constant shearing stress, this instrument is recommended for the measurement of viscosity at a constant mean rate of shear, which allows a comparison to be made between the consistencies of different non-Newtonian liquids. Methods of calculation and experimental data are given to illustrate the application of this viscometer in studying the rheological properties of several different asphalts.

<div align="right">W. F. FAIR, JR.</div>

[1]. Rotary Viscometer for Determination of High Consistencies. Ind. Eng. Chem., Anal. Ed. **14**, 340 (1942).

Concrete and Mortar

"In these disturbed times little work is being done on the Rheological properties of concrete and mortar. Our working

subcommittee in A.S.T.M. C-1 has completed some very interesting experiments, but these are not available as yet for publication or review."

<div align="right">F. O. ANDEREGG.</div>

Glasses and Slags

The Structure and Constitution of Glass. Eric Preston. J. Soc. Glass Tech. 26, 82 (1942).

Some consequences are considered of the conclusion that. in viscous silicates four oxygen atoms are attached to a silicon atom forming a tetrahedral unit, which is the fundamental unit of structure in glassy as well as in crystalline silicates. It is pointed out that there are certain reservations, as yet incompletely considered, attaching to the random network theory, for as the concentration of silica decreases the minimum particle size completely satisfying all the requirements of ratios of silicon, oxygen, and metal atoms decreases also until at 33.3 molecular percent, silica individual tetrahedra must exist. A preliminary attempt is made to correlate this decreasing particle size, or co-ordination group, with known physical and chemical properties of glasses.

Several Stages in the Solidification Processes of Silicate Glasses. A. Smekal. Z. Physik. Chem. B48, 114 (1940) Cf. Ceram. Abstr. 21, 38 (1942).

Influence of Ion Radius and Valence of Cations on the Viscosities of Silicate Melts. K. Endell and H. Hellbrugge. Angew. Chem. 53, 271 (1940).

The results obtained by measurement of the viscosity of silicate melts were treated theoretically. If other factors were excluded, on the addition of equal numbers of cations to the SiO_4 network of silica glass, the resulting viscosities were lower the greater the valence of the cation. This was said to be due to number of Si-O-Si bonds broken. In comparing the effects of R_2O and RO additions on the viscosity of silica glass, it was assumed that R_2O produced a complete separation of the SiO_4 tetrahedra while the RO acted to bond them. When cations of the same valence were considered, those with higher field strengths formed strong R-O bonds which resulted in a lower viscosity. It was concluded that the variation of viscosities of sodium silicate melts with changing Si/O ratios indicated the presence of the metasilicates or orthosilicates in the fluid state.

Liquids and Solutions

Viscosity—Temperature Functions of Liquids. A. H. Nissan. Phil. Mag. 32, 21 (1941).

A single curve is obtained for all members of the normal hydrocarbons when the logarithm of the viscosity is plotted against T/T_B , where

T $\simeq$ absolute temperature of measurement

T_B = boiling temperature at atmospheric pressure

An artificial temperature ordinate scale is constructed by graphical methods, so that the plot becomes a straight line. It is shown that all the pure liquids tested are governed by a general equation which gives a straight line when used with the artifical temperature ordinate,

$$\log \mu = K' - K_1' \left(\frac{T}{T_B}\right) + K_2' \left(\frac{T}{T_B}\right)^2 - K_3' \left(\frac{T}{T_B}\right)^3 \text{------}$$

The function T/T_B is used since many of the homologous series give the same straight line for all members. Other derived formulae enable the viscosity-temperature relationship of a pure liquid to be determined from the values of its viscosity at two temperatures.

It is concluded, from the many relationships studied, that all pure liquids of any type, with the known exception of helium, are governed by one law for which several formulae are given. It is assumed, as shown in the above equation, that an increase in temperature tends to change the viscosity, the direction of change depending on the relative values of the constants and T/T_B. Thus it is concluded that a general equation may exist, governing the change of viscosity of fluids with temperature, independent of the state of the fluid.

J. M. GEIST

Viscosity Nomographs for Organic Liquids. D. S. Davis, Ind. Eng. Chem. 33, 1537 (1941).

The following equation correlating viscosity and density is used to construct a nomograph for the rapid determination of the viscosity of any organic liquid at a given density·

$$\log (\log \eta) = I \, d/M - 2.9$$

where η = viscosity in millipoises

M = molecular weight

d = density in gm/cc.

I = viscosity-constitutional constant which is evaluated for each compound from a summation of general atomic and structural constants.

As can be seen from the nature of the equation, the viscosity scale is short and crowded. The viscosity scale is lengthened by use of special nomographs which can be used only for the ninety listed compounds.

J. M. GEIST

Variation of Viscosity of Cellulose Acetate Solutions with Concentration and Nature of Solvents. M. Takei and H. Erbing. Kolloid Z. 95, 207 (1941). A correction. Cf. Rheology Bull. XIII. No. 1.

Table I.

Bredee and deBooys

Solvent	k	A
Ethyl lactate	72.4	2.83
Methyl glycol acetate	73.9	2.73

H. M. SPURLIN

Brittleness of Liquids. M. Kornfeld and M. Ryvkin. J. Phys. (U.S.S.R.) 2, 183 (1940).

At a rate of impact deformation of about 20 m. per sec. for a liquid having a viscosity of approximately 5×10^2 poises, a brittle destruction was observed. This differed greatly from Tammann's conclusion that a viscosity of 10^{12} to 10^{13} poises was the boundary between the liquid and solid states where the body became brittle.

Metals

A Study of the Collapsing Pressure of Thin-Walled Cylinders. R. G. Sturm. University of Illinois Bull. Eng. Expt. Station Bull. Series 329, Nov. 11, 1941.

This study deals with the failure of thin-walled cylinders or cylindrical vessels by instability when these vessels are subjected to external pressure. This problem arises in the design of large pipe lines, submarines, vacuum bottles and vacuum distillation tanks. The work consists of a theoretical analysis of this problem and comparisons with experimental results.

The analysis is based upon the following argument: If the external forces acting on the shell can hold it in a deflected position compatible with continuity, equilibrium and boundary conditions, such that the magnitude of the deflections are indeterminate, the shell is considered in a state of neutral equilibrium. For external pressure the critical or collapsing pressure of a circular cylindrical vessel is considered as the lowest pressure at which neutral equilibrium is obtained. The method of analysis is to consider the cylinder in its deflected shape and from the geometry of the resulting strains, to derive the relation between the applied load and the deflection. The critical load is determined by setting the coefficient for the deflection equal to zero for which case the deflection is indeterminate.

While the derivation is made on the basis of elastic action, a workable approximation for determining the collapsing pressure for stresses above the elastic limit has been developed and correlated with tests. The effects of combined stresses are also discussed, particularly with respect to the beginning of plastic action.

The particular significance of the work lies in the fact that it gives a practically useful method of computing collapsing pressures of stiffened and unstiffened vessels and serves as a

basis of arriving at code specifications. This work also emphasizes the great need for further study of plastic deformations and the effects of combined stresses upon the beginning and progress of plastic deformations.

<div align="right">R. G. STURM</div>

Rubber

Rheologic and Elastomeric Measurements of Rubber Products. F. Hoppler. Rubber Chem. Tech. 15, 5 (1942).

In this paper, a brief description of the Hoppler "Consistometer" is given. It consists of a vertical rod driven by a dead load applied by means of a lever system. The lower end of the rod can be equipped with spheres, cones, cylinders, etc., which are forced into a sample confined in a chamber at a rate which is measured by a dial indicator gauge. Provision is made to maintain the sample at a definite temperature. Although it is stated that the instrument is an "absolute" Consistometer and certain viscosity results are expressed in poises, it is difficult to agree with the author's definition of his instrument. The paper suffers in the attempt to include measurements of a very large number of properties of rubbers and rubber solutions without adequate details as to technique and method of calculation. Nevertheless, some of the data giving "viscosity" as a logarithmic function of temperature are interesting. In general, the discussion of results is confused and without much regard to previous work in this field.

Introduction of the Bending Strength Test as a Means of Dtermining the Freezing Point and Changes in Elastic Properties of Soft Rubber at High and Low Temperatures. E. A. Koch. Rubber Chem. Tech. 14, 799 (1941).

In this work, test strips were placed upon a pair of horizontal knife edges and frozen at —75°C. The strips were then deadloaded midway between the knife edges and the temperature allowed to rise at a more or less controlled rate. The temperature at which bending deflection occurred was termed the "freezing temperature". Although no compounding formulae are given in the article, it is interesting to note that the freezing point for comparable natural rubber and Buna-S Stock was the same (—66°C.) The value given for Perbunan was —45°C.

On the whole, the apparatus and technique employed by Koch appear to be simple and effective, especially where only a limited number of samples are to be tested. Measurements of bending modulus at low temperatures were made in addition to the freezing point determinations.

Brittle Point of Rubber upon Freezing. M. I. Selker, G. C. Winspear and A. R. Kemp. Ind. Eng. Chem. 34, 157 (1942).

In this work, test strips were clamped radially around the perifery of a sector, which was rotated rapidly by hand in a tank containing a solution, the temperature of which could be con-

trolled.   A rigid arm was mounted on the tank, so that the strips were successively bent at a sharp angle against it.   The temperature of the solution was varied to the point where the strips broke against the rigid arm.   This temperature was recorded as the "brittle point".   It was stated that it could be determined to within plus or minus 0.1°C. for samples from a given sheet of material.

It was found that the brittle temperature of soft vulcanized rubber is independent of state of cure in the range of industrial curing practice.   For rubber-sulfur compounds, an almost linear relationship was found between brittle temperature and combined sulfur.   Addition of reinforcing pigments produced little effect, but coarse fillers raised the brittle temperature.

Measurements were made with a number of synthetic elastomers.   It is interesting to note that the brittle temperatures for Buna-S and Perbunan were —65.5°C. and —45.5°C., respectively, agreeing closely with the "freezing point" determined by Koch (see preceding abstract).   For a natural rubber gum stock, however, the brittle temperature was —59.5°C. and for tread stocks —56.5°C.

<div align="right">J. H. DILLON</div>

Theory

Stickiness, Tackiness and Spinnability.   D. Josefowitz and H. Mark.   India Rubber World **106**, No. 1, 33 (1942).

It is attempted here to give a molecular interpretation of the phenomenon of stickiness, tackiness and spinnability; these three terms are used here interchangeably as they are considered to represent the same intrinsic behavior of a material.

A system is defined as tacky when it exhibits the following two main characteristics:

a.   Two separate parts of the system merge fairly rapidly if brought in contact at room or slightly elevated temperature and at small pressure.

b.   After merging it shows a certain resistance to forces of stress or shear, if an attempt is made to separate the two parts again.

Such systems are in respect to their behavior somewhat intermediate between elastic solids and viscous liquids, and it is easy to understand that there is a very wide range as to the extent each of the above conditions are fulfilled.   At sufficiently low temperatures tackiness disappears completely.   A solution of rubber in benzene, for instance, which is distinctly sticky at room temperature or slightly below becomes hard and brittle at the temperature of dry ice; while, on the other hand, alcohols and glycols show typical stickiness at temperatures of about —40°C., which in turn disappears again at still lower temperatures.   This proves

that a certain degree of mobility is essential to produce stickiness which is exactly what one would expect from condition (a) above.

A convenient measure for the ease with which the molecules of a substance or certain parts of these molecules can move and eventually adapt themselves to the influence of an external force is the viscosity of the substance. The viscosity is best expressed here in terms of "time of relaxation" which is a measure of the average time required by a molecule to relax into an unstrained condition while under the influence of an external force.

If we take a very dilute solution of cellulose nitrate in acetone and gradually increase its concentration we will observe that, while the viscosity increases continuously the tackiness at first will increase, until it reaches a maximum and finally at high concentrations it will practically disappear. Many similar experiences indicate that tackiness is somewhat related to viscosities between 100 and 10,000 poises or relaxation times of 10^{-7} to 10^{-4} seconds. The chain-like molecules or their parts must have a certain mobility in order to fulfill condition (a), and to merge easily with each other. But they must not slip too easily along each other in order to comply with condition (b), which requires a certain resistance to stress and shear. Many chain polymers show a range of oily consistency (Polymerization degree P.D. $<$ 50) without stickiness. Then follows a range (P.D.=50— 300) of a more viscous, typically sticky condition. Above this range (P.D. $>$ 300) the material becomes tough and hard and no longer adheres.

From the above consideration it seems that the following conditions might be suggested for tackiness, stickiness and spinnability: the phenomena are related to the presence of easily moveable chain segments or chain ends of an average length of about a hundred links (P.D. =100). If they are shorter the chains merge, but their mutual forces are too small to prevent slippage. If on the other hand, these segments are much longer the chains adhere considerably to each other and therefore merging is not readily accomplished when two samples are brought into contact with each other.

Calculation of Viscosity from Stormer Viscometer Data. J. A. Geddes and D. H. Dawson. Ind. Eng. Chem. **34,** 163-167 (1942).

To explore the possibility of describing the consistency of paints in more fundamental units, a submerged-paddle viscometer was calibrated with five truly viscous oils (6.03—33.7 poises). Correlation of the viscosity of these oils with Stormer data was obtained by making a kinetic-energy correction. The formula developed is limited with respect to several variables, including temperature and container size. It is suggested that maximum tolerances of 0.25°C be imposed in all liquid and paint measurements. Although containers from half-pint upward may be used,

measurements made in containers of different size cannot be intercompared without correction. A table gives consistency values in Krebs units corresponding to Stormer speeds of 24—40 seconds/100 revolutions and driving weights of 75—1000 grams.

<div align="right">E. C. HENRY</div>

Modern Theories of Plasticity. Anon. Chem. Age **45**, 128 (1941).

The prevalent belief that plasticity was due to particles of clay being separated by films of water in such a manner that the liquid surface adhered to and bound the solid surface was now being replaced by the view that the separation of the surfaces was due to a repulsion between them. This repulsion was estimated by determining the equilibrium moisture content when the mixture was compressed under constant load between porous pistons. To account for the observed rates of flow of water through plastic clay, it had been suggested that a tendency towards a regular arrangement built up of layers of water in crystalline form existed in the water near the clay surface. The rate of destruction of this arrangement with distance from the surface, caused by thermal agitation and the presence of ions, was expected to be proportional to its value at any point. Two such systems, based on opposing surfaces, necessitate mutual destruction of this arrangement at the midway point, and energy was required to bring the surfaces closer together. This appeared as a repulsion between the surfaces, increasing as the separation decreased. The rigidity of the plastic body was due to this network of repulsive forces. The increase in magnitude of the forces with decrease in moisture content resulted in the well known hardening of clays. On application of shear, the particles slide over one another; on its removal, a similar force system remained, and the material retained its deformed shape.

<div align="right">E. PRESTON</div>

New Books

Ten Lectures on Theoretical Rheology. Markus Reiner, D. Sc. Tech. Published by Rubin Mass, P.O.B. 990, Jerusalem, Palestine. 144 pp. $2.50 or 10s. 6d.

Contents

Preface

Notes. Bibliography. Notation. Index.

Dr. Reiner is one of the pioneers of rheology. In 1928 he assisted Prof. Bingham in organizing rheology as a new branch of science. In 1930-31 he gave a series of lectures on Mathmatical Rheology at Lafayette College, Easton, Pa., which was repeated in improved form at Princeton University, Princeton, N. J., in 1931-32. He has since done further original work and lectured on rheology, and in 1941 summarized the present position of Theoretical Rheology in a series of lectures given at the Hebrew University, Jerusalem, Palestine. These lectures, amplified by notes, are now in print for publication. The book will be an up to date source of information on this subject for the Rheologist, either scientific or industrial, and the Physicist, Chemist or Engineer working on rheological problems.

Letters to the Editor

Sir—

You ask in regard to Abstracts. I am trying to make a very complete bibliography on rheology, and I have something over 10,000 references that are, of course, multiplying rapidly. I am looking for an opportunity to publish them, but do not see how you can utilize the material which I am accumulating in any way in the Bulletin. I see no reason for publishing Abstracts which are given in full in **Chemical Abstracts** or **Science Abstracts.** It seems to me that all that is necessary is references to these Abstract journals.

EUGENE C. BINGHAM

Sir:

I have not yet received my copy of the Rheology Bulletin. I understand that this Bulletin is published quarterly, and therefore I should have received a copy in May, since I have the February issue. If there is any reason why this bulletin has not been published or sent out, I would sincerely appreciate information to this effect.

R. M. LEVY

APPLICATION

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

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

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

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