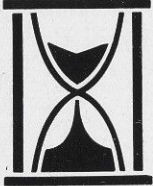


π α ν τ α



Σ Ε Ι

---

# RHEOLOGY BULLETIN

Vol. XVI, No. 3

August 1945

Publication of THE SOCIETY OF RHEOLOGY

---

## TABLE OF CONTENTS

### Contributed Papers

- Rheological Systematics, by Markus Reiner..... 53

### Meetings

- Ultracentrifuge Conference..... 69  
British Rheologists' Club  
Report of 4th Annual Meeting..... 70  
British Rheologists' Club Abstracts..... 72  
Society of Rheology, 1945 Fall Meeting..... 74

- Abstractors in this Issue..... 75

### Rheology Progress Abstracts

- Apparatus and Methods..... 76  
Cellulose..... 77  
Ceramics..... 82  
Colloids..... 83  
Glass..... 84  
Liquids..... 85  
Lubricants..... 86  
Microscopy..... 87  
Polymers..... 87  
Proteins..... 88  
Rubber..... 88  
Theory..... 89

HERMAN MARK, President  
Department of Chemistry  
Polytechnic Institute of Brooklyn  
Brooklyn, New York

W. F. FAIR, JR., First Vice-President  
Mellon Institute of Industrial  
Research  
Pittsburgh, Pennsylvania

P. J. FLORY, Second Vice-President  
Goodyear Research Laboratory  
Goodyear Tire and Rubber Company  
Akron, Ohio

NELSON W. TAYLOR, Editor  
Minnesota Mining and  
Manufacturing Company  
St. Paul, Minnesota

TURNER ALFREY, Publishing Editor  
Monsanto Chemical Company  
Springfield, Massachusetts

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

H. F. WAKEFIELD, Treasurer  
Bakelite Corporation  
Bloomfield, New Jersey

## RHEOLOGY BULLETIN

*Published Quarterly for*

THE SOCIETY OF RHEOLOGY

by Interscience Publishers, Inc.  
New York, N. Y.

The Society is dedicated to the Development of the Science  
of the Deformation and Flow of Matter and is one of the  
Five Founder Societies of The American Institute of Physics

*Nonmember Subscriptions: \$2.00 Annually  
Single Copies: 75¢*

Send manuscripts and editorial communications  
to Nelson W. Taylor, Minnesota Mining and  
Manufacturing Company, St. Paul, Minnesota.

Send orders for subscriptions and back issues to  
the Society of Rheology, 57 East 55 Street,  
New York 22, New York.

# RHEOLOGICAL SYSTEMATICS

MARKUS REINER (JERUSALEM)

1. **F**OR many years in America, Bingham (1929, 1930) and his school have made various proposals for a consistent nomenclature in rheology as a prerequisite for a rheological systematics. These proposals were partly accepted by the American Society of Testing Materials. Later, the Amsterdam Academy of Sciences seconded Bingham in its two *Reports on Viscosity and Plasticity*. In recent years these efforts were followed by British rheologists, notably Scott Blair and collaborators (1940, 1942). The present writer was active in this field some years ago (1931, 1932), basing the classification not so much on properties as on *ideal materials* having certain properties *which can be treated mathematically and serve as "pictures" of the real materials*. It was proposed these ideal materials be named after the scientists who first postulated their existence. This method of designation indicates the character of the different "bodies" as *mathematical idealizations*. Accordingly, the term "Euclid solid" was used for the (nonexisting) "rigid" body and "Pascalian liquid" for the (equally non-existing) "ideal" liquid. These two bodies, in which no rheological material constants appear, belong to mechanics and are outside the range of rheology. Rheology is entered with the *Hooke solid* from one side and the *Newtonian liquid* from the other. The former is a perfectly elastic solid, the latter a "simple" viscous liquid. If we add to these the *St. Venant body*,\* a solid which has a yield point below which its deformation is elastic, but above which it flows plastically at constant stress, it will be shown in the present paper that all other "rheological bodies" can be considered as built up through a combination of these three, a statement subject to qualification in regard to "dilatancy," which is discussed in section 6.

2. However, we must first take account of a basic phenomenon affecting any classification of rheological properties. It is a fact that, *under hydrostatic pressure, all materials—solids and liquids alike—behave in the same manner*. When uniformly compressed from all sides they behave in the manner of *perfectly elastic solids*, provided, of course, that the test piece is truly homogeneous. As Lord Kelvin pointed out, "by compression between the dies used in coining the density of gold may be raised from 19.258 to 19.367." But such "permanent set" is due to the porosity of the coin and an indication of its structure; it is not inherent to the material forming the structure. If the pressure is truly hydrostatic, which requires that it was acting within the pores also, there is no per-

\* St. Venant (1871) first described such a material mathematically.

manent set and no plastic deformation in a solid, no flow in a liquid, only an entirely recoverable elastic volumetric strain, the result of volume elasticity. In other words, materials do not differ rheologically in cubical dilatation (positive or negative), *all rheological differences are revealed under shear only* (or, more generally, distortion).

3. Considering shear only, Scott Blair (1940) has compiled a list of eight "essential rheological properties." For reasons which will become clear later on, his list here is slightly modified and extended as follows:

- |                         |                          |
|-------------------------|--------------------------|
| I. Viscosity (Fluidity) | VI. Structural Viscosity |
| II. Elasticity          | VII. Strain Hardening    |
| III. Firmoviscosity     | VIII. Strength           |
| IV. Elasticoviscosity   | IX. Thixotropy           |
| V. Plasticity           | X. Dilatancy             |

In a rheological table, Scott Blair listed a number of industrial materials with gradings of zero to five for each of the rheological properties in a semiquantitative way, as: (0) nonexistent, (1) very low, (2) low, (3) moderate, (4) fairly high, (5) very high. It then became evident that the materials could be grouped in *classes* in accordance with the more or less marked presence of the different rheological properties. For instance, milk, honey, and oil together form (with water and others) the class of true fluids in which the "species" milk, honey, etc., are distinguished by the different values of their viscosities. If this procedure is followed up and the rheological table extended to cover all materials for which rheological data are available and brought up to date as rheological research advances, one fact should not be overlooked. It can be considered as a rheological axiom that every *real* material possesses *all* rheological properties in varying degrees *in accordance with the conditions of the case*. In thin layers, a liquid such as water can exhibit rigidity; in the shape of a thin rod, a solid like lead will show viscous flow. Only the *ideal* materials are limited in their properties—*because this is how they are defined*. They can therefore serve for the representation of real materials *in different degrees of approximation*. In a first approximation, steel can be considered as a Hooke body, in a second approximation as a St. Venant body, and in a third as a Bingham body (about which see later), etc.

4. From Scott Blair's classification of rheological properties and his table of real materials we therefore proceed to the *classification of the ideal materials*. This can be done in two stages: (1) qualitatively, by a "structural formula"; (2) quantitatively, by a "rheological equation." The qualitative classification starts from the three simplest rheological bodies, the Hooke solid, the Newtonian liquid, and the St. Venant plastic, which we denote symbolically by H, N, and StV, respectively. To build up materials with more complicated properties, we employ a well-known device as apparently first used by Poynting and Thom-

son and later developed by Burgers and the writer (1943). We represent the Hooke solid by a perfectly elastic spring, the Newtonian liquid by a dashpot, and the St. Venant plastic by a weight resting on a table with "solid" friction between both (see Fig. 1). The only rheological property of the H spring is property II, its elasticity measured by the modulus of rigidity,  $\gamma$ ; of the N dashpot, property I, its viscosity, measured by the coefficient of viscosity,  $\eta$ ; and of the StV weight, property V, its plastic resistance measured by the yield stress,  $\vartheta$  (significantly named by Bingham, the "friction constant").

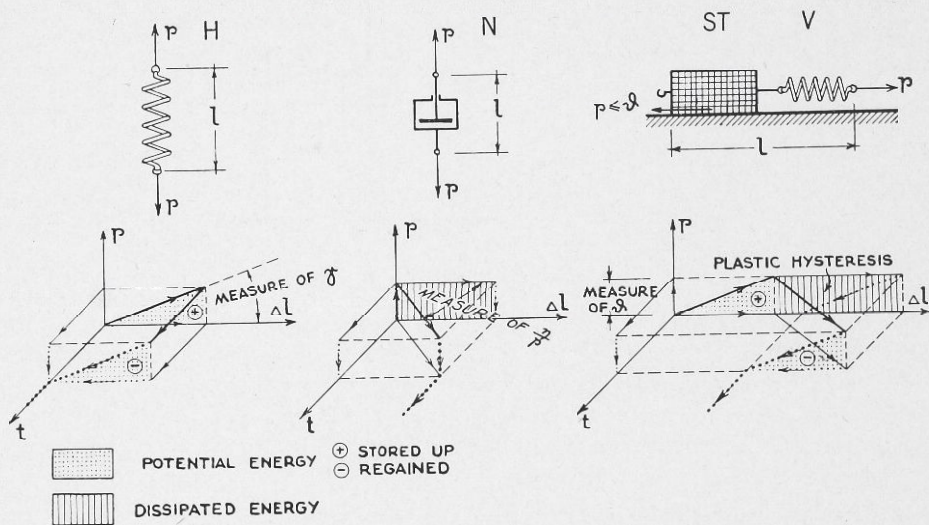


Fig. 1.—Structural elements.

As in Broome's graphs, the dotted lines represent behavior on removal of load. In working out the diagrams, the inertia of the mechanism has been neglected and the elastic strain assumed as following instantaneously the applied force.

If we now combine the H and N elements, as shown in Figure 2, it will be seen that this represents a model for a solid which is elastic, but exhibits: (a) elastic fore- and aftereffects, *i.e.*, a time lag in the appearance and disappearance of elastic strains; (b) elastic hysteresis and therefore also viscous damping of oscillations. These "imperfections of elasticity" have been included by Jeffreys (1929) under the term "firmoviscosity," which is listed above (as in Scott Blair's list, albeit under a different designation) as property III. The corresponding ideal material has been called *Kelvin solid*. Similarly, Figure 3 shows a model (a) for a liquid which exhibits "instantaneous" (as Bingham calls it) elasticity, or (b) for a "solid" the elastic stresses of which relax and which exhibits creep.

These properties have been included by Jeffreys under the term “elastoviscosity,” listed above as property IV (not mentioned separately by Scott Blair in his list). The corresponding ideal material has been called a *Maxwell liquid*.

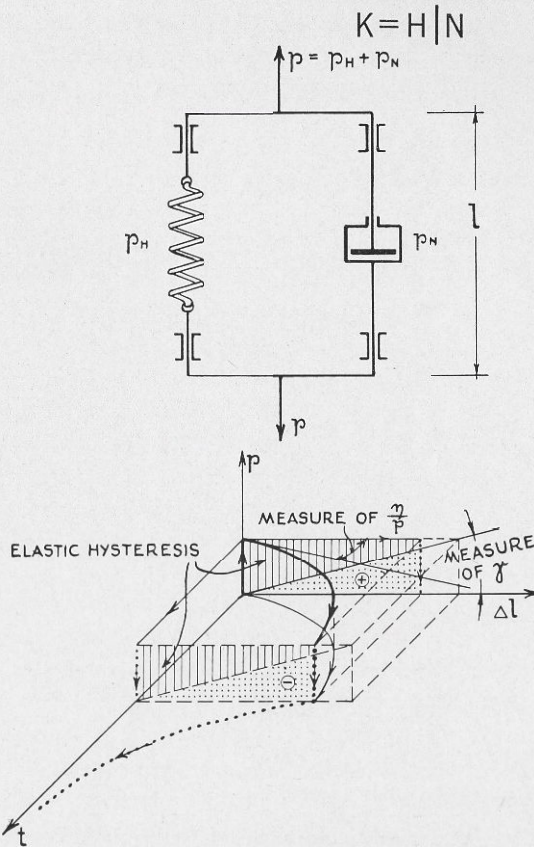


Fig. 2.—Model for a Kelvin solid.

The mechanisms in the figures show extensions and pulls, but one should not forget that these stand for shearing strains and shearing stresses, respectively. Also, the stress-strain relations have been pictured as linear; but the models can be applied in a general manner for nonlinear relations as well.

In Figure 2 the spring and the dashpot are combined in *parallel* arrangement; in Figure 3 they are combined in *series*. Indicating “parallel coupling” by a vertical dash (|) and “coupling in series” by a horizontal dash (—), we can write the following *structural formulas*, using obvious abbreviations:

$$M = H - N; \quad K = H | N \quad (1)$$

In the working of these models no other rheological properties enter than the elasticity of the spring and the viscosity of the dashpot. Therefore, the properties "elastic foreeffect," "elastic aftereffect," "elastic hysteresis," "instantaneous

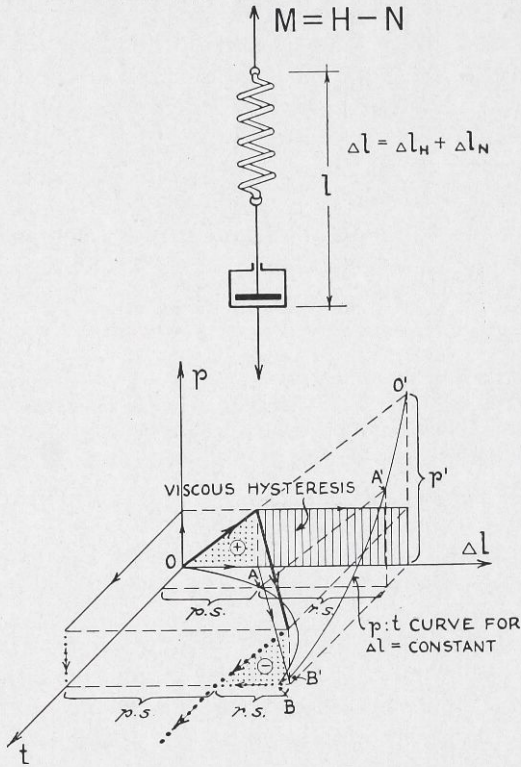


Fig. 3.—Model for a Maxwell liquid.

- OAB = elastic recovery for elongation  $\Delta l$
- O'A'B' = relaxation curve for stress  $p'$
- p.s. = permanent strain
- r.s. = recovered strain

elasticity," "relaxation of stresses," and "creep" can all be expressed by the two fundamental properties of elasticity and viscosity.

A material involving the StV body is the one with structural formula (2).

$$B = N - StV \quad (2)$$

Its model is shown in Figure 4. It will be recognized that this is a Bingham body.

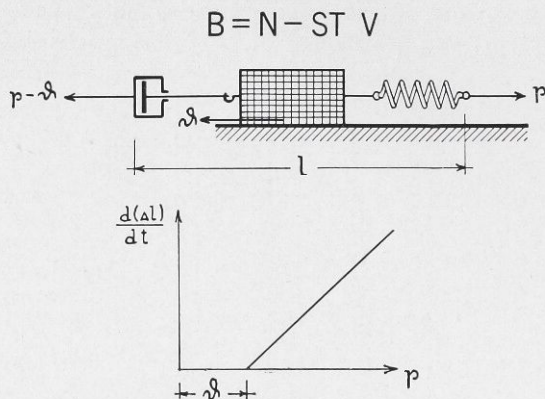


Fig. 4.—Model for a Bingham body.

It should be noted that, in contradistinction to the spring and the dashpot, the StV element is not symmetrical in respect to its ends. When coupling a StV element in series, it is therefore necessary to indicate whether the connection is to the "weight" or to the "spring." When using the symbol StV we shall assume that "St" stands for the weight and "V" for the spring.

A body in which three elements are combined is given by structural formula

$$\text{Schw} = H - N - \text{StV} = M - \text{StV} = H - B \quad (3)$$

It represents the 0.5% gelatin sol with which Schwedoff experimented in 1890 in a coaxial cylinder instrument. He exerted a torque upon the internal cylinder which was rotated against the elastic resistance of the gelatin by a certain angle. To maintain a constant deflection, the torque had gradually to be reduced as in a Maxwell liquid; but Schwedoff found that the sol, in contrast to a Maxwell liquid, apparently maintained a small residual deformation permanently. This requires the connection, in series, of a StV element to the M body.

It is not necessary to work out models for all the different materials. *For the purpose of the qualitative classification of a material, it is sufficient to write the structural formula from the information provided by the tests to which the material has been subjected.*

5. As an example of the classification of a given material qualitatively, let us treat the investigations of Schofield and Scott Blair (1932, 1933a, 1933b, 1937) on flour dough. The authors first stretched out long cylindrical pieces of dough for a measured time, at the end of which the cylinders were cut loose. It was found that part of the extension was recovered, but part was permanent



(Fig. 1 in Schofield and Scott Blair, part I). This showed that while flour dough (FD), because of the permanent extension of the cylinders, is not a Hooke body, it has a Hooke component; and in a first approximation we write  $FD = H - X$ , where  $X$  represents another element or elements to be deduced from further experiments. In the next series of experiments, it was found that the elastic recovery decreased with time under stress in accordance with an exponential law (Fig. 4 in the same paper). Comparison with our Figure 3 here shows that we must write  $N$  for  $X$ , or that in a second approximation  $FD = H - N = M$ . This was confirmed by further experiments, in which the decay of internal stresses in pieces of dough which had been stretched and held stretched, was followed (Fig. 6 in Schofield and Scott Blair, part I). The shape of the curve conformed to our Figure 3 for  $\Delta l = \text{const.}$  The second report of these authors describes observations in which the rate of extension of cylinders of dough, hung vertically and allowed to elongate under the action of gravity, is related to the stress. It was found that, while the rate of extension generally decreased with decreasing stress, there was a finite stress at which the rate of extension vanished, in fact, a yield point. This shows that a St. Venant element must further be added; and in a third approximation  $FD = H - N - \text{StV} = M - \text{StV} = H - B = \text{Schw.}$  It had, however, been noticed that a "considerable time often elapses between the release of the stress and the cessation of contraction." This indicated an elastic aftereffect, to the investigation of which the third report is devoted. For an elastic aftereffect, a  $K$  body must be coupled on. As the structural formula for  $FD$  contains a  $\text{StV}$  element, the question arises as to which end of the  $\text{StV}$  element the  $K$  body is to be connected. (Compare the paragraph in small type on page 58.) Experiments (Fig. 2 in report III) showed that the elastic aftereffect makes its appearance in strains *below the yield point*. This means that the  $K$  body must be connected at the spring end. It could be formed there by parallel coupling of the spring with an  $N$  element. The same figure, however, illustrates that, beside the "lagging" elastic recovery, there is also "instantaneous" recovery, *i.e.*, the spring of the  $\text{StV}$  element is not impaired in its working and the  $K$  body is therefore connected to it "in series." We accordingly obtain, in a fourth approximation, formula (4).

$$\text{SchScB} = H - N - \text{StV} - K = M - \text{StV} - K = H - B - K = \text{Schw} - K \quad (4)$$

Figure 4 in report III confirms the formula for strains above the yield point. The formula embodies all observations made by Schofield and Scott Blair, but in addition also those of Wolarowitsch and Samarina (1935). Scott Blair, on page 27 of his book (1938), remarks that to apply "Bingham's principles to . . . flour doughs. . . is contrary to the author's [Scott Blair's] experience." But in view of the presence of a  $B$  element in  $\text{SchScB} = H - B - K$ , it can be understood that *in steady flow* flour dough must behave as a Bingham body.

6. This example shows that a material with the most complicated rheological behavior can be adequately represented by a structural formula. The example also shows that, in the relations between shearing stress, shear, and their rates, which give rise to *the most complicated properties*, these can be reduced qualitatively to the three fundamental rheological properties, I, II, and V, listed in section 3. Of these, *elasticity* is that property by virtue of which the strain work performed by the external forces in a deformation is stored up as potential energy and the deformation (which in this case is called "strain") is therefore *recoverable*.\*

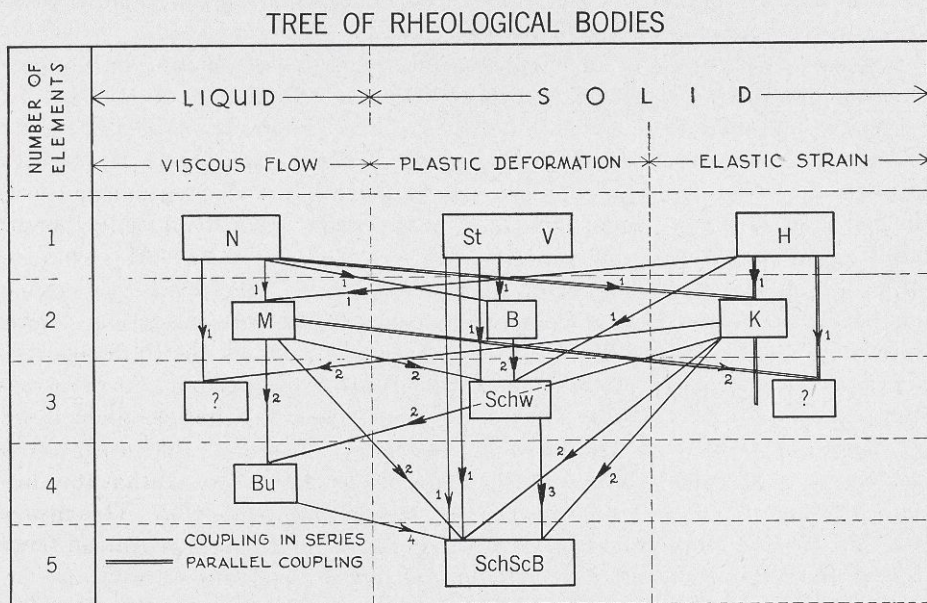


Fig. 5.—Tree of rheological bodies.

N = Newton	StV = St. Venant	H = Hooke
M = Maxwell	B = Bingham	K = Kelvin
Schw = Schwedoff	Bu = Burgers	SchScB = Schofield-Scott Blair

The figure beside the arrow indicates the number of elements.

When the strain work is dissipated (converted into heat) and the deformation (which in this case is called "flow") is nonrecoverable, we speak of *viscosity* if the resistance to flow depends upon the rate of deformation (viscous flow), and of *internal friction* if it is independent of the rate of deformation (plastic flow). When the elastic energy is gradually dissipated through lapse of time, we speak of *relaxation*, which, however, as we have shown, is not an independent property.

\* Compare *Nature*, 149, 702 (1942).

There is, however, a fourth fundamental property which cannot be derived from the above three: property X, *dilatancy*. Dilatancy refers, not to a relation between shear and shearing stress, but to a *change of volume caused by shear*. Wherever dilatancy comes into play, another element must be added in the structural formula. Disregarding dilatancy for the present and consulting Figure 5,\* we see how a system of rheological bodies can be built up *in accordance with the number of fundamental structural elements making up the body*. We see that, while three ideal bodies (M, B, K), each one made up of two elements are known, rheology has so far made use of one only, consisting of three, four, and five elements. Many others can be imagined, and they all can be arranged in a hierarchy of rheological bodies, starting with the three *groups* of "solids," "plastics," and "liquids," each one divided into the *families* of Newtonian, Maxwellian, etc., liquids. St. Venant, Bingham, Schwedoff, etc., plastics, and Hooke, Kelvin, etc., solids, respectively.

7. We have so far dealt with rheological properties I, II, III, IV, V, and X, of which I, II, V, and X are fundamental, while III and IV are derived and can be expressed through I and II. We now turn to properties VI and VII. These express *quantitative* relations in respect to fundamental properties. For instance, VII implies an increase of yield stress with strain; but de Waele has drawn attention to the existence of strain *softening*. Property VI refers to a decrease of viscosity with increasing rate of strain, while theoretically, an increase of viscosity is also possible (the latter has been described, wrongly it seems to me, as a case of dilatancy). Schofield and Scott Blair have discovered in flour dough an increase of viscosity with strain (not *rate* of strain) similar to the ordinary strain hardening. Generally these properties show that  $\eta$ ,  $\gamma$ , and  $\partial$  must not necessarily be constants, but are to be considered as parameters or coefficients which themselves may depend upon stress and strain and their rates. If, for instance,  $\eta$  is not a constant, but decreases with increasing stress, such a material shows the property of what Ostwald called "structural viscosity"; it belongs to the class of what Green called "pseudoplastics" or what Reiner (1929) called "non-Newtonian liquids." The last term has been widely accepted; but, being purely negative, it was originally meant to be provisional only. Considering that a Maxwell liquid also is *not* Newtonian, a better scheme would seem to be to call all liquids whose only fundamental property is viscosity *Newtonian*, whether  $\eta$  is a constant or not. If it is desired to distinguish the latter from the former, the latter can be called *generalized* Newtonian liquids and the former *simple* Newtonian liquids. This principle of designation can generally be applied, and we would have to divide each "family" into different "classes" of Newtonian liquids, Maxwell liquids, Hooke solids, etc., etc. However, here the structural formula breaks down and we must proceed from qualitative to quantitative classification by

---

\* Compare Treloar's suggestions in *Nature* (1942).

means of *rheological equations*. A rheological equation is, according to Hersey (1932), the relation connecting shearing stress with shear (and their derivatives in respect to time). Denoting shearing (tangential) stress by  $p_t$  and shearing strain by  $e_t$  and using for the time derivatives Newton's dot, the following are the fundamental rheological equations (in which  $t$  is dropped for simplifying the writing):

$$\left. \begin{array}{l} \text{Newtonian (viscous) liquid} \\ \text{Hooke (elastic) solid} \\ \text{St. Venant (plastic) solid} \end{array} \right\} \begin{array}{l} p = \eta \dot{e} \\ p = \gamma e \\ p = \vartheta \end{array} \quad (5)$$

The rheological equations of materials built up of two elements are accordingly

$$\left. \begin{array}{l} \text{Maxwell liquid} \\ \text{Kelvin solid} \\ \text{Bingham body} \end{array} \right\} \begin{array}{l} \dot{e} = p/\eta + \dot{p}/\gamma_l \\ p = \gamma_s e + \eta_s \dot{e} \\ p - \vartheta = \eta_{pl} \dot{e} \end{array} \quad (6)$$

No essentially new constant appears in any of these equations, but indices must be used in order to avoid confusion. We accordingly write  $\eta_s$  for what Lord Kelvin (1875) first called "solid" viscosity,  $\gamma_l$  for the elastic modulus of a liquid in accordance with Maxwell, following Green,  $\eta_{pl}$  for the plastic viscosity, which Bingham calls "stiffness."

The rheological equation of a material built up of three elements is the following one of the Schwedoff body:

$$\dot{e} = (p - \vartheta)/\eta_{pl} + \dot{p}/\gamma_l \quad (7)^*$$

It should be noted that the first two equations of (6), being of the form:

$$dy/dx + My = N \quad (8)$$

permit of solutions of the form:

$$y = e^{-\int M dx} (\int N e^{\int M dx} dx + C) \quad (9)$$

where  $e$  is the basis of natural logarithms. We accordingly have for the Maxwell liquid:

$$p = e^{-\gamma/\eta t} (p_0 + \gamma \int_0^t \dot{e} e^{\gamma/\eta t} dt) \quad (10)$$

and for the Kelvin solid:

$$e = e^{-\gamma/\eta t} \left( e_0 + \frac{1}{\eta} \int_0^t p e^{\gamma/\eta t} dt \right) \quad (11)$$

---

\* Compare Reiner (1932), where the notation and the terminology only are different.

8. We shall now show how, if the structural formula is known, the rheological equation can be derived, and shall take our example again from the flour dough experiments of the Schofield and Scott Blair. These workers express the rheological equation of their material, translated into our notation, as follows:

$$e = p/\eta + \dot{p}/\gamma_l - \dot{\alpha} \quad (12)$$

where  $\dot{\alpha}$  represents the elastic aftereffect. We note that they do not take into account that flour dough possesses a yield point. Their rheological equation, therefore, represents only part of their experimental findings; as a matter of fact it corresponds to structural formula (13):

$$\text{Bu} = \text{M} - \text{K} \quad (13)$$

which can be derived from the second form of formula (4) by omitting the StV element. Its model can easily be pictured. It appears in Burger's article, already quoted. It was used by Lee and Markwick to explain the rheological behavior of bituminous materials. To the rate of strain  $\dot{e}$  of the complete body, the strains  $e_M$  and  $e_K$  of the components  $M$  and  $K$  contribute, so that:

$$\dot{e} = \dot{e}_M + \dot{e}_K = p/\eta + \dot{p}/\gamma_l + \frac{d}{dt} \left[ e^{-\gamma/\eta_s t} \left( e_0 + \frac{1}{\eta_s} \int_0^t p e^{-\gamma/\eta_s t} dt \right) \right] \quad (14)$$

After carrying out the differentiation this gives as the rheological equation of the body:

$$\dot{p} = p \frac{\eta + \eta_s}{\eta \eta_s} + \dot{p}/\gamma_l - \frac{\gamma}{\eta_s} e^{-\gamma/\eta_s t} \left( e_0 + \frac{1}{\eta_s} \int_0^t p e^{\gamma/\eta_s t} dt \right) \quad (15)$$

If we compare this expression with (12), we see that our method has carried us one step further, revealing at the same time that, in the summary expression  $\dot{\alpha}$ , two material constants are contained.

9. To give an example of the last division of the rheological families into rheological classes, it must be remembered that the postulation of nonlinear laws is a comparatively recent development. The existence of generalized bodies was realized by Maxwell when, in his quoted paper, he said "it is possible that in some bodies  $\tau$  (the time of relaxation) may be (not a constant, but) a function of  $p$ ." It was, however, not until the existence of structural viscosity was discovered that nonlinear laws were proposed.\* Considering these, the simple Newtonian liquid for which the viscosity  $\eta$  is a constant or  $\varphi = 1/\eta = c$ , forms a class within the family of Newtonian liquids together with the Weissenberg liquid for which:

\* Hodgkinson postulated for cast iron a generalized Hooke solid for which  $p = \gamma e - ce^2$  but this law fell into oblivion.

$$\varphi = \varphi_0 + cp^2 \quad (16)$$

the Kraemer-Williamson liquid for which:

$$\varphi = \frac{\varphi_0 + \varphi_\infty p^2/c}{1 + p^2/c} \quad (17)$$

and a liquid proposed by Reiner and Rievin (1927) for which:

$$\varphi = \varphi_\infty - (\varphi_\infty - \varphi_0)e^{-p^2/c} \quad (18)$$

In the "tree" of rheological bodies we shall ultimately have many such names under each family designating the classes. However, as has been stated, this division is not yet advanced very far; there are very few names which could be entered for the classes now; and this is where the classification of Scott Blair and Caffyn is very useful.

10. As Reiner (1933) has shown, every monotonously increasing function,  $y = f(x)$ , which can be extrapolated toward the origin ( $x = 0, y = 0$ ) can be approximated by a power function,  $y = \alpha x^\beta$ , where  $\alpha$  and  $\beta$  are two parameters. This analytical fact is at the root of many "power laws" which make their appearance in different branches of physics and physical chemistry. Reiner has discussed the objections by which these "laws" must be regarded as convenient *interpolation formulas* only; but as such they are useful. In our case, until we have rheological equations for the many classes of nonlinear bodies at our disposal, we can, with Scott Blair and Caffyn, use power formulas to fill in the blanks in our rheological tree.

Granted that all rheological behavior is dependent upon values of the four variables  $p, \dot{p}, e,$  and  $\dot{e}$ , we can define a coefficient ( $\alpha_0$ ) by:

$$\alpha_0 = p^{\alpha_1} \dot{p}^{\alpha_2} e^{\alpha_3} \dot{e}^{\alpha_4} \quad (19)$$

where  $\alpha_0, \alpha_1, \alpha_2, \alpha_3,$  and  $\alpha_4$  are characteristic for the material under consideration. For instance, for the simple Newtonian liquid  $\alpha_0 = \eta, \alpha_1 = 1, \alpha_2 = 0, \alpha_3 = 0, \alpha_4 = -1$ , while for the generalized Newtonian liquid  $\alpha_1 > 1$ ; for the simple Hooke solid  $\alpha_0 = \gamma, \alpha_1 = 1, \alpha_2 = 0, \alpha_3 = -1, \alpha_4 = 0$ , while for the generalized Hooke solid  $\alpha_1 > 1$ .

If it is desired to include true plastics,  $p$  must be understood as the excess of the actual stress over the yield stress. Scott Blair and Caffyn write their equation in the form (using our notation):

$$\psi = p^\beta e^{-1} t^K \quad (20)$$

but this equation is not essentially different from (19). By differentiating both parts of Equation (20) in respect to time, we introduce  $\dot{p}$  and  $\dot{e}$ , and if we eliminate time  $t$  from this equation and (20), we get an equation in which  $p, \dot{p}, e,$  and  $\dot{e}$  and certain coefficients appear in which the  $t$  does not appear explicitly and which again can be approximated by (19).

RHEOLOGICAL EQUATIONS

Number of Elements	Liquid	Plastic Solid	Elastic Solid
1	<p><b>N</b></p> $\dot{e} = p/\eta$ <p style="text-align: right;"><math>\infty</math></p>	<p><b>StV</b></p> $p - \vartheta = 0$ <p style="text-align: right;">0</p>	<p><b>H</b></p> $p = \gamma e$ <p style="text-align: right;">0</p>
2	<p><b>M</b></p> $\dot{e} = p/\eta + \dot{p}/\gamma_l$ <p style="text-align: right;"><math>\uparrow</math> <math>\gamma_l</math></p>	<p><b>B</b></p> $\dot{e} = (p - \vartheta)/\eta_{pl}$ <p style="text-align: right;"><math>\uparrow</math> <math>\eta_{pl}</math> <math>\infty</math></p>	<p><b>K</b></p> $p = \gamma e + \eta_s \dot{e}$ <p style="text-align: right;"><math>\uparrow</math> <math>\eta_s</math></p>
3	$\dot{e} = \dot{p} \frac{\eta + \eta_s}{\eta \eta_s} - \frac{\gamma}{\eta_s} e^{-\gamma/\eta_s t}$ $\left( e_0 + \frac{1}{\eta_s} \int_0^t p e^{\gamma/\eta_s t} dt \right)$	<p><b>Schw</b></p> $\dot{e} = \frac{p - \vartheta}{\eta_{pl}} + \frac{\dot{p}}{\gamma_l}$ <p style="text-align: right;"><math>\uparrow</math> <math>\gamma_l</math></p>	$p = \gamma e + e^{-\gamma t/\eta_s} \left( p_0 + \gamma_l \int_0^t \dot{e} e^{\gamma t/\eta_s} dt \right)$
4	<p><b>Bu</b></p> $\dot{e} = p \frac{\eta + \eta_s}{\eta \eta_s} + \frac{\dot{p}}{\gamma_l} - \frac{\gamma}{\eta_s} e^{-\gamma/\eta_s t}$ $\left( e_0 + \frac{1}{\eta_s} \int_0^t p e^{\gamma/\eta_s t} dt \right)$		$p = \gamma e + \eta_s \dot{e} + e^{\gamma t/\eta_s} \left( p_0 + \gamma_l \int_0^t \dot{e} e^{\gamma t/\eta_s} dt \right)$
5		<p><b>SchScB</b></p> $\dot{e} = (p - \vartheta) \frac{\eta_{pl} + \eta_s}{\eta_{pl} \eta_s} + \frac{\dot{p}}{\gamma_l} - \frac{\gamma}{\eta_s} e^{-\gamma/\eta_s t}$ $\left[ e_0 + \frac{1}{\eta_s} \int_0^t (p - \vartheta) e^{\gamma/\eta_s t} dt \right]$	

11. For the rest, the reader is referred to the report of Scott Blair and Caffyn. As the whole subject is still in a very preliminary stage, names for different classes have not been entered in Figure 5. Nor have their rheological equations been listed in the accompanying set of rheological equations of the families only, where the rheological coefficients can either be constants for the "simple" bodies, or depend upon stress and strain and other coefficients. When the latter is the case, *i.e.*, when the fundamental properties of the material change their magnitude in the course of the rheological process through which the material is passing, this is generally an indication of a change in the internal structure of the material. For instance, the internal structure of a strain-hardened mild steel is different from one coming out of the rolling mill, the change consisting in a breaking up of the large into small crystals; the internal structure of a rubber solution in flow is different from its structure when at rest, the change consisting in a liberation of immobilized solvent. From the rheological behavior of a material, therefore, conclusions can be drawn about its internal structure. This was carried out by Reiner and Schönfeld-Reiner for rubber-toluene solutions and termed "structural analysis." We can accordingly combine properties VI and VII with many similar properties under the term "rheological destruction," where "destruction" should be understood to mean "reduction of structure."

Property IX, thixotropy, is also a property resulting from a change of structure of the material. Its distinction from structural viscosity consists in that, in the case of thixotropy, *time* enters *explicitly* as a determinant. Another property of this kind is the "aging" of steel (compare Nadai, p. 25) by which its yield point increased during a period of rest. Property IX should include all such phenomena and may generally be termed *aging*.

12. We still must deal with property VIII, "strength." Every body can sustain certain states of stress and strain between zero and a definite upper limit. When this limit is exceeded, the body decomposes into two or several parts: it *breaks*. This upper limit is the strength of the material. Reiner and Weissenberg have expressed the strengths of the different kinds of rheological materials in terms of *strain energy*. From an atomistic point of view, strength is not an independent property (*vide* Andrade), but such considerations belong to "metarheology."

Revising, in the light of the above, the list of essential rheological properties, we would have the five *fundamental* properties of viscosity, elasticity, plasticity, dilatancy, and strength, through a combination of which other properties such as firmoviscosity, elasticoviscosity, plasticoviscosity, etc., as well as such properties as toughness, brittleness, etc., can be expressed. In addition, the two phenomena of *rheological destruction* and *aging* give rise to such properties as structural viscosity, strain hardening, strain softening, etc.

There are many technological properties which do not come under Scott Blair's essential properties and which defy classification. Sometimes they can be



expressed in terms of essential properties. Green (1941), for instance, has reduced "tack" to a combination of viscosity and yield stress. Such properties, however, as the "covering power" of a pigment (Green, 1942) or "seepage," etc., would simply have to be listed in a glossary.

### SUMMARY

A rheological systematics is built up through an *hierarchy of ideal materials* as shown in Figure 5. Of these, three are elemental; and it is shown how all others can be expressed qualitatively through these three by means of *structural formulas*. *Rheological equations* as listed in the table, page 65, describe the quantitative behavior of the materials. The parameters appearing in the rheological equations are characteristic coefficients or material "constants," and the rheological properties are determined by the numerical values of these coefficients. Leaving cubical dilatation apart, we find five *fundamental properties*, viz., viscosity, elasticity, plasticity, dilatancy, and strength, from which other essential properties can be derived. The coefficients may be constants, but in many cases their values are affected by the phenomena of *rheological destruction and aging*.

### Bibliography

- Andrade, E. N. da C., "The ultimate strength of metals," *Science Progress*, No. 120, 593-610 (1936).
- Anon., "Classification of rheological properties," *Nature*, **149**, 702 (1942).
- Bilmes, L. A., "A rheological chart," *Nature*, **150**, 432-433 (1942).
- Bingham, E. C., "Some fundamental definitions of rheology," *Proc. Am. Soc. Testing Materials*, **29**, II (1929); *J. Rheol.*, **1**, 507-516 (1930).
- Broome, D. C., *Nature*, **149**, 702 (1942).
- Burgers, J. M. See reference following.
- Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam, *First Report on Viscosity and Plasticity* (1935); *Second Report* (1938).
- Green, H., "The tackmeter, an instrument for analyzing and measuring tack," *Ind. Eng. Chem., Anal. Ed.*, **13**, 632-639 (1941).
- "The physics of pigments in dispersed systems," *J. Applied Phys.*, **13**, 611-622 (1942).
- Hersey, M. D., "Future problems of theoretical rheology," *J. Rheol.*, **3**, 196-204 (1932).
- Hodgkin, E., in *Report of the Commissioners appointed to inquire into the application of iron to railway structures*, London, 1849, p. 47.
- Jeffreys, H., *The Earth*, Cambridge Univ. Press, London, 1929.
- Kelvin, Lord (Sir W. Thomson), "Elasticity," in *Encyclopaedia Britannica*, Ninth Edition, 1875. Also Papers 3, London, 1890.
- Lee, A. R., and Markwick, A. H. D., "The mechanical properties of bituminous surfacing materials under constant stress," *J. Soc. Chem. Ind.*, **56**, 146T-156T (1937).
- Nádai, A., *Plasticity*, McGraw-Hill, New York and London, 1931.
- Poynting, J. H., and Thomson, J. J., *Properties of Matter*. Griffin, London, 1929.
- Reiner, M., "Die Hydrodynamik disperser Systeme," *Naturwissenschaften*, **19**, 878-880 (1931).
- "Outline of a systematic survey of rheological theories," *J. Rheol.*, **3**, 245-256 (1932).
- "A system of rheological notation," *J. Rheol.*, **3**, 264-267 (1932).
- Ten Lectures on Theoretical Rheology*. Rubin Mass, Jerusalem, and Nordeman, New York, 1943.

- Reiner, M., and Riwlin, R., "Zur Hydrodynamik von Systemen veränderlicher Viskosität," *Kolloid-Z.*, **43**, 72-78 (1927).
- Reiner, M., and Schoenfeld-Reiner, R., "Viskosimetrische Untersuchungen an Lösungen hochmolekularer Naturstoffe," *Kolloid-Z.*, **65**, 44-62 (1933).
- Reiner, M., and Weissenberg, K., "A thermodynamic theory of the strength of materials," *Rheology Leaflet*, No. 10, 12-20 (1939).
- Schofield, R. K., and Scott Blair, G. W., "The relationship between viscosity, elasticity, and plastic strength of soft materials as illustrated by some mechanical properties of flour doughs," *Proc. Roy. Soc. London A*, **I**, **138**, 707-718 (1932); **II**, **139**, 557-566 (1933); **III**, **141**, 72-85 (1933); **IV**, **160**, 87-94 (1937).
- Scott Blair, G. W., *Introduction to Industrial Rheology*. Churchill, London, 1938.
- A Survey of General and Applied Rheology*. Pittman, London, 1944. "The measurement of some industrial materials," *J. Sci. Instruments*, **17**, 169-177 (1940).
- "Classification of rheological properties," *Nature*, **149**, 197-198 (1942).
- Scott Blair, G. W., and Caffyn, J., "The classification of rheological properties of industrial materials in the light of power-law relations between stress, strain, and time," *J. Sci. Instruments*, **19**, 88-93 (1942).
- Treloar, L. R. G., *Nature*, **149**, 197-198 (1942).
- Wolarowitsch, M. P., and Samarina, K. I., "Untersuchungen der plastischen Eigenschaften des Mehlteigs nach der Methode eines rotierenden Zylinders," *Kolloid-Z.*, **70**, 280 (1935).

## ULTRACENTRIFUGE CONFERENCE

**T**HE ALL-DAY CONFERENCE on the Ultracentrifuge in Polymer Research, under the joint auspices of the Polytechnic Institute of Brooklyn, the Society of Rheology, and the Metropolitan Section of the American Physical Society, was held June 2, 1945, at the Polytechnic Institute, Brooklyn.

James Burton Nichols, research chemist of the du Pont Experimental Station, presided. In his introductory remarks, he pointed out that most of the work done by Svedberg, a Nobel Prize winner in physics, and currently of the University of Upsala, Sweden, and most of the work so far published on the ultracentrifuge deal with protein molecules, which as a rule are very uniform in size, either fairly round or elliptical, with similar shape.

The conference dealt with data obtained as the result of applying the ultracentrifuge to the study of linear high polymers. In this category are the molecules found in synthetic rubber, gelatin, starch, nylon, polystyrene, cellulose acetate, and vinyl resins. In solution these molecules appear in myriad forms, in the shape of long flexible threads of different lengths. Even these long molecules take on different characteristics, some being long and straight and others being straight for a time and all tied up in bunches at the end. Even at low concentration the threadlike molecules tend to get entangled, coming to grips with each other; and to produce proper results they have to be disentangled. The ultracentrifuge gives exact data on the size and the shape of large molecules in solution and on particle size distribution curves.

The discovery that polyvinyl chloride, one of the most important raw materials for manufacturing transparent and flexible plastics, is composed of two distinct components, was announced by Kurt G. Stern, Paul Doty, and Seymour Singer of the High Polymer Research Bureau, Polytechnic Institute of Brooklyn. In using the ultracentrifuge to determine the molecular makeup of polyvinyl chloride it was found that this material, unlike other linear high polymers, shows two separate "peaks" during sedimentation. The presence of the two peaks indicates that polyvinyl chloride is composed of two components sufficiently different in particle size and average molecular weight to be resolved separately in the ultracentrifuge. Ordinarily polymer materials tested by the ultracentrifuge show a single sedimenting boundary. The two components, chemically both polyvinyl chloride, will give rise to very different materials. By controlling, analyzing, and observing polymer solutions with the ultracentrifuge, it is possible to select the best material for a specific purpose. These two peaks probably represent two different polymerization reactions, one of which produces a long-chain molecule and one a short chain.

Two other materials now being studied with the ultracentrifuge are cellulose acetate, which is being studied in collaboration with Milton Harris of Washington, and a biological material which represents nuclear protein isolated from the nucleus of living cells.

# BRITISH RHEOLOGISTS' CLUB

## A DISCUSSION ON THE MEASUREMENT OF TACK

(Report of the Fourth Annual Meeting, Oct. 21, 1944) Chairman,  
E. N. da C. Andrade, F.R.S.

A TOTAL OF TWELVE PAPERS were presented at this symposium. Very brief abstracts are given herewith. For fuller details, the reader is referred to *Paint Technology*, October, 1944, pages 211-221.

### 1. "Tacky Adhesion," N. A. de Bruyne

Equations of J. Stefan (1847), Osborne Reynolds (1886), G. I. Taylor and Hardy and Bircumshaw (1925), and J. R. Scott (1931) all of which deal with viscosity and yield value as primary factors, are examined and found to be unsatisfactory for the complete evaluation of tack. A surface tension equation from Poynting and Thomson (1934) is shown to be significant only at small separations. The time factor is recognized as important. The author reaches the conclusion that an empirical simulative test is still the most useful for predicting tacky behavior.

### 2. "Tack of Printing Inks," R. F. Bowles

The time factor is very important. Printing takes place in about 0.01 second. Since organic liquids do not vary greatly in surface tension, this property plays a minor role in explaining variations of tack. Bowles believes that, under rapid printing conditions, the fluid ink assumes the properties of an elastic solid under high tension. "A thixotropic gel will show tack; whereas, a dilatant gel will be non-tacky."

### 3. "The Effective Work of Adhesion," R. S. Rivlin

Tapes of surgical adhesive plasters are stripped from a smooth stainless steel surface. The effective work of adhesion is found to be approximately inversely proportional to the time of stripping, and to be greatly increased by lowering the temperature. The author observes the formation of threads, and believes that energy is stored up in the adhesive before detachment, the storage being greater when Young's modulus is low. He believes that "sticky" and "tacky" represent different concepts.

### 4. "Tackiness of Paint," E. W. J. Mardles

Nontacky paints are required for rapid drying of airplane finishes. Some apparently dry films show syneresis of liquid which will cause sand or other particles to adhere. Some anhydrous lanolin paints show tacky and thixotropic

properties. Wetting is essential to tack. A small robust Stormer viscometer operating at different rates of shear was very useful in the development of non-tacky paints.

### 5. "Time and Tack," F. A. Askew

If the energy for rapid stretch exceeds that for creating new air-liquid surfaces, separate threads will form. The behavior of a liquid trapped between two surfaces will depend on the speed of approach or recession. "If the force is applied very suddenly indeed, the joint will behave like a solid one and break; if the force is applied slowly, viscous flow may occur before the break, and the material will be described as 'tacky'."

### 6. "What is Tack, in Varnish, and in Rubber," C. R. Pye

According to various views, tack is viscosity, adhesiveness, self-adhesion, stickiness, stringiness. Much thought should be given to this matter before measurements are made.

### 7. "Measuring the Tack of Rubber," J. R. Scott

Workers in rubber technology regard tack as an expression of self- or auto-adhesion; cf. Zhukov and Talmud (1935). A tacky material must flow readily under small stresses. Rapid self-diffusion of molecules is also necessary so that two tacky surfaces will fuse together when brought into contact. Pressures and times must be standardized in order to reproduce experimental results. Aging of the surface, oxidation, and orientation, may play a strong role.

### 8. "Adhesion and Autohesion in the Rubber Industry," C. M. Blow

#### *Classification by Type of Adhesion*

A. Nonadhesive	Nonautohesive	GR-S and reclaim natural rubber.
B. Nonadhesive	Autohesive	Natural rubber.
C. Adhesive	Autohesive	Rubber-resin (surgical plasters).
D. Adhesive	Nonautohesive	GR-S resins.
		GR-S-natural rubber reclaim.

### 9. "Tackiness and Stickiness of Rubber," W. H. Stevens

"It was not until some time after the attack on Pearl Harbor and the development of large scale manufacture of general purpose synthetic rubber in America that the rubber manufacturing industry began to realize what an important property tack was, and to what a great degree it had been a specific property of natural rubber." The distinction between *adhesion* to a different surface and self-adhesion or autohesion (as when two pieces of natural rubber are brought into contact) is very important. Stevens believes tack can be described for the tire industry as strong natural adherence of two rubber surfaces.

## 10. "Stringiness," W. H. Banks

Stringy materials are not purely elastic, but probably also show non-Newtonian flow, *i.e.*, elastic-plastic.

## 11. "The Stability of Threads," P. H. Plesch

Plesch proposes an equation for the stability of a thread which is being elongated:

$$(r \cdot RT/2B) \cdot \log(\eta/A) = \gamma$$

where  $r$  = radius,  $\eta$  = viscosity,  $\gamma$  = surface tension, and  $B$  and  $A$  are constants. Therefore, as  $r$  diminishes,  $\eta$  must increase, in order to maintain stability.

## 12. "Tack of Asphalt and Bitumen," D. C. Broome

Depending on the use or on the method of testing, bituminous materials will show different physical aspects. Tack is much more than mere viscosity. It may include ability to form threads (*Spinnbarkeit*), or thixotropy. It may be related to adhesion *on first contact*, but not to permanent adhesion.

## BRITISH RHEOLOGISTS' CLUB ABSTRACTS

Circular No. 8 of the British Rheologists' Club, issued December, 1944, contains rheology abstracts under the following titles:

"The electrical and elastic properties of amorphous polar polymers," R. F. Tuckett, *Trans. Faraday Soc.*, **50**, 448 (1944).

"The liquid state," J. H. Hildebrand, *Proc. Phys. Soc. London*, **56**, 221 (1944).

"A molecular theory of the viscoelastic behavior of an amorphous linear polymer," T. Alfrey, *J. Chem. Phys.*, **12**, 374 (1944).

"Network structure and elastic properties of vulcanized rubber," P. J. Flory, *Chem. Revs.*, **35**, 51 (1944).

"A new extrusion plastometer," H. A. Schultz and R. C. Bryant, *J. Applied Phys.*, **15**, 360 (1944).

"Drift and relaxation of rubber," M. Mooney, W. E. Wolstenholme, and D. S. Vilars, *J. Applied Phys.*, **15**, 324 (1944).

"Hysteresis losses in high polymers," H. S. Sack, J. Motz, and R. N. Work, *J. Applied Phys.*, **15**, 396 (1944).

"GR-S, an elastically inverted polymer," H. A. Braendle and W. B. Wiegand, *J. Applied Phys.*, **15**, 304 (1944).

"Rapid determination of elastic constants of glass and other transparent substances," W. T. Szymanowski, *J. Applied Phys.*, **15**, 627 (1944).

"Viscosity of water," J. R. Coe, Jr., and T. B. Godfrey, *J. Applied Phys.*, **15**, 625 (1944).

"Rate of rise of water in capillary tubes," G. Pickett, *J. Applied Phys.*, **15**, 623 (1944).

"Rate of rise of water in capillary tubes," W. A. Rense, *J. Applied Phys.*, **15**, 436 (1944).

"Poisson's ratio at high temperatures," F. L. Everett and J. Miklowitz, *J. Applied Phys.*, **15**, 598 (1944).

- "Miniature and micro suspended level viscometers," M. M. Lapitzky and S. Thompson, *J. Inst. Petroleum Tech.*, **30**, 349 (1944).
- "Preliminary list of definitions by Standardisation Sub-Committee No. 11," *J. Inst. Petroleum Tech.*, **30**, 249 (1944).
- "On the temperature dependence of plastic deformation and creep," J. Frenkel, *J. Phys. U. S. S. R.*, **11**, 49 (1940).
- "Contribution to the theory of viscosity of macromolecular substances," J. J. Hermans, *Kolloid-Z.*, **106**, 22-29 (1944).
- "Beiträge zur Kenntnis der Viscosität der Milch" [Contribution to our knowledge of the viscosity of milk], W. Spöttel and K. Gneist, *Milchw. Forsch.*, **21**, 214-234 (1942).
- "The viscosity of evaporated milks of different solids concentration," E. F. Deysher, B. H. Webb, and G. E. Holm, *J. Dairy Sci.*, **27**, 345-355 (1944).
- "Beiträge zur Messung der Konsistenz von Käse. I. Bericht: Bestimmung der Fließgeschwindigkeit" [Contributions on the measurement of the consistency of cheese. I. Report on the determination of flow rate], G. Schwartz and O. Fischer, *Milch. Forsch.*, **21**, 110-124 (1942); also *Deut. Molkerei Ztg.*, **63**, 448 (1942).
- "Report of viscosity panel: Institute of Petroleum," *J. Inst. Petroleum Tech.*, **30**, 42 (1944).
- "Physical-chemical properties of textile Nylon yarns," Sales section of Nylon Division du Pont de Nemours & Co., *Rayon Textile Monthly*, **25**, 169, 221 (1944).
- "Fluidity determinations on flax cellulose," W. A. White and T. N. Richardson, *J. Textile Inst.*, **35**, 5, T53 (1944).
- "The fast and slow extension of some plastic materials," R. N. Howard, *Trans. Faraday Soc.*, **39**, 267 (1943).
- "Flow of visco-elastic materials in capillaries," A. C. Merrington, *Nature*, **152**, 663 (1943).
- "Experiments on plasticity, I and II," H. H. Macey, *Trans. Brit. Ceram. Soc.*, **43**, 5 (1944).
- "Effect of concentration and pH on the viscous and electrochemical properties of hydrogen bentonites," J. N. Mukherjee, N. C. Sen Gupta, and M. K. Indra, *J. Phys. Chem.*, **47**, 553 (1943).
- "Structure and physical properties of plastics," L. W. Turner, *Chem. Industries*, **52**, 492 (1943).
- "Evaluation of rheological constants from tensile and compressive tests," W. Lethersich, *J. Sci. Instruments*, **21**, 68, 111 (1944).
- "The stress distribution at the neck of a tension specimen," P. W. Bridgman, *Am. Soc. Metals, Preprint*, October, 1943.
- "The percentage stress strain diagram as an index to the comparative behavior of materials under load," H. J. Gilkey and G. Murphy, *Iowa Eng. Expt. Sta. Bull.*, No. 159 (1944).
- "Viscosity of recent container glass," H. A. Robinson and C. A. Peterson, *J. Am. Ceram. Soc.*, **27**, 129 (1944).
- "Analytical and integrative aspects of the stress-strain-time problem," G. W. Scott Blair, *J. Sci. Instruments*, **21**, 80 (1944).
- "A falling co-axial cylinder viscometer for the rapid measurement of high viscosities," H. L. D. Pugh, *J. Sci. Instruments*, **21**, 177 (1944).
- "A precision extensometer and its use for the measurement of Poisson's ratio," W. Lethersich, *J. Sci. Instruments*, **21**, 180 (1944).
- "Some applications of the Nutting-Scott Blair equation," L. Bilmes, *J. Sci. Instruments*, **21**, 183 (1944).

# SOCIETY OF RHEOLOGY, 1945 FALL MEETING

**T**HE 1945 ANNUAL MEETING of the Society of Rheology will be held October 26 and 27 at the Hotel Pennsylvania, New York City. Dr. W. F. Fair, Jr., Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania, is chairman of the Program Committee. Interest in rheological work has definitely increased in recent years, and the attendance and discussions during the last two annual meetings indicate that progress in this field may be greatly accelerated, especially in industrial rheology, when censorship restrictions on scientific publications are relaxed. Earlier in the year the officers of the Society decided to proceed with plans for the customary Fall Meeting for 1945, although realizing that such plans must necessarily be tentative, and subject to revision and restriction complying with government regulations. The recently announced modified restrictions for scientific meetings will permit us to hold our annual meeting as usual, since the permissible number of out-of-town attendants is considerably larger than the number of out-of-town members who have ever attended our annual meetings. The program for the 1945 meeting is given below.

## PROGRAM

*October 26 and 27, 1945*  
*at the Hotel Pennsylvania, New York City*

### *Friday Morning*

- 9:00- 9:30 Registration.
1. 9:35-10:05 Anomalies of Flow. E. C. Bingham, Lafayette College, Easton, Pa.
  2. 10:10-10:40 The Rate Process Theory of Flow, Applied to Viscous Liquids. A. Bondi, International Lubricant Corp., New Orleans, La.
  3. 10:45-11:15 The Effect of Plasticizers on the Viscoelastic Properties of Vinyl Resins. Capt. W. Aiken, T. Alfrey, A. Janssen, and H. Mark, U. S. Quartermaster Corps.
  4. 11:20-11:50 Stress-Strain Curves of Viscoelastic Materials. Turner Alfrey, Jr., Monsanto Chemical Co., Springfield, Mass.

Luncheon.

### *Friday Afternoon*

5. 2:00- 2:30 Dilute Solution Viscosity of Heterogeneous High Polymers. R. S. Spencer and R. F. Boyer, Dow Chemical Co., Midland, Mich.



6. 2:35- 3:05 New Developments in Empirical Flow Methods for Plastics. R. Burns, Bell Telephone Laboratory, New York, N. Y.
7. 3:10- 3:40 Theory and Application of the Parallel Plate Plastometer. G. J. Dienes and H. F. Klemm, Bakelite Corp., Bound Brook, N. J.
8. 3:50 Annual Business Meeting.

*Saturday Morning*

9. 9:00- 9:30 Viscosity of Cellulose Acetate Solutions. W. Badgley and H. Mark, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.
10. 9:35-10:05 A Viscometer for Measurements during Thixotropic Recovery; Results with a Compounded Latex. M. Mooney, United States Rubber Co., Passaic, N. J.
11. 10:10-10:40 The Viscosity of Three Burma Oils at High Pressures. R. B. Dow, F. S. Veith, and C. E. Fink, Pennsylvania State College, State College, Pa.
12. 10:45-11:15 Use of the Aniline Point in Predicting the Pressure Coefficient of Viscosity of Hydrocarbon Oils. R. B. Dow and C. E. Fink, Pennsylvania State College, State College, Pa.
13. 11:20-11:50 Strain Hardening Under Combined Stresses. W. Prager, Brown University, Providence, R. I.
14. 11:55-12:25 An Interpretation of Some Useful Properties of Textiles in Terms of a Molecular Model. George Halsey and H. Eyring, Princeton University, Princeton, N. J.

---

## ABSTRACTORS IN THIS ISSUE

A. BONDI

C. K. BUMP

R. LEININGER

R. M. LEVY

J. A. PASK

S. ZERFOSS

BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY (B.I.P.C.)

# RHEOLOGY PROGRESS ABSTRACTS

## APPARATUS AND METHODS

### THE X-RAY EXAMINATION OF PLASTICS.

W. T. ASTBURY, *Chemistry & Industry*, No. 14, 114-16 (April, 1945).

By means of twelve x-ray diffraction patterns of thermoplastics, the author shows to what extent the state of orientation and aggregation of linear high polymers can be followed at present. The thermosetting resins are not discussed in detail because their x-ray diagrams belong to the higher reaches of diffraction analysis which have been little explored in the case of the complex amorphous bodies. It makes no difference in the preparation of an x-ray photograph of a thermosetting resin whether the product is in lumps, in films, or drawn out into fibers; the result is the same. With the thermoplastics, whose configurations and states of aggregation depend on temperatures and previous thermal and mechanical treatment, x-rays offer a valuable means of following what is happening.

B.I.P.C.

### AN INVESTIGATION OF THE DETERMINATION OF MOLECULAR WEIGHTS OF HIGH POLYMERS BY LIGHT SCATTERING.

P. M. DOTY, B. H. ZIMM, and H. MARK, *J. Chem. Phys.*, **13**, 159-66 (1945).

The determination of the molecular weights of large molecules by measuring the turbidity of the solution and the change in index of refraction with concentration is discussed. The apparatus, its calibration, and the technique used are treated, together with a comparison between molecular weights measured by this method and other methods. The effect of polymolecularity is also present. 10 references.

B.I.P.C.

### IMPACT TESTING OF PLASTICS, PART II. Factors Which Influence the Energy Absorbed by the Specimen.

DAVID TELFAIR and H. K. NASON, *Modern Plastics*, **22**, 145-9, 186, 188 (1945); cf. B.I.P.C., 13:482.

The purpose of the present paper is to discuss such factors as dimensions of the test specimen, the notch, the rate of stressing, and temperature, as they apply to the impact testing of plastics. The most important conclusions are summarized as follows: The energy of fracture depends on both the force required and the deformation produced, but the type of rupture (brittle or ductile) depends on the material, the temperature, and the speed and state of stress. If the failure is brittle, the energy absorbed may be correlated directly with the dimensions of the specimen, the elastic modulus, and the maximum tensile stress which the material can exhibit. In general, the type of break (brittle or ductile) depends on the ratio of shearing strength to tensile strength of the material under examination and any test condition, such as the notch, the temperature, or type of specimen which affects the ratio, will determine the manner of breaking. A brittle break will occur if the tensile stress reaches its critical value before the shear stress; otherwise, the material will deform ductily until failure. Ductile to brittle transitions have been observed

in metals by increasing the speed of testing and a related phenomenon would undoubtedly exist in plastics of many types, since the yield point in tension of cellulose acetate and nitrate increases with increasing rates of stressing rate. Plastics are more sensitive to temperature changes than metals and a change in the ratio of maximum shear strength to maximum tensile strength with change in temperature will result in different types of breaks. Data are presented to show the influence of dimensions of the test specimen on impact values as well as the influence of the notch, fibrous fillers versus non-fibrous fillers, and rate of stressing. The importance of notching technique is brought out by tabulated data obtained from breaking bars in thirteen different testing laboratories. The tensile strength of many commercial plastics is shown to bear a straight-line relation when plotted against the log of the rate of stressing from  $10^{-2}$  to  $10^3$  p.s.i. per minute. The present distinction between static and impact tests may disappear when a better knowledge of the behavior of a plastic test sample is obtained for several conditions of temperature, testing speeds, and states of stress (as determined by size and type of sample and presence of notches). 29 references. B.I.P.C.

## CELLULOSE

### VISCOMETRIC CHAIN LENGTH OF WOOD CELLULOSE IN TRITON F SOLUTION.

EDWIN L. LOVELL, *Ind. Eng. Chem., Anal. Ed.*, **16**, 683-5 (1944).

Use of aqueous dimethyldibenzylammonium hydroxide (Triton F) as a cellulose solvent for the determination of the average chain length by the viscometric method, in dilute solution, is suggested. A suitable experimental technique is described in detail. Intrinsic viscosity data for a number of cotton and wood celluloses in Triton F are compared with the corresponding degree of polymerization values obtained viscometrically after nitration, and a linear relationship is established. The results are compared with cuprammonium viscosity values, as used in the wood cellulose industry. 14 references. B.I.P.C.

### VISCOSITY AND MOLECULAR WEIGHT. III. The Heterogeneity Coefficient.

s. COPPICK, *Paper Trade J.*, **119**, 36-42 (T.S. 256-62) (Dec. 28, 1944); *Tech. Assoc. Papers*, **27**, 211-17 (1944); cf. B.I.P.C. 14:135.

Wood pulps are known to be very heterogeneous as regards both the species and chain length of the component polysaccharides. This nonuniformity leads to divergence from both the theoretical and empirical relationships between viscosity, concentration, and infinite dilution functions which appear to be valid for more uniform preparations. This adds further complications to viscometric methods for the determination of the average molecular weight of commercial wood pulp cellulose. The divergence is followed during sulfate pulping. The results indicate that the distribution of chain length changes during pulping in such a manner as to give viscosity relationships similar to those obtained for blends of a number of pulps. These results confirm the "equalizing" effect of pulping which has been reported by others.

Since most commercial pulps may be considered as blends of various proportions of raw and well-cooked fibers, these factors are always present and cannot be neglected in the interpretation of viscosity data. The results indicate that the relationship between viscosity, concentration, and molecular weight must contain a "heterogeneity coefficient." This quantity is worked out for various degrees of sulfate pulping, and the data indicate that its value is unity solely for well blended, thoroughly cooked, or purified pulps. However, with raw cooks the "heterogeneity coefficient" increases to such an extent as to make viscosity interpretations very inaccurate if the heterogeneity effect is neglected. 33 references.

B.I.P.C.

#### VISCOSITY AND MOLECULAR WEIGHT. IV. Acid and Basic Methods.

S. COPPICK, *Paper Trade J.*, **120**, 37-40 (T.S. 7-10) (Jan. 4, 1945); *Tech. Assoc. Papers*, **27**, 219-22 (1944).

A comparative study is made of the various methods for determining the solution viscosity of wood pulps. These include cuprammonium, cupriethylenediamine, and nitrate viscosities. The molecular magnitude of wood polysaccharide is evaluated from the various solution viscosity data determined at various stages during the purification of wood cellulose. The results indicate that nitrate viscosities are much more reliable than either of the basic methods for celluloses containing residual lignin. Noncellulose encrustants interfere with the solution of the polysaccharide to such an extent as to produce an entirely erroneous picture of the degradation which occurs during the purification of wood cellulose. By suitable calibration, the nitrate method for determining the degree of polymerization may be brought into agreement with the TAPPI standard cuprammonium method. 23 references.

B.I.P.C.

#### A STUDY OF THE CUPRAMMONIUM VISCOSITY OF CELLULOSE USING THE HOEPLER VISCOSIMETER.

W. D. HISEY and C. E. BRANDON, *Paper Trade J.*, **120** (2), 43-52; **120** (3), 41-44 (1945).

A study was made of the Hoespler viscometer for the measurement of the viscosity of cellulose dispersed in cuprammonium hydroxide. It was found that this instrument was very satisfactory for this purpose and has an inherent error approximately one-half as great as that of the TAPPI Standard T 206 M. The variables of the viscosity test, which included copper and ammonia concentrations, dispersion time, temperature, cellulose concentration, etc., were studied with the particular object of reducing the time required for the viscosity determination. A rapid method was devised. It was found that the specific gravity of pulp dispersed in cuprammonium under TAPPI standard conditions was 0.945 instead of 0.96 as given in the standard method. It was also found that the tolerance for the ammonia concentration given in T 206 M is too large for accurate work.

R. M. LEVY

## THE INFLUENCE OF VELOCITY GRADIENT ON THE RELATION BETWEEN VISCOSITY AND CONCENTRATION IN CUPRAMMONIUM SOLUTIONS OF CELLULOSE.

W. JAMES LYONS, *J. Chem. Phys.*, **13**, 43-52 (1945).

The numerous equations which have hitherto been employed to relate the viscosity of solutions of high polymers to the concentration of the solute have neglected to recognize explicitly the influence which velocity gradient (rate of shear) has upon the observed viscosity of non-Newtonian liquids. Consequently, the theoretically important, intrinsic viscosity, calculated on the basis of these equations from data obtained on a solution in the anomalous region, is found to have a different value for each velocity gradient prevailing during measurement. A modification of the Baker-Philippoff equation has been developed empirically having the advantage that it yields a uniform value for the intrinsic viscosity of a given solution, regardless of changes in velocity gradient. The new equation has been found to agree well with data on cuprammonium solutions of cellulose in concentrations below 0.5 g. per 100 ml. 11 references.

B.I.P.C.

## THE PRACTICAL ASPECTS OF CELLULOSE VISCOSITY FOR MILL CONTROL.

R. M. LEVY and W. D. HARRISON, *Southern Pulp Paper J.*, **7**, 26-7 (1944); *Paper Mill News*, **68**, 12, 14, 16 (Jan. 6, 1945).

Reference is made to the use of cupriethylenediamine as a solvent for the disperse viscosity of cellulose and the recently developed wet-disintegrator for processing moist pulp samples directly without previous drying (*cf.* B.I.P.-C., **12**:179; **14**:201). The utility of this test in direct process control in the papermaking industry is outlined, including the rapid detection of degradation of cooked pulp, preferably after pretreatment with sodium chlorite to remove the lignin, for bleach control, and for evaluating the uniformity of pulp for papermaking purposes. There appears to be a certain critical viscosity value above which a further increase does not seem to bring significant increases of desirable properties, such as sheet strength and folding endurance. The correct interpretation of viscosity data is not always easy, complex factors being introduced through variations in the raw material, cooking procedure, and resulting chemical actions. In spite of this, the use of viscosity as a quality measure in conjunction with other physical and chemical tests is becoming of increasing importance.

B.I.P.C.

## POLYMOLECULARITY AND MECHANICAL PROPERTIES OF CELLULOSE ACETATE.

ARNOLD M. SOOKNE and MILTON HARRIS, *Ind. Eng. Chem.*, **37**, 478-82 (1945); *J. Research Natl. Bur. Standards*, **34**, 467-77 (1945).

The tensile strength, ultimate elongation, and folding endurance of films prepared from a series of cellulose acetate fractions and blends were studied. When the mechanical properties are plotted against the intrinsic viscosities (or relative weight-average degrees of polymerization), the results for the fractions and different blends fall on separate curves. In contrast, when the mechanical properties are plotted against the number-average degrees of polymerization, the results for the fractions and all of the blends fall

approximately on a single curve for each property. The results are shown to be qualitatively consistent with the hypothesis that the mechanical properties of blends are the weight-averages of the properties of their components. They indicate the importance of the determinations of the number-average degree of polymerization by either osmotic pressure or other methods in studying commercial polymolecular materials. 10 references. B.I.P.C.

### CELLULOSE ACETATE FRACTIONS; INTRINSIC VISCOSITY AND OSMOTIC MOLECULAR WEIGHT.

ARNOLD M. SOOKNE and MILTON HARRIS, *Ind. Eng. Chem.*, **37**, 475-7 (1945); *J. Research Natl. Bur. Standards*, **34**, 459-65 (1945).

The intrinsic viscosities and osmotically estimated number-average molecular weights of a series of cellulose acetate fractions have been measured. It was found that, within the range of chain lengths investigated (number-average molecular weight up to 130,000), the number-average molecular weights are proportional to the intrinsic viscosities in acetone solutions, in agreement with Staudinger's rule and the results of Kraemer. An estimate is provided of the relative homogeneity with respect to molecular size of the fractions and the starting material from which they were prepared. B.I.P.C.

### RECENT PROGRESS IN CELLULOSE CHEMISTRY.

W. BADGLEY, V. J. FRILETTE, and H. MARK, *Ind. Eng. Chem.*, **37**, 226-32 (1945).

Recent progress is reported in the field of cellulose and its derivatives in three respects: (1) the size and shape of cellulose molecules in dilute solution; (2) the polymolecularity of cellulose acetates; and (3) the existence of more or less easily accessible areas in bulk cellulose, particularly in fibers. The first and last items are apparently closely related to important mechanical properties of films and fibers made from cellulose or cellulose derivatives, such as ultimate tensile strength and elongation to break. They seem to be particularly important for the so-called transversal properties, such as resistance to folding, bending, and shearing, but they influence other important technical qualities, such as moisture regain, swelling, dyeing, softness, and luster. The rate of exchange of the hydroxyl hydrogen in cellulose samples with deuterium was investigated. The second point appears to be of interest for the behavior of spinning and casting solutions, particularly for the degree of orientation and crystallinity which can be expected if such solutions are subjected to certain coagulating and stretching operations. 42 references. B.I.P.C.

### INTERCHAIN ORDER AND ORIENTATION IN CELLULOSE ESTERS.

W. O. BAKER, *Ind. Eng. Chem.*, **37**, 246-54 (1945).

A continuous series of states of short-range molecular order from amorphous to crystal-like has previously been shown to result from appropriate heat treatment, solvent action, etc., in solid cellulose esters and other linear polymers. The order-disorder proportion strongly influences physical properties of the solids, and is affected by rate of cooling during molding, by subse-

quent aging, etc. These studies, aimed at describing, by means of the fine structure, the principal mechanical behavior of thermoplastic cellulose derivatives, have been extended to various oriented states of cellulose esters and mixed esters. These include orientation (Sisson's classification) found in fibers (uniaxial), parts of injection moldings (imperfect uniplanar, uniaxial, and biaxial), and rolled sheets (uniplanar or selective uniaxial, *i.e.*, biaxial). X-ray diffraction was principally used to indicate structure and orientation. The simplest operation of pressing or rolling an unoriented sample produces the lowest degree of orientation, uniplanar. At the same time, some disruption of ordered regions appears to occur during the deformation, and strained positions are occupied by some of the chain segments. These may lead to slow dimensional changes, especially in moisture-sensitive polymers. Cold pressing resembles low-temperature compression molding in this effect. Similarly, when a highly ordered annealed fiber is cold-rolled to give a selective uniaxially oriented ribbon, local strains are introduced. Then, subsequent reordering is demonstrated by the diffraction diagrams after heat or solvent treatment. This improved local ordering is accompanied by no change, or sometimes slight increase in over-all orientation. These effects are shown particularly clearly for cellulose triesters and highly substituted acetate butyrates. Increasing concentrations of plasticizer in both unoriented and oriented sections gradually cause disordering of the chains quite like that in quenched polymers. In the mixed esters, such as the acetate butyrates, high total substitution is required, as might be expected, for high degrees of crystallinity. Lower total substitution, however, with more hydrogen bonding, tends to raise the melting point. These competing factors appear to cause the bending back toward the butyral side of the melting point *vs.* composition curves of Malm, Fordyce, and Tanner. In this and all other instances, chemical composition must always be considered in predicting the physical effects of varying order in inter-chain packing. 47 references.

B.I.P.C.

#### A TUMBLING DEVICE FOR PREPARING CELLULOSIC DISPERSIONS.

S. A. SIMON, *Textile Research J.*, **15**, 82-3 (March, 1945).

A new tumbling device for preparing cellulosic dispersions in cuprammonium or other solvents is described which was developed in the laboratories of the Chicopee Research Division. The usual end-over-end action is supplemented by a very slow rotation of the viscometer about its own axis, so that successive passes of the agitating plunger are distributed around the circumference of the viscometer rather than localized on two opposite sides, as in the usual devices. The sensitivity and accuracy of the new instrument seem much improved, a single test in place of the previous four separate tests giving sufficiently precise results. One illustration.

B.I.P.C.

#### PHYSICAL AND CHEMICAL MEASUREMENTS ON REGENERATED CELLULOSE FIBERS.

NILS GRALEN and OLOE SAMUELSON, *Svensk Papperstidn.*, **48**, 1-5 (Jan. 15, 1945) (in English; German and Swedish summaries).

Measurements of the degree of polymerization (DP) and of the polydispersity of cellulose have proved of great value for the determination of the

quality of regenerated cellulose fibers. Two samples of staple fiber of different grade were studied by means of several physical and chemical testing procedures. The molecular weight and polydispersity of the cellulosic fibers were determined by sedimentation in the ultracentrifuge and by diffusion. In addition, the fibers were examined by x-rays; the pentosan molecular weights calculated from viscosity measurements according to Staudinger give lower values than those obtained from sedimentation and diffusion. In addition, the fibers were examined by x-rays; the pentosan contents, the copper number, and alkali solubility were also determined. Tensile strength and elongation to rupture were found to depend to a large extent upon the experimental conditions employed. The resistance to washing of the fibers was studied by boiling in soap solution. From a textile viewpoint, one of the staple fiber samples was of lower quality than the other (which was of a standard grade). A high DP and low polydispersity were found to correspond with high strength, low copper number, and slight alkali solubility. 25 references. B.I.P.C.

## CERAMICS

### **SYMPOSIUM ON "REVIEW OF ENAMEL TESTS." II. Review of Tests for Fineness and Consistency of Enamel Slips.**

C. M. ANDREWS, *Bull. Am. Ceram. Soc.*, **23**, 475-7 (1944).

The author reviews the test methods for determining fineness and consistency of enamel slips. The screen and settling tests for fineness and use of Bingham plastometer, Irwin consistometer, Gardner mobilometer, pressure flow, hydrometer, and viscosity tube for measurement of consistency are described and compared for their practicability in plant control. J. A. PASK

### **SOFTENING POINT OF GLASS BY FIBER ELONGATION METHOD AND IMPROVEMENTS IN APPARATUS AND PROCEDURE.**

ARTHUR H. FALTER, *J. Am. Ceram. Soc.*, **28**, 5-8 (1945).

The improved apparatus is described in detail. Individual curves show the results of softening point (corresponding to a viscosity of approximately  $10^{7.6}$  poises) tests on glasses over a range of 260°C., in which the agreement for five individual homogeneous glass specimens varies from 1° to 6°C.

J. A. PASK

### **SOME PROPERTIES OF SODA-SILICA GLASSES AT HIGH TEMPERATURES.**

KUAN-HAN SUN and HURD W. SAFFORD, *J. Am. Ceram. Soc.*, **28**, 11-15 (1945).

One section of the paper presents a study of *viscosity* data for glasses in the system  $\text{Na}_2\text{O}-\text{SiO}_2$  within the temperature range of 800° to 1400°C. Equations by which calculations of viscosity from composition may be made are derived.

J. A. PASK

### **FACTORS INFLUENCING FLUXING ACTION OF VARIOUS OXIDES IN LOW-TEMPERATURE BOROSILICATE GLASSES.**

HOWARD R. SWIFT, *J. Am. Ceram. Soc.*, **28**, 33-36 (1945).

Strontium, barium, and lead oxides were studied as fluxes in low-temperature borosilicate glasses by using the button-flow method. The method



consists of fusing the buttons on a ground-coated, steel panel and then lowering the panel to a vertical position and noting the flow, which is a function of viscosity, in a given time.

J. A. PASK

### SOME CLAY-WATER PROPERTIES OF CERTAIN CLAY MINERALS.

R. E. GRIM and F. L. CUTHBERT, *J. Am. Ceram. Soc.*, **28**, 90-95 (1945).

Computed values are given for the thickness of the water film adsorbed on the surfaces of the various clay minerals when clays composed of such minerals develop specific plastic characteristics. Based on such values, the following concept of clay-water relationships is presented. The dominant factor determining the plastic properties of clays is the rigidity of the water held on the surfaces of the clay minerals, and the point of beginning of the transition of completely rigid water to liquid water is marked by great changes in such properties. Each type of clay mineral seems to have a characteristic ability to stabilize water, and the exchangeable ions also exert an influence. The reaction between water and kaolinite or halloysite may require considerable time so that there is frequently a time lag after mixing clays composed of such minerals before the plastic properties are fully developed. Applications of the foregoing concept in the fields of geology, ceramics, and soil mechanics are suggested.

J. A. PASK

## COLLOIDS

### ELECTRICAL ANISOTROPY OF XEROGELS OF HYDROPHILE COLLOIDS. PART I.

S. E. SHEPPARD and P. T. NEWSOME, *J. Chem. Phys.*, **12**, 244-8 (1944).

A number of colloid materials—proteins, plastics, cellulose acetate, and the like—have been coated in sheet form and “fibred” internally by stretching to 100% or more elongation. Circular disks were cut from the fibred sheets, and their degree of orientation measured in an (alternating) electric field. Account is given of the relation of the orientation measured to field strength, thickness, humidity, and moisture content. It was observed that induced electrical anisotropy is not shown by all kinds of natural and synthetic colloids; thus, it is not shown by organophile xerogels but only by the hydrophile ones. With most of these the electrical response depends upon the relative humidity and the absorbed water content, but with polyvinyl alcohol the effect was independent of the absorbed water.

B.I.P.C.

### ELECTRICAL ANISOTROPY OF XEROGELS OF HYDROPHILE COLLOIDS. PART II.

S. E. SHEPPARD and P. T. NEWSOME, *J. Chem. Phys.*, **12**, 513-19 (1944).

An improved, though still relative, quantitative expression has been derived for the electrical anisotropy (E.A.). The E.A. is a linear function of the elongation up to a certain limit, as is also the optical birefringence. The relation of electrical to optical anisotropy has been studied in greater detail. A more critical discussion in terms of atomic model structures if given of the hypothesis that E.A. in the compounds studied is due to the formation of con-

tinuous parallel chains of hydrogen bridges, having electronically conducting character. The materials studied were: polyvinyl acetate and its hydrolyzed stages down to polyvinyl alcohol; and cellulose acetate and its hydrolyzed stages down to (hydrate) cellulose.

B.I.P.C.

## GLASS

### THE STRENGTH OF GLASS FIBRES. Part I. Elastic Properties.

J. B. MURGATROYD, *J. Soc. Glass Tech.*, **28**, 368-87 (1944).

The value of Young's modulus and of the modulus of rigidity of glass fibers of stated composition decreases as the fiber diameter is reduced; and the viscosity of the glass also falls in value with the decrease in elastic moduli. Heating the fibers to 400° causes an increase in the modulus of rigidity, but not in Young's modulus, and on heating to 520° or higher Young's modulus is increased as well as the modulus of rigidity. The viscosity of the glass is also increased by heat treatment. The author interprets the results as meaning that the process of drawing a glass fiber causes profound changes in the constitution of the glass. The suggested structure is such that long chains of molecules are formed lying parallel to the direction of drawing, and the lateral bonds between the chains are few. Heat treatment at low temperatures permits the formation of some lateral bonds, resulting in a stiffening of the structure. At the higher temperature levels the chain structure should break up, but is prevented from doing so to the fullest extent by the dimensions of the very fine fibers. It is suggested that heat treatment should also cause a reduction in strength due to the formation of strong lateral bonds and the consequent loss of "ductility."

### THE STRENGTH OF GLASS FIBRES. Part II. The Effect of Heat Treatment on Strength.

J. B. MURGATROYD, *J. Soc. Glass Tech.*, **28**, 388-405 (1944).

An apparatus is described for the rapid determination of the breaking strain of glass fibers. The effect of heat treatment on the strength is shown to follow the changes in the elastic moduli recorded in Part I. The strength is reduced to about 70% of the original value by heating to 400° for 30 minutes, and to about 50% by heating to 520° for the same period. Distribution curves of the breaking strains are compatible with a random distribution of "flaws," which increase in number when the fibers are heated.

### THE MECHANISM OF BRITTLE RUPTURE IN GLASS.

J. B. MURGATROYD, *J. Soc. Glass Tech.*, **28**, 406-31 (1944).

Griffith's "crack theory" and the weak molecular bond theory of the strength of glass are tested by strength phenomena recorded by different investigators, and it is concluded that modifications are necessary to these theories to account for the facts. The suggestion is made that Griffith "flaws" consist of pockets of quasiviscous material surrounded by larger three-dimensional aggregates, and that when the pocket material has yielded to an applied stress the fact that it then carries no load makes the pocket the equivalent of a "hole"

in the glass. Such a "hole" would act as a stress concentrator. In this way the time elapsing before breakage occurs is explained as being due to the time required for the stress in the quasiviscous material to relax. By means of a model representing the stress concentration at a pocket an equation is derived relating the breaking strength,  $P_B$ , with time. Values of the breaking strength calculated from this equation,  $P_B - a = b/t \cdot k$ , are in good agreement with published experimental results.

#### THE DETERMINATION OF THE ELASTIC AND VISCOUS PROPERTIES OF GLASS AT TEMPERATURES BELOW THE ANNEALING RANGE.

G. O. JONES, *J. Soc. Glass Tech.*, **28**, 432-62 (1944).

An experimental survey has been made of the elastic and viscous properties of a soda-lime-silica glass at temperatures in and well below the annealing range, using specimens cut from drawn sheet and a bending method for observing the development of the strain under an applied stress. The results indicate that, down to quite low temperatures, the whole of the strain is made up of a purely viscous part, plus a completely reversible elastic part. The reversible elastic strain may again be divided into an instantaneous component and a delayed component which appears rapidly at first and then approaches asymptotically to a maximum value. It was often impossible to continue the measurements until the whole of the delayed elastic strain had appeared, and a method was developed for the analysis of the strain-time curves, based on the observation that only that part of the delayed strain which had already appeared under load was later recovered on removal of the load, and on the assumption that the form of the decay function was similar for both deflection and recovery. The total delayed elastic strain for a given applied stress is a function of the temperature, increasing from about 3% of the instantaneous elastic strain at 200° to about 75% at 444° ( $T_g$ , the transformation point for this glass, was 534°). Above this temperature it became increasingly difficult to separate the instantaneous and delayed parts of the elastic strain, and this is suggested as the main reason for the many differences between the present results and the conclusions of N. W. Taylor and co-workers, which were based on work at these higher temperatures. The true viscosity of this glass at 350° was  $10^{17.8}$  poises, appreciably lower than would be expected from an extrapolation of the curve obtained at higher temperatures, and supporting the conclusions of H. R. Lillie based on the measurement of viscosities in the range  $10^{13}$  to  $10^{16}$  poises. This value of viscosity is substantially higher than measured values previously reported in experiments on glass. Some theoretical and practical implications of the results are discussed.

## LIQUIDS

#### VISCOSITIES AND RHEOCHORS OF ALDEHYDES, NITRILES AND OF SECONDARY AND TERTIARY AMINES.

J. NEWTON FRIEND and W. D. HARGREAVES, *Phil. Mag.*, **35**, 619-631 (1944).

Data are given on the viscosity of various amine, aldehyde, and nitrile derivatives up to the boiling point. Rheochors derived in the previous

work (*Phil. Mag.*, **34**, 643, 1943) were used in this paper. The formula for the rheochor is as follows:

$$R = M(10^3\eta)^{1/8} (D + 2d)$$

where  $M$  is mol. wt.,  $D$  is density of the liquid,  $d$  is density of the vapor, and  $\eta$  is viscosity. Values for  $R$  from the previous work are as follows:

C, 12.8	C <sub>6</sub> H <sub>5</sub>
H (in C—H), 5.5	attached to alkyls, 100.7
H (in O—H), 10.0	attached to other groups,
O (etheric), 10.0	102.7
O (ketonic), 13.2	CN, 33.0
Covalent bond, 0	NH, 13.6
Coordinate bond, -0.4	N (-), 6.6
Cl, 27.3	Satd. 6-member C ring, -5.6
NH <sub>2</sub> , 20.6	

In this paper the observed and calculated  $R$  values are compared for 6 aldehydes, 9 nitrile derivatives, 8 secondary amines, and 7 tertiary amines.

S. ZERFOSS

## LUBRICANTS

### SOME TECHNICAL ASPECTS OF LAUNCHING LUBRICANTS.

C. W. BOHMER, *Inst. Spokesman*, **3** (Nov., 1944).

Launching friction data (which are remarkably consistent within themselves) are compared with a number of rheological properties of the applied launching greases, such as yield value, viscosities, and consistencies over a wide range of temperature conditions. So far, a basis for the correlation of field and laboratory performance has not been found.

A. BONDI

### EFFECT OF MINERAL OIL POUR POINTS ON FLOW CHARACTERISTICS OF LUBRICATING GREASES.

C. W. GEORGI and J. F. O'CONNEL, *Inst. Spokesman*, **3** (Dec., 1944).

Within the temperature range of 10° to 210°F. and rate of shear range of 10 to 1000 sec.<sup>-1</sup>, the grease viscosity was found practically independent of base oil viscosity and flow characteristics, and essentially a function of soap type and concentration.

A. BONDI

### SOME ASPECTS OF LUBRICATION.

E. M. LEAHEY, *Pulp Paper Mag. Can.*, **45**, 961-7 (1944).

The author describes the outstanding characteristics of lubricants and tests for their evaluation, with special emphasis on the deleterious effect of contaminants such as water and acidity. Assuming that the lubricant in question is chemically inert and that proper steps have been taken to keep it in that condition—namely, that the contaminants are removed as readily as they are formed—the most important property of a lubricating oil is its viscosity. Its significance, measurement, and effect on other properties are discussed. Tables and graphs are included, as well as a bibliography with 20 references to more complete information on the subject. The article has been written, not

for the specialist, but for the benefit of engineers unfamiliar with the theories of lubrication.

B.I.P.C.

## MICROSCOPY

### PRINCIPLES OF MICROSCOPE ILLUMINATION AND THE PROBLEM OF GLARE.

WILFRID TAYLOR DEMPSTER, *J. Optical Soc. Am.*, **34**, 695-710 (1944).

The author discusses the adjustments necessary for obtaining glare-free illumination in microscopy; effective illuminations depend equally upon the condenser, the field stop, and the illuminant proper. In general, there are two extremes in the practical use of illumination—illumination for high resolution and illumination for maximum contrast. The microscopist should ordinarily vary his illumination as he works to obtain the advantages of each type. The conditions of each are fully described.

B.I.P.C.

### VISUAL FACTORS IN MICROSCOPY.

WILFRED TAYLOR DEMPSTER, *J. Optical Soc. Am.*, **34**, 711-17 (1944).

The author discusses the problem of vision through a microscope; the literature relative to high visual acuity is reviewed. Conditions for high visual acuity and visual comfort are outlined. 42 references.

B.I.P.C.

### ELECTRON MICROSCOPY.

JAMES HILLIER, *Can. Chem. Process Ind.*, **28**, 728-36 (1944).

The author discusses electron microscopy with particular emphasis on both the interpretation and the significance of the results, which are in the form of highly magnified geometrical representation of the specimens under investigation. Stress is placed upon the fact that the electron information gives no information beyond that. On the other hand, it is pointed out that there exist relatively unexplored techniques of utilizing the physical properties of the electron beam in various types of analysis. 166 references.

B.I.P.C.

### MICROSCOPY WITH LIGHT, ELECTRONS, AND X-RAYS.

G. D. PRESTON, *J. Sci. Instruments*, **21**, 205-13 (1944).

The relation of the optics of light, x-ray, and electron microscopy is discussed, so as to allow a comparison of the methods, their differences, and their special advantages. 14 references.

B.I.P.C.

## POLYMERS

### A SURVEY OF THE SYNTHETIC FIBERS.

WILLIAM D. APPEL, *Am. Dyestuff Repr.*, **34**, 21-4. Discussion 24-6 (Jan. 15, 1945); *Rayon Textile Monthly*, **26**, 17-20 (Jan., 1945).

The paper summarizes the available data on the important properties of the synthetic fibers and compares them with similar data for cotton, wool,

and silk. Tabulated data for composition and structure, dimensions, tensile strength in dry and wet condition, extensibility, modulus of elasticity, relative stiffness, relative toughness, density, and effect of temperature are given, as well as a graph indicating the different moisture absorption of textile fibers. The data on these fibers have been assembled from the viewpoint of their use as engineering materials. Whether a fiber is of natural growth or manufactured from natural cellulose or protein, or wholly synthetic, is not important to the future of the industry. The most important factor is what the fiber will do, and that depends upon its properties. Price is another determining factor, and there is a limit to the number of fibers which can be produced on an economic basis. The future will create from the best of the synthetic and natural fibers new products better fitted than before to meet the ever increasing requirements of use.

B. I. P. C.

## PROTEINS

### ELASTICITY OF KERATIN FIBERS. II. Influence of Temperature.

HENRY B. BULL, *J. Am. Chem. Soc.*, **67**, 533-36 (1945).

The stress on human hair was measured over a temperature range of from 17° to 60° at various stretches, both for extension and for contraction, and the four-fifths life of the stress is reported. The stress was resolved into that due to internal energy and that due to heat motion. It was found that the force of contraction due to the internal energy is, in general, very much larger than that due to entropy change. It is concluded that the elastic element involves principally the internal energy which is in contrast with rubber.

R. LEININGER

### STUDIES ON THE DOUBLE REFRACTION OF FLOW. II. The Molecular Dimensions of Zein.

J. F. FOSTER and J. T. EDSALL, *J. Am. Chem. Soc.*, **67**, 617-25 (1945).

The theory of double refraction and its application to the determination of molecular length is reviewed briefly. By the use of a new apparatus providing velocity gradients as high as 30,000 sec.<sup>-1</sup> and the use of high viscosity solvents as propylene glycol it was possible to study zein which is a relatively short corpuscular protein. Results obtained are in good agreement with those obtained by sedimentation, diffusion, and viscosity measurements when compared on the basis of a prolate ellipsoidal molecule 300-400 Å. in length.

R. LEININGER

## RUBBER

### PHYSICAL-CHEMICAL INVESTIGATIONS OF GOLDENROD RUBBER. IV. Increase in Viscosity and Formation of Photogels by Irradiation of Goldenrod Rubber in the Absence of Oxygen.

MORRIS M. GRAFF and EVALD L. SKAU, *J. Phys. Chem.*, **49**, 1-4 (1945).

The viscosity of goldenrod rubber solutions in benzene can be increased until gelation occurs by irradiation in the presence of catalysts such as benzophenone, carbon tetrachloride, and benzaldehyde, but in the absence of oxygen.

C. K. BUMP

**DEPENDENCE OF POLYMER PROPERTIES ON TEMPERATURE OF POLYMERIZATION.**

MAURICE L. HUGGINS, *J. Am. Chem. Soc.*, **66**, 1991 (1944).

Huggins presents an argument alternative to that of Alfrey, Bartovics, and Mark, *J. Am. Chem. Soc.*, **65**, 2319 (1943), on the dependence of polymer properties on the temperature of polymerization.

**THE MOISTURE RELATIONS OF TEXTILES. A SURVEY OF THE LITERATURE.**

P. W. CARLENE, *J. Soc. Dyers Colourists*, **60**, 232-7 (1944).

Most of the work of outstanding importance on the moisture absorption of textiles has been published during the last twenty years. The author reviews the results of the more important investigations during this period under the headings: the absorption and desorption of water by fibers; the influence of moisture on the physical characteristics of textile fibers; and the effect of processing upon the moisture absorbency of textiles. 56 references.

B.I.P.C.

**SOME REMARKS ON THE FATIGUE OF TEXTILES.**

W. E. ROSEVAERE, R. C. WALLER, and H. MARK, *Rayon Textile Monthly*, **25**, 452-4 (1944).

The authors divide the mechanical properties of solids, including textile fibers, into three classes. (1) Properties depending directly upon the molecular structure. The deformations which the test specimen suffers under the stress of the test are relatively small and reversible or nearly reversible. (2) Properties depending upon molecular structure plus the presence of weak spots (imperfections of various kinds). No satisfactory agreement exists between calculated and observed values. As an example, the ultimate theoretical breaking strength is always many times larger than the observed values. The theoretical value for cotton is 150,000, but the observed value is only 1500. The deformation which occurs during testing is not more or less reversible than in case 1, but represents an irreversible change during which the sample is destroyed. (3) Properties depending upon molecular structure plus existing and potential weak spots. The latter are the result of prolonged and combined physical and chemical influences, usually referred to as endurance or fatigue failures. These failures depend not only upon the numbers and the nature of imperfections actually present in the sample at the beginning of the fatiguing process, but also upon the readiness of the sample to produce additional weak spots throughout this process. The factors involved in the individual phases of the fatiguing process are analyzed.

B.I.P.C.

**A RELATION BETWEEN VISCOSITY AND REFRACTIVE INDEX.**

R. T. LAGEMANN, *J. Am. Chem. Soc.*, **67**, 498-99 (1945).

A linear relationship was found in each of seven homologous series of organic liquids between the molecular refraction and the viscosity constant as

defined by Souders. From this relation the viscosity can be calculated from the refractive index and vice versa for any liquid falling in the series described whose density and molecular weight are known. C. K. BUMP

### **CREEP CHARACTERISTICS OF PLASTICS.**

WILLIAM N. FINDLEY, *Modern Plastics*, **22**, 153-9, 194, 196 (Dec., 1944).

The author presents a mathematical equation to represent the creep-time behavior of plastics which he claims can be applied more accurately than previously employed equations, one of which is almost universally used in testing metals. This interpretation has been applied to creep of several plastics with good agreement. The results for plastics indicate that this method of interpretation may permit reliable extrapolation of creep data for the prediction of creep behavior at times greater than the extent of available tests. Illustrations of the instruments used in the tests, a number of diagrams, and one table listing the creep characteristics of several plastics are included. 22 references. B.I.P.C.

### **MECHANISM FOR THE RELAXATION THEORY OF VISCOSITY. (Letter to the Editor.)**

R. E. POWELL and H. EYRING, *Nature*, **154**, 427-8 (1944).

Powell and Eyring discuss the work of Eley and Pepper on the plastic flow of plasticized cellulose derivatives which showed that the "flow velocity of compression of cylinders and extrusion of rods depends exponentially on stress at moderate stress" but that at high stresses the flow velocity approaches linearity with stress. Powell and Eyring have observed the above in greases, paints, and clay slips, and claim generality for the phenomenon for liquid-solid dispersions previously described by the Bingham yield-value equation. A theoretical explanation is offered, accompanied by a diagram for a lime-base grease. The authors assume that the breaking of two types of bonds (a strong and a weak bond) are involved in this process and derive their equations on this basis. S. ZERFOSS

### **(Letter to the editor.)**

D. D. ELEY and D. C. PEPPER, *ibid.*

In a discussion of the above letter Eley and Pepper question the necessity of the two bond types-assumption for all system and stress the need of more data on plastic flow. S. ZERFOSS

### **THE RHEOLOGICAL CONCEPTS OF VISCOSITY AND YIELD VALUE.**

HENRY GREEN, *Interchem. Rev.*, **3**, 105-11 (Winter, 1944).

The author discusses the meaning of two of the important factors determining plastic flow, shows the relationships underlying plastic flow, and describes some instruments for measuring viscosity. B.I.P.C.