

THE RHEOLOGY LEAFLET

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No. 15 November, 1940

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THE RHEOLOGY LEAFLET
NOVEMBER 1940

WE HAVE A NEW NAME. The Executive Committee of the Society of Rheology voted at its meeting on October 19th to change the name of the RHEOLOGY LEAFLET to RHEOLOGY BULLETIN. This change will take place starting with the February issue for 1941. We hope you will like the new name as representing more accurately the type of publication which it represents in its present form.

CLASSIFICATION OF MEMBERSHIP. Up until now we had three classifications of membership: (1) Sustaining membership at a minimum of \$25.00 per year which included the Leaflet, the Review of Scientific Instruments, and the Journal of Applied Physics. (2) The regular membership at \$6.00 per year, \$5 of which was applied to a subscription to the Journal of Applied Physics, leaving \$1 for the Leaflet and all other expenses. (3) Associate membership at \$2.00 per year which included a subscription to the Leaflet.

The Executive Committee has voted to change this lineup to the following: (1) Sustaining membership the same as before; (2) Subscribing membership at \$7.00, \$2 of which is for dues and the Leaflet, and \$5 for a subscription to the Journal of Applied Physics at the reduced rate applicable to members; (3) Regular membership at \$2.00 per year which includes dues and a subscription to the Bulletin.

OUR NEW MEMBERSHIP COMMITTEE. President Hunter has appointed the following Membership Committee: D. K. Berkey, Chairman, Colgate University; E. C. Bingham, Lafayette College; J. W. McBurney, U. S. Bureau of Standards; R. H. Ewell, Purdue University; W. F. Fair, Mellon Institute; J. H. Dillon, Firestone Tire and Rubber Company, Akron, Ohio.

THE BRITISH RHEOLOGIST'S CLUB. A notice has just been received from G. W. Scott Blair, of the British National Institute for Research in Dairying, telling of the formation of The British Rheologist's Club. The first president of the club is Professor G. I. Taylor, F. R. S. The provisional committee of three consists of Dr. V. G. W. Harrison, Dr. G. W. Scott Blair, and Dr. H. R. Long. Membership is open to anyone residing in the British Commonwealth who is interested in rheology. Dues are five shillings a year. The activities of the Club must depend largely upon war conditions; and it is hoped that the Club may be re-organized at the end of the war, on a

more formal basis particularly with a view to co-operation with Societies having similar aims in this and other countries.

For the present it is proposed to hold occasional informal meetings when and where conditions permit and to arrange visits to laboratories where rheological methods are in use.

The periodical issue of a duplicated circular to members will be started as soon as possible. This will feature such items as short accounts of progress in specific industrial and academic rheological problems; requests for information contributing to the solution of problems; abstracts of papers on rheological subjects, more especially those published in technical or trade journals not usually seen by members, including foreign periodicals; news and views concerning rheology generally.

RUBBER IN COMPRESSION

E. G. Kimmich, A. S. T. M. Bulletin No. 106, p. 9-14 (1940)

This work is primarily concerned with the compression stress-strain relationship as a function of "shape factor" and degree of slippage of the loaded surfaces. The shape factor is defined as the ratio of average loaded area to free area of the rubber test piece, provided the loaded areas are initially parallel planes. The clear-cut results of this paper illustrate that this simple definition of "shape factor" is quite satisfactory for the various shapes of test piece studied. The author's remarks concerning unnecessary complications introduced in the use of the shape factor introduced by R. W. Brown. (S. A. E. Journal **47**, 432, (1940) appear quite justified.

The compression modulus at 20 per cent deflection with well lubricated surfaces is shown to be independent of shape factor over a wide range of shape factors. Compression modulus vs. shape factor curves with bonded surfaces (zero slippage) are given for rubber stocks of various hardnesses. The data presented are typical of those obtained by many others workers in this field. However, the simple method of presentation used is a definite contribution from the standpoint of the engineer and might well serve as a pattern for further work in this field.

J. H. Dillon.

HYSTERESIS IN CRYSTALLIZATION OF STRETCHED VULCANIZED RUBBER FROM X-RAY DATA

G. L. Clark, Marian Kabler, E. Blaker, and J. M. Ball
Ind. Eng. Chem. 32, 1474-1477 (1940)

The initial and subsequent hysteresis loops of two vulcanized

gum stocks in tension were obtained by the usual testing methods and the corresponding changes in state of crystallization were measured by the x-ray diffraction-densitometric method. The crystallization vs. elongation curves thus obtained are of great interest particularly in the marked lag in the decay of crystallization upon retraction shown in the case of one of the two rubber stocks.

The choice of an impact method for determining resilience may appear unfortunate to some workers in this field. However, the work may be considered an excellent beginning for a more complete study of this type. Such a study should yield valuable fundamental information.

J. H. Dillon

VISCOSITIES OF LINEAR POLYMERS

The high viscosity of polymeric substances distinguishes them from low molecular weight materials more readily than any other physical property. Not only are molten polymers themselves highly viscous, but small amounts of them dissolved in mobile solvents are able to increase the viscosity greatly. In general, the greater the molecular weight the greater the viscosity of the polymer or its solution. In fact, Staudinger has proposed a simple quantitative relationship between the molecular weight of a linear polymer and the amount by which the viscosity of a dilute solution of the polymer exceeds that of the pure solvent.

Recently it has been shown (J. Am. Chem. Soc., **62**, 1057 (1940)) that the viscosity of molten linear polyesters depends in a simple manner upon the molecular weight. At constant temperature the viscosity of the polyester (without diluent) is related to the weight average molecular weight M_w according to the relationship.

$$\log \eta = A + C \sqrt{M_w}$$

where A and C are constants. Since the polyesters, like all other synthetic polymers, are composed of a great many molecular species differing in size, it is unnecessary to use an average molecular weight. The particular average upon which the viscosity depends has been found to be the weight average, defined by

$$M_w = \sum w_x M_x$$

where w_x is the weight fraction of molecules having a molecular weight M_x .

The temperature variation of the viscosity is the same for polymers having widely differing average molecular weights. Furthermore, the temperature coefficient of the viscosities of these polymers is not many times larger than those for analogous monomeric compounds. These facts lead directly to the conclusion that viscous flow depends upon successive rearrangements of small sections of the long polymer molecule; it does not occur through simultaneous movement of the molecule as a whole.

The relationship between viscosity and molecular weight provides a simple means for accurate determination of polymer molecular weight. Perhaps of greater importance, it offers some insight into the mechanism of viscous flow in polymeric substances.

Paul J. Flory

FLOW PHENOMENA IN METALS

Several years ago there appeared a number of articles in the magazine "Steel" on the plastic forming of metals written by Professor Erich Siebel and translated by John H. Hitchcock. This series of articles touched on a great number of fundamental problems in connection with plastic flow of metals, pointing out fundamental characteristics as determined by special tests and correlating them with the actual behavior of metals under relatively large plastic deformations encountered in actual forging, drawing, rolling and extruding operations. In connection with this series of articles a relatively complete bibliography of related subjects may be found. Interest in the fundamental behavior of metals when forced to flow under pressure has been reflected by the popularity of such books as "Plasticity" by A. Nadai and "Elasticity, Plasticity and Structure of Matter" by R. Houwink.

Recently articles on the "Flow of Metals" by G. Sachs, Case School of Applied Science, have been published in the Iron Age, February 1 and 8, 1940, which review the present state of academic knowledge of the basic principles underlying the flow of metals in forming operations, and correlates these known principles with experimental data. The first of the articles by Dr. Sachs shows the results of considerable test data plotted in various ways to illustrate the effects of a number of the factors influencing the flow of metals under load. The effect of strain hardening is pointed out in a general way and is shown to vary greatly for different materials, but in general, it still follows Ludwik's laws. The second of the articles by Dr. Sachs deals with the fundamental mechanics of extrusion and drawing and

shows the results of various tests dealing with extrusion temperatures and speeds and with drawing temperatures, speeds and die angles. In connection with Dr. Sachs' article are a number of references to related subjects.

A paper by Dr. Hugh D. Mallon entitled "The Plastic Flow of Metals," published in the March, 1940, issue of *Metallurgia*, discusses the nature and offers a hypothesis for explaining the type of deformation which takes place. The essential idea involved in this hypothesis is that on and near the surface of the specimen deformation takes place by rotation and slip along certain crystallographic planes until fracture finally takes place, while the crystals near the core of the specimen will be subject to tension in more than one direction with the result that this intercrystalline slip cannot take place. As the elongation proceeds the surface crystals elongate and fracture with the result that slip will take place in the next layer of crystals. This process will continue until the slip crystals penetrate toward the center of the piece, ceasing only when the tensile stress has exceeded the tensile strength of the material.

A paper in the April, 1940, issue of the *Journal of the Institute of Metals* by G. Welter and S. Morski entitled "Dynamic Tensile Properties and Stress-Strain Diagrams of Some Constructional Materials" gives experimental results obtained by straining various metals at deformation speeds ranging from 1 to 5 meters per second as compared to the usual rate of 10 millimeters per minute. Dynamic stress-strain curves for copper, brass, aluminum, duralumin, zinc, and three plain carbon steels indicate that both the tensile strength and elongation were greater at high speed deformation than for usual speeds for all materials except zinc. Zinc showed a slight increase in tensile strength but definite reductions in elongation and reduction of area.

A symposium on the tension test dealing with the ductility of metals was held in Atlantic City, New Jersey, June 24 to 28, 1940. Of this symposium the papers dealing directly with plastic flow characteristics or ductility of the material were "The Limited Significance of the Ductility Features of the Tension Test" by H. W. Gillett and the paper entitled "The Tension Test" by C. W. MacGregor.

R. G. Strum

POLYMERS IN SOLUTION.

Studies on reactions relating to carbohydrates and polysaccharides. LVIII. The relation between length and viscosity of the polyoxyethylene glycols. Reid Fordyce and Harold Hibbert. *J. Am. Chem. Soc.* 61, 1912-5 (1939).

The viscosities of long chain polyoxyethylene glycols are measured in CCl₄ and dioxane at 20, 40 and 60°. In all cases a linear relationship between viscosity and molecular weight is found within the weight range 810-8200. Below 810 a sharp departure from the linear form results. In the above range the following formula expresses the data: $\eta_{sp}/c = K'_m M + B$ (η_{sp} sp. specific visc., c concentration, M molecular weight), thus showing a modification of Staudinger's formula to be necessary at lower molecular weights.

In the reviewer's opinion investigations of the type described above on well defined and possibly homogenous high molecular weight substances are very important especially in view of the fact that viscosity measurements are often used for the determination of molecular weights in polydisperse systems.

The influence of Brownian movement on the viscosity of solutions. R. Simha. J. Phys. Chem. 44, 24-34 (1940).

The present state of the hydrodynamic theory of the viscosity of dilute solutions of non-spherical particles is discussed. Particular attention is given to the case in which the orientation tendency of the flow is negligible compared with the intensity of the rotary Brownian movement. A formula connecting the viscosity with the dimensions of the suspended particles assumed to be rigid ellipsoids of revolution is given. The limitations of the theory are critically discussed.

Viscosity and the shape of protein molecules. J. W. Mehl, J. L. Oncley and R. Simha. Science, 92, 132-3 (1940).

The results of the previous paper are applied to solutions of thirteen proteins using viscosity data of various authors. The results for the dimensions of the protein molecules so obtained give in most cases good agreement with those calculated from sedimentation-diffusion data. The degree of solvation of egg albumin and thyroglobulin respectively in water is estimated from a combined use of sedimentation and viscosity results.

The viscosity-fluidity relations of proteins. Henry P. Treffers. J. Amer. Chem. So. 62, 1405-9 (1940).

The fluidity of various proteins is found to be a linear function of the concentration over a wide concentration range. The fluidity is

additive for mixtures of rabbit eu-and pseudoglobulin, and for horse albumin and globulin fractions.

The reviewer believes that the linear relationship is a consequence of the fact that the relative viscosity of a solution can be generally written as a power series in the concentration:

$$\eta_{rel.} = 1 + \gamma_1 C + \gamma_2 C^2 + \dots$$

Robert Simha.

BITUMINOUS MATERIALS.

In previous issues of the "Rheology Leaflet" mention has been made of publications dealing with attempted correlations of penetration results (1) with rheological properties and with descriptions of capillary rise viscometers (2) for bituminous materials.

In connection with penetration data it will be recalled that reference was made to an article by Mack (3) who stated that by calculation of a constant "c" from penetration results, the plasticity of an asphalt could be determined. Mill and Harrison (4) severely criticize the assumptions made by Mack, and the misleading conclusions drawn therefrom in regard to penetration- viscosity relations. They point out that Mack's reasoning is mathematically unsound, that his proposed relations can only hold under certain conditions which are inconvenient practically, and that penetration equations are less simple than appears from Mack's suggestions.

Two interesting contributions to the literature of capillary rise viscometry have recently appeared. The first, by Anderson, Wright, and Griffen (5) describes a modified Ostwald instrument which has three capillaries of decreasing bore arranged in series with intervening bulbs, so that the operator may measure the time of rise in the most appropriate section. The authors claim that for liquid asphaltic road materials this instrument is to be preferred to the Koppers viscometer because of the possible poor selection by the operator of the proper pressure to be applied in the latter instrument. It seems to the writer that this triple-capillary assembly may be much harder to fill and to clean, especially if it should be used in measuring the viscosities of the more fluid road tars, than the easily removable single capillary unit.

A more recent article by Lewis and Halstead (6) critically reviews the mathematics of the Koppers capillary rise viscometer, and presents data showing experimental results gathered for a wide consistency range of various asphaltic road materials at different temperatures. It is interesting to note that these authors use different distances of rise, to get appropriate times, rather than a change in the

capillary bore as suggested above.

They conclude that this capillary rise viscometer gives generally satisfactory results for asphaltic road materials over the range of 100 to 6,000,000 centistokes approximately, and especially recommend this instrument for the determination of viscosities of liquid asphaltic materials. They confirm the straight line relationship between double log kinematic viscosity and log absolute temperature, and report temperature susceptibility factors and lack of suitable correlation between kinematic viscosities and float test results for various asphalts at different temperatures.

Tar technologists may be interested in the suggestion by Blakeley (7) that viscosity and specific gravity data may be used to determine the type of coke oven road tar samples.

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3. J. S. C. I., 1939, 58, 306
4. J. S. C. I., 1940 59, 66
5. Ind. Eng. Chem., Anal. Ed., 1940, 466
6. Public Roads, 1940, 21, No. 7, 127
7. J. S. C. I., 1940, 59, 87

W. F. Fair, Jr.

HIGH PRESSURE EFFECTS.

"The Effects of High Pressure On the Activity of Pepsin and Rennin;" J. E. Matthews, Jr., R. B. Dow, and A. K. Anderson; J. Biol. Chem. 135, 697, 1940.

One aspect of this paper is related to rheology, namely the effect of pressure on reaction rates. It was found that the activities of dilute solutions of pepsin, and of rennin, in water decreased with pressure and length of exposure time at constant temperature. The loss of activity appeared to be result of denaturation of protein by pressure. The existence of more than one reaction rate was found under pressure conditions, and in no case was the reaction a monomolecular one. While the product of denaturation by pressure appeared to be similar to that of denaturation by heat, it was shown that the physical conditions are quite different. No hydrolysis effects were discovered as a result of the pressure treatment.

R. B. Dow.

PLASTIC BEARING MATERIALS

Properties and Performance of Plastic Bearing Materials,
L. M. Tichvinsky, A. S. M. E. Transactions for July, 1940.

The article describes the bearing materials bonded with synthetic resin. Rather complete data are given on the laminated materials, including physical properties as well as the results of various bearing performance tests. This information was gathered from various publications, as well as from testing in the author's laboratory.

All bearing materials bonded with synthetic resin can be divided into three types in accordance with their internal structure.

(1) The bearings of the first type are made from various plain or graphitic molding powders. Numerous kinds of bearings for light and medium load applications are made from these materials. Guide bushings for high-speed spindles, or gland materials for sealing purposes, are typical examples of the use of this material; these bearings perform under all types of friction, namely, dry boundary, and fluid. The application of these materials is rather limited because, as they are very brittle and fragile, impacts of even small magnitude may cause failure. Those made of graphite powder have a rather high heat-transfer coefficient.

(2) The second type comprises the most important and widely used bearings. Such bearing material is obtained by molding at high pressure and temperature sheets of woven textile fabric treated with an organic binder.

Laminated bearing material is strong and tough. Bearings made of such materials perform efficiently when lubricated with water in which case the latter serves as lubricant and as a cooling agent. Almost any liquid (except strong alkalis) can be used, and although it might be recommended sometimes to add a lubricant, e.g. tallow or suitable emulsion, to the water, these bearings do not require oil or grease.

(3) Bearing material of the third type is based on an internal felt-like structure. It is obtained by impregnating a felt of fibrous fillers consisting of cellulosic fluff, linters, and similar materials. The resin is generally precipitated from a thin aqueous solution (sodium hydroxide) on and in the felt-forming fibers.

The materials range in their physical properties between the brittle powder molding and the extremely tough and strong laminated materials. The original article should be consulted for data on moduli of elasticity, compressive-strength, heat conductivity, and general performance of some of these bearing materials.

ORGANIC PLASTICS

Physics of the Styrene Plastics. Technically Important Properties of the Polystyrenes. F. Horst Muller. *Wiss. Veroffentl. Siemens-Werke* 19, No. 1, 110-33 (1940)—The properties of polystyrene are given for a range of temperatures. The effects of drawing upon the change in strength is ascribed to orientation of the molecules into straight chains.

The Tensile Strength of Polystyrene Glass as Depending on the Temperature. Ernst Jenckel and Paul Lagally. *Z Elektrochem.* 46, 186-8 (1940)—The tensile strength of threads of polystyrene has been determined over a range of temperatures and was found to have a maximum at 50°C. Maxima such as this indicate that at this point the factor of brittleness is becoming less important and that the plastic is beginning to soften. Curves such as this might well be compared with hardness curves over the same temperature range.

Measurement of the Rheological Properties of Some Industrial Materials. G. W. Scott Blair. *J. Sci. Instruments* 17, 169-77 (1940)—The author lists the significant rheological properties of a new material as viscosity, elastic modulus, elastic after-effect, rate of shear or stress, the change of slope of the viscosity-stress curve, the amount of breakdown under shear which is only recovered slowly or not recovered at all, work or strain hardening, and tensile strength. Some description is given of methods for determination of these properties. He lists the rheological properties of a large number of industrial products, many of which are not commonly controlled by scientific methods.

Viscosity Variations in Methacrylic Ester Polymer Solutions. D. E. Strain. *Ind. Eng. Chem.* 32, 540-1 (1940)—Toluene is a solvent for methyl, propyl, and butyl methacrylate polymers while alcohols are non-solvents. However, the viscosity of the toluene solutions is greatly reduced by the presence of alcohols. Ethylene chlorhydrin, methyl acetate and methyl ethyl ketone have similar effects. No theoretical explanation is offered.

Measurement of the Flow Temperature of Thermoplastic Molding Materials. L. W. A. Meyer. *ASTM Bull.* No. 105, 23-6 (1940)—Four types of plastometers were used in an attempt to determine the relationships between the values found for five different thermoplastic resins. The Rossi-Peakes, Mooney and Dillon instruments showed straight line relations for all five materials. The Rossi-Peakes apparatus correlated with the Williams parallel plate plastometer only for

vinyl co-polymer and polystyrene, but not for ethyl cellulose, methyl methacrylate or cellulose acetate.

Dynamic Determination of the Elastic Modulus of Plastics. Kurt Frolich. *Kunststoffe* 30, 10-12 (1940.)—This method is based upon a determination of the fundamental vibration frequency of a thin sheet of the material. The elastic modulus can then be calculated by a formula. Vibration of the test sample is caused by an air blast of controlled frequency. The vibrating end holds a small piece of iron. The frequency is determined by means of the poles of an electro-magnetic circuit, an amplifier and a galvanometer.

H. F. Wakefield

Influence of Size of Molecule on the Properties of Industrial Thermoplastics. E. G. Couzens, J. A. Hetherington and L. W. Turner, *Chem. and Ind.* 59 209, March 30, 1940—The article is an extended review with some original data on the properties of cellulose and vinyl plastics.

The property of toughness is understood to be a combination of impact, tensile strength, extensibility, Young's Modulus and bending strength magnitudes. Each of these values has standards of measure but experience proves that the values of some differ widely with the method of test used; some, for instance polyvinyl formal, are very sensitive to such factors as the depth of notch used in a test bar. Values are always changed greatly by rate of application of load for all these strength measures. The size of molecules measured by classical methods can sometimes in one series be related to the measured strength but for each measured property there is a maximum above which increase in molecular weight does not register on the strength value. As between different plastics, the same molecular weight values do not mean the same strength values.

Then the authors call attention to the confusion in determined molecular weight numbers where nitrocellulose gave the same values by two methods, namely viscosity and osmotic pressure but the same two methods do not at all agree with the polystyrenes. The higher the temperature at which the polystyrene is produced the less the agreement between these two methods, so that, by reference to Staudinger, an initial temperature change from 20 to 80° C. made no molecular weight difference on the osmotic pressure molecular weights but gave molecular weights which varied in ratio of 3:1 when measured by viscosity methods.

The authors showed that apparent molecular weight measured at higher concentration is very sensitive to the proportion of low viscosity and high viscosity material used in the mixture. Data given also shows the dependence of the concentration curve on the solvent used, for instance, cellulose diacetate starts at lower value in formic acid solvent as compared to acetone but the formic acid specific viscosity curve increases faster and exceeds that of acetone at values above 0.2% concentration. Thus, even below 0.5% concentration the ratio of determined values shift from 26,000:23,000 to the reverse ratio 38,000:31,000. Such conditions cannot even be remedied by use of different constants for different solvents affecting the same polymer sample.

The application of load to a plastic results in increased density until flow starts; the density remains constant until an increase occurs later with reduced flow prior to the breakdown under load.

The determined molecular weights were concluded to be of no value for comparison of plastics of different chemical structure. The discussion of the paper gives the inference that the determining factor is the size of that portion of the chain situated between cross-bonds connecting one chain with its neighbors (in this connection, see the paper by Kistler, *J. Applied Physics* **11** 769, (1940)). Curves of dielectric loss against temperature were said to show great differences between solvents used with the same polymer which was thought to be the effect of force acting between the solvent and the polymer. Force between solvent and polymer was also used to explain the retardation of evaporation of the solvent mixture as compared to the free solvent.

H. L. Bender

The Thermoplastic Behavior of Linear and Three-Dimensional Polymers.... S. S. Kistler, *J. Applied Physics* **11** 769, (1940)—The relationship between the structure of the linear molecules, their side bindings and their physical properties is stressed. The word linear seems here to mean polymer and the side structures to involve both secondary force binding and true chemical linkage.

It is not clear to the reviewer that the Table 1 lists such relative **hydrogen** or secondary binding forces between the two molecules as is needed for the stated conclusion that the table shows the relative side attraction between linear polymers where these groups are present as the side chains.

The theory of large radical sizes and of radicals displaced in space by plasticizers seems logical but without direct evidence as bear-

ing on the strength of such polymer masses.

The curves show that all polymers drop in measured strength above certain critical temperatures, these critical temperatures being around room temperature for many linear polymers and above room temperature for the so-called cross-linked polymers, such as phenol-formaldehyde and some copolymers.

These differences in critical strength temperatures are said to be due to primary bonding. If so, there must be all shades of primary bonding either in strength or else in numbers. The author seems inclined to view the differences as being due to variation in comparative number of such primary cross-bonds. The main difference between the two classes is said to be the degree of extension at rupture, small for three dimensional and large for linear polymer structures. The main strength effect is thus considered as due to secondary forces the slippage of which allows overloading of such primary bonds as may be present. From the indications of force data there is thus no direct evidence for primary bonds but the author did not point out this alternate since the original definitions involved the assumption of some primary cross-linkages. Later on, when the effect of increased viscosity (supposed to be increased molecular weight) was found not to increase the moving portion, then the molecule is supposed to move in part only, at one time. In this case also the determined data here gives no basis for the assumption that the molecule is larger than the moving unit.

The imagined mechanism of flow as given here involves flow of a portion of long chain molecule without disturbance of the balance of its own chain; perhaps the chain even acting as a brake to make the flow even more local in nature.

This local movement is necessarily related to a cross-area of chain portion in the place of shear and this, times the distance moved, will give a "viscous volume" quantity which when found to be large is expected to define a large volume of the moving groups since the various distances moved are expected to be in the same order of magnitude per each such jump—as shall not disturb the remaining connected atoms in each polymer. The picture is given of a moving unit surmounting a barrier which entails $\frac{1}{2}$ energy push and $\frac{1}{2}$ free glide for each moving group producing such a "viscous volume" effect. Then the resulting equation:

$$N = \frac{\Delta f}{\sin h Bf/T}$$

gives a viscosity which should not be a linear function of the applied large force. Thus, for Gelva a 4 per cent change in shearing stress

sometimes produces a four-fold change in viscosity expressed as poises; that is to say, the chosen mathematical formula agrees in order of magnitude with the experimental facts.

Experiments show that a sudden reduction of load is followed by a period of recovery preceding the start of relaxation under the new conditions of experimental load. This slowness in response to load makes for irregular experimental values if the stresses per cross-section are varied. The best conditions are thus found at constant load with measurement of elongation rates. From three experimental curves it was then found possible to calculate the viscosity at the same per cent elongation. The activation energies to start the particles in motion are found from the determined "viscous volume" values and are found to vary from 54,000 to 86,000 for various tested Gelva polymer masses and to be as high as 170,000 for Formvar 15-95. These activation energy values go up with the elongation (Fig. 6) and the movements go down with the per cent elongation.

The influence of molecular weight (or should one say viscosity measure) on the determined movements and on calculated activation energy is not at all evident. Thus, the moving group is either not the molecule, or else the molecular weights for the different vinyl acetates are constant in which latter case the known differences in viscosity would have to be due to other causes than the variations in molecular weights. For some unknown reason one low viscosity sample shows a high activation energy which is explained as being low enough in chain length to be within the border of crystallization ranges. High activation (E) energy is reflected in rapid softening with raise of temperature.

Rubbers have large "viscous volume" values and small activation energies; otherwise the picture is the same as for resinous polymers. Milling of latex rubber results in great lowering of the activation energy. This is considered due to smaller pieces in the milled rubber rather than to smaller distance of motion. The extreme activation energies (40,000) found are only $\frac{1}{4}$ of the value needed to break a carbon to carbon bond so in order to break bonds they are assumed to be partly weakened as by oxygen pick-up, since a full carbon to carbon bond requires four times the observed experimental value.

The author reasons that activation energy values are a measure of the moving part and that the viscous volume is then a measure of the internal viscosities, high volumes meaning quick retraction.

The assumption, then, of cross carbon linkage in polymers is

discarded as to strength effects but is retained as an explanation for variation in extension effect under load and for variations in plastic deformation under load. Activation energy values found indicate that the average bond broken is not a carbon to carbon value and therefore such carbon bonds are only broken after some initial reaction to weaken the bond, such a case being oxygen addition to rubber bonds followed by breakdown on milling procedure.

The reviewer wonders if all these artificial devices, such as movement of a part of a molecule, are needed to uphold the original assumption that polymers necessarily involve carbon to carbon long chain and cross-chain bonding, an assumption originally made to explain the fact of:

(a) high determined molecular weight values, which in themselves are not in good agreement.

(b) high strengths of polymers as compared to easily meltable crystals. Compare, however, to the metals and rocks.

(c) high viscosity effects in solutions. Compare, however, the viscosity changes from solvent to less solvent liquids.

Perhaps an easier way is not to make the carbon to carbon bond assumption.

H. L. Bender.

VISCOSE RAYON: STRESS-STRAIN PROPERTIES

II. Effect of Rate of Load

By H. R. Bellinson, Textile Research, vol. X, June 1940,
No. 8, pp 316-322. (A Textile Foundation Publication).

The effect of varying the rate of load upon the strength, breaking stretch and load-stretch diagram of viscose yarn is described. Tests were made on an inclined-plane machine, in which the rate of increase of load is constant throughout any one test.

The strength increased as the rate of loading is increased

$$S = 2.3R + K$$

where S is the breaking strength at rate of load R, and K is related to the inherent strength of the material. The breaking stretch appears to be unaffected by change in rate of load. The only portion of the load diagram which appears to be definitely affected by the rate of load at which the test is performed is the "elastic limit," which increases with the rate of loading.

H. F. Schiefer.

WORKABILITY AND PLASTICITY OF CONCRETE AND MORTAR.

The following discussion is confined to systems of broken solids composed of hydraulic cements and aggregate. These solids are to be mixed with sufficient water to allow them to be conveniently placed, but little if any segregation should occur during ordinary handling.

Hydraulic cements include hydraulic lime, natural cement, portland cement, aluminous cement and mixtures of hydrated lime or clay with portland cement. These cements have the property of hardening under water. Portland and aluminous cements are clinkered or fused during burning and contain few particles ground below 1 micron. In the other, weaker cements, the particles are often quite fine. Indeed, as in hydrated limes, the larger particles are mostly clumps of the very small unit crystals. The finest particles play an extremely important role in the placing of concretes and mortars.

Aggregate is usually divided into fine and coarse, the separation generally being by means of a screen with openings of about 6 mm. For masonry mortars the upper size may run to only about 2 or 3 mm.

The aggregate may have been worn into a more or less rounded shape by water or glacial action. It may also be produced by crushing natural rock or industrial slags. Considerable variation in particle shape is observed. It is the presence of this aggregate which complicates the analysis of the rheological properties of concrete and mortar.

The functions of the aggregate are manifold. The most important one is to lower the cost. The aggregate reduces the shrinkage as excess water evaporates from the mass. It serves as a system of keys against the development of fracture planes. In placing the concrete, the inertia of the aggregate greatly helps to flow the concrete or mortar into place. This may readily be observed by mixing the cement neat, that is, with water only. The mix is then much like clay and water, coherent and with an appreciable yield value. On adding fine sand and then coarser sand and finally gravel progressively, with more water to keep the mass workable, the character of the mass changes greatly. The aggregate grains roll over each other and through the cement paste, reducing its coherency and yield point. A little experience will indicate when a properly balanced mix has been obtained. If a suitable selection of sizes is chosen, the smaller grains act as ball bearings over which the larger grains roll. This rolling is obviously affected by the particle shape, suggesting an advantage in using rounded aggregate.

The packing of the aggregate is of importance from an economic standpoint and for the durability of the product. Two systems of good packing have been proposed by Furnas (1), on the basis of mathematical analysis. In the one giving best packing, only two or three sizes of material are used to give an intermittent or gap grading. The other method, involving a continuous grading from fine to coarse, had also been worked out empirically by Anderegg (2).

In portland cement (2) the best grading is logarithmic. In sands for mortars (2), the ratio of the fractions, separated by standard sieves should be 1.2 for rounded particles and about 1.15 for irregular grains, such as crushed marble. The less regular particles have more voids and hence require more fines to fill in. In concrete, with a much larger range in sizes, this ratio of successive size fractions may vary from 1.2 to about 1.4.

It is an interesting empirical fact that the same graduation of continuous sizes, which gives excellent packing, also gives excellent workability. The mathematical analysis of this has not been worked out. Another coincidence is that in crushing natural stones, many machines grind to a product approximating this ideal, continuous grading.

The ease of placing of a harsh working concrete can frequently be greatly improved by the addition of small amounts of fine sand. At the same time, a reduction in water requirement is often secured. The addition of fine sand must be made with caution, since if too much of any one size is added, it interferes with proper packing and workability (2, 3). In the same way, if the cement contains an excess in any one size, its packing and workability are interfered with (2).

Extending the principles of void filling to the cement portion of the system, a finer material than portland cement can often be used to advantage. But with such particles, the layer of absorbed water or lyosphere becomes quite important. Assuming a thickness of $\frac{1}{2}$ micron for this layer, the bulking of a particle 1 micron thick would be 700 per cent. As in any plastic system containing heterogeneous constituents, this lyosphere plays an extremely important role.

On adding water to the dry mix, the first portion is absorbed on the surface to build up a tightly held layer of moisture. Then any voids present have to be filled and after that, as water is added, the particles become separated so that their mobility is increased. According to this conception, mixing water performs three initial functions; it is absorbed on the surface of all solid grains; it fills the voids between the grains; and it separates or floats the solid particles to give better workability. After the first two functions are satisfied, a relatively small addition of water usually changes the mobility considerably.

The first water molecules apparently line up on the solid surfaces according to the polarities. They are held tightly at certain points in very definite orientations. These orienting forces then seem to line up many layers of molecules. Estimates vary for the thickness of such highly oriented water from 25 to 40 A. Outside of this layer the molecules still feel the effect of the orienting forces, but to a lessening degree. The decrease is apparently logarithmic, according to Massey (4), who has studied clay between porous pistons. The outer portions of the lyosphere, being held much less rigidly than the inner portions are susceptible to movement under mechanical pressure, but require a certain minimum force to start flowing or yielding. This force is called the yield point.

The thermal agitation of the molecules in the outer layers aids the yielding, so that the yield point is determined by a combination of temperature and of the rate of load application. For very small pressures applied over a considerable time, there may be some perceptible flow, corresponding to the cold flow in many thermoplastic organic materials. This may be connected with the distribution of thermal

energies among molecules, which follows a well known exponential distribution law derived by Maxwell. According to this viewpoint, Bingham's classical critical yield point for plastic systems would need revision. It has been frequently observed, experimentally, that many plastic systems do not have a straight line relationship between flow rate and pressure in the lower part of the curve.

Based on Massey's observations, logarithmic relationships might be expected to hold and Roller (5) has found that plotting the log. of the deformation of a plastic body under a steadily increasing load against the log. of the load, a straight line may be drawn through the experimental points. Again, Gauss (6) on pushing thin portland cement pastes through capillary tubes found the log. of the pressure to be proportional to the log. of the flow rate. By varying the water content, a family of parallel, straight lines would be obtained. Different cements had different constants, including the slope of the curve and the intercept with the pressure axis. These differences are apparently caused by variations in fineness.

Small amounts of certain wetting agents have interesting effects. Commercial stearic acid, tannic acid, oxidized rosin, and several others have been applied commercially. It was first thought these polar-non-polar molecules had the ability to line the capillaries with their non-polar ends to resist water inflow. More recently it has been observed that air froth is formed in the mass when these agents are added. The bubbles have excellent mobility and an appreciable amount of water is apparently absorbed or bound at their surfaces.

While the compressive strengths of concrete may be diminished by included air, its durability is often increased. The reason for this lies in the phenomenon of "bleeding". Sufficient water has to be added to concrete to float the particles so that they may be worked into place. On standing the solids settle and part of the water travels upward. It may be trapped under the larger particles, but most finds its way to the surface. It tends to follow definite paths. After the concrete has dried out, these paths permit the ready ingress of corrosive solutions, such as sulfuric acid from winter rains. They also permit salt and ice crystals to grow in oriented directions to gradually disrupt the concrete. The finest of the aggregate and the fine air bubbles are very helpful in holding the mixing water immobilized. In this way bleeding is reduced and few if any capillaries are formed.

Several attempts have been made to devise apparatus for studying workability quantitatively. But the interplay of the various fac-

tors is so complicated that the surface of the problem has hardly been scratched. A new attack is needed based on thorough analysis. For this purpose the following statements are tentatively offered:

WORKABILITY is the ease with which mortar or concrete can be worked into place. Masonry mortar must flow off the trowel readily and yet be coherent. It must be sufficiently sticky to adhere to the ends of the units. Stucco mortar must flow out uniformly into a thin layer under the plasterer's trowel. Concrete must flow around reinforcing. A synonym of "mobility".

PLASTICITY results from the water absorbed at the surfaces of solids and of air bubbles. Plasticity will be assumed to be proportional to the interfacial area. Synonyms of plasticity used in practice are "fatness" and "stickiness".

CONSISTENCY is determined by several factors, but for purposes of simplification, it will be defined as "wetness". It is assumed to be proportional to the amount of water added after the absorbed layers are built up and voids are filled. This wetness-water floats the particles apart and is necessary in most mortars and concretes. It is believed that use of the word in this sense, while opposed to best rheological practice, is in line with common usage in the concrete and mortar fields.

In addition to surface areas and wetness, the size distribution of all the solids, especially of the finest sizes, must be accurately determined. Information must be obtained as to the shapes of the particles. The distribution of air bubble sizes must be worked out, as well as the thickness of the water immobilized at their surfaces.

The principles covering workability will best be determined by making up synthetic systems with factors under definite control. Flow rate-pressure curves should be determined and curves for other types of deformation over wide ranges of consistency should be worked out for systems of several definite gradings.

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