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THE OCTOBER MEETING.

Your program committee has done an excellent job. As of May 1st, they have received and accepted a total of fifteen papers—of which five are "invited" papers, and ten are "contributed". Several other papers have been promised, but their titles have not yet been received. Titles and abstracts, (original and 2 carbon copies), of additional papers should reach the program committee by July 1st to avoid delay in scheduling. The final dead-line for the receipt of titles and abstracts is August 1st.

Our program committee consists of:

R. H. Ewell, Dept. of Chemistry, Purdue University, Lafayette, Indiana.
W. F. Fair, Jr., Mellon Institute, Pittsburgh, Pa.
A. I. McPherson, National Bureau of Standards, Washington, D. C.
A. Nadai, Research Laboratory, Westinghouse Electric and Manufacturing Company, Pittsburgh, Pennsylvania.
H. F. Wakefield, Development Laboratory, Bakelite Corp., Bloomfield, N. J.

The following is a list of the papers which have been accepted so far:

Invited Papers.

1. FLOW OF ROCKS, David Griggs, Dept. of Geophysics, Harvard University, Cambridge, Massachusetts.
2. HIGH TEMPERATURE CREEP IN METALS, Saul Dushman. General Electric Company, Schenectady, N. Y.
3. THE RHEOLOGY OF TOBACCO MOSAIC VIRUS, Max Lauffer, the Rockefeller Institute for Medical Research, Princeton, N. J.

Contributed Papers.

1. VISCOSITY AND FRACTIONATION OF HIGH POLYMERS, H. Mark, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.
2. RELATIONS BETWEEN VISCOSITY OF SOLUTIONS AND PHYSICAL PROPERTIES OF HIGH POLYMERS, Robert Simha, Columbia University, New York, N. Y.
3. A THEORY OF THE VISCOSITY OF SOLUTIONS CONTAINING ELECTROLYTES, Charles Clark, R. E. Powell and Henry Eyring.


The meeting will be held at Hotel Pennsylvania, October 24 and 25. A complete program will be published in the next issue of the Rheology Bulletin.

The Optical Society of America and the Acoustical Society of America expect to hold meetings at the same time in Hotel Pennsylvania. Your program committee is trying to arrange for joint activities (get-together, dinner, etc.), with these sister societies of the American Institute of Physics.

A NEW DEPARTMENT.

It has been suggested that a section of the Bulletin be opened for "Letters to the Editor". Letters should be short (say 100-200 words) and should be intended either as announcements or as discussions on matters of Rheological interest.

OUR BRITISH COUSIN.

The inaugural meeting of the British Rheologists' Club was held at the University of Reading on November 16, 1940, there being about twenty-five present of the current membership of sixty-five. The Bulletin of the club is published at the Institute of Physics of the University of Reading, Berks, England, the first number bearing the date of January, 1941. It contains club notes, a paper by Dr. V. G.
W. Harrison on Rheology in the Printing Ink Industry in a division headed “Rheology In Industry,” and nineteen abstracts with critical comments and the initials of the abstractor, in all eight pages. The Bulletin is sent gratis to the members.

Recent Papers On Rheology in the Journal of Applied Physics. F. Seitz and T. A. Read have a paper in the February and March issues on the Theory of the Plastic Properties of Solids. The authors first define slip, creep, twinning and rupture, and then treat each of these topics for four cases of pure single crystals, single crystals of alloys, pure polycrystalline materials and polycrystals of impure materials and alloys. These subjects are skillfully treated in such a way as to avoid too much mathematics without making the paper sound hazy or indefinite.

W. E. Trumpler Jr. has an article in the March issue on Relaxation of Metals at High Temperature, in which he describes an automatic machine for determining by means of short-time test the long-time transformation of a purely elastic strain into a permanent strain while the length of the specimen remains unchanged.

CORRELATED ABSTRACTS

RUBBER


In this paper experimental results are reported in a field that is not new; but the experiments are quite extensive and a new technique is developed for measuring the extent of crystallization. Percent crystallization in stretched raw rubber is deduced, not from the intensity of the diffraction spots in the x-ray crystal diagram, but from the reduction in intensity of the amorphous halo of the stretched rubber in comparison with that of the unstretched rubber. The results show that as the elongation increases, the crystallization increases asymptotically to about 80 per cent at an elongation of 700 per cent. The lowest measured crystallization is 20 per cent at an elongation of 250 per cent. Following an apparent custom among rubber technologists, the author extrapolates linearly the lower portion of the crystallization-elongation curve and concludes that crystallization "sets in" at about 150 per cent elongation. However, the data suggest that the proper extrapolation might be along a curved line to the origin with a zero slope at this point. To the reviewer such an extrapolation seems more plausible. The question could probably be settled if the measurements could be extended down to 10 per cent crystallization. Reduced temperatures might be required to reduce plastic flow.

The measurements of crystallinity in stretched rubber are based
on the ratio of spot to halo intensity. Data are reported for per cent crystallization for a number of different cures of a variety of rubber stocks subjected to a wide range in elongation and other test conditions. Among the results reported is the fact that percent crystallization is reduced by raising the temperature to 99° C.; and when the temperature is brought down to room temperature again, crystallization of vulcanized rubber regains its initial value, while that for the raw rubber does not.

In reporting comparison of percent creep after 3 1/2 months under constant load, and percent crystallinity, both as a function of per cent elongation, the author states that crystallization sets in at about that elongation at which the creep passes through a maximum. However, the existence of this maximum in the creep curve appears to depend largely upon an extrapolation of the creep curve to zero percent creep, based on the elongation, at zero percent elongation. This reviewer has not seen published any experimental data which would suggest such an extrapolation. He would expect to find that percent creep approaches a finite value as the percent elongation approaches zero. Regardless of this uncertainty, however, the fact remains established that percent crystallization shows a marked increase at that elongation at which percent creep begins to decrease markedly.

**Determination of Scorching of Rubber in Synthetic Compounds by Use of the Mooney Plastometer—J. V. Weaver, Rubber Age, Volume 48, pages 89-95 (1940).**

**A Torsional Hysteresis Test for Rubber—M. Mooney and R. H. Gerke, India Rubber World, Volume 103, pages 29 to 32 (1941).**

These papers present two new rheological tests for rubber, the first raw rubber, the second for cured rubber.

In the first set raw mixed stock is run in the shearing disc plastometer continuously at 250° F. until the viscosity reading begins to increase markedly. If a reading of 100 is reached in less than 12 minutes, the stock is likely to scorch in processing. If the time for the reading of 100 is greater than 12 minutes, the stock will probably process satisfactorily. This paper was awarded a cash prize offered by the N. Y. Rubber Group in 1940 for the best original paper in the field of rubber technology.

In the second rheological test of light aluminum circle suspended from a die-cut test piece of cured rubber constitutes a torsional pendulum; and the hysteresis is determined from the rate of damping of the pendulum oscillations. The test is simple, though accurate, and the test piece can be cut from a sample of any initial shape. The main disadvantage is that the frequency of the oscillation must be limited for observational purposes, and cannot be adjusted to approximate the frequencies usually involved in service conditions.

M. Mooney.
BITUMINOUS MATERIALS.

In a recent paper Scott Blair (1) tabulates various materials, including bituminous substances, the rheological properties of which are of practical importance. He regards as worthy of study viscosity, elastic modulus, elastic after effect, rate of shear, change of slope of viscosity-stress curve, breakdown under shear with slow or no recovery, work hardening, tensile strength and temperature susceptibility.

Later Pryce-Jones (2) continued this discussion, differing in certain aspects from Scott Blair's suggestions, and described a double Couette type instrument which may be used to show the differences in different materials establishing and measuring non-Newtonian flow, elasticity, etc.

Another interesting paper has been presented by Lee and Warren (3) who point out that the customary empirical tests used to evaluate bituminous materials have little correlation with important characteristic properties of the binders used in aggregate mixtures. These authors used coni-cylindrical, modified Ostwald and falling cylinder type viscometers to cover the ranges studied, namely $10^{-2}$ to $10^9$ poises, for a number of different bituminous binders. They state that most asphaltic bitumens do not show a simple proportionality between stress and rate of shear and in fact exhibit marked elastic and thixotropic properties. From angular rotation results obtained with the coni-cylindrical instrument, portions of the curve may be assigned to elastic effects, thixotropy, or internal structure, equilibrium viscosity conditions for particular stresses and recovery upon removal of stress. The investigators measured different bitumins under different conditions, for finding the deviation from Newtonian flow, and they suggested a definition of plastic properties encountered at the lower temperatures. They believe that differences in plastic and elastic properties are more important than variations in temperature susceptibility, and conclude that for binder aggregate mixtures more binder is required when the binder is more plastic in nature, and the more plastic the binder, the greater the resistance to deformation.

In another paper Lee and Warren (4) describe in detail the coni-cylindrical viscometer mentioned above.

Continuing this type of investigation Lee, Warren and Waters (5) attempt to correlate bituminous surfacing results with the flow properties of binders and laboratory aggregate mixtures. They state that the properties of the binder-aggregate mixtures are directly influenced by the nature of the binder used, and they determine the optimum binder content from deflection-time curves. They suggest the use of a "plastic-flow index" to aid in evaluation of various types of binders and mixtures, the plastic properties depending partly upon the aggregate composition and partly upon the binder. Non-plastic California
bitumen and (Newtonian) tar binders have a plastic flow index of 2 at optimum binder content of mixtures; variations from this value are related to the plastic properties of the binder. Experimental results indicate that the rate of flow of the mixture of binder and aggregate is inversely proportional to the viscosity of the binder.

Hocott and Buckley (6) describe a rolling ball and inclined tube viscometer which may be used to determine the viscosity of subsurface oil samples at reservoir temperatures and pressures, the instrument being adaptable to a wide range of viscosities. The authors report the viscosity of oil to be at a minimum at the saturation pressure and to increase with release of dissolved gas as the reservoir pressure drops.

REFERENCES

(2) J. Sci. Inst. 18, 39 (1941).
(3) Assoc. Aspli. Pav. Tech. 11, 340 (1940)
(4) J. Sci. Inst. 17, 63 (1940)
(5) J. Inst. Petrol. 26, 101 (1940)
(6) Petrol Tech. 3, No. 3

W. F. FAIR, Jr.

PAINT AND LACQUER.

No fundamental work of importance has appeared during 1940 on the rheology of purely paint products. Several instruments have been described, among which should be mentioned the modifications and improvements in the turbosviscometer to permit greater accuracy and convenience. (Paint and Varnish Production Manager 20: 174-8; Farben Zeitung 45:20-1, 35).

The relationship between turbosviscometer reading and efflux viscometer reading and the conversion of one to the other is discussed briefly.

An instrument called a “thixoviscometer” was described in full by Arnold and Goodeve (J. Phys. Chem. 44: 652-70). It was developed for measuring thixotropy and anomalous viscosity. The system carbon black—mineral oil was investigated and the results critically analyzed. The instrument should prove of value in similar studies on paints and lacquers.

The authors conclude from their study of the carbon black suspensions, that the structure which forms depends upon actual contact of the plate-like carbon particles with one another. The “residual” viscosity of the suspension was accounted for by the Newtonian viscosity of the liquid plus the volume effect of the carbon particles. The non-Newtonian viscosity was found to be the sum of a series of impulses transmitted from layer to layer through the liquid. The theory developed gives a quantitative description of thixotropy and defines the conditions under which it occurs.
The distensibility of paint and varnish films, and its measurement was the subject of a paper by S. Mark (Paint Manufacturer 10:150-4). Established methods of measurement were critically considered.

A review of the thixotropy and viscosity of paint products and the relationship of these properties to paint technology has been prepared by W. Beck (Verfkroniek 13:27-31, 48-53, 68-72).

An increasing appreciation of the importance of thixotropy in the flow and leveling of paints is evident in the literature. This has resulted in the development of specially treated pigments for the production of paint with controlled thixotropic properties and in modifications of paint compositions for the same purpose. As yet, however, instruments for routine measurement of this important property are not sufficiently simple and rugged.

J. D. Jenkins.

**THEORY OF CREEP IN CONCRETE.**

Creep in concrete is defined (1) as the nonelastic deformation of concrete under sustained loading. Since it tends to distribute the stress its action is usually beneficial, especially in mass concrete. This deformation is to be considered separate from the deformations due to various chemical and physical growths, or from swelling or shrinkage due to moisture or temperature changes. Creepage in cement products appears to be due to a "seepage" phenomenon. Moisture moves out of the gel at points of stress concentration, permitting the gel to collapse and so partially relieve the stress. Hence the factors that aid creep include: a high water content or water-cement ratio, as providing more opportunity for gel collapse; high humidity during loading as this resists evaporation and hence moisture flow in the capillaries; age at loading, as the older the cement the more it has dehydrated itself and the less opportunity for collapse; size of specimen, the larger the specimen the slower the evaporation rate, so that the rate of creep is reduced, although it may eventually reach the same value as a more slender specimen: the mix proportions, the size and shape of the aggregate, the type of cement and the temperature all affect creep through their effect on the amount of moisture present and its rate of movement out of the gel. Creep decreases with time and approaches a limiting value so that it is convenient to use a hyperbolic equation to predict creep in concrete. Creep under tensile stress appears to be about one third as great as under compression. It may reach a magnitude of 0.01 per cent.

Autogenous Volume Changes in Concrete have been discussed by Harmer E. Davis of the University of California. (2) Under this term comes those volume changes which occur as water is brought into combination with the cement constituents, whether chemically
or by more or less rigid absorption within the gel structure of the products of hydration. It may reach a magnitude as great as 0.1 per cent, which is sufficient to cause considerable trouble under certain conditions. The effect varies considerably with the type of cement, certain portland-possuolana cements exhibiting far more volume reduction over a period of years than other cements. The fineness of the cement is also a factor.

F. O. Anderegg.


HIGH MOLECULAR WEIGHT POLYMERS.

The determination of average molecular weight of particle sizes for polydisperse systems. Elmer O. Kraemer, J. Franklin Inst. 231, 1 (1941). The different types of molecular weight averages and the corresponding experimental methods, e. g. osmotic pressure, solution viscosity combined with Staudinger's rule, or light absorption, for the determination of these averages are discussed. Equations based on hydrodynamic formulae for the viscosity of ellipsoidal solutions and previously developed for homogenous systems cf. Rheology Leaflet. No. 15, 7 (1940) are extended by the author to mixtures. It is assumed thereby that a distribution formula of the same type as that previously postulated for the molecular weight distribution of macromolecular systems can be applied to the axis ratios of the suspended particles.

The molecular weights of rubber and related materials. G. Gee Trans. Farad. Soc. 36, 1162 (1941). Molecular weights of crepe samples are measured by means of osmotic measurements in several solvents like benzene, ether and benzene-methyl alcohol mixtures in a 100:15 volume ratio. Solutions in a poor solvent or in a mixture of a poor solvent with a precipitant approach ideal behavior at low concentrations. By comparison with ultracentrifuge data of Kraemer and Lansing (J. Am. Chem. Soc. 57, 1369 (1935) the Staudinger constant is determined and viscosity data are employed to calculate weight average molecular weights. The constants vary from $5.8 \times 10^{-4}$ for tetralin to $10.8 \times 10^{-4}$ for ethylene dichloride. The Staudinger rule is found valid for rubber solutions within a molecular weight range from 60000 to 350000. Non-uniformity coefficients for non-fractionated materials are calculated from a comparison of osmometric and viscometric data. The molecular weight of sol rubber is higher than that of gel rubber.

Investigations of fractionated and unfractionated high molecular weight substances using independent methods and various solvents are very desirable and should be systematically undertaken for all materials of interest.

Robert Simha.
VISCOSITY OF SUSPENSIONS.

The suspension of solids in mixed liquids. E. W. J. Mardles, Trans. Farad. Soc. 36, 1190 (1940). The viscosity and the settling process of kaolin and other solids in liquid mixtures such as ether-alcohol, water-alcohol and others is examined. The behavior is similar to that of cellulose, soap or protein solutions in mixed solvents. Friction and thixotropy in suspensions of non-polar liquids is remarkably reduced by the addition of polar substances such as oleic acid or linseed oil, and by the addition of materials absorbed by the dispersed particles.

The viscosity of suspensions in non-aqueous liquids. E. W. J. Mardles, Trans. Farad. Soc. 36, 1008 (1940). Suspensions of kaolin graphite and other solids in pure organic liquids show a relative viscosity increasing with increasing viscosity of the suspension medium. This might be due to the fact that the relaxation time for the orientation process of the immersed particles due to the shear is comparable with the time necessary for them to pass through the capillary tube. The viscosity ratio further decreases with increasing temperature. Suspensions of graphite show much lower friction than those of silica, independently of the medium.

It should prove interesting to investigate the viscosities in capillary apparatus of various dimensions and also in a rotating cylinder apparatus, especially in connection with the above hypothesis. Robert Simha.

RHEOLOGICAL PROPERTIES OF COTTON.

The rheological properties of cotton have yielded some valuable suggestions as regards fiber structure and conversely, the generally accepted structure of cotton provides a good basis for the elaboration of its mechanical properties. Cotton and other native celluloses differ from the regenerated or "once-dispersed" types in possessing longer chains and a higher orientation of chains in the lengthwise direction of the fiber and in having a sub-division of the fiber structure into fibrils. It is assumed that purified cotton is constitutionally homogeneous and consists of long, unbranched chains with anhydro-B-glucose as the repeating unit.

Although the mature fiber is a flattened, convoluted ribbon, it may be visualized as a hollow cylinder 10μ to 20μ in diameter whose walls consist of concentric layers of spiralling fibrils. The fibrils are more or less uniform and distinct entities about 1μ in diameter and extremely long. It is apparent that such a gross structure plays a not inconsiderable role in over-all fiber behavior. For example, a major part of the elongation of a fiber under stress seems to represent merely the straightening of the coiled fibrils. Aside from such effects, the properties of the fiber are largely the summation of those of the con-
stituent fibrils which, in turn, are determined by the structure of the native cellulose. Average chain lengths in intact cotton are probably about 2000 glucose units and correspond to a polymer weight of approximately 320,000. Such chains are disposed more or less parallel to the lengthwise direction of the fibril. In consequence of a periodic lateral coherence of adjacent chains the fibrils contain discontinuous, crystalline units or crystallites 600-1000 Å. U. long and 55-60 Å. U. thick. Thus, it can be seen that the crystallites are probably connected together by the primary valence chains of an expanded or amorphous network. Since the crystallites are comparatively rigid, the surrounding amorphous network functions as articulations.

**Extensibility.** Cotton fibers extend only about 8 per cent at rupture and, of this, about two-thirds is contributed by the straightening and denser packing of fibrils. The remaining 3 per cent originates within the fibrils and is recoverable. Extension in the latter case is directly opposed by primary valence chains. Young's moduli varying from 2 to $8 \times 10^{10}$ dynes per sq. cm. have been recorded for single cotton fibers.

**Rigidity.** Mean rigidities of various cottons have been found to range from 0.010 to 0.111 dynes per sq. cm. Correlations indicate that one of the governing factors in rigidity is fiber wall-thickness.

**Plasticity.** The fiber structure outlined above appears to be compatible with the low, true plasticity of cottons which, in the absence of moisture, obeys Hooke’s law. Fibers can be deformed but the deformation is largely semi-permanent and sets up strains which can be made to disappear with prolonged soaking in water. At the same time the fiber may recover from the amorphous chain network, the enhanced plasticity of wet cotton can be traced to the swelling and extension of the articulations produced by water. The moisture-recovery effects in deformed fibers are suggestive of an elastic after-effect which may be an elastic relaxation phenomenon. The crease-resistance of cottons is perhaps of this origin.

**Mercerization.** Mercerization augments such mechanical properties of cotton as elongation and plasticity and, in addition, activates the chemical properties. The change in mechanical properties has been traced to a permanent increase in the amount of amorphous or expanded cellulose in the treated cotton. In other words mercerization widens the articulations and the dependent properties change accordingly.

R. F. Nickerson.

**PLASTICS.**

New Instrument for Rheological Studies of Plastic Substances, C. R. Bailey, Ind. Eng. Chem. Anal. Ed. **13**, 173 (1941). This instrument, while rather complicated, seems to have distinct value in
the accurate determinations of the mechanical properties of the weaker gels and soft plastics. The transition or borderline states between easily recognized fluids and bodies which everyone considers as solid have been neglected, largely because of a lack of suitable apparatus. In this paper, its use has been confined to bentonite lyogels. The results of this work have been reported in J. Phys. Chem. 45, 493 (1941).


**Strength and Permissible Loading of Polyvinyl Chloride Resins**, Walter Buchmann Z. Ver. deut. Ing. 84, 425-31 (1940). The author gives the mechanical properties of polyvinyl chloride plastics at various temperatures.

**The Measurement of the Elastic Modulus of Plastics**, W. Kuntze and F. Pfeiffer, Kunstoffe 30, 293-6 (1940). This article describes an apparatus which measures elasticity of molded organic plastics and avoids the complications due to plastic deformation. The method depends upon the resonance periods of two pendulums swinging from arms attached to the lower end of a suspended rod of the material under test.

In the last few years during the phenomenal growth of the "plastics" industry, we have noticed a process of change in the previously accepted usages of the words "plastic" and "plasticity." One instance may be used as a typical example. In modern Plastics, Vol. 18, No. 9, Page 72 (May) 1941, we find an article Plasticity of Molding Compounds by Robert Burns, which was presented at the 43rd annual meeting of the American Society of Testing Materials, June 24, 1940. The article is reprinted by permission of that Society. An apparatus is described in which either thermosetting or thermoplastic materials may be tested by extrusion through a die having seven capillaries two inches in length with the diameters graduated in size from .015 in. up to .093 in. Since the paper was originally presented, several objections have been found to its use and the author is reported to have conceded the difficulty in obtaining reproducible data with the apparatus.

A significant point about the article is the use of the word "plasticity" by one of the author's standing in the plastics industry. As used in this article, "plasticity" is synonymous with flow. This is the common, if not universal, usage in the industry. It is contrary to the usage recommended by the ASTM, to the definition in Webster's International dictionary and to the classical meaning in the field of physics and engineering. Examples of this same changing use of the
word can be found in most of the technical articles dealing with plastics and is most common in the advertising and sales literature. The word "plastic" is often used to characterize the solid material remaining after application of a solution of an oil, resin or organic high polymer to solid surfaces or as an impregnation into cloth. There is nothing one can do about this trend but it may be that in the future, a new word will be required to describe the amount of retained deformation.

H. F. Wakefield.

The Theory of Absolute Reaction Rates and Its Application to Viscosity and Diffusion in the Liquid State, J. F. Kincaid, H. Eyring and A. E. Stearn, Chemical Reviews 28, 301-65 (1940). This is a highly mathematical summary used as a background for a theory of absolute reaction rates. This is developed into equations for viscous flow in liquids and the theory is applied to both normal and associated liquids. The theory may be used to calculate the viscosity of liquids from thermodynamic data.

Viscous flow is considered to take place by the activated jumping of a unit mass from one configuration to a second normal state. Thus flow involves an energy of activation and a rate mechanism. The energy for viscous flow is related to the energy needed for vaporization in many low boiling chemicals. The heat of activation for such flow is usually close to one-fourth the heat of vaporization of a molecule the size of the unit of flow. For long molecules the moving units from this rule are seen to be short segments of some twelve to twenty chain atoms.

THE VISCOUS FLOW OF LARGE MOLECULES.
W. Kauzmann and Henry Eyring
J. Am. Chem. Soc. 62, 3113 (1940)

This twelve-page article treats the mechanism of the flow of large molecules. It starts with the data that three or four times as much heat is required to vaporize a small molecule as is needed to cause a molecule to flow. Thus the space or hole for the moving liquid molecule is one-fourth the size of the vapor molecule as measured by energy of formation. In searching for a connection between viscosity and volume Eyring and his co-workers held viscosity constant with increase of temperature by the use of sufficient pressure to hold the volume constant. Since all simple substances have a viscosity of 0.02 poise at the melting point, then they are all considered as having about the same number of holes or the same expansion in order to melt. Prevention of such expansion prevents melting.

The heat to cause vaporization of chain organic molecules increases in a straight line up to about eight carbons in the chain. Be-
yond that point there seems to be some less heat needed per added carbon and this is considered as caused by a rolling up of the chain even in the vapor state. Now as the molecule gets longer than five carbons, there is a decided falling off per carbon on the heat needed for flow and at about 30 carbons the heat flow no longer reflects the increase of chain length.

For chains of longer than 30 carbons the energy measure indicates that the molecule is no longer moving as a unit but in segments each of which in flow requires the same energy as though it were a free molecule. Thus the fluidity in poises goes down as the specific volume goes down for hydro-carbons from C5 to C14. Above C14 there is a factor acting to reduce the fluidity or to increase viscosity. At this point in chain length the influence of movements or portions of the chain are thus detected. As the data picture becomes less clear with chain lengths above 30 carbons, one must here speak of average chain lengths since any attempt to separate the long chains into definite fractions give fractions which themselves prove to be average.

The observed low activation energy of these long polymer chains is too low to activate a whole chain of over about 30 carbons and Flory has published temperature coefficients of viscosity for several polymers as independent of the measured molecular weights of the polymers. Ref. J. Am. Chem. Soc. 62, 1057, (1940).

Thus it seems evident that melted polymers flow in segments. So that with regard to most phenomena the polymer segments act more or less like independent molecules but for viscosity effects the random motion of segments must become coordinated in order that the molecule as a whole can move in the direction of flow. This coordination is a time factor.

The authors thus indicate that the effect of chain size for large molecules is not expected to be found in activation energy, nor in melting phenomena but rather in those phenomena such as viscosity which deal directly with time factors. The highly viscous flowing polymers would be considered as consisting of movements below that of the full-sized chains but a sequence of such movements can displace the total long molecule in a desired direction.

This, then, is a theory stating that long molecules move both physically and chemically as though they were made of short (30 chain atoms) segments which sometimes seem nearly independent and at other times must coordinate to pass an energy barrier. Such coordination is mainly concerned with time as a factor.
A THEORY OF THE THERMODYNAMIC PROPERTIES OF LARGE MOLECULES.

R. E. Powell, C. R. Clark and Henry Eyring.

Previously in reviewing the data of P. J. Flory, Kauzmann and Eyring had concluded that melted polymer systems flow only as a result of a random forward motion of segments of some twenty to forty carbon chain atoms and independently of any larger measured particle or molecular sizes. (See Rheology Bulletin, Vol 12, No. 1, page 4. for report by H. Mark.)

This present paper is a physical viewpoint of the kinetic process to see why a chain molecule may well be expected to act in segments of some thirty chain atoms.

Having found that the total energy of activation for viscous flow is approximately 8 K cal, the authors now divide this total energy into two parts:

(a) Energy to rotate the chain.
(b) Energy to make a hole and move the segment therein.

They reason that the energy to rotate about a single C-C bond for 180° is approximately 3 K cal, but that here somewhat less energy would be needed to slightly twist each of several successive bonds until the same 180° position is reached. Having decided that this second type of motion would require approximately 2 K cal, then a mathematical solution for the number of small units movements gives n = 33. Thus a picture is drawn of rotation where each 33 carbon chain atoms may equal half turn without the need of any weak link in the chain. There is left then an activation energy of about 6 K cal available for forward motion which energy is sufficient to vibrate a section of some 30 chain atoms. Flow is a preponderance of vibration effects in one direction.

This same type of reasoning as to flow effects is applied to that thermal motion which becomes so evident as a liquification effect at the melting point. The same picture of flow (here flow by melting) as a result of segment motion leads to a maximum range of melting points since there is a maximum effective segment size. The maximum melting point is then the segment melting point or the same range as a melting point for a material with a complete molecule the same size as the chain segment found in long molecules. The length of such long molecules does not register on the melting point scale. That is, the melting point will be determined only by the properties of the segments for all long individual molecules. The linkage of other materials, such as solvents, other long molecules or even solid surfaces, to such a long molecule may of course influence its melting failure towards either higher or lower temperatures.

A plate of the available data shows that paraffins, olefines, alco-
hols and acids all approach, with increasing chain length a maximum value of around 122 C for the melting failure. This maximum value divided by the known increment for each chain carbon gives about 20 carbon chain atoms as a value for the maximum effective chain segment.

There are thus two motions to consider, one for a total long molecule and the other for an effective segment of such a long molecule. Consideration of these two different motions leads to two distinct pictures of flow depending upon dilution of a solid in a solvent or of pieces in a melt. The fact that the flow of pieces in their own melt does not vary in kind with concentration leads to the conclusion that the flow is by like segments of both the solid and its melt and does not depend upon the size of the unmelted segments. In a pure melt of long polymers the segments of 20 to 30 atoms in length find holes and conditions for motion as segments. However the complete molecules are greatly hindered so that the low pressure flow is determined as to type by the segment and not by the length of the molecule. The same result is found to a large degree in concentrated solutions, of polymers in solvents. However, the solvents used have such small molecular size as compared even to the segments that as solutions become more dilute the cavities are filled by small solvent molecules and the segments of the long molecule can no longer move unless it displace solvent. The osmotic pressure thus changes with dilution until the true osmotic pressure of the total unit piece is the only pressure found. That is, the calculated molecular weight increases with dilution until a maximum value is found in a very dilute solution and the equation for dilute solutions of long polymers is equivalent to Van't Hoff's classical expression:

$$\frac{11V_0}{RT} = N_2$$

from which the average size of the long molecule can be obtained, but of course only in solutions so dilute as to avoid the effect of segment motion.

The changes of osmotic pressure with concentration can then be so plotted as to show the total piece size as an intercept and the segment size as a slope of a straight line. Under such conditions any one polymer series shows a constant segment size in any one solvent. Some apparent differences as between data with different solvents are interpreted as effects of interaction with the solvent itself. If the polymer molecules cluster or associate the region of effective dilution may be below a workable range. The presence of cross-linkage bonds leads to the same unworkable condition as to polymer size and segment size.

It is interesting that for cellulose derivatives the moving segment is found as that of two glucose units. Rubber is variable and high
due, it would seem, to some cross-linkage bonds always present.

Vapor pressure data on solutions of different long molecules such as oleyl oleate and dioleyl thepsate give indications that the effective moving piece is about the same size, yet these products are known to have quite different sized molecules. Here the size is calculated to be about one half or one third the known size, that is, a segment of 16 or 17 chain atoms is the maximum found. For raw rubber, it is a segment of 25 chain atoms. Thus the vapor pressure data does not measure the full-sized piece in dilute solutions as does the osmotic pressure and the two different measurements indicate respectively the moving segment and the total polymer unit.

The surface tension is also independent of the total polymer size and the data of surface tension gives only the moving segment size. The unit effective in producing surface tension calculated from the temperature coefficient of surface tension by Eötvös equation gives chain lengths of about 12 atoms fairly constant for materials from molecular weights of 288 to 890.

The normal mixing of two low molecular materials gives an entropy increase. The addition of a low polymer to a high polymer gives an entropy decrease which will be superimposed upon the normal entropy increase of mixing.

High polymers involve both a moving segment and a moving total polymer unit whereas low molecular substances (below a chain atom length of about ten) involve only a moving total molecule.

In measuring the size of polymers on the molecular weight scale, one may get either the limiting segment size or the total polymer size or any intermediate value between these two extremes may be obtained according to conditions used.

The reviewer’s comments may be summed as follows:

In measuring molecular weight effects of organic materials for all values over 200, one is now forced to consider two possibilities:

A. That of moving segments which reach a constant and comparatively low value.

B. That of moving pieces of larger or total size.

1. These molecular values may, under other conditions, become constant. If these can be separated into constant fractions and determined as constant numbers, then one is dealing with a molecular substance for the larger moving unit and these are classical chemical substances.

2. These may be fractionable into constant fractions but give distribution curves of different size pieces even on repeated fractionation. Furthermore the same average sized lots from different procedures always show different properties.
in one or more directions, even if alike in many other respects. Such inconstant mixtures are called polymers and the average polymer size pieces may be measured. So far there is no direct proof that they are ever of any definite or known molecular size. This lack of proof is covered by the term “colloidal molecules” for the maximum moving unit of polymers. There is a recent tendency to include all these rather indefinite colloidal molecules under the term long molecules which term encourages one to think one knows more than the data justifies as to shape, size and molecular condition of polymers.

The Analogy Between the Mechanism of Deformation of Cellulose and That of Rubber, P. H. Hermans, J. Phys. Chem. 45, 827-36 (1941). An eight page general article with 37 references showing how cellulose, especially when in a swollen state, acts under deformation similar to a rubber. The stronger forces of cellulose yield on swelling much as the forces of rubber yield to increased temperature. Thus swollen cellulose will give a stress-strain curve like rubber at room temperature. In special cases, the special cellulose has an extensibility of 600%. Raw rubber can be cooled to crystals. Swollen cellulose can be dried to crystals. Rubber can be extended to form crystals and so also can cellulose. The stretching process is, however, less reversible with cellulose than with rubber, and the cellulose crystals are too strong to be melted without decomposition. Photomicrographs are shown of stretched cellulose dried and pulverized to show long needle particles and these look much the same as stretched and frozen rubber pulverized to a fine state.

The deformation of cellulose gels is said to show that cellulose molecules are best considered as curled flexible rods until they are forced to orientate or crystallize by motion.

H. L. Bender.
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