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## THE RHEOLOGY LEAFLET

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### **ANNUAL MEETING FOR 1939**

The Eleventh Annual Meeting was held as scheduled at the National Bureau of Standards on the 13th and 14th of October, 1939. The sessions were well attended and the comments upon the program were quite favorable. The Society is truly grateful to the local Committee on Arrangements for the time and thoughtfulness which made the meeting such a success.

#### Symposium on Rheology in Science and Industry

The greater part of this symposium was not presented for general release and cannot be reproduced in this publication. After a most courteous welcome by Dr. Lyman J. Briggs, Director of the Bureau the symposium was opened by Dr. A. S. Hunter.

The first contribution was by **Dr. J. H. Dillon** of The Firestone Tire and Rubber Company. His review, which is given here in slightly reduced form is titled **"Rheology in the Tire Industry."** 

#### INTRODUCTION

The principal basic materials entering a tire plant are; Crude rubber, latex, fabric, steel bead wire, and rubber pigments. All these materials present rheological problems which must be dealt with in the laboratories of a tire factory. For the sake of brevity, however, this discussion will be confined to the rheological applications of rubber in tire manufacture.

#### RHEOLOGICAL PROCESSES IN TIRE MANUFACTURE

Briefly stated, the treatment of rubber in most types of rubber manufacture consists in first mechanically breaking down the highly elastic crude rubber into a less elastic moldable state; second, incorporating certain materials called "pigments" (softening, vulcanizing, and reinforcing agents, fillers, and age resistors), third; fabrication to the desired shape; fourth, molding under pressure; and fifth, restoring the elastic properties by heating while under pressure in the mold (vulcanization or "cure"). The methods of executing these processes in a tire plant are shown schematically in the chart (Fig. 1).

The crude rubber enters the tire plant in 250 lb. bales of smoked sheets or crepe. The bales are cut into several smaller pieces which are then ready for the 1st fundamental process, "mastication" or "massing". Referring to the chart, we see that there are two basic methods of massing. Much crude rubber is now massed in the machine called a plasticator. It consists of a variable pitch screw turning in a cylindrical chamber with corrugated walls. The cut bales are fed into a hopper at the high pitch end of the screw and the rubber is forced through the barrel to the low pitch end where it is under extremely high pressure and temperatures of 300° F. and higher are generated. It is then extruded from a die in the form of a rough sheet. The mechanical working caused by the screw combined with a certain amount of oxidation at high temperature produces the desired breakdown. The older method is accomplished on a mill. The mill consists of two hollow steel rolls rotating as shown with the front roll surface speed somewhat lower than that of the back roll. Cooling water is sprayed against the inside walls of the rolls. The cut bales are placed on the rolls and allowed to go through the bite until the rubber knits into a hot dough. It then tends to follow the front roll and is cut and folded back on itself repeatedly by a millman or an automatic knife so as to accelerate the grinding and tearing action.

A comparison of the two methods shows that the plasticator method is more economical but does not give as uniform breakdown as the mill method. The type of breakdown is not quite the same in the two machines for, because of the higher temperature generated in the plasticator, the oxidation action is proportionately greater than in the case of the mill. Obviously, the massing operation involves rheological study and control both of the crude rubber and the massed product. It should be mentioned that crude rubber is sometimes washed on a corrugated mill with water sprayed into the bite. Only a small fraction of crude rubber is washed, however.

The next rheological process is mixing. The more modern Banbury mixer is somewhat like a huge bread mixer with a high pressure ram at the top. The walls are water cooled. The rubber and pigments are introduced at the top and ground up together under high pressure. In spite of the water cooling, high temperatures are generated in the mixer. Hence, in most cases, the sulfur is not introduced in the Banbury, in order to avoid premature vulcanization (set-up). In some cases, only carbon black is introduced with the rubber into the Banbury. The resulting rubber-black mixture is called a black masterbatch. The other pigments are added on a mill usually located directly below the dumping gate. The older mill mixing method is still very important. It is similar to the mill massing process except that the pigments are added and worked into the rubber with the aid of manual cutting or an automatic knife. The final mixing of a stock often consists of milling together masterbatches of the various pigments with rubber which may have been mixed in a Banbury or on a mill.

It might be well to inject a few words about rubber pigments at this point. Every pigment used in a first line tire stock has a definite function. No "fillers", that is, materials added only to reduce cost are used. Sulfur is the principal vulcanizing agent. Various organic accelerators such as Mercaptobenzothiazole are used to reduce the time of vulcanization. Such accelerators also produce better physical properties in the vulcanizate. Zinc oxide is added to activate the accelerator and to produce higher heat conductivity. The principal reinforcing agent is carbon black, used particularly in tread compounds. Other organic materials called antioxidants are added to improve the aging properties of the stocks. Still other materials called softeners are added to the rubber early in the milling process to facilitate breakdown.

The cement mixing operation is also included in the chart since cements are used in the tire building operation. Cements are made by stirring massed rubber or compounded rubber into a solvent by means of paddles or screws. In some cases, "dips" are made in this manner. "Dips" are used for impregnating the cord fabric in order to produce adhesion between rubber and fabric. Other types of cements and dips are made directly from latex and water dispersions of other materials. Cement mixing is a science in itself and requires considerable rheological research and control.

After the massed rubber has been properly mixed with the required pigments to form compounded stocks, it must be fabricated into the proper form for tire building. The two principal fabricating methods are extrusion ("Tubing") and calendering. However, before the stock can be tubed or calendered, it must be warmed up and sometimes refined. The warm-up process accomplishes two objects; namely, temporary softening due to increased temperature and thixotropic softening. This is usually accomplished on a small mill and the "warmed-up" rubber is run directly into a tuber or calender. The refining operation is accomplished with a mill having a very small roll clearance (bite) so that any undispersed pigment lumps are broken up. Most inner tube stocks are refined in an effort to avoid thin spots.

The extrusion process in tire manufacture is limited to the formation of inner tubes, treads, and beads. In the formation of beads, which give tire rigidity and hold it to the rim, semi-hard rubber stock is extruded from a die through which the required number of strands of steel wire are pulled. The rubber-bound wire bundle thus formed is then wrapped with rubber-coated fabric. Inner tubes are extruded from a circular slit formed between a die and mandrel. The tube walls are water-cooled and a lubricating powder such as soapstone is blown into the extruded tube to prevent the tube walls from sticking together. Treads are "tubed" in a similar manner except that no mandrel is required. Because of the high carbon black content of tread stocks, they are very stiff and generate very high temperatures in extrusion under the high pressures necessary. Many rheological problems arise in the tubing operation for the tuber screw causes additional breakdown of the stock which tends to vulcanize at the high extrusion temperatures.

Thus, great care must be used in interpreting results of consistency measurements made on the stock before entering and after leaving the tuber, respectively. In some cases, an extruded stock appears softer than the feed stock when, in reality, it has set-up (prevulcanized) more than the desirable amount. Consistency measurements at several temperatures generally will detect this condition.

The calendering process is illustrated in two of its applications in the chart. In "gum calendering" a "warmed" stock is forced between the heated rolls and rolled out into a thin sheet. The center roll is generally slightly hotter and runs faster than the other rolls. Sidewalls and sometimes combined tread and sidewalls are formed with calender rolls having grooves of appropriate shape and size. The thin gum strips and tread cushion are formed on rolls that are slightly crowned to compensate for deformation of the rolls. The carcass stock is calendered to the cord fabric as shown in the chart. When the fabric has been previously dipped in some sort of rubber solution or dispersion, the surface speeds of the rolls are equal and the process is called skimming. When the fabric has not been dipped, it is usually necessary to employ differential speeds on the various rolls in order to work the carcass stock more deeply into the fabric. The rheological problems found in calendering are similar to those associated with tubing. As in the tubing process, the stock recovers in thickness after

passing through the rolls and the control of gage is a problem which requires great skill on the part of the operator even when one of the several commercial automatic roll clearance regulators is employed. Rheological uniformity of the warm-up stock is very important.

After tubing and calendering, the tire manufacturing process ceases to be strictly rheological. The next group of operations consists in cutting the various tubed and calendered elements to the size required for a tire. For example, the cord fabric is cut on the bias and is either plied up in pairs of plies with reversed angles or built into bands of two plies each. The process of tire building involves laying the various elements on a drum and, by means of various wrapping and "stitching" operations, producing a cylindrical structure. This cylindical structure is placed between two platens and compressed into a toroidal shape while a thick-walled inner tube called a "bag" is inserted.

The resulting "bagged green tire" is inserted into a mold which is closed under high pressure and is then cured (vulcanized) with hot water or steam in the bag and the mold heated with steam or other means. The molding process, of course, involves rheological work.

#### **RHEOLOGICAL TESTING**

The so-called "plastic flow" of unvulcanized rubber is measured with three general types of instrument; namely, the parallel plate compression type, the extrusion type, and the shearing disk type. In general, because of the complex nature of the rate of shear versus shearing stress relationship, these flow measurements are empirical in nature. However, the shearing disk plastometer can be used for absolute measurement of consistency at a given rate of shear, temperature and thixotropic equilibrium. Both the compression and extrusion plastometers are sometimes used to measure elastic recovery as well as consistency. Measurements of consistency of the crude rubber as well as of the massed and compounded stocks are usually routine operations.

The evaluation of vulcanized rubber stocks involves too many physical tests to describe in this brief talk. Of these, the tensile test on dumbell or ring specimens is the oldest and most thoroughly standarized test. Both tensile strength at break and modulus at various elongations are obtained at speeds generally in the range 10 - 30 inches per minute. Another standard test is the hardness or penetration test made with a spring or dead weight-loaded plunger projecting beyond a flat "foot". Resilience and hence hysteresis are measured by rebound of a falling ball or pendulum hammer. The "T-50" test which involves measurement of the temperature of retraction of samples frozen in an extended state is finding increased support as a method of determining state of cure (degree of vulcanization). Measurement of modulus and hysteresis at low elongations and high frequencies (the conditions of tire service) is made by several methods but has not yet become standard among rubber technologists.

The endurance type of test is used in a great many forms. One important type of endurance testing machine which yields results of great practical value is the flexometer in which heat generation is studied and resistance to blowout is measured.

In addition to measurements on the rubber stocks going into a tire, the raw fabric must be evaluated by tensile and dynamic flexing measurements. The plastic flow of raw cord is another property which is measured in order to predict the inflation growth of tires. The fabric-rubber bond is evaluated by adhesion and endurance tests. The dips and cements are evaluated by various types of viscosity and film strength tests.

Tests made on finished tires are the final criteria of the effectiveness of laboratory tests. Tires are tested both on indoor machines and in road service for tread wear, separation, flex break, growth, etc.

### NEW PROBLEMS IN RUBBER MANUFACTURE

The materials going into tires are constantly being changed, thus necessitating changes in construction. Conversely, improvements in construction often develop the need for new types of stocks and fabrics. A typical example of this trend was the introduction of rayon as a tire fabric. Thereafter followed long and painful researches in an effort to develop a method of tire construction which was compatible with its properties. At the present time there is much interest in synthetic rubbers, such as the German "Buna". They have very different properties from those of natural rubber and require a whole new method of testing and analysis. The possibilities of direct use of latex in rubber products are very interesting and will without doubt introduce more complicated problems for the rheologist in the rubber industry.



G. G. Sward, Institute of Paint and Varnish Research discussed "Rheology in the Paint and Varnish Industry".

As in many other industries, rheological properties are widely used in the paint and varnish industry for manufacturing control, purchase specifications, and for resarch. Most of the devices used are the well-known types of viscosity cup, torsion, falling ball, bubble, Mobilometer, etc. No single device appears to meet all requirements. For the plant control of paints, the Gardner Mobilometer and the Krebs modification of the Stormer viscometer are the most important devices used. Determinations obtained with these devices are made solely to assist in controlling the uniformity of the paint, and bear no simple relation to the practical property of ease of brushing. In the cooking of varnish the consistency of the hot cook is often used as a signal for the end of the cooking stage. The consistency of the finished varnish is almost universally determined with the Gardner-Holdt bubble tubes, that of nitrocellulose and other lacquers, with the viscosity cups.

An interesting problem is the leveling of brushed films, involving as it does a careful control of the thixotropic characteristics of the paint.

The nature of resin solutions in the many types of solvents and thinners used in the paint industry has been studied by means of viscosity measurements.

**Dr. L. H. Adams,** director of the Geophysical Laboratory of the Carnegie Institution, described how even the earth's bedrock is subject to flow under pressure. The flow of rock is a distinct problem in Geology and must be considered in connection with changes in the contours in the mountains and ocean floors. Beds of solid stone which could only shatter or crumble if intense pressure were applied at the earth's surface will flow like molasses when miles deep. The reason for this is that the stone is supported from all sides and loose particles have no place to flow. This flowing ability of the earth explains how mountains have been lifted and oceans have sunk. Recently these conditions have been artificially reproduced by causing marble blocks to flow within a steel jacket by exerting a pressure of 200,000 lbs. per square inch.

**Dr. Wilmer Souder** of the Bureau of Standards, specialist in dental materials reported that while amalgam. fillings for cavities have been successfully standardized there has not yet been developed a natural color false plate which will not lose its shape. The reason for this is that the plastic materials in these natural color plates flow or sag under pressure. This problem of flow has been solved in the manufacture of amalgam but the person requiring a fill denture still must choose between one which is darker than his gums but wears well, or the type that is a perfect match with his gums but which will deform during use. Work is being continued in the Bureau with the hope that eventually more suitable materials will be developed with properties of rigidity, toughness and stability which may be standardized on scientific principles.

In addition to the announced program **Dr. A. S. Hunter** gave a paper on "The Influence of Applied Stresses Upon Physical Properties of Rayon". He pointed out the fact that the physical properties that are often attributed to yarns may be of a temporary nature and they may not really represent the fundamental properties of the system in question. Frequently applied stresses impart new properties to yarns and if these stresses are removed by allowing the yarns to relax in hot water, marked adjustments may occur so that the now relaxed yarns will possess physical properties which may be utterly different from those originally measured. This condition should be recognized in the evaluation of textile samples. A request has been made that Dr. Hunter reformulate his outline into an extended summary for publication in a future Leaflet.

#### **INSPECTION TRIPS**

Friday afternoon was devoted to inspection trips, each guest selecting the laboratory or institutions in which he had the greatest interest. From reports on these trips they may be considered to have been a very valuable part of the meeting. Specialists in the various fields of interest to the Rheologist were most courteous in explaining their objectives and their technique.

#### THE CONVENTION DINNER

The dinner which was held at the Wardman Park Hotel on Friday evening had not been announced in the Leaflet for final arrangements had not been completed. About thirty-five members enjoyed the excellent food and the stimulating intellectual fare. Dr. Lyman J. Briggs described the fundamental scientific work in progress and contemplated by the Bureau and discussed the importance of Rheology in the broad outline of scientific knowledge. He then introduced the principal speaker of the evening and recounted his many contributions to fundamental physical science. The speaker, Dr. Paul R. Heyl, Chief of the Sound Section of the Bureau of Standards is well known to readers of The Scientific Monthly as a writer on things both physical and philosophical who combines an imposing familiarity with higher mathematics and a no less considerable sense of humor. Possibly his outstanding contributions to science have been the redetermination of the constant of gravitation, G, (Bureau of Standards Journal of

Research, Vol. 5, December, 1930.) and his absolute determination of the value of gravity, g, (Paul S. Heyl and Guy S. Cook. Ibid. Vol 17, December 1936.). In connection with this work he had the opportunity to examine the records of the Royal Society of London and in his talk entitled "Eighteenth Century Science from the Archives of the Roval Society" he told us about some of the material he uncovered. From this unusual opportunity Dr. Heyl drew much that is truly amusing, in particular the sad case of the noble lady who met her end from spontaneous combustion, and at the same time many incidents that we today may consider with profit. The Royal Society had to confute the same sort of perpetual motion schemes as the ones the Bureau of Standards must explain today. [While the earlier scientists did not have the same concepts of energy that we now have they showed considerable ingenuity in demonstrating the fallacy of the various devices presented. Dr. Heyl reminded us that while science has scored many advances in the last century there still remain many mysteries to be solved. So many of the basic problems of science still await solution that after all, the attitude of the research worker today should not be so different from that of his predecessor 150 or 200 vears ago. The electron is one of these mysteries. While physicists today know about momentum and kinetic energy which their seventeenth century predecessors did not, the present task is to decide whether the electron is a particle of a train of wayes.

#### SATURDAY MORNING PROGRAM

The first hour was devoted to consideration of the report of the Committee on Definitions and Nomenclature. A Summary of Criticisms had been prepared by Dr. Mooney and these criticisms were discussed in considerable detail but with no general agreement. The final decision of the members present was that the report should be revised in some manner so that the criticisms could be embodied in it and that it should then be presented to the entire membership either by mail or through the Leafelt so that a ballot could be taken. This will be carried out during the first part of 1940.

#### A Three-Dimensional Model to Demonstrate The Relationship Between Principal Strains and Simple Shears, Abstract by M. Mooney.

The model represents in proper space relationships the axes of principal strains in a deformation at constant volume and the axes of the corresponding simple shears. The model consists of two sets of Cartesianaxes mounted inside a large spherical glass flask. A stationary set of axes represents the principal strains and a movable set with the same origin represents the axes of simple shears. A series of neutral lines is painted on the surface of the sphere, a different color being used to represent each different ratio, r, of algebraic maximum to algebraic minimum principal strain. When the movable axes are set so that all three intersect the sphere in the neutral line for a particular value of r, the orientations thus determined is a possible orientation of axes with respect to which the particular deformation consists of shears only, with no elongation along the axes.

Note On The Use Of The Rolling-Ball Viscometer For Measureing The Effect Of Pressure On The Viscosity Of Liquids, by Raymond B. Block. This paper occasioned considerable discussion. The publication medium has not yet been decided.

Computation Of Some Physical Properties Of Lubricating Oils At High Pressures, by E. B. Dow and C. B. Fink is to be published in the Journal of Applied Physics.

**Neglected Fields Of Rheology**, by **E. C. Bingham.** This was a most interesting review of some phenomena which are ordinarily not considered in terms of rheology but which on close examination prove to be largely problems of flow. It is hoped that this entire review will be available for publication in the near future.

**Psycho-Rheology by G. W. Scott Blain (1)** and **F. M. V. Coppen (2)**, National Institute for Research in Dairying, University of Reading, England.

Rheology has been defined as the science of the deformation and flow of matter, and is concerned with changes of form (strains) produced by the application of stresses of various kinds during finite

1) Rheologist 2) Psychologist

periods of time. The phenomena of rheology are thus described in terms of stress (generally shearing stress) S, strain  $\sigma$ , and time t, and these are generally given in c.g.s. units, except when measurements are made for purely practical purposes, when arbitrary units, sometimes convertible into c.g.s. units, are used.

Matter has from the earliest times been thought of in terms of three states, solid, liquid and gaseous, and these categories appeared all the more convenient to the classical rheologists when it was found that solid materials showed a simple relationship between S and  $\sigma$  over wide limits, S being proportional to  $\sigma$  (Hooke 1678), and that liquids obeyed an almost equally simple law, S being proportional to rate of flow d  $\sigma$ /dt (Newton 1685).

It was some time before it was realised that the usefulness of rheology to the community must depend on its application to materials which obeyed neither of these simple laws, although Palissy, a practical rheologist, discussed the flow properties of pastes and doughs as early as about 1540 without making any specific assumptions about the S:  $\sigma$ : t relation.

Trouton and Andrews (1) were probably the first to make a detailed study of the flow properties of a material which deviated but slightly from truly fluid behaviour. (Pitch). They showed, in effect, that the introduction of a small term to allow for the anomalies, permitted a Newtonian type of equation to be applied. This type of treatment was much more fully developed in the work of Bingham (2) and, for special cases, in the theoretical analyses of Buckingham (3), Reiner (4) and many others.

At the other end of the scale, work on imperfect elasticity in materials such as muscle, rubber and fibres had led to modifications in Hooke's law to allow for incomplete or non-instantaneous recovery. Finally, for materials in which viscous and elastic properties are about evenly balanced, two-term equations have been proposed, one term allowing for viscous flow being Newtonian in form, and the other being an elastic (Hookian) term. In some cases the latter term is itself modified to allow for elastic after-effect. As an example may be quoted the equation of Schofield and Scott Blair (5) in which de/dt, the rate of extension of a dough cylinder is given by

$$\frac{de}{dt} = \left(\frac{1}{n}\frac{ds}{dt} - \frac{d\alpha}{dt}\right) + \frac{s}{\eta} ,$$

where n is the shear modulus,  $\eta$  is the viscosity, and d  $\alpha$  /dt a term to allow for elastic after-effect.

This equation proved useful in application to the properties of flour doughs, but there are two facts about it which must be borne in mind. First, n and n, which are constants for solids and fluids respectively, are very far from constant for doughs and secondly, the calculation of n and  $\mathbf{n}$  depends on a division of the strains actually observed into two parts, a recoverable part, and a non-recoverable part. The line of demarcation between these two is not hard and fast. but depends on the time during which recovery is allowed to proceed. Dough shows true hysteresis apart from after-effects, which means that the elastic elements will never recover completely, so that their permanent strains have to be included, together with the slipping of the units past each other, all within the heading of plastic flow; nor can these two essentially different types of strain be, in fact, differentiated. These facts do not in any way diminish the value of two-term equations, but in considering the alternative suggestions that follow. they should be borne in mind.

In practice, in many industries the rheological properties of materials are assessed subjectively by touch and handling. Apart from rupture properties (crumbliness, shortness, etc.) and stickiness, which are not so directly connected with the  $S : \sigma$ : t relation, the properties most generally assessed are firmness (and its opposite, softness) and spring (springiness, opposite deadness). Firmness is one of those conceptions not exclusively associated with any one set of physiscal dimensions. If a person is asked to compare the weights of two objects, although he may be influenced by differences in volume, he will, whatever the materials, at least attempt to restrict his judgment to differences in mass. But if asked to compare for firmness two samples of a truly viscous bitumen he will judge by viscosity, whereas if rubber samples are presented, his judgment will depend on compression moduli differences.

An interesting experiment consisted in presenting subjects, one in each hand, with a sample of rubber and one of bitumen of the same size and shape. When adequate precautions were taken to eliminate right-handedness, temperature variations and so forth, it was found that in judging firmness, if a single bitumen sample was compared with a series of rubbers of varying modulus, a reversal of opinion could be obtained over quite a wide range of moduli if the time during which compression was allowed was varied. Thus the rubber sample would appear softer for a half-second compression, but the bitumen was chosen as softer if four seconds were allowed. Similarly a range of viscosities was found over which reversals could be obtained in comparing with a single rubber sample. In comparing two samples of cheese or flour dough which differ in spring as well as in firmness, it is clear that the time factor is very important, and also that firmness has dimensions which depend on the spring of the materials.

We have carried out experiments  $(6)^*$  on the smallest differences in firmness (viscosity) which can be correctly detected eighty times out of a hundred for about a dozen subjects, using samples of California bitumen of viscosity of the order of 10 poises. That these samples were very nearly true fluids was established by the method of Rheograms (vid. Schofield and Scott Blair) (7). There were no significant differences between subjects taken as individuals, and a "threshold" (in the above sense) of 30 per cent was obtained.

A similar experiment was carried out using samples of rubber differing slightly in compression modulus  $(8)^*$ . In this case, there were significant differences between individuals, but if a mean is taken, the threshold is found to be 9%. The compression moduli of the samples were of the order of 10 c.g.s. units.

In both these experiments, the subjects were judging firmness, and it is interesting to enquire why they could judge with three times the accuracy in the case of approximately elastic rubber that they could for viscous bitumen. In the former case, the dimensions of firmness were those of a modulus, i.e. of a stress. In the latter they were those of a viscosity, i.e. stress x time. There is some reason to suppose from other evidence that differential thresholds do increase with increasing complexity of dimensions, but it is difficult to pursue this line of thought much further until the laws of psychological dimensions have been worked out. At present all that is known is that they differ from those of physical dimensions, e.g. in physics a strain is dimensionless, whereas in the subjective measurement of strains, two lengths have to be judged. It is interesting that the dimensions of viscosity and compression modulus differ by one t. Unlike stress and strain, time is not directly perceived by any sense organ, but is inferred indirectly. This may be connected with the very big difference in threshold here found.

The dimensions of firmness being thus dependent on spring, one is led to enquire as to the dimensional status of the latter property. It is clear that in the extreme cases of true fluid and solid, firmness being

<sup>\*</sup> This work is in process of publication in detail in the Proc. Roy. Soc. Lond.

judged by viscosity and shear modulus\* respectively, we can write:

 $\Psi = S\sigma^{-1}t = \eta$  (fluid)  $\Psi = S\sigma^{-1} = n$  (solid) when  $\Psi$  is firmness

Our hypothesis is that for materials which show intermediate properties we may write:

$$\Psi = S\sigma^{-1}t^{k}$$

It will be seen first that  $\Psi$  has dimensions which depend on k, and secondly that k becomes unity for a true fluid,  $\Psi$  being the viscosity, and zero for an elastic solid,  $\Psi$  being the modulus.

k is in fact the spring, and is seen to be dimensionless.

The fact that in industry rheological properties of materials are directly compared although they differ in physical dimensions has not received the attention it deserves. It is of interest to study an extreme case of this type of mental synthesis, and for this purpose a very large number of people is being asked to state, without undue meditation, which seems to them the larger, an elephant or a second of time. The experiment is by no means complete, but it already appears certain that only quite a small proportion are unable to give any comparison. The majority select the elephant as the larger, but a few prefer the second. In many cases rationalisations are given, but in some cases the judgment appears to be spontaneous.

The experiments described above suggest a method for investigating the alleged superiority of experts in various industries to judge rheological properties of materials by feel. Binns (10) has already shown that the supposed superiority of testers, ascribed to long experience and even to heredity, to judge the quality of wool-tops is only a fact when sight is used in making the judgments, and Katz (11) has made a study of bakers' judgments of flour dough quality, and concludes that their special skill is not in the main due to any abnormal capacity to judge rheological properties of the dough.

In our experiments on bitumen and rubber already mentioned, two of our subjects were highly skilled cheesemakers. They did not show any superiority to other subjects in the viscosity experiment, and a  $\chi^2$  test indicated a significant inferiority in the case of the compression modulus.

<sup>\*</sup> For the materials discussed, the compression modulus may be taken as a simple multiple of the shear modulus. It is hoped to extend the treatment later to cover the the case of materials whose Poisson ratio differs appreciably from 0.5.

It therefore seems likely that experts are not superior in judging subjectively rheological properties of materials by reason of any enhanced tactual acuity, and three other possibilities present themselves: (1) In the case of materials showing such properties as work-hardening and structural viscosity, a reversal of judgment would be obtained in making a comparison if stresses used and hence strains produced were varied. As already noted, differences in time of compression will produce reversals in judgment for pairs of materials differing in spring. The expert might be superior in his capacity to reproduce the joint movements of his hands in respect to stresses and times, (2) The expert might be superior in his capacity to recognize rheological conditions which he had earlier learned to associate with desirable or undesirable qualities in his material, (3) The expert may be superior only in respects which have nothing to do with the judging of rheological properties. He is probably able to make better use of the information given him by his senses due to his knowledge of the requirements and conditions in his industry.

Experiments are in progress in which 20 subjects are being tested, six of whom are "experts", in order to test the first two suggestions. The investigation is still far from complete, but it does not appear so far as though the experts were showing any superiority.

Other factors as well as experience in technological testing are of interest. In the experiments with viscous bitumen samples, although  $\chi^2$  tests showed no significant differences between individuals as such, it appeared that the younger and less educated subjects were somewhat superior to the older and more highly educated, though it was not possible to separate the effects of age and education.

The group of those subjects who are normally engaged in routine laboratory analysis ( $\rho$  - group) was definitely superior.

In the experiments with rubber samples there was more differentiation. Again the  $\rho$  group and the younger and less educated subjects showed superiority.

It must be borne in mind in connection with these conclusions that comparatively few subjects have been tested and much further work requires to be done.

#### SUMMARY:

1). The classical treatment of the rheological behaviour of complex systems is discussed. In this treatment strains are arbitrarily divided into recoverable and non-recoverable parts, and all the data are forced

into the double framework originally designed for true fluids and solids respectively.

2). An alternative treatment is tentatively proposed more consistent with the psychological factors involved in subjective testing which plays such a large part in industrial rheology

3). Experiments are described on the measurement of the smallest differences detectable by feel in the case of viscous bitumens and elastic rubbers, and it is shown that the latter can be judged with three times the accuracy of the former. The reason for this is discussed in terms of dimensional theory.

4). The nature of the alleged superiority of the expert in judging rheological properties of industrial materials is considered in the light of the experiments described.

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# REPORT OF THE BUSINESS SESSION OF THE SOCIETY OF RHEOLOGY, OCTOBER, 1937.

The following officers were declared elected to serve for two years:

- A. S. Hunter, President,
   E. I. duPont de Nemours and Co., Station B, Buffalo, N. Y.
- J. H. Dillon, First Vice-President, Chief Physicist, Research Laboratory Firestone Tire and Rubber Co., Akron, Ohio
- H. R. Ewell, Second Vice-President, Department of Chemistry, Purdue University, Lafayette, Indiana
- W. P. Davey, Editor, Department of Physics, The Pennsylvania State College, State College, Pa.
- H. F. Wakefield, Associate Editor, Research Division, Bakelite Corporation, Bloomfield, N. J.
- H. R. Lillie, Secretary-Treasurer, Research Divison, Corning Glass Works, Corning, N. Y.

The minutes of the preceeding meeting were read and accepted.

The report, of the retiring Secretary-Treasurer was read and accepted. Dr. M. Mooney was appointed chairman of the Committee on Arrangements for the 1940 meeting. The following program committee for the 1940 meeting was appointed by President Hunter: R. B. Dow, chairman, E. C. Bingham, H. R. Ewell, H. F. Wakefield, G. R. Sturm, W. F. Bartoe, J. W. McBurney.

A discussion of the Rheology Leaflet seemed to indicate that the membership wishes (1) editorials, (2) reviews of work in particular fields, (3) articles on applied rheology.

The editors plan to increase the usefulness of the Leaflet to Industry by printing a series of practical articles written by specialists in different fields. The following contribution from Dr. W. F. Fair, Jr., of the Mellon Institute is presented in accordance with that plan.

# RECENT INVESTIGATIONS ON THE FLOW PROPERTIES OF BITUMINOUS MATERIALS

During recent years considerable progress has been made in the study of the rheological properties of bituminous materials. Space permits the description of only a few of the investigations which emphasize the importance of absolute determinations, and illustrate the methods used in studying the fundamental properties of these complex substances.

Volkmann, Rhodes, and Work (1) showed that the capillary rise viscometer could be well adapted to measure the viscosity of coal tars in absolute units, Rhodes, Volkmann and Barker (2) pointed out the value of this type of instrument as a viscometer capable of covering a wide viscosity range of bitumens. Later the same authors (3) showed that the capillary rise instrument could be used as a reference medium for various types of empirical viscometers of limited range, and published conversion tables by means of which such results may be converted to absolute units. They also indicated that coal tars exhibit viscious flow, and confirmed the earlier work of Ubbelohde and coworkers (4) showing that the curve obtained by plotting log log viscosity of coal tars against log absolute temperature is linear, again emphasizing the importance of absolute viscosity determinations in connection with the evaluation of viscosity-temperature criteria.

It should be noted that the capillary rise viscometer is used over a wide but relatively fluid range, and hence should not be used at temperatures where the viscosity of the materal is over approximately one million centistokes.

To investigate the flow properties of more viscous materials, Traxler and Schweyer (5) suggest the use of the falling co-axial cylinder viscometer. By using light or heavy falling cylinders in this instrument of suggested appropriate dimensions the investigator may study a wide range of viscous materials to give a rapid determinations of viscosity in absolute units. In another publication (6) they show how increase in viscosity of asphalts with time may be studied by means of this viscometer. They found that several asphalts, and some filled bitumens, increased in viscosity upon standing, but that re-melting yielded materials of about the original viscosity. Thus they concluded that the viscosity increase was due mostly to age hardening, possibly by development of internal structure, rather than to extensive evaporation of volatile components. Continuing these investigations, Traxler and Coombs (7) determined the viscosities of several different types of asphalts, and found that some exhibited anomalous flow characteristics, thought to be due to age-hardening processes, which were reversible by heating, and also found that the same asphalts showed surface patterns when treated with solvents. This leads to the hypothesis of a progressive formation of internal structure, unstable to heat and to working, possibly dependent upon gradual isothermal sol-gel transformations.

Traxler (8) later pointed out the importance of absolute determinations in a paper describing empirical tests, and methods of measuring the viscosity of fluid and viscous asphalts. He suggested the use of a capillary or falling coaxial cylinder viscometer for more fluid asphalts, the latter or rotating cylinder viscometer for viscous asphalts, and for non-viscous (such as air blown) asphalts the rotating cylinder instrument. Of great value in stimulating research in this field is the emphasis made by Traxler and his co-workers on the importance of obtaining stress-rate of shear diagrams to determine the nature of flow of different asphalts.

Attempts have been made from time to time to develop simpler means of estimating the magnitude of flow properties of bitumen. Thus Thelen (9) suggested means of determining flow-shear diagrams from penetration measurements. Rhodes and Volkmann (10) criticized Thelen's definitions and proceeded to develop, by a method of successive penetrations, a procedure by which to approximate the viscosity and obtain flow diagrams for some representative coal-tar pitches. Traxler and Moffatt (11) report that this method of successive penetrations is not sound (possibly because of unjustified assumptions in the derivations concerning the flow during penetration) since occasionally negative yield values are found for certain asphalts.

This method may, however, be of some qualitative value at least to find the order of magnitude of the yield value for a non-viscous sample, or the approximate temperature at which changes in general flow characteristics might occur.

An extremely interesting method of investigation has been followed by Vokac (12) who proposed using a compression test not on the bitumen alone, but on the sample of whole pavement, to measure the physical characteristics of different paving mixtures. By emphasizing the time factor in applying loads, this investigator (13) developed relations and flow diagrams to differentiate by laboratory testing between types of paving, and points out the analogy between compressive stress and shear stress, and between rate of volume displacement and rate of shear. Upon continuing this work with actual service mixtures Vokac (14) claims to have observed extremely better correlation between compression tests and service performance, than was found for any of the other customary empirical methods now in use. As a further contribution he has suggested (15) determining compressive strengths of paving mixtures at different temperatures to arrive at a mixture susceptibility index, analogous to a viscosity-temperature susceptibility factor, to aid in the comparison of different asphaltic paving compositions with changing temperature.

Another field to which tar and asphalt chemists have lately turned their attention concerns the properties of soils and clays, because of the growing importance of soil stabilization and the necessity of developing methods to distinguish between soils of different physical characteristics. Among the attempts to put this work on a more fundamental basis is the proposal by Rhodes (16) to adapt a dough testing machine for soil stabilization evaluation before and after the addition of coal tar, in the belief that some types of dynamic test on wet soils would be better correlated to field results. Using a Brabender Plastograph, which draws a graph showing the resistance to paddle mixing as water is uniformly added, he reports distinctive curves (inverted-V-shaped) with critical points showing marked differences between soils previously known to give good service results, and those known to be extremely unstable. Similar curves showing consistency in grammeters against time (or % water) may then be obtained with tar treated soil to show the improvement possible by stabilization, which appears to depend upon the amount and kind of -200 mesh material in the soil.

Of interest in this connection is a paper by Roller (17) who studied the compression of cylinders of clays, cements, and other materials, under increasing load and arrived at certain conclusions concerning the plastic flow of these substances. Methods similar to this may be important in the future to those interested in soil stabilization evaluations.

The above cited papers have been chosen for comment here because they all stress the importance of absolute measurements and the use of complete rheological data in dealing with the fundamental properties of these complex mixtures. It is to be hoped that more attention will be paid to this type of investigation to increase our knowledge of the flow properties of bituminous materials. Mellon Institute W. F. FAIR, JR.

21.

October 21, 1939.

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### MISCELLANEOUS NOTES OF INTEREST TO RHEOLOGISTS

#### A CORRECTION

On page 16 of the February 1939 Rheology Leaflet, in Dr. M. Mooney's article, "Stress and Rate of Strain; An Elementary Analysis," the values given for the shears  $\alpha y'z'$  and  $\alpha x'y'$  should be interchanged.

The Trustees of the John and Mary R. Markle Fund have awarded the sum of \$2900 for research upon the viscosity of the blood to be carried out at Lafayette College under the direction of Dr. Eugene C. Bingham. The experimental work will begin as soon as a suitable man can be found for carrying on the work. The historical survey of the field is already in progress.

It is interesting to note in view of the discussion now going on in regard to the Rheological Definitions that the American Society for Testing Materials has a committee on Rheological Definitions. Mr. Robert Burns, Acting Chairman, reports favorable action of that committee on the new revision of the "Tentative Definitions of Terms Relating to Rheological Properties of Matter," with A. S. T. M. designation E34-37T. The definitions must now be submitted to the entire Society.

We are happy to announce that the work of the Bureau of Standards on the determination of the Viscosity of Water as the basic viscosity standard has been resumed. It will be recalled that this important research was originally instigated and financed by the Society of Rheology.

#### RHEOLOGICAL MEMOIRS

For many years Prof. E. C. Bingham has advocated the publication of a series of translations of classic papers in rheology. Through his initiative, such publication has now been undertaken, and the first number of the series IX and 101 pp., 15x23 em., 10 figs. has been issued, and can be obtained from Rheological Memoirs, Easton, Pa., at the price of \$2.00 in paper covers, or \$2.50 bound in cloth.

This first number of the projected series contains a translation of the classic paper of Poiseuille on the flow of water through capillaries, published in 1846 in the Memoires presentes par divers savants a la acad roy. des scienc de l'Institut de France. This investigation was a part of Poiseuille's study of the mechanics of the circulation of blood in animal bodies. It provided the first demonstration of the laws of viscous flow, an experimental determination of the law of viscous flow in capillaries, and data on the absolute viscosity of water which compare favorably with the most accurate measurements ever made of this quantity. The reader may be surprised to learn that nowhere did Poiseuille use the term "viscosity". This paper of Poiseuille's is the first and historically the most important chapter of the whole extensive literature devoted to viscosity. Since his work on blood began began before 1840, this is a centenary which deserves recognition.

Historically, a translation of such a paper is of obvious value, and presumably every technical library will welcome it. These older scientific papers, however, are deserving of a wider popular interest, which they would receive if their educational value were more fully appreciated. Once a successful analysis has been developed in any field of science, the ideas employed harden into a rigid framework, which is accepted uncritically by the student, and seems to him self-evident and inescapable. Nothing can better restore the intellectual flexibility that should characterize the research worker than a study of the original work that laid the framework of our present thought. In these original papers we can see at first hand the formulation of concepts which are familiar to us, but which were novel creations to their authors.

The continuation of the Rheological Memoirs will depend upon the support given this first number. If this is well received, further numbers are planned to include among others, the studies of Schwedoff on plasticity (which he called the "rigidity of liquids") and of Petroff upon lubrication. It is proposed to put in each volume enough numbers to make about 500 pages. It is to be hoped that the welcome given the Poiseuille number will warrant the issue of the others.

# TWELFTH ANNUAL MEETING OCTOBER, 1940

The invitation of Dr. Roy Chapman Andrews to hold our 1940 meeting in October at the American Museum of Natural History has been accepted. The following committee has been appointed and the members are invited to cooperate with them with suggestions and contributions:

- R. B. Dow, Chairman, Pennsylvania State College, State College, Pa.
- E. C. Bingham, Lafayette College, Easton, Pa.
- R. H. Ewell, Purdue University, Lafayette, Indiana
- H. F. Wakefield,Bakelite Corporation,230 Grove Street,Bloomfield, N. J.

R. G. Sturm, Freeport Rd., & Catalpa St., New Kensington, Pa.

- W. F. Bartoe,
  Rohm and Haas Company,
  222 W. Washington Street,
  Philadelphia, Pa.
- J. W. McBurney, 300 South Building, U. S. Bureau of Standards, Washington, D. C.

H. R. Lillie, Corning Glass Works, Corning, N. Y.

#### APPLICATION

Mr. H. R. Lillie, Secretary Research Division Corning Glass Works Corning, N. Y.

I hereby apply for membership in the Society of Rheology for the year \_\_\_\_\_ as follows:

- [ ] Sustaining membership (including subscriptions to both Journal of Applied Physics and R. S. I. \$25.00 or more
- [] Regular membership (including subscription to **Journal of** Applied Physics) \$6.00 (foreign, \$6.50)
- [] Associate membership \$2.00 (foreign, \$2.50)

All members receive a subscription to the Rheology Leaflet.

Please also enter my subscription for the following additional periodicals published by the American Institute of Physics:

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