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TABLE OF CONTENTS

    With this issue we are making a change in the method
of printing the BULLETIN. In the past the BULLETIN was
first set up by linotype and printed in the conventional
manner taking only a few impressions of each page. The
mathematical expressions which could not be duplicated by
the printer were then drawn in by hand. After this, the
single printed copy was reproduced with some decrease in
size, by the method known as photolithography. This oper-
ation, as well as the assembling of the BULLETIN, is per-
formed by the Sackett and Willhelms Lithographing Corporation.
The present change consists only in substituting typewritten
copy for the linotype printing.

    The BULLETIN will not be as attractively printed but
the reduction in cost will be considerable. It will be
possible to increase the number of pages and still be within
our former budget.

REPORT ON THE 1942 FALL MEETING

The Annual Meeting of the Society of Rheology was held at the Hotel Pennsylvania, New York City, on October 30 and 31. Joint luncheon and dinner on Friday were eaten together with the Optical Society of America and with the American Mathematical Society. The papers presented before the Rheology Society were of excellent quality, and attracted a large and attentive audience. In the present issue of the BULLETIN we are pleased to publish rather detailed abstracts of most of these technical papers. Unfortunately not all of the authors had supplied manuscripts at the time of going to press, but the reader may be referred to brief abstracts of these papers in the September 1942 issue of the BULLETIN.

THE PROPERTIES OF LIQUID SULFUR

Richard E. Powell and Henry Eyring
Princeton University, Princeton, N. J.

It is assumed that S_λ is 8-membered rings and S_μ is long sulfur chains, so the equilibria in liquid sulfur are given by

$$\frac{X}{8}S_8(\text{ring}) \rightleftharpoons S_X(\text{chain}) \qquad 0 < X < \infty$$
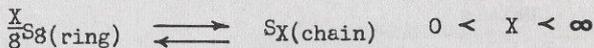
The equilibrium constant K_x is formulated for this reaction, and is, with the numerical values necessary to fit the experimental data,

$$K_x = e^{-\frac{27,500}{RT} + \frac{23.84}{R} - \frac{x}{27,000}}$$

The average chain length Z is given by

$$1/Z^2 = 1/27,000Z + K_8/8$$

and therefore decreases with increasing temperature. The weight fraction of chains ϕ is given by

$$\phi = \frac{1 - Z/27,000}{2 - Z/27,000}$$

and therefore rises toward an upper limit of 50% at high temperatures. This result is in agreement with the data on percent insoluble sulfur of Smith and Holmes and of Hammick et. al.

The effect of added impurities such as iodine is calculated: the result is that a fraction M of added impurities reduces the chain length according to the equation.

$$1/Z = 1/Z_{initial} + 2M$$

The viscosity is calculated upon the assumption that the $S_{8(ring)}$ obeys a viscosity equation like that for simple liquids, that $S_{x(chain)}$ obeys a viscosity equation like that for chain polyesters, and that the viscosity of the mixture of the two is given by $\eta = (\eta_{rings})^{1-\phi} \cdot (\eta_{chains})^{\phi}$. The equations for the viscosities are, with the numerical values necessary to fit the experimental data.

$$\eta_{rings} = \frac{Nh}{128} e^{-\frac{2.0}{R} + \frac{8,300}{RT}}$$

$$\eta_{chains} = \frac{Nh}{128} e^{\frac{9000}{RT} + \frac{0.35 \, Zw^{1/2}}{R}}$$

Fair agreement is obtained between calculated viscosities and those observed by Bacon and Fanelli, both for pure sulfur and for mixtures containing iodine.

RHEOLOGICAL PROPERTIES OF RUBBERLIKE MATERIALS

Arthur Tobolsky and Henry Eyring,
Princeton University, Princeton, N. J.

Rubberlike substances are composed of long molecules that are linked together at some points by primary or secondary cross bonds to produce an effective netted structure. The bulk of the substance however is composed of the coiling molecular chains between the cross linking points. Thus in effect we have a network pervaded by a liquid composed of the mobile segments of the same long molecules as those forming the network. The elastic properties are conferred by the fact that the long molecules spend most of their time in coiled configurations. This gives rise to the peculiar entropy elasticity of rubber like substances.

Attention is centered on the creep, relaxation, and hysteresis in rubberlike substances. These are treated in terms of molecular rate and flow processes.

For the ith kind of deformation unit the following equation of motion holds:

(A)
$$ds/dt = \frac{1}{G_i} \cdot \frac{df_i}{dt} + n_i \lambda_i \frac{kT}{h} e^{-\frac{\Delta F_i^{\mp}}{kT}} \cdot 2 \sinh \frac{f_i \cdot \lambda_i}{2N_i kT}$$

where ds/dt is the rate of strain, f_i the stress distributed on deformation processes of type i, N_i the number of such processes in parallel. G_i: is the elastic modulus, λ_i the

3

distance jumped and ΔF_i^{T} the free energy of activation for this type of unit process. f_i is therefore the force acting on each process of type i. $\overline{N_i}$

In rubberlike material there are three main deformation types: Primary network units, secondary network units, and mobile chain segments. Most of the stress is concentrated on the network units, which obey equations of type A. Breaking of primary cross bonds can be neglected for many experiments. For segment motion, when stresses are rather low, equation A reduces to the equation of Maxwell by expanding the hyperbolic sine.

It is assumed that the stresses distribute in such a way that the rate of strain for all deformation processes is the same.

For certain experiments such as creep under constant load, relaxation of stress at constant elongation and extrusion, elastic deformation coupled with slipping at secondary network bonds are of most importance. Mathematical formulae describing the behavior of rubberlike materials in these experiments are developed on the basis of the equations of motion described below. In these cases the non linear relation between stress and rate of strain in A appears well suited.

A consequence of these laws is that the creep vs. log time (in constant load experiments) or stress vs. log time (in constant elongation experiments) are straight lines over a considerable range, a result which is in agreement with much experimental data.

Since the equations of motion are written in terms of molecular constants, it should be possible to obtain information on these constants by analysis of data. It has been found for example that there is a rough proportionality between the number of secondary bonds per unit area and the initial deformation or stress.

In vibrational experiments it has been found that the measured viscosity ranges between $10^3 - 10^5$ poises for rubberlike substances, whereas the effective viscosity for constant load, relaxation and extrusion experiments is very much higher. This means that in these experiments secondary network bonds have no time to slip, but the viscosity is due to the relaxation of chain segments in the amorphous regions pervading the network.

Mathematical formulae are derived which show that for these kinds of experiments the measured modulus is a non-decreasing function of frequency, and the measured viscosity a non-increasing function of frequency.

4

THE PENETROMETER METHOD FOR DETERMINING THE
FLOW PROPERTIES OF HIGH VISCOSITY FLUIDS

W. W. Pendleton, Westinghouse Research Laboratories,
East Pittsburgh, Pa.

A review of the literature has shown that there was no reliable method of measuring the flow properties of fluids, such as asphalt, in the range of viscosity 10^6 to 10^{12} poises where the flow is "generally viscous." The theory of the penetrometer has been developed in this paper to a point where absolute viscosities may be determined both for "viscous" flow (viscosity independent of rate of shear) and for "generally viscous" flow (viscosity dependent on rate of shear). The new penetrometer method was checked (1) with the capillary viscometer for viscous flow using coal tar pitch, and (2) with the revised axially moving cylinder method for generally viscous flow using a high melting blown asphalt. For any one temperature, the flow properties of a generally viscous material are defined by the log shearing stress—log rate of shear straight line relationship from which viscosity may be determined at any desired rate of shear. The slope, $\underline{n}$, of this line is required in the calculation of rate of shear both for the penetrometer and for any other standard viscometer method. An independent means of observing $\underline{n}$ was developed both for the penetrometer and for the moving cylinder method. Earlier viscosity formulas for standard instruments based on viscous flow are invalid when used to express the flow properties of generally viscous fluids.

The penetrometer formulas for generally viscous flow are as follows:

1. <u>Shearing Stress</u>:

$$\tau_{az} = \frac{M}{P-K'} \cdot 3.12 \times 10^5 \qquad \text{dynes/cm}^2 \qquad (1)$$

where: M = mass of load in grams.

P = penetration in decimillimeters.

K' = needle point correction parameter.

a = largest needle radius in cm.

Z = depth of penetration in cm.

2. <u>Rate of Shear</u>:

$$\dot{\gamma}_{az} = \frac{(m-1) \cdot P}{5(m+1)t} \cdot \left[1-\left(\frac{a}{b}\right)^{m-1}\right] \qquad (2)$$

where: b = radius of container in cm.

5

$$t = \text{time in seconds.}$$

$$m = \text{slope of } \log \mathcal{T} - \log \dot{\gamma} \text{ line.}$$

3. Viscosity

$$\eta_{az} = \frac{Mt \cdot (m+1)}{P \cdot (P-K') \cdot (m-1)} \left[1 - \left(\frac{a}{b} \right)^{m-1} \right] \cdot 1.56 \times 10^6 \tag{3}$$

The formulas for the flow properties using the moving cylinder method are as follows:

1. Shearing Stress:

$$\mathcal{T}_a = \frac{M \cdot g}{2 \pi a L} \tag{4}$$

where g = acceleration of gravity

a = rod radius in cm.

L = length of rod in contact with material in cm.

2. Rate of Shear:

$$\dot{\gamma}_a = \frac{V_a (m-1)}{a \left[1 - \left(\frac{a}{b} \right)^{m-1} \right]} \qquad \text{reciprocal seconds.} \tag{5}$$

where V_a = velocity of movement in cm/sec.

3. Viscosity

$$\eta_a = \frac{a \mathcal{T}_a}{V_a (m-1)} \cdot \left[1 - \left(\frac{a}{b} \right)^{m-1} \right] \tag{6}$$

For viscous fluids the value of n is unity and equation (6) goes into the indeterminate form of $\frac{0}{0}$. However, by application of L'Hospital's rule the form reduces to

$$\lim_{m \to 1} \left[\frac{1 - \left(\frac{a}{b} \right)^{m-1}}{m-1} \right] = \ln \frac{b}{a} \tag{7}$$

Equation (7) substituted in equation (6) produces the familiar formula given by others for the moving cylinder method.

The means of determining n by experiment are as follows:

1. For the Penetrometer:

$$C = \frac{1}{m+1} = \frac{d(\log P)}{d(\log t)} \tag{8}$$

Where: C = the slope of the log P - log t line.

6

2. **For the moving cylinder:**

$$m = \frac{d(\log v)}{d(\log \tau)} \tag{9}$$

The parameter K' in equation (1) is a variable depending on penetration up to 54 decimillimeters and is a constant equal to 23 thereafter. For less than 54 decimillimeters the following equation was derived:

$$K' = P(0.849 - 0.00788P) - 0.0562 \tag{10}$$

Using the moving cylinder method it was found that the elastic properties of the asphalt accounted for a greater part of the movement than the flow properties. Also it was found that the flow properties depend on the extent of working and the previous heat treatment of the sample. Strain hardening was also observed by both methods.

The power function law relating shearing stress and rate of shear has been found to hold, for the asphalt studied, over the range of rate of shear from 10^{-5} to 10 reciprocal seconds.

In addition to speed of operation and precision, the penetrometer has the advantages of minimizing the elastic effects and reproducibility without extensive heat treatment and preworking. Entire shearing stress-rate of shear curves can be determined with one load and one penetration using a succession of time intervals.

THE SOLIDIFICATION OF FLUID LUBRICANTS BY PRESSURE

R. B. Dow, Aberdeen Proving Ground, Md.

For determining the pressure-volume relations of a substance at extremely high pressures, it is customary to compress the substance in a strong steel chamber into which a leak-proof piston is forced by a hydraulic jack or similar device. Adams[1] has described such a simplified apparatus, much like that used in the present study although in details it followed more closely the designs of Bridgman[2]. To study freezing of fluid lubricants under pressure the procedure adopted was to make piston displacement - pressure measurements at constant temperature. The piston displacement was read by vernier calipers and the pressure measured in the conventional manner of Bridgman by observing the change of resistance of a manganin gauge that had been calibrated previously against the freezing pressure of mercury at 32° F.

The apparent solidification of fluid lubricants at high pressures as reported by Hersey and Shore[3], and Kleinschmidt[4]

was determined by viscosity measurement, both studies being made with the rolling-ball viscometer. Some degree of solidification was assumed to have occurred when the ball ceased to roll at a certain pressure at constant temperature. The present investigation by making use of the static, piston displacement method made it possible to observe volume change which, with a knowledge of pressure and temperature, would enable the thermodynamics of solidification or freezing to be studied, e.g., application of the Clapeyron equation.

A Pennsylvania Bright Stock sample at 32° and 100°, lard oil at 73° and 100°, sperm oil at 140°, and a typical hydraulic oil at 100°F. were examined over a pressure range of about 10,000 kg/cm^2. The freezing of mercury at 32° was observed for comparison purposes. The accuracy and precision was such that volume changes could be read off to within 0.1%, this figure also representing the greatest departure from a smooth curve of piston displacement versus pressure. No volume discontinuity within the experimental error was detected for the oils, but in the case of mercury the piston displacement changed by about 6% with no permanent increase of pressure during freezing at 7640 kg/cm^2. However, in the case of lard oil at 73° it was found that solid material remained for a short while after the pressure was suddenly dropped from about 5,000 kg/cm^2 to atmospheric and the apparatus was suddenly dropped from about 5,000 kg/cm^2 to atmospheric and the apparatus taken apart as soon as possible. It is thought that solidification of Newtonian oils by pressure does not involve an appreciable volume discontinuity as observed during freezing, but may result in the formation of a labile substance similar to the vaseline-like consistency obtained during a cold test.

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1. L.H. Adams,Rev.Sci.Insts.7,174,1936,Figure 1.
2. P.W. Bridgman,Physics of High Pressure,McMillan 1931,pg. 42
3. M.D. Hersey and H. Shore,Mech.Eng.50,221,1928
4. R.V. Kleinschmidt,Trans.A.S.M.E. APM-50-4,1928

PROGRESS REPORT ON THE VISCOSITY OF OILS AS A
FUNCTION OF TEMPERATURE AND PRESSURE

R. B. Dow, Aberdeen Proving Ground, Md.

A previous report[1] discussed the application of the A.S.T.M. Viscosity-Temperature Chart D 341-37T to viscosity-temperature-pressure relations for four typical hydraulic oils. The present report considers the adequacy of the Chart in representing these data for a wide variety of mineral oils that have been studied by the author and colleagues at The Pennsylvania State College during the past five years. The A.S.T.M. Chart represents quite well the following kinematic

viscosity-temperature relationship of fluid lubricants at atmospheric pressure:

$$\log\log(kv. + 0.8) = A\log T + B$$

T is the absolute temperature F., and A and B are constants. It has been found that the loglog kinematic viscosity varies linearly with the log absolute temperature at constant pressure over a pressure range of 20,000 psi. for some twenty different oils of wide geographic range, and probably can be applied with some accuracy over a higher pressure range since the decrease of slope with increase of pressure is relatively small.

Some of the characteristics of the Chart are of special interest. If the viscosity isobars remain parallel throughout the experimental range, the proportional decrease of the viscosity coefficient with temperature rise for a constant pressure difference would be much greater than has been observed for most liquids experimentally. Moreover, the proportional increase of viscosity with pressure at constant temperature would be the same at all temperatures, a result contrary to fact. If the isobars should converge toward a pole at the high temperature end of the Chart, i.e., increasing in slope as the pressure increases, the temperature change of viscosity would appear to be as is observed for most liquids, and the pressure effect would be less at the higher temperature, a result that agrees with Bridgman's[2] study of viscosity of pure liquids at high pressure. But the results of the present study show definitely that for oils the isobars converge toward a pole at the low temperature end of the Chart, as shown by the fact that the slope decreases with increase of pressure. This result is surprising and indicates that oils under pressure do not have the same viscosity-temperature characteristics as pure liquids. This may be in accord with some of the unusual viscosity-temperature relations at atmospheric pressure that have been found by other investigators. Further studies should be made at various pressures and at as many different temperatures as possible in order to confirm the present results. The A.S.T.M. Chart appears to be the most practical way of representing the viscosity-temperature-pressure relations of oils that is available at present. It would be interesting to obtain similar data and apply this Chart to pure liquids.

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1. Paper read at Annual Meeting, N.Y. City, 1941
2. P. W. Bridgman, Proc.Amer.Acad.Arts and Sci. 61,57, 1926

THE FLOW AND RECOVERY PROPERTIES OF VISCOSE RAYON YARN

Jack Press, Virginia-Carolina Chemical Corporation,
Carteret, N. J.

Flow (loads of 0.1-1.0 grams/denier*) and recovery tests of 10^{-2} to 10^6 seconds duration at 70°F. and 65% R.H. indicate the following:

I. The time required to reach 3/4% extension is inversely proportional to the load; 0.4 g/d requires only 100 seconds while 0.2 g/d requires over 1,000,000 seconds. The recovery rate after 3/4% extension is the same as the extension rate. This range of extension is completely elastic, involving no permanent change in the sample. It probably represents the maximum movement of molecular segments in the more amorphous regions before weaker secondary bonds begin to break.

II. The time required to reach a constant extension of 4% is inversely proportional to the load. The recovery rate after 4% extension is much slower than the extension rate. However, after removing internal strains by wetting and then drying, the sample does recover completely. In this region of extension the incomplete, conditioned recovery indicates an increase in viscosity due to steric hindrance, while the complete wet recovery indicates no permanent deformation. In the amorphous regions some secondary bonds have been broken and the molecular chain segments have begun to change positions, but do not have sufficient translational and rotational freedom to move into new equilibrium positions of strong interaction.

III. The rate of flow from 10^3 to 10^6 seconds for loads of 0.1-0.4 grams/denier increases with increase in load, whereas from 0.4-0.8 grams/denier it remains approximately constant, indicating an increase in viscosity directly proportional to the increase in load. The non-reinforcing range of 0.1-0.4 grams/denier has attained a maximum extension of 4% (at 0.4 g/d) after 10^6 seconds and is explained by (I) and (II). The rate of recovery for extensions above 4% is much slower than the extension rate. Also, the recovery is not complete even after wetting and drying. This indicates a further increase in viscosity with some molecular segments now having sufficient translational and rotational energy to move into new equilibrium positions. The % permanent deformation for extensions above 4% remained constant in the short time tests (10^3 seconds) at about 19% of the extension (0.65, 0.80, and 1.0 g/d gave values of 19.3%, 17.8%, and 19.4%) while in the range from 10^3 - 10^6 seconds the % permanent deformation increased with load (0.5, 0.65, and 0.80 g/d gave values of 19.2%, 27.2% and 31.2%). The constancy of permanent deformation/extension for the short time tests indicates that the mechanism is one mostly of translational movement which is proportional to extension,

whereas in the <u>long time</u> tests the increase of permanent deformation/extension, with load, indicates that here the rotational freedom with increasing energy stored in the molecular segments is beginning to play an important part.

IV. The <u>short time</u> (10^3 seconds) flow and recovery results for 0.8-1.0 grams/denier loads are similar to those in (III) except for a much stronger re-inforcement. The long time (10^6 seconds) flow tests at 1.0 g/d all broke before completion. This indicates a strong short time reinforcement which gradually relaxes until the sample breaks. The value of 0.8-1.0 g/d for the long time conditioned tenacity (<u>normal</u> tenacity approximately 2.0 g/d) is very similar to the <u>normal</u> <u>wet</u> tenacity of approximately 1.0 g/d and indicates a possible similarity in internal load distribution and breaking mechanism for long time conditioned tests and very short time wet tests. Further work on this aspect of the problem is in progress.

* (1 g/d equals approximately 20,000 #/sq. in. for viscose rayon).

ON RELAXATION EFFORTS IN HIGH POLYMERS

Robert Simha, Department of Chemistry,
Howard University

The mechanical behavior of amorphous bodies like inorganic and organic glasses and high polymers represents a complex superposition of properties characteristic for an elastic solid and a viscous liquid. Maxwell's well known relaxation theory of viscosity represents an attempt to account for this behavior. It defines a relaxation time as ratio between viscosity and shear modulus. However, it is not able to account for the fact that a state of flow is reached asymptotically by these substances and that recovery after removal of the load proceeds in a similar manner.

Already some fifty years ago it was suggested by Thomson and Wiechert that the behavior of these materials under stress may be characterized by a whole set of relaxation rates giving a whole set of stresses which combine to a resulting internal stress. Information of a similar character can be gained from dielectric dispersion data on polar high polymers such as phenolic resins and polar vinyl derivatives. The broadness of the dispersion curves obtained has been connected by Fuoss and Kirkwood with the existence of a whole distribution of dielectric relaxation times.

Considering a relaxation frequency as a rate constant for a particular molecular process leading to relaxation of a stress component, we can correlate energies and entropies of activation to the different regions of the frequency

spectrum. The broadness of this spectrum in the case of a high polymer is then essentially a consequence of the particular effects characteristic for long chain molecules possessing internal flexibility of shape.

Three different mechanisms can be roughly distinguished as responsible for the spectrum. First, the thermal diffusion of the chain segments in the field of shear. Although not identical from an hydrodynamic point of view with their movements in an electric field, this leads to relaxation frequencies (of the order of magnitude of fractions of a second) similar to those responsible for dielectric dispersion which is caused by the rotational diffusion of the polar segments in the electric field.

Second, the change in average shape caused by the application of stress. Larger changes in free energy result here and the relaxation times are large. They increase with the size of the molecule and its internal stiffness. According to Frenkel the relaxation time of an isolated chain connected with its ability to assume various shapes with varying corresponding values of the entropy is proportional to the degree of polymerization. It is furthermore inversely proportional to the internal diffusion coefficient which describes the thermal motion of one chain and relatively to the other. The forces between the chains will tend to shift the result towards larger values of the relaxation times which will be of the order of magnitude of minutes.

Third, we have the region of the distribution curve pertaining to the relative translational displacement of whole chains. The relaxation times are large because the corresponding energy barrier is determined by the interaction of whole chains. Flow in the sample will become preponderant after a period of time large compared with these relaxation times, corresponding to an order of magnitude of hours, days or longer. Formation of cross links will increase these times, while leaving those frequencies which determine the elastic properties, practically unchanged, if the relative degree of cross-linking is small. Crystallization has the same effect. It furthermore makes the spectrum narrower by oppressing long chain effects and in this manner affects the elastic properties also.

Inhomogeneity in respect to size will primarily affect the largest relaxation times and therefore the flow properties of the sample, the lower end of the molecular weight distribution having a plasticizing effect.

Experimentally it should be possible to gain information of the different bands in the spectrum by investigating the absorption and dispersion of supersonic waves. Creep curves can be utilized for the same purpose, at least for the regions of the spectrum with relaxation times larger than the period

of time necessary for the first reading in recording the creep. If the creep-time curve is known and can be expressed in an analytical form then a procedure derived by the author in J. Appl. Phys. 13, 201 (1942) gives the distribution curve of relaxation rates.

In a symposium recently held by the Faraday Society on the structure and reactions of rubber Eley and Tuckett discussed some aspects of the connection between molecular structure and elastic properties of rubber-like and plastic materials. They considered this question starting with one characteristic time constant which in this case will represent some kind of an average. Knowledge of the whole distribution will throw further light on these questions, similarly as a knowledge of the whole molecular weight distribution is required rather than average values only in considering high polymeric systems. The time constants connected with the transition temperatures for the expansion coefficients of these systems must also have a relation to parts of the spectrum responsible for relaxation of stress.

MECHANICAL PROPERTIES OF CONCENTRATED POLYSTYRENE SOLUTIONS

John D. Ferry, Harvard Medical School, Boston, Mass.

From measurements of the viscosities and rigidities of concentrated solutions of polystyrene in xylene, a description of the mechanical behavior of this system can be made, and interpreted in terms of molecular structure.

An unfractionated sample of polystyrene, of average molecular weight 120,000, was studied over a concentration range of 15 to 52%, between temperatures of -5° and 30°. The viscosities were measured in a modified Stormer viscosimeter, and their dependence upon shearing stress, temperature, and concentration was determined. The propagation of transverse fibrations was followed by stroboscopic examination of the strain double refraction. The velocities of propagation and the dispersion and damping were measured.

The reciprocal apparent viscosity was a linear function of shearing stress, following the equation

$$\eta' = \eta /(1 + b\epsilon) \tag{1}$$

where η' and η are the apparent viscosity and the viscosity extrapolated to zero shear, and ϵ is the shearing stress. The parameter b, which is inversely proportional to the polystyrene concentration up to 30%, is interpreted as a reciprocal modulus of rigidity. This modulus has the value 1.1×10^4 g dyne cm^{-2}, where g is the weight fraction of polystyrene.

The variation of viscosity with temperature followed the usual exponential relationship, $\eta = Ae^{Q/RT}$. The energy Q, which is 2100 cal. for the pure solvent, rises from 3800 cal. at a concentration of 15.4% to 10,700 cal. at 52.3%. The viscosity at 25° C., which is 0.0059 poises for the pure solvent, rises from 15.5 at a concentration of 15.4% to 116,000 poises at 52.3%.

At a concentration of 52.3%, the elastic recoil following removal of the load was measured. The magnitude of the return corresponded to a modulus of rigidity of 1.0×10^4 dyne cm^{-2}, in agreement with the value of 1/b (eq. 1) at this concentration (1.2×10^4). The course of the return did not follow an exponential relation, but if it be described by an average relaxation time, the latter varies from 28 sec. at 30.5° to 98 sec. at 2.7°, and follows the equation $\tau = A'e^{Q'/RT}$; and Q' = 9300 cal., which is close to the corresponding value for the viscosity at this concentration.

The propagation of transverse vibrations was analyzed in terms of the equation for an exponentially damped plane wave,

$$\gamma = \gamma_o\, e^{\,i(\omega\tau - 2\pi x/\lambda) - x/x_o} \qquad (2)$$

and an assumed Maxwellian relaxation of shearing stress. The relaxation time was calculated from the dispersion (at the lower concentrations) as $\tau = 1/\omega$ at the frequency where $G(\omega) = 0.83\, G^o$; and it was calculated from the damping (at higher concentrations) as $\tau = \pi x_o/\omega\lambda - \lambda/4\pi\omega x_o$. Here ω is the circular frequency, G^o the modulus of rigidity at high frequencies, λ the wavelength, and x_o the critical damping distance.

The value of τ from both dispersion and damping was 4×10^{-4} sec., independent, to a first approximation, of temperature and concentration.

The modulus of rigidity G^o, at 25°, ranged from 0.8×10^4 dyne cm^{-2} at a concentration of 15.3% to 3.8×10^5 at 52.3%. Its variation with temperature (up to 40%) followed the equation $G^o = A''e^{Q''/RT}$, and Q'' = 1500 cal., independent of concentration.

All these data are interpreted in terms of two rigidity mechanisms, setting $G^o = G_1 + G_2$ and $\eta = G_1\tau_1 + G_2\cdot\tau_2$ (following Kuhn and Bennewitz and Rötger). If G_1 is identified with the modulus obtained from the viscosity and recoil measurements, which is proportional to the concentration (up to 30%), then G_2 is found to be proportional to the third power of the concentration (up to 30%). If τ_2 is identified with the relaxation time of the transverse vibrations, which is independent of concentration, then τ_1 is found to vary markedly with concentration.

It is suggested that mechanism 1 involves deformation by alignment of long chain molecules and relaxation of stress by motion of whole chains or long segments of them; and that mechanism 2 involves deformation by bending of carbon-carbon bonds, when segments of chains are stretched between "points of entanglement," and relaxation of stress by motion of short segments of chains.

THE GIESELER METHOD FOR MEASUREMENT OF THE PLASTIC CHARACTERISTICS OF COKING COALS

Glenn C. Soth and Charles C. Russell

The softening of coking coals when heated in the absence of air is believed by coke oven operators to account, at least in part, for the character of the coke produced. Although a large number of determinations of the softening of coal have been made in many different types of apparatus, the interpretation of these results has been the subject of much controversy among coal technologists. The term "coking coal" is difficult to define but for the purposes of this paper it is used to describe a coal which shows flow characteristics when heated in the absence of air at a rate of heating ordinarily obtained in coke ovens.

Coal, being a heterogeneous material, differs from pitches, tars, or oils, familiar materials on which plastometric or viscometric studies are made. Plastic properties or flow characteristics of tars and oils are relatively permanent and changes occurring during measurement are generally reversible, while the plastic properties of coal are transient and changes occurring during plasticity tests are generally irreversible. A description of the changes in coal at various temperature levels when the coal is heated to increasingly higher temperatures indicates that during the time the plastic properties can be measured, the coal substance is also decomposing. This results in measurements of coal plasticity being made on a heterogeneous system consisting of some solid infusible matter, some liquid coal substance, and some gaseous material produced in the decomposition of the coal and present in the system as bubbles.

The use of the term "plasticity" and reference to the "plastic properties" of coal has been the subject of much discussion. Since there is no terminology to describe the flow characteristics of coal which agrees with accepted rheological definitions the terminology used in this paper is arbitrary. The term "plasticity" together with the reciprocal term "fluidity" has been used to describe the coal system when it is in a state to exhibit flow characteristics. The term "maximum fluidity" has been used to describe the coal system when it is in a state to exhibit flow characteristics. The term "maximum fluidity" has been used to describe the system when

the flow characteristics appear to be present to the greatest
degree. The work described in the paper is directed toward
establishing a scientific basis for the measurement of the
plastic characteristics of coking coals as an improvement over
the empirical methods now in use.

The general schemes used in different types of apparatus
which have received the most attention in this country are
described. Of these instruments, the Gieseler type plastometer,
operating on a principle similar to that employed in the Stor-
mer viscometer, was selected as giving the most satisfactory
results for test of all ranks of coking coals as well as appear-
ing to give results which showed most promise of being convert-
ible to absolute units.

A complete description of the plastometer is given, in-
cluding dimensions of the various parts of the apparatus, the
preparation of the coal sample to be used, the method of placing
the test sample in the plastometer retort, and the procedure
of operation of the plastometer. Modifications in the retort
which are improvements over the designs of the Gieseler plasto-
meter appearing in the literature are given in detail.

A method of plotting the results is given which allows
tests for all different ranks of coking coals to be reported
on the same basis. These results, showing stirrer movement
in dial divisions per minute plotted on a logarithmic scale
against temperature plotted on an arithmetical scale, allow
comparison of the plastic properties of different coking coals
relative to one another, both in respect to the degree of
plasticity and also the temperature interval during which flow
characteristics are measureable. Results show that the maxi-
mum fluidity in divisions per minute dial movement is re-
producible within 20% and that the temperatures of significant
points in tests may be duplicated within 5° C.

In order to permit expression of the plastic properties
of coking coals in a manner possessing more scientific meaning
than the empirical units of divisions per minute dial movement,
the plastometer was calibrated by using several pitches whose
viscosities had been measured by the falling co-axial cylinder
and the capillary rise methods. This calibration for express-
ing dial movement from 0.1 divisions per minute to 15,000
divisions as "equivalent viscosities" covers the wide range
of results which had been obtained for many kinds of coking
coals. The range, expressed in absolute viscometric units,
corresponds to the range 6.4×10^7 poises to 6.6×10^2 poises.
Experimental results showed that if it were described to in-
crease this range by using variable loads acting to turn the
stirrer of the plastometer, separate calibrations would be
necessary at each loading because of frictional resistance in
the plastometer.

Typical results of tests of several different ranks of coking coal are given and discussed. Some generalizations are given, acknowledging that within different ranks of coal, many exceptions to these generalizations may occur. As the rank of the coal decreases, from low volatile rank, through medium volatile to high volatile rank, the maximum fluidity increases, the temperature range of plasticity increases, beginning plasticity occurs at lower temperature, temperature of maximum fluidity decreases, and the temperature of the end of the plastic range decreases. Within the high volatile A rank of coal, the maximum fluidity begins to decrease again and likewise the temperature range of the plastic interval; this decrease continues so that with many coals in the high volatile B rank no plastic properties are shown when the coals are tested under the conditions of the Gieseler test.

Retort residues from these plastometer tests indicate that some correction may be necessary in estimating the relative plastic properties of coking coals. The residues show that the degree of swelling of the sample during the plastic state is variable. Some coals, generally the coals of lowest rank and of highest rank exhibiting plastic characteristics show little or no swelling during tests. Other coals may swell to a volume several times the space occupied by the original sample at the start of the test. Thus, during a test, some coals have a plastic system containing much more gaseous phase than others, in which phase the plasticity is negligible. These retort residues also indicate that it is incorrect to consider the stirrer movement, converted to poises by the method of calibration described in the paper, as representing actual viscosity or plasticity of a single phase. Rather, the qualification of the absolute units as "equivalent viscosity" expresses the concept of the plastic characteristics of coals as being of a different kind than the viscosity of pitches or tars.

From 1929 to 1933 The Society of Rheology published the Journal of Rheology, each volume running to about 550 pages. In 1933 the new journal "Physics", now called "Journal of Applied Physics" began to publish the rheological material. Sale is announced of back volumes of the Journal of Rheology at the following prices. Complete set (3 vols.) $16.25; yearly back number rate $5.50; single copies $1.50.

Each of the issues contain Contributed Articles and Abstracts.

A list of the Contributed Articles follows:

Vol. 1 No. 1 October 1929.

The Theory of Plastic Flow in the Rotation Viscometer. By Marcus Reiner.
The General Law of Flow of Matter. By Marcus Reiner.
The Plasticity of Solvated Colloids. By S. E. Sheppard and R. C. Houck.
A Modified Plastometer for Industrial Use. By D. V. Gregory, G. M. Rassweiler, and K. C. Lampert.
The Plasticity of Solids. By Wheeler P. Davey.
Flow Relationships in Nitrocellulose Dispersions. By David R. Wiggam.
A Multiple Bulb Consistometer. By Winslow R. Herschel.
Internal Friction and Structure of Solvated Colloids. By Elmer O. Kraemer and Robert V. Williamson.

Vol. 1 No. 2 January 1930.

The Rheology of Soil Pastes. By G. W. Scott-Blair.
Plastic and Pseudo-Plastic Flow. By A. De Waele.
Plastic Study of Nitroglycerin-Nitrocotton gels. By L. C. Pritchett.
Consistency in the Application of Coatings to Paper. by R. M. Cobb and D. V. Low.

Capillary Siphons. By Eugene C. Bingham and Daniel Figlioli.
A Study in the Fluidities and Densities of the Octyl Alcohols. The Association of Liquids. By Eugene C. Bingham and Logan B. Darrall.

Vol. 1 No. 3 April 1930.

The Viscosity of Dilute Lyophilic Dispersions. By Elmer O. Kraemer and George R. Sears.
The Kinetic Energy Correction in Fluid Flow. By S. Bradford Stone.

Vol. 1 No. 3 April 1930. (cont'd.)

In search for a General Law of the Flow of Matter.
By Marcus Reiner.
The Plasticity of Protoplasm. By William Seifriz.
A New Consistometer and its Application to Greases and
to Oils at Low Temperatures. By Ronald Bulkley
and F. G. Bitner.
The Slippage Correction in the Equation of Plastic Flow.
By R. V. Williamson.
Classification of Plastics and Definition of Certain
Properties. By E. Karrer.

Vol. No. 4 July 1930.

James Leonard Marie Poiseuille. By Marcel Brillouin.
The Fluidity of Liquids. By S. E. Sheppard and R. C.
Houck.
Chemical Constitution and Association. By Eugene C.
Bingham and Holmes J. Fornwalt.
The Correction in Viscometry When Using Capillary Tubes
Which Have Trumpet-shaped Openings. By Eugene C.
Bingham and Richard R. Thompson.
On the Flow of Viscous and Plastic Materials Along an
Initially Empty Long Narrow Glass Tube. By G. W.
Scott-Blair.
A Method of Measuring the Relative Plasticity of Pastes
and Doughs. By C. H. Bailey.
On the Determination of the Fluidity of Water as a Ref-
erence Standard. By Eugene C. Bingham.
The Data of Poiseuille on the Flow of Water. By Eugene
C. Bingham.

Vol. 1 No. 5 October 1930.

Plasticity and Viscosity as Criteria of Molecular
Aggregration. By S. E. Sheppard.
The Colloidal Structure of Egg White as Indicated by
Plasticity Measurements. By J. L. St John and
E. L. Green.
On the Rate of Shear in Capillary Tubes. By Winslow H.
Herschel.
Rheology Definitions Make Progress. Some Fundamental
Definitions of Rheology. By Eugene C. Bingham.

Vol. 2 No. 1 January 1931.

A Contribution to the Theory of Thixotropy. By E. A.
Hauser.
Rheology Index. By Eugene C. Bingham.

Vol. 2 No. 2 April 1931.

The Thixotropy of Pseudo-Plastic Systems. By
    A. deWaele.
The International Comparison of Viscometers. By
    S. Erk.
The Law of Elasticity for Isotropic and Quasi-Isotropic
    Substances by Finite Deformations. By H. Hencky.
The Relation between the Plasticity of a Two Component
    Solid-Liquid System and the Degree of Wetting of
    the Solid by the Liquid. By F. E. Bartell and A.
    Hershberger.
On the Deviations of the Pressure Drop in a Cappillary
    from the Poiseuille Law. By S. Erk.
Explicit Formulas for Slip and Fluidity. By Melvin
    Mooney.

Vol. 2 No. 3 July 1931

The Static Rigidity of Plastic Clays. By Charles Terz-
    aghi.
The Effects of Salts on the Extensibility of Protoplasm.
    By William Seifriz and Janet Plowe.
The Orientation of Dipole Molecules in a Viscous Medium.
    By John Warren Williams and J. L. Oncley.
Preferred Orientation in Silver Foil Produced by Cold
    Rolling. By Cleveland B. Hollabaugh and Wheeler P.
    Davey.
Viscosity and Absorption in Colloidal Solutions. By
    Elmer O. Kraemer and George R. Sears.
An Analytical Study of Leveling. By R. K. Waring.

Vol. 2 No. 4 October 1931

Slippage in a Non-Newtonian Liquid. By Markus Reiner.
Quasi-Laminar Capillary Flow. By R. L. Peek, Jr. and
    W. R. Erickson.
Some Physical Concepts in Theories of Plastic Flow.
    By R. L. Peek, Jr. and D. A. McLean.
The Flow of Colloids Which Show Anomalous Viscosity.
    By H. Kroepelin.
Notes on the Ring and Ball Method. By Fred C. Eaton.
The Flow of Dry Sand through Capillary Tubes. By
    Eugene C. Bingham and Robert W. Wikoff.
The International Comparison of Viscometers. By
    S. Erk (Errata)
Notes on the Fluidity of Water in the Vicinity of 20°C,
    Report by the Committee on Viscosity Standards.
    By Eugene C. Bingham, Chairman.

Vol. 3 No. 1 January 1932

The Cause of Fluctuations in Rising Mixtures of Gas and
    Liquid. By J. Versluys.

Vol. 3 No. 1 January 1932. (cont'd.)

Fundamental Equations and Definitions concerning the
Mechanics of Isotropic Continua. By K. Hohenemser
and W. Prager Gottingen.
Dimensional Analysis of Plastic Flow. By Mayo D. Hersey.
On a Simple Model Explaining the Hardening Effect of
Poly-Crystalline Metals. By H. Hencky.
The Influence of Nitrogen in Mild Steel on the Ability
Developing Flow Layers. By C. W. MacGregor and
F. R. Hensel.
Some Physical Properties of Wiping Solders. By D. A.
McLean, R. L. Peek, Jr., and E. E. Schumacher.
Thixotropy and Plasticity. 1—The Measurement of Thixo-
tropy. By Elliott L. McMillen.
The Mixture Law. By Eugene C. Bingham and Delbert F.
Brown.
The Fluidities of Non-Aqueous Mixtures. By Eugene C.
Bingham and Horace E. Rogers.
Viscosity Measurements in Molten Glass. By Howard R.
Lillie.

Vol. 3 No. 2 April 1932

Thixotropy and Plasticity. 11—An Empirical Equation
Expressing Thixotropic Fluidity Changes. By Elliott
L. McMillen.
Thixotropy and Plasticity. 111—The effect of Thixotropy
upon Plasticity Measurements. By Elliott L. McMillen.
Future Problems of Theoretical Rheology. By Mayo D.
Hersey.
Purification of Materials by Vacuum Distillation. By
Earl W. Flosdorf and Arthur E. Palmer.
Elastic After-Effect in Metals. By M. F. Sayre.
The Engler Viscometer and the Theory of Laminar Flow at
the Entrance of a Tube. By L. Schiller.
Approximate Calibration of Apparatus for Measuring Abso-
lute Viscosity. By C. H. Weiss and M. Louis.
The Fluidity Method for the Determination of Association. 1.
By Eugene C. Bingham and Laurence W. Spooner.
Outline of a Systematic Survey of Rheological Theories.
By Markus Reiner.

Vol. 3 No. 3 July 1932

The Flow of Solid Metal Aggregates. By C. H. M. Jenkins.
High-Pressure Capillary Flow. By Mayo D. Hersey and
George H. S. Snyder.
The Pachimeter as an Instrument for Testing Materials,
with Special Reference to Clays, Soils, and Flours.
By G. W. Scott Blair and R. K. Schofield.
The Viscosity of Potassium Chlorate in Aqueous Solution.
By G. Raymond Hood.

Vol. 3 No. 3 July 1932. (cont'd.)

An Electro-Rheic Effect of a Thixotropic Gel. By
E. Karrer.
Some Physical Properties of Pure Ricinoleic Acid:
The Refractive Index, Specific Gravity, and Vis-
cosity. By Emile Andre and Chas. Vernier.
An Ancient Problem in Rheology. By Eugene C. Bingham.
Parallel Plate Plastometry. By R. L. Peek, Jr.

Vol. 3 No. 4 October 1932

Contribution to the Study of Viscous Friction and the
Application to the Theory of Lubrication. By
Pierre Mercier.
Contribution to the Study of the Flow of Viscous Liquids.
By C. Camichel and Collaborators.
The Structural Properties of Anisotropic Solutions of
Soap as Determined by a New Centrifugal Falling
Ball Method. By James W. McBain and Otto O. Watts.
Viscosity Problems in Igneous Rocks. By Robert Balk.
A Further Study of Association by the Fluidity Method.
By Eugene C. Bingham and Harold L. DeTurck.
A Method for Determining Diffusion Constants of Colloids
which Show Mechanical Birefringence. By Paul Boeder.
The Mechanics of Plastic Deformation: The Flow of Dur-
alumin through Orifices. By S. I. Goybkin.

Orders may be placed with the American Institute of
Physics, 175 Fifth Ave., New York, N. Y.

CREEP PHENOMENA IN HIGH POLYMERS

H. Leaderman, Massachusetts
Institute of Technology,
Cambridge, Massachusetts

The mechanical behavior of high polymers such as fatigue, impact, internal friction, and cold flow behavior cannot be deduced from simple load-deformation tests. In order to understand better the nature of the mechanical properties of high polymers and of the relationship between these properties and constitution, it is necessary to carry out more detailed investigations of mechanical properties.

When a constant load is applied to a high polymer, it is found in general that the deformation is not constant but increases gradually with time; creep is said to take place. After removal of load the residual deformation gradually decreases with time; creep recovery takes place. Under certain circumstances, for example, suitable mechanical pretreatment, the residual deformation following load removal may eventually disappear entirely. The specimen is then said to be mechanically conditioned.

Fig. 1 shows the deformation-time behavior for a loading history in which a constant load is applied for 24 hours and the specimen allowed to recover following removal of load for a subsequent 24 hours. Figs. 1 (a) and 1 (b) show respectively the deformation behavior of a specimen previous and subsequent to mechanical conditioning. The creep and recovery behavior in Fig. 1(b) can be considered as being of the nature of a delayed elasticity (or "primary creep") superimposed upon the instantaneous or Hooke's Law elasticity. In general, the delayed elastic deformation is a function of the previous load history.

The nature of the delayed elasticity in glass and other materials was considered many years ago by Boltzmann. He proposed an empirical Superposition Principle concerning the relationship between load, time, and deformation in this material. This Principle seems to be consistent with the experimental data on the delayed elastic behavior of glass and to be a basis for the study of the delayed elasticity in high polymers. The Principle may be stated as follows. If a load P is applied to a body at zero time, and if F is a form factor and E the appropriate modulus, the instantaneous deformation is given by (FP/E). The deformation subsequently increases by the delayed deformation, assumed to be proportional to the instantaneous deformation and a function of time $\psi(t)$. Hence the deformation x_t at time t due to the load P applied at zero time is assumed to be given by:

$$x_t = (FP/E)\left\{1 + \beta \psi(t)\right\} \tag{1}$$

The deformation at time t due to several loads P_θ applied at previous times Θ is assumed to be the <u>simple summation</u> of the deformations which would be due to each load acting alone, i.e.

$$x_t = \sum_{\Theta = -\infty}^{\Theta = t} (FP_\theta/E)\left\{1 + \beta \psi(t-\Theta)\right\} \tag{2}$$

Eq. 2 is the one form of Boltzmann's Superposition Principle. If the validity of this equation can be demonstrated experimentally, then this Principle might be of help in elucidating the mechanism of deformation of high polymers as related to chemical constitution.

Two methods are convenient for testing the validity of Eq. 2 in a previously mechanically conditioned high polymer. First, a constant load is applied at zero time and the deformation due to load application observed as a function of <u>time under load</u> for a period -- say 24 hours -- at the end of which the deformation has reached a limiting value or is at least proceeding slowly. The load is then removed, and the (negative) deformation due to load removal observed as a function of <u>recovery</u> time. These two deformations should be identical and furthermore the deformation at any particular instant should be proportional to the load used in the test. Such a test is called a <u>long-duration</u> test. In an alternative method, a given load is applied for say ten minutes, removed, reapplied ten minutes later, again removed, and so on. From observation of the changes in deformation with time of the material in such a test the deformation as a function of time can be computed for a simple creep test as above by means of the Principle. Such a test is called a Superposition Test (Fig.2). It seems that for small longitudinal deformations (up to say 5%) the Superposition Principle is obeyed by high polymers.

A mechanical model which consists of a spring in parallel with a unit with a finite Maxwell relaxation time obeys the Superposition Principle. The normalized creep function for this model is of the form:

$$\psi(t) = 1 - e^{-t/\tau} \tag{3}$$

Data on the creep of high polymers indicates however that the delayed elastic behavior of such materials can be represented by an equivalent model possessing not a single relaxation time but a <u>continuous distribution</u> of such times according to Wiechert.

24

Fig. 1

LOAD

DEFORMATION
(a)

DEFORMATION
(b)

0   24   48 HRS.

TIME

Fig. 2

LOAD

LONG DURATION
TEST

CREEP I   CREEP II

RECOVERY I   RECOVERY II

DEFORMATION

LONG DURATION
TEST

SUPERPOSITION TEST

TIME, MINS.

0   10   20   30   40

25
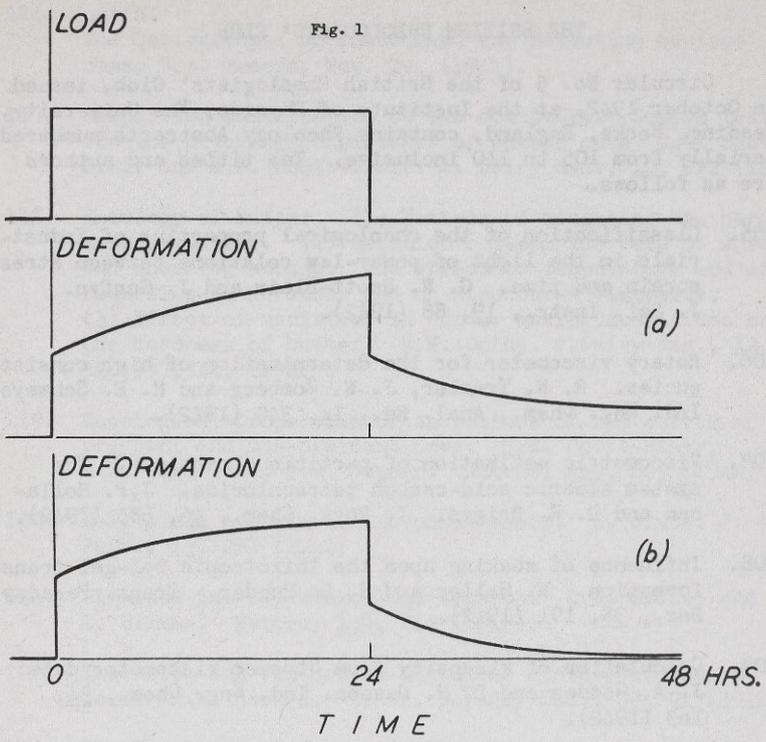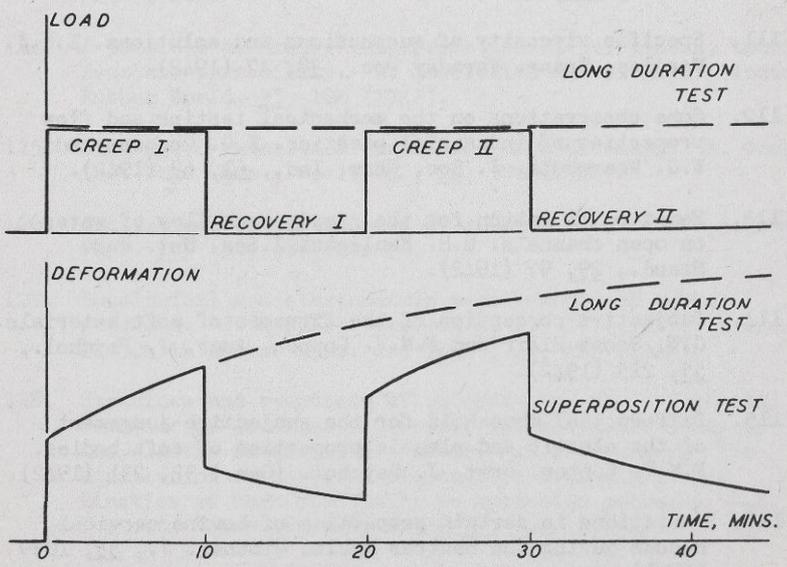
Circular No. 5 of the British Rheologists' Club, issued in October 1942, at the Institute of Physics, The University, Reading, Berks, England, contains Rheology Abstracts numbered serially from 105 to 140 inclusive. The titles and authors are as follows.

105. Classification of the rheological properties of industrials in the light of power-law relations between stress strain and time. G. W. Scott-Blair and J. Garfyn. J. Sci. Instr., 19, 88 (1942).

106. Rotary viscometer for the determination of high consistencies. R. N. Traxler, J. W. Romberg and H. E. Schweyer. Ind. Eng. Chem., Anal. Ed., 14, 340 (1942).

107. Viscometric estimation of particle dimensions. The system stearic acid-carbon tetrachloride. J.P. Hollahan and D. R. Briggs. J. Phys. Chem., 46, 685 (1942).

108. Influence of shaking upon the thixotropic sol-gel transformation. W. Heller and H. L. Roeder. Trans. Faraday Soc., 38, 191 (1942).

109. Calculation of viscosity from Stormer viscometer data. J. A. Geddes and D. H. Dawson. Ind. Eng. Chem., 34, 163 (1942).

110. A type of plastic deformation new in metals. E. Orowan. Nature, 149, 643 (1942).

111. Specific viscosity of suspensions and solutions. E.W.J. Mardles. Trans. Faraday Soc., 38, 47 (1942).

112. Some observations on the mechanical testing and flow properties of industrial plastics. E.G. Couzens and W.G. Wearmouth. J. Soc. Chem. Ind., 61, 69 (1942).

113. Equation of motion for the steady mean flow of water on open channels. G.H. Keulegan. J.Res. Nat. Bur. Stand., 29, 97 (1942).

114. Subjective conception of the firmness of soft materials. G.W. Scott-Blair and F.M.V. Coppen. Amer. J. Psychol., 55, 215 (1942).

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121. Firmness in compression and tension. D.C. Broome and L. Bilmes. Nature, 149, 413 (1942).

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123. Highly elastic deformation in polymers. A.P. Alexandrov and J.S. Lazurkin. Acta Physicochem. U.S.S.R., 12, 647 (1940).

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127. Rheological and elastometric measurements of rubber products. F. Hoppler. Kautschuk, 17, 17 (1941). Translation in Rubber Chem. and Tech., 15, 115 (1942).

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131. Frictional phenomena. A. Gemant. J. Appl. Phys. $\underline{12}$, 530, 626, 718, 725, 827, (1941); $\underline{13}$, 22, 90, 210, 290, 355 (1942).

132. An extension of Saint Venant's principle, with applications. J.N. Goodier. J. Appl. Phys., $\underline{13}$, 167 (1942).

133. On the resistance to the uniform motion of a solid through a viscous liquid. R.B. Block. ibid, $\underline{13}$, 56 (1942).

134. Rubber in vibration. S.D. Gehman. ibid, $\underline{13}$, 402 (1942).

135. Relation between viscosity of solutions and physical properties of high polymers. R. Simha. ibid, $\underline{13}$, 147 (1942).

136. Theoretical approach to the problem of yarn strength. R.R. Sullivan, ibid. $\underline{13}$, 157 (1942).

137. Studies in lubrication, X.F. Morgan, M. Muskat and D. W. Reed. ibid. $\underline{12}$, 743 (1941).

138. Elastic after-effects and dielectric absorption in glass. N.W. Taylor. ibid. $\underline{12}$, 753 (1941).

139. Structure and dynamics of liquids. W.E. Roseveare, R. E. Powell and H. Eyring. ibid, $\underline{12}$, 669 (1941).

140. Correlation between elastic moduli and viscosity of liquids and plastics. A. Gemant. ibid, $\underline{12}$, 680 (1941).

METALS

A THEORY OF THE STRENGTH OF METALS.-Lawrence Bragg*,
Nature, 149, 511 (May 9, 1942).

The author combines certain portions of Taylor's (Proc.
Roy. Soc. A145, 362 (1934) dislocation theory of slip with
Wood's (Proc. Roy. Soc. A172, 231 (1939) concept of a lower
limiting "crystallite" size in cold worked metals to arrive
at the following expression for the elastic strength of a
metal:

$$T = \alpha \, ns/(t-t_o)$$

Where T is the limiting stress for elastic failure, a con-
stand approximating unity, n the coefficient of rigidity for
a poly-crystalline aggregate of the particular metal and s
the interatomic distance for the slip plane in the slip di-
rection. t is the side of the "average" crystallite existing
in the metal and t_o the limiting size below which the metal
becomes brittle. Wood's calculation's of the crystallite
size are based on the broadening of xray diffractions lines
which accompanies cold work and which might also be attribut-
ed to "wrinkling" as "crimping" of the planes of the lattice.
Bragg suggests that in either case the above formula should
apply since if the second picture of the effect of deformat-
ion is preferred t above would refer to the periodicity of
the "crimps" in the lattice planes.

<div align="right">J. R. LOW, JR.</div>

*(Substance of a lecture delivered at Royal Institution
   March 31, 1942)

A TYPE OF DEFORMATION NEW IN METALS.-E. Orowan, Nature,
149, 642 (June 6, 1942).

The author describes a type deformation in single crys-
tals of cadmium and zinc which is distinct from slip, twin-
ing or "flexure gliding". When single crystal wires of
cadmium oriented with the (0001) plane nearly paralled to
the wire axis were loaded in compression, sharp "kinks"
appeared in the surface which could not be accounted for by
any of the usual deformation mechanisms. The glide planes
in the two parts of the kink are mirror images across the
"kink plane" but the lattice orientations are not. The
"plane of kinking" need not be a crystallographic plane; its
orientation depends on stress conditions. The author suggests
that slip may begin in many or all cases by this mechanism
and suggests that this mechanism would account for the ob-
served orientation of Lueders lines in mild steel and the

phenomenon of a sharp yield point.

J. R. LOW, JR.

ON THE THEORY OF FINITE DEFORMATIONS OF ELASTIC
CRYSTALS.-R. Furth, Proc. Roy. Soc., A 180, 285 (1942).

The general theory of finite deformation of cubic crys-
tals at zero temperature is developed to a second order approxi-
mation, and the cases of (1) a uniform hydrostatic pressure,
(2) a tension in the direction of one of the axes, (3) a shear
along the (0,1,0) planes and (4) a shear along the (0,1,1)
planes of the lattice, are worked out in detail. A number
of 'second order effects' (deviations from Hooke's law) are
predicted which in case (1) have been observed and measured
by Bridgman, and the remaining cases certainly can be detect-
ed and measured by suitable experimental arrangements.
Assuming the particular force law between the particles of
the lattice which was first introduced by Mie and Gruneisen,
and later used in the investigations of Leonnard-Jones and
Born and his collaborators, and using some of the results of
the latter authors, the constants governing the above-mention-
ed second-order effects are expressed in terms of the con-
stants governing the force law, and calculated numerically
for a number of special values of these constants. Thus by
comparing the calculated values of these constants with the
results of measurements at low temperature the unknown force
law could probably be determined.

CRYSTAL THEORY OF METALS: CALCULATION OF THE ELASTIC
CONSTANTS.-K. Fuchs and H. W. Peng, Proc. Roy. Soc., A 180,
451 (July 3, 1942).

The approximate equations of motion for the electrons in
a cyclic lattice of a metal or set up with the help of the
self consistent field. The displacement of the ions are then
considered as pertubations of the motion of the electrons.
The change of the boundary is compensated by a co-ordinate
transformation. The change of the potential energy of the
lattice due to a homogeneous deformation is calculated by
the perturbation method. The calculated values of the elastic
constants are found to be in satisfactory agreement with the
observed values on Li, Na, K, and Cu.

The relationship between viscosity, yield value, tack,
thixotropy and concentration is investigated experimentally
on pigments suspended in oils.

Stress-strain curves and apparent viscosity-rate of
shear curves are shown for three different viscometers, a
capillary, a rotating cylinder and a falling sphere type.
The apparent viscosities of the same suspension obtained on
the three instruments vary widely, which is to be expected
since apparent viscosities of plastics decrease with rate
of shear and since the rate of shear used differed on each in-
strument. The stress-strain curves seem to have been obtain-
ed by increasing the rates of shear from one measured point
to the next. These curves appear curvilinear throughout all
speeds. From this it is concluded that paints and pigment
systems do not conform with Bingham's equation and that sub-
sequently this curvature is due to an existence of yield value
in such systems. However, this is not necessarily so. In
the case of the rotating type viscometer straight lines could
have been obtained if stress-strain curves were measured at
decreasing rates of shear immediately following the ones ob-
tained at increasing rates of shear. In that case the curvili-
nearity of the up-curve would be caused by thixotropic break-
down.

Yield value and specific viscosity measurements are made
on suspensions of pigments in liquid media at various pigment
concentrations. It was found that the suspensions having the
higher yield values also had the higher specific viscosities
and vice versa. Only above a certain minimum concentration
did the suspensions start to show signs of yield value. But
by increasing the concentration above that minimum the yield
values increased rapidly.

The yield value and viscosity of the suspension is pro-
foundly influenced by the kind of pigment and liquid media
contained in the suspension, since presumably the degree of
flocculation is influenced by these two ingredients. The de-
gree of flocculation of particles in suspension is indicated
by measuring sedimentation volumes. A high sediment volume
is found for pronounced flocculation and vice versa. There-
fore, various pigments were suspended in a hydrocarbon mixture
(7% concentration) and sediment volumes were compared with
specific viscosities. It is found that both decrease toget-
her as expected. The same was done with silica in various
liquids with similar results for yield values and sedimen-
tation volumes.

It has been also found that the viscosity of the medium plays an important part in determining yield value and specific viscosity. In low viscosity liquids such as hexane the author claims that particles orientate more quickly and therefore at higher concentrations by reason of their quicker movement interfere more readily with each other resulting in higher yield values. To demonstrate this the viscosity of silica suspensions in a heavy and light oil was plotted against various concentrations.

The existence of structure in suspensions of low concentration where no yield value is evident, is shown by using a rotating cylinder (Stormer viscometer). At these low concentrations it was found that structure not only exists but increases by increasing the time of rest before the measurement. Therefore it is concluded that the structure does not suddenly develop above a minimum concentration but exists also at lower concentrations, even though it is difficult to detect. However, this structure below the minimum concentration according to all indications seems to be viscous and thixotropic rather than one due to simple flocculation.

Viscosity coefficients fulfilling Einstein's viscosity equation, but differing from 2.5, are given for various suspensions. Coefficients as high as 12 have been obtained. Among others, values for these coefficients are given for Bentonite suspended in mineral oil hydrocarbons of various viscosity. It was found that the coefficient increases with an increase in viscosity of the medium, being especially sensitive below 5 centipoises. As an explanation for the dependence of the coefficients on the viscosity of the medium it is stated that the particles in the more viscous media take longer to orientate causing more disturbance by eddying with a consequent increase in viscosity.

It is shown that the specific viscosity of an 11.5 per cent suspension of kaolin in petroleum spirit decreases with additions of oleic acid, wool fat, or boiled linseed oil. With smaller additions the decrease is more rapid than with larger ones. This decrease is taken as indication of thixotropic structure but it may be rather due to surface changes, especially since the sediment volumes decrease accordingly. The sedimentation volumes of the mixed liquids were found to be usually less than the ones obtained with either single liquid.

The tack or pull-resistance as used in the tests is the force in grams required to pull up from a paint film a flat glass finger of 12.5 mm in diameter. Such conception of tack is dangerous since it does not include the time of break, and is only a one point method. From the measurements of pull resistance of various suspensions it is shown that pull resist-

ance develops above the same minimum pigment concentration
at which yield value appears. From this the conclusion is
drawn that pull resistance is mostly dependent on yield value,
which, however, is only a fact at low rates of shear since
the yield value becomes less and less significant as the
rates of shear increase.

A short description is given of a metal outflow visco-
meter cup to be used in laboratory work.

RUTH N. WELTMAN

HIGH-SPEED ROTATIONAL VISCOMETER OF WIDE RANGE, CONFIR-
MATION OF THE REINER EQUATION OF FLOW.-Henry Green, Ind.
Eng. Chem., Anal. Ed. 14, 576 (1942).

The first part of this paper explains the advantages
inherent in the rotational viscometer when used for measur-
ing plastic materials like paints, printing inks, etc. The
second part describes a rotational viscometer designed speci-
fically for this type of work.

The equation of plastic flow in a rotational viscometer
was originally published by Reiner and Riwlin in 1927 and
later republished by Reiner in the Journal of Rheology in
1929. Prior to this time rheologists had no way of determin-
ing yield value and mobility except by using capillary tube
viscometers. The author points out that the capillary tube
method employs the erroneous assumption that a straight line
relationship exists over the upper part of the consistency
curve. Buckinham mathematically disproved this straight
line conception, but in doing so left no apparent means for
measuring the consistency factors of plastic materials, for
the solution of his own equation was found quite impractical.

This condition was rectified with the publishing of
Reiner's equation. Unfortunately neither Reiner nor anyone
else had given data tending to prove the correctness of his
equation; consequently that very valuable contribution to
rheology became buried in the literature and has remained
practically unused ever since. The author shows in his paper
that the Reiner equation can be rewritten in a form that is
easy and practical to solve; and then gives data that prove
the equation is entirely valid.

A plastic material, flowing through a capillary tube,
will hold together in a solid mass unless the shearing stress
is greater than the yield value. The shearing stress, how-
ever, is always larger at the wall of the capillary than at
the center; consequently shear takes place first at the wall
and then developes inward toward the center as the stress is
gradually increased. In the capillary tube, shearing into

complete laminar flow is not attained until the shearing
stress is infinite. This is the reason that a capillary
tube cannot give a straight line relationship between stress
and rate of shear. The situation is entirely different in
the case of rotational viscometers. Here complete laminar
flow can be induced with relatively small finite shearing
stresses; hence a linear relationship can be had. This is
the basis of Reiner's work and is the reason why the rotat-
ional viscometer is inherently better than capillary types
for obtaining consistency curves of plastic materials.

In order to obtain consistency curves from which yield
value and mobility can be derived it is necessary to have a
means for varying the r.p.m. over a sufficiently large range.
In addition, the difference between the lengths of the cup
and bob radii must be made small enough so as to reduce the
non-linear portion of the curve to an insignificant amount.
The dimensions used are: Radius of cup = 1.5 cm. Radius
of bob 1.3 cm. Depth of the bob immersed, 5.1 cm.

The viscometer is operated by a 0.25 h.p. synchronous
motor. The r.p.m. is varied by means of a Graham (Briggs
and Stratton Corp.) continuously variable transmission.
The range covered is from 5 to 400 r.p.m. The cup is immersed
in a temperature controlled bath and is rotated by means of
a shaft which enters from the bottom of the bath. The tors-
ion members are helical steel springs. There are six of these
springs, which is sufficient to cover the range of mobilities
and yield values found in paint and printing ink products.

The author is mainly concerned with measuring printing
inks. These materials are invariably thixotropic; hence
they "break down" while being measured in a viscometer. In
order to obtain a record of this breakdown the consistency
curve is run in both directions i.e. up and down. The up-
curve is run first, starting with the lowest convenient r.p.m.
The r.p.m. is increased in equal steps and the corresponding
torque read. When the top r.p.m. is attained the down-curve
is commenced and the r.p.m. is reduced until the bottom of
the curve is reached. During the running of the up-curve
thixotropic breakdown occurs, and consequently the curve is
bow-shaped. In making the down-curve, however, the velocity
gradient is steadily decreased and no further breakdown occurs.
It is shown by numerous graphs that the down-curve follows
the Reiner formula of flow.

Two new terms are employed in the paper. One is plastic
viscosity in place of the reciprocal of mobility. This has
been done mainly for convenience in the printing ink industry
where the term viscosity has been used for years and the term
mobility is practically unknown. In thixotropic materials
the plastic viscosity decreases as the material breaks down;
hence its value is dependent on the top r.p.m. employed.

For each particular velocity gradient (derived from the top
r.p.m. and the dimensions of the instrument) the material
attains a definite thixotropic level, which is apparent from
the linearity of the down-curve. It is on account of the ex-
istence of such a level that plastic viscosity and yield value
of thixotropic materials can be measured; but it should al-
ways be stated at what velocity gradient the measurement has
been made. When the up- and down-curves are plotted toget-
her a so-called thixotropic hysteresis loop is formed. Under
rigidly standardized conditions the area of this loop indi-
cates the magnitude of the thixotropy. No loop means no de-
tectable thixotropy.

HENRY GREEN
Interchemical Corp., New York, N. Y.

THE TACKMETER, AN INSTRUMENT FOR ANALYZING AND MEASURING
TACK.—Henry Green, Ind. Eng. Chem., Anal. Ed. 13, 632 (1941).

Many years ago the concept of "tack" was introduced into
the printing ink field. In the present article an analysis
is made of tack from the inkman's point of view. The analy-
sis does not include rubber-like or elastic materials but
otherwise is comprehensive.

In the ink industry tack is defined by the finger tap-
out test. This is described as follows:

"The ink is first rubbed out into a sufficiently thin
layer with the finger tip, either on a nonporous material like
glass or on coated paper. The finger tip is next firmly press-
ed into the film and then drawn suddenly away. When this
motion is repeated a number of times in rapid succession, the
sensation of stickiness arises, caused by the pull-resistance
of the ink exerted on the finger tip. The amount of this pull-
resistance is adjudged to be the tack".

An analysis of tack, then, becomes an analysis of the
pull-resistance between two parallel plates, the intermediate
space being filled with ink. Assuming that the causes of
pull-resistance in a non-elastic material are not know, tack
might arise from five different sources: (1) adhesion, (2)
cohesion, (3) surface tension, (4) viscosity, and (5) yield
value.

An examination of the finger test shows that the ink
does not rupture abruptly nor does it strip clean from any
portion of the fingertip or from the paper surface. It
divides by necking down. This means that no work is done
against the force of adhesion, and so adhesion must enter the
picture only indirectly. The absence of adhesion would make
pull-resistance impossible, but increasing the adhesion

(between the ink and finger or ink and paper) would not in-
crease the pull-resistance. The author also discards cohes-
ion and surface tension as being relatively unimportant, hav-
ing no direct bearing on the tack of materials like printing
inks. Thus by a process of elimination, tack is found to de-
pend on the resistance to flow arising from the factors vis-
cosity and yield value.

An instrument capable of analysing pull-resistance of
inks must have three qualifications. It must be designed so
as to make possible the individual variation of each of three
factors while the remaining two are constant. These factors
are, area of the fingertip, initial film thickness, and rate
of pull. The Tackmeter has these qualifications. It is a
metal finger (operating over a plate) attached to a combin-
ation of levers which are activated by a series of weights.
The whole is mounted on a temperature controlled water bath.
The initial film thickness is adjusted by a micrometer screw.
The finger area is varied by having a number of different
size finger tips. The rate of pull is changed by using differ-
ent activating weights. The metal finger is fastened into
a flat metal bar hinged at one end. The free end of the bar
can be pulled upwards by means of levers to which it is attach-
ed. On the end lever in this series are suspended the differ-
ent pulling weights.

A drop or two of ink is placed on the center of the
above mentioned plate. The metal finger is then brought
down in contact with the ink. The finger is prevented from
sinking through the ink until it reaches the plate by means
of two metal strips, one on each side of the ink. The init-
ial film thickness is now regulated with the micrometer screw.
A large weight (500 grms.) is placed on the flat bar to hold
it in place and some suitable small pulling weight is suspended
from the end lever. When the large weight is lifted, the
small weight begins to pull the finger upward. During the up-
ward motion the ink necks down to a fine thread but does not
necessarily break as the pull-resistance has by then become
negligible. The upward pulling motion is terminated by means
of a set-screw after the finger has been raised about 2 m.m.
The time of the upward motion (time of necking down) is measur-
ed with a stopwatch.

The Tackmeter has shown the following: (a) the rate of
pull is directly proportional to the activating force (pull-
resistance) in excess of the yield value intercept; (b) pull-
resistance is inversely proportional to the square of the
initial film thickness; and (c) pull-resistance is directly
proportional to the fourth power of the finger tip radius.
From these facts empirical equations can be set up:

$$T_{1/t} - \frac{U}{Kt} + Cf$$

36

$T_{1/t}$ is the tack or pull-resistance at the rate of pull $1/_t$; U is the plastic viscosity; C is an instrumental constant; and K is $D^2/\pi R^4$, D being the initial film thickness and R the radius of the finger tip area.

There is a decided advantage in the printing ink industry in putting tack on a relative basis by comparing the tack of an unknown with the tack of a standard substance. The equation for relative tack is

$$(\text{Relative tack}) \ T/T^o = \frac{U}{U^o} + \frac{\text{Const. } tf}{U^o}$$

If t is the time of the printing press, then t is quite small and the last term of the equation becomes negligible. Relative tack then becomes equal to relative viscosity. The advantage in this conclusion is that a suitably constructed rotational viscometer, capable of measuring plastic viscosity, can be employed for measuring relative tack.

<div style="text-align:right">

HENRY GREEN
Interchemical Corp., New York, N. Y.

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THE PHYSICS OF PIGMENTS IN DISPERSED SYSTEMS.-Henry Green, Research Laboratories, J. Applied Phys. 13, 611-622 (1942).

The object of this paper is to show the relationship between the microsocpy of pigment-vehicle suspensions and their rheological properties. Very little has appeared in the literature in this field.

The industrial rheologist, whose interest is in products like paints, printing inks, etc., must deal with condensed or crowded, systems, o.e. with high pigment-vehicle ratios. This crowding results in particle contact producing various types of pigment structure. Such structure has a pronounced effect on the consistency flow curve. All this is in marked contract with what happens in the very dilute suspensions usually employed in academic studies on rheology.

The elements of pigment microscopy are first outlined. This includes the definitions of individual particle, hard aggregate, ultimate working unit and flocculate. The photomicrographic method for making particle size measurement is briefly described and the equations for the important average diameters are given.

Next, the microscopy of pigment suspensions is explained. This comprises the technique for making the mount. A drop of the material (paints, printing inks, etc.) is placed on a microscope slide and then covered with a clear drop of

its own vehicle. The coverglass is pressed down upon it with a slight rotary motion. The edge of the drop will thus be made to diffuse somewhat into the surrounding vehicle and when examined with a microscope this edge will show the nature of the pigment structure.

In pigment-vehicle suspensions of the kind examined, structures range from highly flocculated to complete defloc-culated forms. The exact nature of the force holding the particle flocculate together is not stated but the existence of such a force is easily demonstrated microscopically. For instance, an isolated flocculate can be distorted without dis-persion by pressing the coverglass with a needle point in the vicinity of the flocculate. When the pressure is released the flocculate often returns to its original form showing that a definite force exists holding the particles together.

This force is one of the causes of yield value. In dilute suspensions, where the distance between the particles is increased by stirring, yield value disappears under the circumstances. In crowded systems, however, the particles are always in contact, consequently yield value is not affect-ed by stirring. If wetting is increased by incorporating a deflocculating agent, yield value decreases. If water or some other flocculating agent is rubbed into the material, the force of flocculation is increased and the yield value also increases.

The final section of the paper treats of the rheology of various suspensions possessing different types of pigment structure. Photomicrographs of these structures are shown with their respective consistency curves attached.

The force of flocculation must manifest itself some way in the consistency curve. Since flocculation produces struct-ure and structure indicates rigidity, it is natural that the effect of flocculation is most apparent in the yield value. Flocculation also increases plastic viscosity.

Suspensions giving Newtonian curves have their particles well deflocculated and fairly large in size. When such par-ticles become molecular in dimension the suspension is like-ly to become pseudoplastic. Dilatent suspensions also have large well deflocculated particles bu the pigment-vehicle ratio is always high and the system completely crowded. Plastic suspensions are always flocculated ones.

The force of flocculation is the intensity factor. The capacity factor is governed by the specific surface of the pigment and by the pigment-vehicle ratio. A microscopical examination of the sample, by the technique given above, will usually reveal the nature of the yield value, i.e. whether it is caused by a strong force of flocculation, by small particle

size (high specific surface) or by a high pigment-vehicle ratio.

HENRY GREEN
Interchemical Corp., New York, N. Y.

RUBBER

MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF POLY-
BUTENES.-Paul J. Flory, Essor Laboratories-Chemical Division,
Standard Oil Development Company, Elizabeth, New Jersey. Ab-
stract of Paper Presented before the Division of Rubber Chem-
istry at the Meeting of the American Chemical Society, Sept.
7-11, 1942.

Viscosity methods provide a most convenient means for
characterizing polymeric materials. Frequently the results
are expressed as "molecular weights" calculated from Staud-
inger's equation, according to which the molecular weight is
proportional to the intrinsic viscosity, $[\eta] = [(\ln \eta_r)/c]_{c=0}$
Recent work on rubber and various syn-
thetic high polymers has cast serious doubt on Staudinger's
method for calculating molecular weights. Unfortunately, sat-
isfactory experimental data for establishing with certainty
the correct relationship between molecular weight and solution
viscosity are exceedingly meager.

In order to establish this relationship for Polybutenes
(polymers of isobutylene), samples of narrowly restricted mole-
cular weight range have been prepared by carefully controlled
fractional precipitation. The intrinsic viscosities of the
fractions have been measured, and their absolute molecular
weights have been determined by the osmotic pressure method.
Over the entire molecular weight range investigated, from 5,000
to 1,300,000, the results are in close agreement with an equat-
ion of the form $M = K[\eta]^a$ where K is a constant and a = 1.64,
instead of unity as required by Staudinger's equation. Houwink
has found that results of Staudinger on comparatively heterogen-
eous polymeric vinyl derivatives can be fitted to a similar re-
lationship, although the molecular weight ranges investigated
were limited.

When applied to heterogeneous polymers the above relation-
ship yields a "viscosity average" molecular weight which is
intermediate between the weight average and number average mole-
cular weights.

Rubber-like Polybutenes possess molecular weights above
500,000, and in some cases they probably reach 10,000,000 or
more. Thus, the molecular weights of these synthetic polymers
exceed those for soluble crude rubber.

THEORY

RELATIONSHIPS BETWEEN VISCOSITY AND SURFACE TENSION OF LIQUIDS.-R. C. Tripathi. J. Indian Chem. Soc., 19, 51 – 54 (1942).

The following three equations connecting viscosity and surface tension have been examined using data of 33 organic liquids, both associated and nonassociated.

(1) $\log \log \eta = 1.2 \, \gamma^{\frac{1}{4}} - 2.9$ (Buehler)

(2) $\eta^{-1} = k \, \gamma^{-\frac{1}{4}} + c$ (Silvermann and Roseveare)

(3) $\log \log \eta = m \, \gamma^{\frac{1}{4}} + c'$ (Modified Buehler Equation)

where η = viscosity

γ = surface tension

k, c, m, c' = constants characteristic of the liquid.

Equation (3) was found to agree with the experimental data better than the other two.

K. H. SUN

LETTER TO THE EDITOR

Sir: In the September issue of the Rheology Bulletin comments on the British Rheologists' Club's Classification of Rheological Properties are invited.

I suggest that we cooperate with our British colleagues in establishing an international standard system of notation.

For example, our British friends represent strain by σ, whereas we use ε. To us, σ always means stress but S is used for this in England. A unified system of symbols would prevent much confusion.

If such a project were successful, it could, perhaps, be extended to include standard definitions.

Very truly yours,

H. K. NASON,

MONSANTO CHEMICAL COMPANY
PLASTICS DIVISION

APPLICATION

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

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

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

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

Membership, (including subscription to Rheology Bulletin.) $2.00

Please also enter my subscription for the following additional periodicals published by the American Institute of Physics, at the rates available to members of the five founder societies:

Review of Modern Physics ....$3.00 (foreign, $3.40)
Review of Scientific Instruments......$3.00 (foreign, $3.50)
Journal of Chemical Physics..........$10.00 (foreign, $11.00)

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