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EDITORIAL

Rheology and Theology

Rheology is the science of the deformation and flow of matter. Theology, according to one authority, is the science that treats of the existence, nature, and attributes of God, especially of man's relations to God. The scope of Rheology is broad indeed, but is very narrow in comparison to that of Theology.

The Holy Bible, in the Christian world at least, is the handbook of Theology. The Rheology Bulletin in its modest way attempts to be the Bible of Rheology. In the Editor's opinion, it doesn't do a very good job. The Holy Bible was the work of many devoted hands, and it condenses and crystallizes the wisdom and the follies and the aspirations of many peoples in many lands, and through many years. The Rheology Bulletin has its wisdom and its follies and its aspirations, too, although its years are few. But it needs more devoted hands, it needs more saintly (?) scribes and epistolarians.

In the February issue your Editor solicited more help from his readers in the form of abstracts, and in fact of unsolicited abstracts. The Editor is too busy to write a letter asking for each and every abstract, and he prays for "showers of blessings" in the form of suitable copy for each issue. Several letters have come in suggesting that there is hesitancy on the part of the writers to furnish such copy for fear they will duplicate the work of another abstractor. The suggested remedy is the assignment of definite journals, to each contributor, making him alone responsible for supplying abstracts along the lines treated by that journal. Certain assignments have already been made. The choice, of course, should be made by the abstractor, since he alone knows what journals are of particular interest to him, but the Editor will advise if a duplication arises in the selection of the journal or journals for abstracting. Help is needed immediately. The actual work of the abstractor is not great. One abstract per month or three per issue would be sufficient, and if fifteen or twenty "saintly souls" would thus cooperate, we would have a Rheology Bulletin that would be worth while, and that might even in due course of time become the Bible of Rheology.

THE 1943 FALL MEETING

The regular annual meeting of the Society of Rheology is scheduled for October 29 and 30 at the Hotel Pennsylvania in New York City. Dr. W. F. Fair, Jr., Chairman of the Program Committee announces that a very good program is being developed, but that he would like to hear from prospective speakers as soon as possible. It is planned to publish brief abstracts of the meeting papers in the next issue of the Rheology Bulletin which will appear in August. Contributors are therefor advised to keep in touch with Dr. Fair at the Mellon Institute, Pittsburgh, Pa., and to furnish him with at least tentative resumes of their work, at an early date.

REVIEW OF THE CONFERENCE ON RUBBER FUNDAMENTALS

On April 3, 1943, the Society of Rheology arranged at the Brooklyn Polytechnic Institute a research conference on "The Present State of the Kinetic Theory of Rubber". Two lectures were given, one by Dr. M. L. Huggins of the Eastman Kodak Research Laboratories, and the other by Dr. L. A. Wood, of the National Bureau of Standards. The following invited discussion speakers attended and contributed to the conference: Drs. T. Alfrey, W. T. Busse, E. Guth, H. M. James, A. R. Kemp, R. Simha, E. Valko and F. T. Wall.

There were about 135 attendents, a large number of which entered the discussion. The meeting was under the chairmanship of Professor P. Debye, of Cornell University.

The theory of rubber-like elasticity was developed in two steps:

1. It was recognized that the free energy changes during the extension of long chain molecules are mainly entropy changes. A statistical theory has been developed to compute the entropy change of isolated long chain molecules with complete free rotation as a function of the distance between the ends of the chain. Such probability considerations lead to the correct order of magnitude of the modulus of elasticity and to its correct dependence upon temperature. However, they cannot represent the shape of the stress strain curve point by point and do not reflect more intricate mechanical and thermoelastic properties.

2. Recent improvements of the theory are being carried out mainly along the following lines:

    (a) To take into consideration the fact that there is no completely free rotation in long chain molecules, but that there exist certain configurations which are preferred from energy considerations. How hindered rotation affects

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the result of the calculation depends mainly upon the internal fine structure of the chain. In general it seems that hindered free rotation makes more elongated configurations of the chain more probable as compared with completely free rotation.

(b) It is to be considered that every sample of rubber is built up by a large number of chains which adhere to each other by Van der Waals forces, and which eventually may also be connected at certain points by strong chemical cross links. In such systems the average length of the individual chain loses its significance for the elastic behavior and has to be replaced by a quantity of the dimension of a length which seems to correspond to the average distance between points of strong attachment between individual chains. The theory has to describe a flexible net-work rather than a system of entangled independent chains in order to reflect the mechanical behavior of the material.

(c) Finally, in order to account for irreversible deformations, one has to consider that the extension of the above net-work is accomplished by a certain amount of irreversible displacements of the fixed points caused by slipping of chains along each other while they are in stretched and parallelized configurations.

NEW BOOKS

The Chemistry of Large Molecules, 275 pp., 65 illus. Price $3.50. Interscience Pub. Inc. 215 4th Ave., New York.

Contents

H. Mark, Polytechnic Institute of Brooklyn.
    "The Mechanism of Polyreactions"
    "The Investigation of High Polymers with X-Rays"

E. O. Kraemer, Biochemical Research Foundation of the Franklin Institute.

    "The Colloidal Behavior of Organic Macromolecular Materials"
    "The Ultracentrifuge and its Application to the Study of Organic Macromolecules"

A. Tobolsky, R. E. Powell and H. Eyring, Princeton University.
    "Elastic-Viscous Properties of Matter"

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R. M. Fuoss, General Electric Company.
    "The Electrical Properties of High Polymers"

C. S. Marvel, University of Illinois.
    "Organic Chemistry of Vinyl Polymers"

Emil Ott, Hercules Powder Company.
    "Chemistry of Cellulose and Cellulose Derivatives"

APPARATUS

USE OF THE BRABENDER PLASTOGRAPH FOR MEASURING THE
WORKABILITY AND PLASTICITY OF BALL CLAYS AND JIGGERING
BODIES.--H. G. Schurecht and Marvin Britton.

Presented before the American Ceramic Society, Annual Meet-
ing, Pittsburgh, Pa., April 22, 1943.

The Brabender plastograph consists of a small mixer or
pug mill which is driven by a freely turning dynamometer
mounted on ball bearings. The resistance which the material
exerts toward mixing is transferred to the dynamometer whose
housing tends to equalize this resistance by turning in the
direction opposite to that of the shaft. The resultant thrust
necessary to pug the clay is transmitted through levers to a
scale and is recorded by an electrically driven recorder
moving the chart at a slow speed synchronized with the time
division of the charts.

It is believed that the resistance which the material
offers towards mixing is proportional to the yield value of
the clay providing the mixing proceeds uniformly. In test-
ing clays the dry ground clay is added to the pugging chamber
and then water is introduced at a constant rate. This causes
the consistency curve to rise to a maximum value due to co-
hesive forces. When an excess of water is added, the curve
again gradually drops to a zero value due to lubrication by
the water; assuming that the consistency values are proport-
ional to plasticity, the plastograph unlike most plastometers
measures this property for all water contents in one run.

With extremely plastic clays there is a tendency for
the clays to form balls which ride above the pug mill pins
and hence satisfactory results are not obtained. This trouble
can be overcome by mixing 25% of the clay with 75% of coarse
sand which prevents balling of the clay and gives much better
results. Careful adjustment of the apparatus is necessary
to prevent large oscillation of the curve. It is believed
that by modifying this apparatus and by using coarse sand
with the material to be tested that the plastograph can be
used to compare the plasticity, workability, and consistency
of clays, ceramic bodies, and masonry mortars.

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AN IMPROVED VOLUMENOMETER.--Joseph C. Richmond, John B.
Peterson, Winslow H. Herschel, J. Am. Ceram. Soc., <u>26</u>, 127
(1943).

Capillaries are used for measuring viscosity, but con-
versely, a knowledge of the viscosity may be used to calibrate
a viscometer, or to investigate the permeability of a porous
material such as brick, and this might also be called Rheology.

The property of brick most commonly measured is the
porosity. Assuming capillary pores, their number and diameter
can be calculated from the permeability and porosity, and it
is with the porosity with which we are here concerned, this
being equal to the difference between the bulk volume and the
solid volume, divided by the bulk volume.

Solid volume is best obtained by the air expansion method,
described in paper by Ray T. Stull and Paul V. Johnson, Jour.
of Research, Nat'l. Bureau of Standards, <u>25</u>, 711 (1940) R.P.
1349. The instrument used is known as a volumenometer, and
an improved form of this instrument has now been described by
Richmond, Peterson, and Herschel.

It consists of three parts, a barometer, expansion
chamber, and evacating apparatus. A brick is placed in the
expansion chamber, in which the pressure is then reduced by
lowering a reservoir containing mercury. The barometer is so
constructed that the pressure in the expansion chamber, both
before and after evacuation, may be read on the same instrument.

From the law that the product of the volume and pressure
of a gas at a given temperature is a constant, it is shown that

$$V_g = A + BH - V_s \qquad (1)$$

where V_g = gas volume in closed system, cm^3

V_s = solid volume of specimen in chamber, cm^3

A = gas volume of closed system, without specimen,
before lowering of reservoir.

B = volume of barometer tube per scale division

H = barometer reading in scale divisions or pressure
(mm) of mercury corrected to standard conditions.

If H' is the reduced pressure, after lowering of
reservoir, the final equation used to calculate the solid volume
is

$$V_s = A + B(H + H') - \frac{CH'}{H - H'} \qquad (2)$$

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The three constants, A, B, and C, must be found in calibration, C being the volume of a glass bulb, with graduations on the connecting tubing at top and bottom. This bulb is full of mercury at the start of test and empty at the end, and the air in the expansion chamber is thus increased in volume by the addition of the volume of the bulb, when the mercury reservoir is lowered.

It was assumed that C equalled 507 cm^3, the volume obtained by calibration of the bulb. The value of B, calculated from the diameter of the barometer tube, 12 mm, and a length of scale division of 0.976 mm, was found to be 0.111 cm^3. Then only the constant A remained unknown.

By tests with steel and glass blocks of known volume, of various sizes, values of A were found to vary from 2285 to 2295, with an average of 2287, which was considered satisfactory as variations in A were not systematic and were no greater than variations in A with V_S constant. If this had not been the case, a reexamination of values for B and C would have been required.

WINSLOW H. HERSCHEL

ASPHALTS AND BITUMENS

MEASUREMENT OF THE "FIRMNESS" OF ASPHALTIC BITUMENS.— D. C. Broome, Petroleum, 5, 122 (1942).

Prior to the invention of machines to measure the "firmness" of pitches, many psycho-physical methods were in use by those skilled in the art of controlling tar distillation. Precision viscometers now take the place of these methods.

In an attempt to define "firmness" reference is made to the Scott Blair and Coppen concept expressed by the relation:

$$\psi = s\sigma^{-1}t^k$$

where:

ψ = firmness

S = stress

σ = strain

t = time

which holds for all materials (it was thought) from pure liquids to Hookean solids. The value of k was found to be unity for pure liquids and zero for solids. In between these extremes, varies depending on the nature of the substance. Actually it is found that "firmness" cannot be expressed in fundamental units because a different value is obtained when a different type of test is run such as tension, torsion, or compression. Also it was found that the value of k was

dependent on stress for certain "rubbery" bitumens. With these materials, firmness is dependent on the rate of application of stress and the extent of deformation.

The penetration test (A.S.T.M.) is useful in determining "firmness" and evaluating "degree of plasticity." Penetrations ought to be carried out at various temperatures, and for hard bitumens, under various increased loads. When bitumens depart from purely viscous flow, different "firmness" values may be found on two specimens showing the same penetration. The difference between the measured "firmness" and the viscosity calculated by using the Saal and Koen formula for penetration may be utilized in showing the "degree of plasticity."

Some of the difficulties encountered in the measurement of "firmness" are the change in rate of shear with constant applied stress due either to thixotropy and structure or to work hardening, the one having the reverse effect of the other; the thermal history, including the phenomenon "age-hardening;" and elastic recovery effects which are allied to the amount of deformation.

It is shown that ductility provides a useful method of determining "firmness" over a wide range of temperature. The effects of varying rate of strain are also easily made known by this method.

Still a further method of measuring "firmness" at elevated temperatures might be the flow or sag of a material under its own weight.

W. W. PENDLETON

RHEOLOGY OF BITUMINOUS MIXTURES RELATIVE TO PROPERTIES OF ASPHALTS.--Charles Mack, Proceedings Assoc. of Asphalt Paving Technologists, 13, 194-255 (1942).

After a discussion of the forces acting on pavements and the rheological properties of asphalts (viscous and plastic flow, thixotropy and elasticity) the author describes methods for measuring the flow properties of asphalts and the mechanical properties of bituminous mixtures (containing 90% sand and silica dust + 10% asphalt). The theoretical aspects of the flow and elastic properties of such mixtures are discussed in considerable detail. Data are given for the flow properties of bituminous mixtures under continuous and successive compressions, for the dissipation of stress therein, and concerning the effects of variation of load and curing on the rheological properties of bituminous mixtures.

R. H. TRAXLER

THE MECHANICAL BEHAVIOR OF BITUMENS.--W. Lethersich,
J. Soc. Chem. Ind., 61, 101-108 (1942).

The mechanical constants of bitumen were analyzed under
static and dynamic conditions including a study of recovery
curves. Lethersich shows that the behavior of a bitumen may
be expressed in terms of a mechanical model containing two
elasticities and two viscosities. The two viscosities increase
with frequency. By means of the model it is shown that when
the tensile strength (ductility) is proportional to the square
root of the rate of loading bitumen fails in a plastic manner,
and that when the tensile strength is independent of rate of
loading, bitumen behaves as a highly elastic solid and fails
in a brittle manner.

The four basic parameters (two elasticities and two
viscosities) were measured for six bitumens covering a viscosity
range of 10^6 to 10^{12} poises. In contrast to the widely vary-
ing viscosities the elasticities did not vary to any great ex-
tent. The physical interpretation of the model developed is
in accord with the colloidal nature of bitumen. Decrease of
viscosity with increase of stress (structural viscosity) in
the opinion of the author is an asset. The penetration test
appears to be of little value except as a qualitative indicat-
ion of the order of the viscosity.

                                        R. N. TRAXLER

    VISCOSITY, PLASTICITY, ELASTICITY AND COLLOIDAL STRUCTURE
OF BITUMENS.--F. Hoeppler, Oel und Kohle, 37, 995-1009 (1941).

The rheological properties of 13 steam-distilled, vacuum
and air blown bitumens were determined by means of the Hoeppler
viscometer (inclined tube and rolling ball) for the range of
temperature -20 to 30°C. The data obtained lead to a theory
of the colloidal structure of bitumens according to which the
disperse phase consists of round solvated micelles (with high
lyosorptive capacity) in equilibrium with the dispersion phase
(mineral oil), depending on the temperature. Logarithmic
linear relations were found between absolute viscosity, pene-
tration, softening point and drip point. The rheological aging
and thixotropy of the blown asphalts were examined. A new
constant the quasi-elasticity modulus, which is introduced as
a characteristic of the elastic properties of bitumen was de-
termined for various asphalts between -30 and 40°C. Thermo-
elasticity was observed in the case of blown bitumen and was
measured at various temperatures.

                                        R. N. TRAXLER

ASSOCIATION OF ETHYL CELLULOSE IN SOLUTION (I) OSMOTIC
PRESSURE (II) AND VISCOSITY.--Erwin Steurer, Z. Physik. Chem.
190A, 1-23 (1941).

These two papers furnish practically the only data in the
literature which enable a clear visualization of the interplay
of solvation and association and the effect of these factors
on the viscosity of solutions of macromolecules. As is shown
by the osmotic pressure data in Figs. 2 and 3,
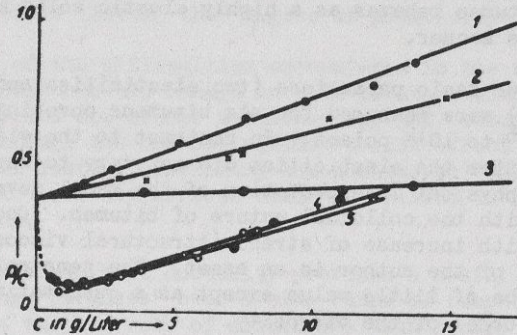
Abb. 2. Konzentrationsabhängigkeit von p c bei Äthylcellulose in Benzol — Äthanol
(90:10 Volum-%. Kurve 1), Chloroform (Kurve 2), Dioxan (Kurve 3), Toluol
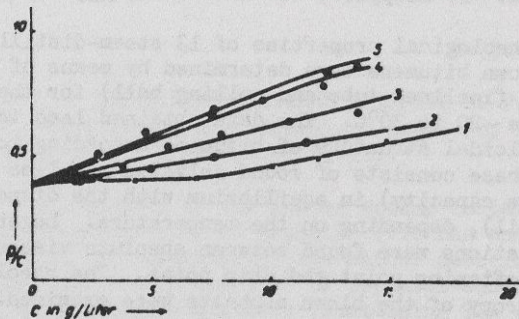(Kurve 4) und Benzol (Kurve 5).

Abb. 3. Konzentrationsabhängigkeit von p c bei Äthylcellulose (51·0% OC_2H_5) in
Benzol bei Gegenwart von Äthanol (Kurve 1 0·25 Volum-% Äthanol, Kurve 2
1 Volum-% Äthanol, Kurve 3 5 Volum-% Äthanol, Kurve 4 10 Volum-% Äthanol,
Kurve 5 50 Volum-% Äthanol).

the sample of ethyl cellulose used (degree of polymerization 197, 51.0% OC_2H_5) is not associated in dioxane, chloroform, or benzene-ethyl alcohol mixtures. In pure benzene or toluene, however, three or four molecules appear to be joined except in extreme dilution. Similar conditions hold for other solvents, pure hydrocarbons leading to association and polar solvents such as benzyl alcohol or cresol preventing association. Model experiments with completely methylated glucose and 2, 3, 6-trimethyl-methylglucoside showed that the latter, containing one hydroxyl group, is also associated in benzene solution, and the former is not associated. Ethyl alcohol is also known to associate to a greater degree in the solvents causing association of ethyl cellulose than in the more polar solvents. It was therefore concluded that the association of ethyl cellulose in non-polar solvents is probably to be ascribed to the un-etherified hydroxyls of the cellulose.

The viscosity data (0.75% concentration) on the same ethyl cellulose-solvent systems showed that the non-associating, polar solvents gave lower relative viscosities than the non-polar solvents. The most valuable distinction between the two types of solvents was furnished by the temperature coefficient of viscosity, a rise in temperature causing a considerably greater decrease in viscosity in those cases where association occurred. About the same ratio of acetone or of acetonitrile to ethyl cellulose in benzene solution was required to secure a normal viscosity-temperature coefficient as was required to prevent association as determined by osmotic pressure. Acetone and acetonitrile had a considerably weaker action than alcohols in preventing association.

It could be concluded from the fact that alcohol had a considerable influence on the viscosity and the slope of the reduced osmotic-pressure curves even after association had been eliminated that solvation by alcohol has at least two distinct actions on the intermolecular forces acting in ethyl cellulose-benzene solutions. The reviewer would like to call attention to a factor not considered by the author, namely, the very considerable influence on viscosity exerted by combined metal ions attached to carboxyls in the ethyl cellulose molecule. As has been shown by several workers (reviewed by Lohmann, J. prakt. Chem., 155, 299 (1940)), the viscosity-increasing influence of metal ions is to a great extent counteracted by alcohols or other polar solvents. If it is assumed that the very strong association of several ethyl cellulose molecules in benzene or toluene was due to the presence of an average of between one and two carboxyls per cellulose chain, a reasonable explanation is obtained for the fact that the association reaction had reached completion at a concentration of about 0.1% and that the reduced osmotic-pressure curve had a quite normal course above this point. It is then also easy to understand why association could be prevented by as little as 0.75% alcohol in the benzene. The influence of further additions

of alcohol on the viscosity and on the slope of the reduced osmotic-pressure curves could then be ascribed to solvation of the free hydroxyl groups of the ethyl cellulose.

H. M. SPURLIN

PLASTICS

FLOW PROPERTIES OF THERMOPLASTICS. I.--W. G. Wearmouth, J. S. Small, Brit. Plastics, 12, 377-379 (1941).

A moulded sample of the plastics was compressed between the plates of a parallel-plate plastometer to a limiting thickness from which the yield value of the material was deduced. The yield value - temperature curves for natural thermoplastics were smooth, but for synthetic resins (cellulose acetates and butyrates (aceto), celluloid, etc.) yield value decreased sharply when a definite temperature was reached, which varied considerably with the resin. The test was useful for determining the safe limiting temperatures, but the data could not be correlated with injection-flow properties. An addition of 30% of crystalline material had only slight effect on the softening range, and it was inferred that intermolecular spaces existed in the resin.

E. PRESTON

RUBBER

THE PLASTIC-ELASTIC BEHAVIOR OF EBONITE.--J. R. Scott, Trans. Faraday Soc., 38, 284 (1942).

Time effects in deformed ebonite are attributed to relaxation, caused by the continuous breaking of secondary valences within the network under the influence of the external stress. Primary bonds form the elastic "component." The increasing instability of the first type of bonds with rise of temperature accounts for the dependence of these rate effects upon temperature. In particular the relation between temperature and permanent set is interpreted on this basis. Various data on natural and butadiene ebonites are discussed.

ROBERT SIMHA

THE KINETICS OF RUBBER-LIKE ELASTICITY.--D. D. Eley, Trans. Faraday Soc., 38, 299 (1942).

Alexandrov's and Lazurkin's deformation-time data (Acta Physicochimica U.R.S.S. 12, 647 (1940) on natural and synthetic rubbers and on methyl methacrylate plastic are evaluated on the basis of the theory of rate processes to obtain the energies and entropies of activation for the relaxation process. The energy is separated into two terms; the first to account

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for the relative displacement of the chain segment upon application of stress, the second to describe the uncurling and stretching of the unit by means of internal rotation. On the basis of the well known results on viscous flow of raw rubber, it is deduced that one C-C bond per isoprene unit in the segment is rotated in the deformation of moderately vulcanized rubber. The effect of vulcanization and of plasticizers is discussed in the light of these concepts and the analogy to the dielectric relaxation in polyvinyl chloride is pointed out. A long discussion follows this article.

This paper as well as the preceding one forms part of a Symposium on the Structure and Reactions of Rubber held by the Faraday Society.

ROBERT SIMHA

SUSPENSIONS AND PASTES

CORRECTION. INTERPRETATION OF VISCOSITY MEASUREMENT OF STARCH PASTES.--B. Brimhall, R. M. Hixon, Cereal Chem., 19, No. 4, 425-441 (1942).

In the abstract, Rheology Bull. p. 14, (Feb.) 1943, formula (1) was omitted. This should read

$$Log \ \frac{4V}{\pi R^3 T} = M \ Log \ \frac{RPg}{2L} + Log \ C$$

In the table following this formula, P equals applied pressure, while g equals the acceleration due to gravity

W. LINDSAY

THEORY

THE VITREOUS STATE: SOME SEMIQUANTITATIVE CONSIDERATIONS.--M. L. Huggins, Presented April 12, 1943 at the American Chemical Society Meeting in Detroit, Michigan. Submitted for publication to the Journal of Physical Chemistry.

The equilibrium between crystalline and noncrystalline conditions in a solid or liquid and the rate at which the equilibrium state is approached are considered as functions of (1) the net energy changes for small internal structural

rearrangements (shifts of position of angle atoms or of orientation of groups of atoms), (2) the activation energies for such rearrangements, and (3) the temperature. Annealing and devitrification phenomena and the necessary requirements for the (practically) permanent existence of a vitreous substance are considered from this standpoint.

MAURICE L. HUGGINS

THE VITREOUS STATE.--M. L. Huggins, K. H. Sun, A. Silverman, Presented April 20, 1943 at the American Ceramic Society Meeting in Pittsburgh, Pa. Submitted for publication to the Journal of the American Ceramic Society.

The difficulty of defining the vitreous state in a rigorous manner, the existence of many borderline cases, and the theoretical requirements which must be met if a substance is to be vitreous are discussed. The following typical classes of vitreous substances are treated in some detail, especially in regard to relationships between their structures and vitreous properties: vitreous sulfur and selenium; vitreous silica; other pure oxide glasses; silicate glasses; inorganic and organic glasses containing hydrogen bridges; organic high polymers.

MAURICE L. HUGGINS

THIXOTROPY AND DILATANCY.--John Pryce-Jones, Jl. of the Oil and Colour Chem. Ass'n. 271, 3, Jan. 1943.

Three of the phenomena found in non-Newtonian fluids are discussed, namely, anomalous viscosity, thixotropy and dilatancy.

For this purpose the author constructed a modified Couette type rotating cylinder viscometer. Realizing that non-Newtonian materials can only be measured in an instrument capable of employing different rates of shear the author designed the viscometer accordingly. Though the author claimed that in an ideal instrument the rate of shear would be continuously variable, he limits his instrument to three different rates of shear of 1.45, 5.09 and 17.80 sec^{-1}, believing that in practice these three different rates of shear are sufficient to distinguish between Newtonian flow, anomalous viscosity, thixotropy and dilatancy. To obtain the three different rates of shear the speed of the cup is changed by a suitable gear arrangement. The bob is suspended on a torsion wire. The diameter of the cup is 2 inches and the one of the bob is 1.5 inches, giving a clearance of 0.25 inches, which is so large that it may cause plug flow even at the highest rate of shear obtainable with this instrument, if the materials being tested have fairly high yield values. By choosing a suitable length of torsion wire for each gear arrangement and by using a true

liquid of 50 poises as a standard the author calibrated the deflection scale in absolute units, letting each scale division correspond to 1 poise. Therefore, for true liquids the deflection reading gives directly the viscosity in poises.

Various materials are measured at the three different rates of shear, and also at one of the rates of shear after they have been left at rest for various definite periods of time after shearing has ceased. According to observations the author divides the materials in five distinct classes.

The first group of materials contains the true liquid, where the deflection readings are independent of the rate of shear and of the time of rest, and give directly the viscosity of the true Newtonian liquid in poises.

The materials of the second group possess true anomalous viscosity, according to the author, where the deflection readings decrease with an increase in rate of shear but are independent of time of rest. According to the author their "viscosities" can not be determined. However, should these materials be plastics and not pseudoplastics, their plastic viscosities could be determined by using higher rates of shear or a different dimensional viscometer in order to reach the straight line portion of the flow curve which is characteristic for plastic materials and from which plastic viscosity and yield value can be obtained.

The third group is comprised of materials, where the deflection readings are independent of the rates of shear but increase, when left at rest for increasing periods of time. This the author identifies with ideal thixotropy.

The fourth group of materials is characterized by an increase in deflection reading with decrease in rate of shear and also with increase in time of rest. All the members of this group possess anomalous viscosity immediately after stirring has ceased. The author calls these materials "False Body" materials, as described in his earlier papers.

According to the definition of thixotropy as given by Freundlich, all materials in group three and four should be classified as thixotropic, since according to Freundlich's definition of thixotropy not a complete isothermal sol-gel-sol transformation is necessary, but any material is thixotropic that becomes less viscous and less elastic on agitation but regains its original value upon rest.

The materials of the fifth class are dilatant, where the deflection reading or "viscosity" increases with rate of shear, but is independent of the time of rest at least at low rates of shear. The author realizes however that a continued shearing at a higher rate of shear may lead to an increase in "viscosity" with time.

The author advances two interesting theories for the existence of anomalous viscosity. 1) Anomalous viscosity may arise through a presence of an oriented structure which breaks down under the influence of shear, but which is immediately restored on the removal of shear or 2) it may arise through the deformation under the influence of shear of the dispersed solid phase particles which regain their normal shape immediately, when shear ceases.

The author concludes that the degree of dispersion in the five stated groups increases in the following order. Anomalous Viscosity, "False Body", Thixotropy, Dilatancy, and Newtonian Flow.

RUTH N. WELTMANN

AN ANALYSIS OF THE THIXOTROPY OF PIGMENT – VEHICLE SUSPENSIONS.—Henry Green, Ruth N. Weltmann, Anal. Ed., Ind. & Eng. Chem., 15, 201 (March 15, 1943).

The analysis of thixotropy, given in this paper is attained by means of the so-called thixotropic hysteresis loop. This is a method that heretofore has been neglected by both rheologists and colloid chemists. There is only slight mention of the loop made in the literature and apparently no one has attempted to develop its mathematical possibilities either empirically or theoretically.

The loop is easily obtained experimentally with a specially designed rotational viscometer (H. Green, J. Ind. & Eng. Chem. Anal. Ed., 13, 576 (1942), the main feature of which is the ability to change r.p.m. rapidly and continuously without stopping the instrument. In making the loop, the operator always commences with the lowest r.p.m. and works in uniform steps toward the top or highest speed. When this is attained the r.p.m. is decreased until the bottom of the curve is reached. When the up-and-down-curves are plotted together a loop is formed, if the material is thixotropic. This is because during the up-curve where the velocity gradient is increasing the thixotropic structure is breaking down. The up-curve is, therefore, bow-shaped. During the down-curve the velocity gradient is no longer increasing and the curve is, in the main, a straight line. A non-thixotropic material gives no loop because there is no breakdown and consequently both the up-and-down-curves are the same.

In order to make their position clear the authors discuss certain debatable points, in regard to thixotropy. From their viewpoint the non-linearity at the lower end of a plastic flow curve is mainly the transition from plug to laminar flow and is no particular indication of thixotropy. The decrease in "apparent viscosity" in a flow curve giving no loop is the result of geometrical necessity and not a proof of thixotropic

breakdown. Suspensions of silica in non-polar liquids are often considered to be highly thixotropic. The authors' viewpoint is that if such materials give no loops as they usually do, they are non-thixotropic, and when forced to flow, do so plastically, and not as the result of breaking down to a sol. As a consequence of this conclusion it would follow that the size of the area of the hysteresis loop indicates the extent of thixotropy, if the time of making the curve and the top r.p.m. is constant. It is claimed that this viewpoint rationalizes the subject.

When a given r.p.m. is applied over a long period of time thixotropic materials will continue to break down until the rate of buildup and breakdown are the same. This is an equilibrium point. If further breakdown is required it can be obtained only by increasing the velocity gradient. Thus two principles are involved in regard to breakdown - breakdown by time and breakdown by velocity gradient. These principles are expressed by two linear equations. The first states that the area of the loop is equal to a constant minus a time factor. The second is, the area is directly proportional to the square of the top r.p.m. (or velocity gradient).

The second of these two equations is derived theoretically as well as empirically. The theoretical derivation depends on an assumption that breakdown (loss in torque on the viscometer) is directly proportional to velocity gradient. The proportionality constant is the loss in torque per unit increase in velocity gradient for any given loop. When this constant is divided by an instrumental factor to make it independent of the instrument it is called the coefficient of thixotropic breakdown. It is the loss in shearing force per unit area per unit increase in velocity gradient. An empirical equation is found showing that the plastic viscosity plotted against the logarithm of the reciprocal of the top r.p.m. squared is a linear relationship. This same equation is also derived theoretically, indicating the correctness of the above assumption - that breakdown is proportional to velocity gradient.

This paper treats the fundamental case where breakdown involves only a loss in plastic viscosity. In a later paper, which is to follow, the double change will be studied, i.e. the effect on both plastic viscosity and yield value when thixotropic breakdown occurs.

HENRY GREEN

LETTER TO THE EDITOR

Sir: The suggestion of Mr. Welch (Rheology Bulletin, Vol. 14, Page 18) that rheological symbols be correlated, where possible, with mechanical symbols is an excellent one, and his tentative system is a good start toward a workable

symbolic vocabulary.

We suggest that accepted thermodynamic symbols be considered, also, in this correlation, since thermodynamic principles are receiving more and more attention in analysis of the kinetics of flow.

The following additions to Mr. Welch's system are proposed:

η_r Relative viscosity $(\eta_{solution} / \eta_{solvent})$

η_{sp} Specific viscosity $(\eta_r - 1)$

$[\eta]$ Intrinsic viscosity $(\lim [\eta_{sp}/c]_{c \to 0} = Ln\ \eta_{sp}/c)$

μ Poisson's ratio

U   Interval energy

KE   Kinetic energy

PE   Potential energy

W   Work λ Relaxation time

S   Entropy

H   Enthalpy $(U + PV)$

h   Planck's constant

n   Number

N   Avagadro's number

π Frequency

I   Moment of inertia

k   Boltzmann's constant

R_n Reynold's number

E_a Energy of activation

Important conflicts which should be resolved are:

E   Modulus of elasticity in tension or
           compression (mechanics)

E   Total energy

Q   Efflux or discharge rate (Welch)

Q   Heat energy (thermodynamics)

It is suggested that T be reserved to mean absolute temperature, and that temperature-centigrade and temperature-fahrenheit be represented by T_c and T_f, respectively.

It might be helpful for the president of the Society to appoint a special committee to draft a suggested system of notation for submission at the fall meeting.

Very truly yours,

MONSANTO CHEMICAL COMPANY
Plastics Division

H. K. Nason

T. Alfrey, Jr.

APPLICATION

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

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

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