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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 operation, as well as the assembling of the BULLETIN, is performed 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 $S_8$ is 8-membered rings and $S_x$ is long sulfur chains, so the equilibria in liquid sulfur are given by

$$\frac{X}{8}S_8(\text{ring}) \leftrightarrow S_x(\text{chain}) \quad 0 < X < \infty$$

The equilibrium constant $K_x$ is formulated for this reaction, and is, with the numerical values necessary to fit the experimental data,

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

The average chain length $Z$ is given by

$$\frac{1}{Z^2} = \frac{1}{27,000}Z + \frac{K_g}{8}$$

and therefore decreases with increasing temperature. The weight fraction of chains $\phi$ is given by

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

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.
The viscosity is calculated upon the assumption that the $S_g$ (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 $\eta = (\eta_{\text{rings}})^{1-f} \cdot (\eta_{\text{chains}})^{f}$. The equations for the viscosities are, with the numerical values necessary to fit the experimental data:

$$\eta_{\text{rings}} = \frac{N_h}{128} e^{-\frac{9000}{RT} + \frac{0.35}{R} \sqrt{\frac{2}{W}}}$$

$$\eta_{\text{chains}} = \frac{N_h}{128} e^{-\frac{2.0}{R} + \frac{8300}{RT}}$$

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

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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 $i^{\text{th}}$ kind of deformation unit the following equation of motion holds:

$$\frac{ds}{dt} = \frac{1}{G_i} \frac{df_i}{dt} + n_i \lambda_i \frac{kT}{h} e^{-\frac{2 \sinh \frac{f_i \lambda_i}{2N_i kT}}{2N_i kT}}$$

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, $\lambda_i$ the
distance jumped and $\Delta F_i$ the free energy of activation for this type of unit process. $f_i$ is therefore the force acting on each process of type $i$. \[ N_i \]

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


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 $10^0$ 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, $n$, 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 $n$ 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. **Shearing Stress:**

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

   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. **Rate of Shear:**

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

   where:
   - $b$ = radius of container in cm.
t = time in seconds.

m = slope of log \( \frac{t}{\log t} \) line.

3. **Viscosity**

\[
\eta_a = \frac{M \cdot t \cdot (m+1)}{P (P - \eta') (m-1)} \left[ 1 - \left( \frac{a}{b} \right)^{m-1} \right] \cdot 1.56 \times 10^6
\] (3)

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

1. **Shearing Stress**:

\[
T_a = \frac{M \cdot \pi \cdot a \cdot L}{2 \pi a \cdot L}
\] (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**:

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

where \( v_a \) = velocity of movement in cm/sec.

3. **Viscosity**

\[
\eta_a = \frac{a \cdot T_a}{v_a (m-1)} \left[ 1 - \left( \frac{a}{b} \right)^{m-1} \right]
\] (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'Hopital's rule the form reduces to

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

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

Where: \( C \) = the slope of the log \( P \) - log \( t \) line.
2. For the moving cylinder:

$$m = \frac{d(\log v)}{d(\log T)}$$  (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:

$$K' = P(0.849 - 0.00788P) - 0.0562$$  (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 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. 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 $32^\circ$ F.

The apparent solidification of fluid lubricants at high pressures as reported by Hersey and Shore, and Kleinschmidt.
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/cm². 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/cm². 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/cm² to atmospheric and the apparatus was suddenly dropped from about 5,000 kg/cm² 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.

1. L.H. Adams, Rev. Sci. Instrs. 7, 174, 1936, Figure 1.
2. P.W. Bridgman, Physics of High Pressure, McMillan 1931, pg. 42

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

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

A previous report 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:

$$\log\log(\nu + 0.8) = A \log T + B$$

$T$ 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 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.

1. Paper read at Annual Meeting, N.Y. City, 1941
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 long time 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 short time \((10^3\) 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 (normal tenacity approximately 2.0 g/d) is very similar to the normal wet 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

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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
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. 12, 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

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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

$$\eta' = \eta / (1 + b \varepsilon)$$

where $\eta'$ and $\eta$ are the apparent viscosity and the viscosity extrapolated to zero shear, and $\varepsilon$ 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 $1.1 \times 10^4$ g dyne cm$^{-2}$, where $g$ is the weight fraction of polystyrene.
The variation of viscosity with temperature followed the usual exponential relationship, \( \eta = A e^{\frac{Q}{RT}} \). 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 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 \( 1.0 \times 10^5 \) dyne cm\(^{-2} \), in agreement with the value of \( 1/b \) (eq. 1) at this concentration \( (1.2 \times 10^4) \). 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 \( T = A e^{Q'/RT} \); 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,

\[
\gamma = \gamma_0 e^{-i(\omega T - 2\pi x/\lambda)} - \frac{x}{x_0}
\]

and an assumed Maxwellian relaxation of shearing stress. The relaxation time was calculated from the dispersion (at the lower concentrations) as \( T = 1/\omega \) at the frequency where \( G(\omega) = 0.83 G^0 \); and it was calculated from the damping (at higher concentrations) as \( T = \pi x_0/\omega - \lambda/4\pi x_0 x_0 \). Here \( \omega \) is the circular frequency, \( G^0 \) the modulus of rigidity at high frequencies, \( \lambda \) the wavelength, and \( x_0 \) the critical damping distance.

The value of \( T \) from both dispersion and damping was \( 4 \times 10^{-2} \) sec., independent, to a first approximation, of temperature and concentration.

The modulus of rigidity \( G^0 \), at 25°, ranged from 0.8 \( \times 10^4 \) dyne cm\(^{-2} \) at a concentration of 15.3% to 3.8 \( \times 10^5 \) at 52.3%. Its variation with temperature (up to 40%) followed the equation \( G^0 = A e^{Q''/RT} \), and \( Q'' = 1500 \) cal., independent of concentration.

All these data are interpreted in terms of two rigidity mechanisms, setting \( G^0 = G_1 + G_2 \) and \( \eta = G_1 T + G_2 T^2 \) (following Kuhn and Bennewitz and Röntgen). 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 \( T \) is identified with the relaxation time of the transverse vibrations, which is independent of concentration, then \( T \) 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 "cooking 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 appearing to give results which showed most promise of being convertible to absolute units.

A complete description of the plastometer is given, including 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 plastometer 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 measurable. Results show that the maximum fluidity in divisions per minute dial movement is reproducible 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 expressing 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 $6.4 \times 10^7$ poises to $6.6 \times 10^2$ poises. Experimental results showed that if it were described to increase 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 Plasticity of Solvated Colloids. By S. E. Sheppard and R. C. Houck.
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.
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.

Vol. 1 No. 3 April 1930.

The Viscosity of Dilute Lyophilic Dispersions. By Elmer O. Kraemer and George R. Sears.
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.

The Fluidity of Liquids. By S. E. Sheppard and R. C. Houck.

Plasticity and Viscosity as Criteria of Molecular Aggregation. By S. E. Sheppard.
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.

Rheology Index. By Eugene C. Bingham.
Vol. 2 No. 2 April 1931.

The International Comparison of Viscometers. By S. Erk.
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 Capillary from the Poiseuille Law. By S. Erk.
Explicit Formulas for Slip and Fluidity. By Melvin Mooney.

Vol. 2 No. 3 July 1931

The Effects of Salts on the Extensibility of Protoplasm. By William Seifriz and Janet Plowe.
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.

Vol. 2 No. 4 October 1931

Notes on the Ring and Ball Method. By Fred C. Eaton.
The International Comparison of Viscometers. By S. Erk (Errata)

Vol. 3 No. 1 January 1932

The Cause of Fluctuations in Rising Mixtures of Gas and Liquid. By J. Versluys.
Viscosity Measurements in Molten Glass. By Howard R. Lillie.

Future Problems of Theoretical Rheology. By Mayo D. Hersey.
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.

High-Pressure Capillary Flow. By Mayo D. Hersey and George H. S. Snyder.
The Viscosity of Potassium Chlorate in Aqueous Solution. By G. Raymond Hood.


An Ancient Problem in Rheology. By Eugene C. Bingham.

Parallel Plate Plastometry. By R. L. Peek, Jr.


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

CREEP PHENOMENA IN HIGH POLYMERS

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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:
\[ x_t = (FP/E) \left\{ 1 + \beta \psi(t) \right\} \]  
\( (1) \)

The deformation at time \( t \) due to several loads \( P_0 \) applied at previous times \( t \) is assumed to be the simple summation of the deformations which would be due to each load acting alone, i.e.

\[ \theta = t \]
\[ x_t = \sum_{\theta = -\infty}^{0} (FP_0/E) \left\{ 1 + \beta \psi(t-\theta) \right\} \]  
\( (2) \)

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 time under load 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 recovery 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 long-duration 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:

\[ \psi(t) = 1 - e^{-t/\tau} \]  
\( (3) \)

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 continuous distribution of such times according to Wiechert.
Fig. 1

DEFORMATION

(a)

TIME

Fig. 2

LOAD

LONG DURATION TEST

CREEP I
RECOVERY I
CREEP II
RECOVERY II

DEFORMATION

LONG DURATION TEST

SUPERPOSITION TEST

TIME, MINS.
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.


116. cont'd.


133. On the resistance to the uniform motion of a solid through a viscous liquid. R.B. Block. ibid, 12, 56 (1942).


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


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


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

The author combines certain portions of Taylor's (Proc. Roy. Soc. A142, 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:

$$T = \alpha \frac{ns}{(t-t_0)}$$

Where $T$ is the limiting stress for elastic failure, a constant 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 direction. $t$ is the side of the "average" crystallite existing in the metal and $t_0$ the limiting size below which the metal becomes brittle. Wood's calculation's of the crystallite size are based on the broadening of x-ray diffractions lines which accompanies cold work and which might also be attributed 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 deformation is preferred $t$ above would refer to the periodicity of the "crimps" in the lattice planes.

J. R. LOW, JR.

*(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 crystals of cadmium and zinc which is distinct from slip, twinning or "flexure gliding". When single crystal wires of cadmium oriented with the (0001) plane nearly parallel 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 observed orientation of Lueders lines in mild steel and the
phenomenon of a sharp yield point.

J. R. LOW, JR.


The general theory of finite deformation of cubic crystals at zero temperature is developed to a second order approximation, 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 detected 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 Leonard-Jones and Born and his collaborators, and using some of the results of the latter authors, the constants governing the above-mentioned second-order effects are expressed in terms of the constants 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.

PROC. ROY. SOC. ABSTRACT


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 perturbations 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.

AUTHORS ABSTRACT

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 instrument. The stress-strain curves seem to have been obtained 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 subsequently 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 obtained at increasing rates of shear. In that case the curvilinearity of the up-curve would be caused by thixotropic breakdown.

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 profoundly 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 degree of flocculation of particles in suspension is indicated by measuring sedimentation volumes. A high sediment volume is found for pronounced flocculation and vice versa. Therefore, various pigments were suspended in a hydrocarbon mixture (7% concentration) and sediment volumes were compared with specific viscosities. It is found that both decrease together as expected. The same was done with silica in various liquids with similar results for yield values and sedimentation 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 viscometer cup to be used in laboratory work.

RUTH N. WELTMAN


The first part of this paper explains the advantages inherent in the rotational viscometer when used for measuring plastic materials like paints, printing inks, etc. The second part describes a rotational viscometer designed specifically 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 determining 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. Buckingham 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, however, is always larger at the wall of the capillary than at the center; consequently shear takes place first at the wall and then develops 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 rotational 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 torsion 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 existence of such a level that plastic viscosity and yield value of thixotropic materials can be measured; but it should always be stated at what velocity gradient the measurement has been made. When the up- and down-curves are plotted together a so-called thixotropic hysteresis loop is formed. Under rigidly standardized conditions the area of this loop indicates the magnitude of the thixotropy. No loop means no detectable thixotropy.

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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 inkmen's point of view. The analysis 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 pressed 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 known, 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 increase the pull-resistance. The author also discards cohesion and surface tension as being relatively unimportant, having no direct bearing on the tack of materials like printing inks. Thus by a process of elimination, tack is found to depend on the resistance to flow arising from the factors viscosity 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 combination 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 different 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 attached. On the end lever in this series are suspended the different 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 initial 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 upward 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 measured 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:

\[
T_l/t = \frac{U}{Kt} + C_f
\]
\( \frac{T_t}{t} \) is the tack or pull-resistance at the rate of pull \( \frac{1}{t} \); \( U \) is the plastic viscosity; \( C \) is an instrumental constant; and \( K \) is \( \frac{D^2}{\eta R^4} \), \( D \) 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

\[
\text{(Relative tack)} = \frac{T}{T_0} = \frac{U}{U_0} + \frac{\text{Const.}}{U_0} \cdot t_f
\]

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.

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The object of this paper is to show the relationship between the microsopy 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, e.g. 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 contrast 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 deflocculated 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 dispersion 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 affected 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 structure 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 particles become molecular in dimension the suspension is likely to become pseudoplastic. Dilatent suspensions also have large well deflocculated particles but 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 POLYBUTENES.—Paul J. Flory, Essor Laboratories—Chemical Division, Standard Oil Development Company, Elizabeth, New Jersey. Abstract of Paper Presented before the Division of Rubber Chemistry 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 Staudinger's equation, according to which the molecular weight is proportional to the intrinsic viscosity,

\[ \eta = C \frac{\eta_v}{c} \]

Recent work on rubber and various synthetic high polymers has cast serious doubt on Staudinger's method for calculating molecular weights. Unfortunately, satisfactory 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 Polybutenies (polymers of isobutylene), samples of narrowly restricted molecular 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 equation 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 heterogeneous polymeric vinyl derivatives can be fitted to a similar relationship, although the molecular weight ranges investigated were limited.

When applied to heterogeneous polymers the above relationship yields a "viscosity average" molecular weight which is intermediate between the weight average and number average molecular weights.

Rubber-like Polybutenies 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


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

(1) \[ \log \log \eta = 1.2 \gamma^{1/4} - 2.9 \] (Buehler)

(2) \[ \eta^{-1} = k \gamma^{-1/4} + C \] (Silvermann and Roseveare)

(3) \[ \log \log \eta = m \gamma^{1/4} + C' \] (Modified Buehler Equation)

where \( \eta \) = viscosity
\( \gamma \) = 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 \( \sigma \), whereas we use \( \xi \). To us, \( \sigma \) 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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