Industrial Rheology
and
Rheological Structures

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Preface

The intention of this book is easily stated. It is to give the laboratory man a workable rheological system: one based on accepted ideas which can be used either for research or for plant control purposes.

It has been the author's desire to avoid writing another textbook, for it has been believed that a greater need exists in a different quarter. That place is in the plant control laboratory. The technologist there in charge usually has only limited time for development work; consequently, he prefers to have all ground work finished and presented to him before tackling his end of the job. It is realized that an attempt to present any one with a "rheological system" is inviting adverse criticism. However, such an act does not prevent any one else from advocating his own ideas on the subject.

Non-Newtonian rheology is a network of conflicting ideas. These ideas are so evenly distributed amongst rheologists that no particular school or group predominates. Consequently, there is no final court of appeals to which one may go with a debatable question and ask for a decision. Each investigator must be his own judge and answer his own questions. It is upon this background that any rheological system is constructed. Hence, the advocate must have ready his apology for his beliefs and acts. In the present case the apology consists of the fact that the system is of sound heritage being based largely on the works of Newton, Poiseuille, Bingham, Buckingham, and Reiner. In addition, the method has been in constant use for the past ten years in the author's laboratory. During this period the "rough spots" have been ironed out, and the system has proved to be practical. It is to be hoped that the foundation has been satisfactorily laid.

Naturally, no claim is made that the method described here is the best possible one. Reasons are given and sometimes explained in considerable detail as to why certain procedures are selected in preference to others. Arguments against accepting some ideas as dangerous or misleading are also given; but actual proof of the correctness of one's choice is quite another matter. Preference is usually a personal affair based mainly on one's own experience.

The author is greatly indebted to Dr. A. E. Gessler, director of research of Interchemical Corporation, and to Dr. D. M. Gans and Dr. Earl P. Fischer, formerly of Interchemical Research Staff for their encouragement and co-operation during the preparation of this work. Also special thanks are due to Miss Ruth Weltmann whose collaboration with the author on numerous rheological papers has done much to make this book possible.

HENRY GREEN

Easton, Pa.
1947

Publisher's Note

We wish to express our appreciation to Ruth N. Weltmann for her invaluable assistance in checking the manuscript, proofreading, and otherwise seeing this book through the press after the untimely death of the author. Miss Weltmann co-operated closely with Mr. Green for more than ten years. She is the author of many papers on rheology and the coauthor with Mr. Green on others.

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PART I

A Rheological System

CHAPTER

1

Some Ideas That Have Retarded Rheological Progress in Industry

During the last 25 years the author has had many opportunities to discuss with technologists the numerous problems encountered in introducing a scientific type of rheology into industrial laboratories either for purposes of research or for plant control work. As the result of arguments that arose, certain objections to scientific rheology (in contradistinction to technical rheology) have dominated to such an extent by their constant recurrence that an examination of their possible merits and faults must be made; for, otherwise, some of the background and reason for this book will not be evident.

First, it should be stated that that part of rheology dealing with viscous materials (Newtonians) like gasoline, alcohol, and water has never been the subject for obstructive argument. Measurements can be made in those cases by "one-point" methods, and the introduction of such procedures in industrial laboratories has never met with resistance. It is only when the investigator finds himself in non-Newtonian fields that he raises an objection to forming a closer alliance with the science of rheology. His reasons are natural enough. Non-Newtonians (paints, printing inks, high-viscosity oils, and the like) require for measurement an entire consistency curve. The one-point method is no longer adequate, but the investigator objects to making multipoint consistency curves. In order to examine his objections, let us list all the principal issues that experience has taught us will be raised in protest against the introduction of a scientific form of rheology in industry. They are:

1. The science of rheology is too complicated for practical use. There are no commercial viscometers available that can give consistency curves for many highly viscous industrial products. The

time consumed in making consistency curves is too long for plant control work.

2. The science of rheology aims at a high degree of accuracy and precision. For practical purposes this is not necessary. "One-point" methods can be duplicated with precision; they are, therefore, "accurate enough."

3. Absolute units are not necessary; therefore, nothing is gained by substituting a method that gives absolute values in place of a relative method.

4. Even if one-point methods are not highly "accurate," *they are at least comparable, because all such measurements are made in the same way.*

Rheology's Reply

1. The science of rheology *is* complicated and will continue to become more so as future progress is made in it. The same objections can be advanced against analytical chemistry, spectrophotometry, spectroscopy, electron microscopy, and many other sciences that industry finds useful. The part of rheology that is necessary for plant control work is not too extensive and is fairly simple. It can be utilized in the plant, as has been demonstrated in certain companies. It is true there are not many viscometers suitable for making consistency curves of highly viscous materials, but such viscometers can be and have been built. When properly constructed, these instruments are rapid enough in operation for plant control work.

2. The main object in applying a sound rheology to industry is *to substitute the multipoint consistency curve for the one-point* method. As may be seen, "accuracy" does not form any part of this motive. Accuracy cannot do so because in the present case the word is practically meaningless. That is, there is no standardized method for determining with 100% assurance the actual yield value and plastic viscosity of a material. There is, therefore, no means for determining accuracy. As for precision, that is only a question of constructing a reliable instrument and then learning how to operate it in exactly the same manner each time. If the method is wrong, precision is simply the ability to duplicate one's mistakes precisely. It should be apparent from what has been said that accuracy and precision, although two ideals greatly to be desired, are not the real arguments for adopting scientific rheology to plant control work.

3. The argument about absolute units is also one that causes unnecessary apprehension and confusion. There is no real necessity to report measurements in absolute units. The only reason rheologists do so is that it gives them a common language in which to compare their results.

4. A one-point method consists of the measurement of a single shearing stress and the particular rate of flow this stress produces in the material under test. The result is a point on an unknown consistency curve. Being but a single point the measurement cannot locate the position and direction of the curve. (The only exception is the case of Newtonians, which give straight-line curves passing through the origin.) Suppose that one-point measurements are made on two or more entirely *different* non-Newtonians. Also suppose that by chance the consistency curves of these materials happen to cross one another at the exact point of measurement. The investigator who believes in the proposition that all materials which are run alike will give results that are comparable will be forced to say that the two or more entirely different non-Newtonians are not different but actually rheologically identical. That, of course, would be incorrect. Therefore, there is no reason to believe that one-point measurements on non-Newtonians are ever comparable *even though they are made exactly alike.*

During the numerous occasions in which these concepts have been advanced and argued, there never seemed to have been any trouble in convincing the one-point investigator that his method was not sound. In fact he always freely admitted this point; but as a rule, after having committed himself to that extent he returned to his laboratory and proceeded to make the same mistakes over again. The reason has long been a puzzle, one that has created considerable food for thought. The solution undoubtedly is that, if the investigator gives up his one-point method, he will have nothing to put in its place. He could, if he chose, study the textbooks on rheology, and obtain a general survey of the science. If he does so, he will discover what each rheologist has accomplished in developing his own particular part of the science. He will find that rheology, as recorded in the literature, is a kind of jigsaw puzzle, one in which the investigator must fit the pieces together himself; that some of the pieces are missing; that rheology contains within itself a collection of contradictory ideas. It is perhaps well to inspect some of the ideas that are most confusing to the beginner. They are:

There is no such thing as a yield value. There is a single yield value. There are three different yield values. The reason for the bending of the lower end of the consistency curve is not known. The curve bends because of slippage. It bends because of the transition from plug to laminar flow. It bends because of realignment of the molecules. It bends because of thixotropy. Thixotropy is not a comparable term and as such cannot be measured. Thixotropy can be measured by a "one-point" method. Thixotropy cannot be measured with anything less than a single consistency curve. Thixotropy cannot be measured with anything less than two different consistency curves. Any solid that can be made to flow is thixotropic. Solid flow *per se* is no evidence of thixotropy. There is no difference between yield value and thixotropy; yield value and thixotropy are not the same phenomenon. Plasticity and thixotropy are always coexistent. Plasticity can exist without the presence of thixotropy. The capillary-tube viscometer is preferable to any other type. The rotational viscometer is preferable to any other type.

Anyone will admit that in such a sea of conflicting ideas the simple one-point method has a substantial appearance. At least it seems to be a straw worth clutching at; and that is apparently what many industrial rheologists are doing. If an investigator is to be dissuaded from this course, he must be presented with a complete and workable system, one that is internally noncontradictory, and one that can be followed through from beginning to end. It was with such a thought in mind that the system in this book has been described and presented to the laboratory man. It is to be hoped that in the course of time he will find it useful and capable of fulfilling its purpose.

CHAPTER

2

The Proper Starting Point for the Rheologist

The most desirable point for the laboratory technologist to commence his study of rheology depends on the type of substance he is required to measure. If his materials are the kind that follow the hypothesis given by Newton—that the rate of shear in a liquid is directly proportional to the shearing stress—then a study of the capillary-tube viscometer is most suitable. On the other hand, if the materials are those, like pigment-vehicle suspensions, which follow a nonlinear law of flow, then a better starting point is with the microscope supplemented only with certain basic facts of capillary viscometry.

The microscope fulfills a double purpose. It shows what is taking place when a material flows through a capillary tube and, in addition, makes possible the study of structure, revealing its relation to the rheological consistency curve. Both purposes are important. Any severance of microscopy from rheology makes it difficult to acquire a mental picture of the internal mechanism of rheological models, and, incidentally, it robs rheology of much of its interest.

The Newton Model of Flow

Before the part played by the microscope is discussed, the concept of Newton for viscous flow and Bingham's modification of it for plastic flow must be described. In Figure 1 is shown what will be called here the *Newtonian Model of Flow*. It consists of two planes A and B, the intervening space being filled with the liquid under test. A tangential shearing stress F is applied at a. The A plane then moves with respect to B, carrying with it the innumerable parallel planes of liquid existing between A and B. Each plane, however, is carried a different distance. The top plane A goes the farthest with respect to the B plane (which remains stationary). When the point b reaches c, the straight line cd marks the distance traveled by all the intermediate planes. If bc is the distance traveled in one second, its length gives the velocity of A with respect to B. Then bc divided by bd becomes the *rate of shear* or *velocity gradient.* This is customarily written dv/dr where v is velocity and r is the distance between the planes. It is obvious, from such a model, that for a given F, dv/dr is constant throughout the mass of material.

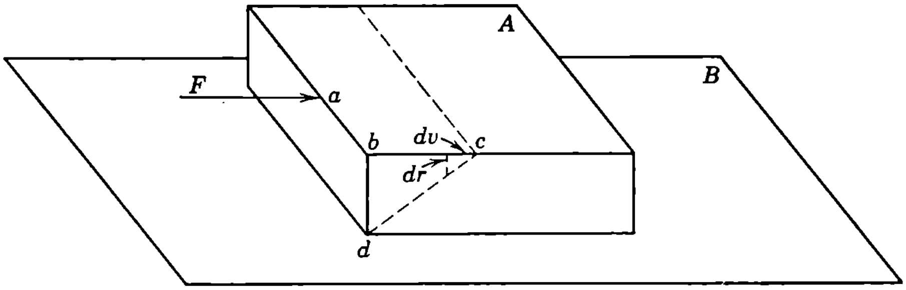


Fig. 1. The Newtonian Model of Flow

Newton assumed that the rate of shear is directly proportional to the tangential shearing stress. His idea is expressed mathematically in the equation,

$$F = \eta \frac{dv}{dr} \tag{1}$$

The proportionality constant η is the *coefficient of viscosity* and is defined as the tangential shearing force per unit area that will produce a unit rate of shear. Equation 1 is applicable only to those liquids whose molecules are not hampered in their motion by the formation of structure or by molecular alignment under high rates of shear.

For plastic clay suspensions in water, Bingham [1] used a modification of the Newton concept. Bingham reasoned that plastic flow could not start until the applied shearing stress exceeded the stress arising from frictional resistance between the clay particles. He expressed his hypothesis by introducing into the Newtonian equation a frictional factor f. Thus,

$$\mu(F - f) = \frac{dv}{dr} \tag{2}$$

where f is the tangential force per unit area just required to start flow. Bingham replaced $1/\eta$ with μ, which he called the *mobility.*

The Capillary-Tube Model of Flow

Unfortunately the Newtonian model of flow, cannot be duplicated in the laboratory, for either the planes A and B would have to be infinite in extent, or, if they were finite, the liquid between the planes would have to retain its shape and position without the benefit of retaining side walls. Both these conditions, naturally, are impossible to produce. The difficulty this limitation introduced was finally overcome years after Newton's time by the Frenchman, Poiseuille (1846), in his investigation of the flow of liquids through capillary tubes. Poiseuille discovered empirically that the volume per second of liquid flowing through a capillary tube is directly proportional to the activating stress. When this became known, mathematicians applied Newton's equation to the capillary tube and derived the following:

$$\frac{V}{t} = \frac{\pi R^4 P g}{8 l \eta} \tag{3}$$

where V/t is the volume of flow per second; P the activating pressure; and R, l, and g the radius and length of the tube and the acceleration of gravity, respectively. In the capillary-tube model of flow, Newtonian liquids give a dv/dr that varies directly with r for a fixed pressure head. r is the radius of any inner cylinder coaxial with the tube. Since R, l, and η are constants for a given tube and material, Equation 3 shows that the volume of flow per second is directly proportional to the pressure head, which is in agreement with Poiseuille's discovery; and so the validity of the Newtonian concept was established without actually employing a Newtonian model of flow. Equation 3 is known as the Poiseuille equation. Its derivation together with the various corrections used with it are given in Appendixes A and B.

At the time of Bingham's original pioneering work on clay suspensions it seemed logical enough to write the flow equation of a plastic in a capillary tube as follows:

$$\frac{V}{t} = \frac{\pi R^4 (P - p) g}{8 l \eta} \tag{4}$$

where p is the smallest applied pressure that will just cause flow. Unlike Equation 3, Equation 4 was not deduced by any mathematical process. It was an assumption only. Now if V/t is plotted against P in Equation 3, for a series of different pressures, a straight-line consistency curve is formed passing through the origin (Figure 2a). Then for plastics, it seemed natural to expect that, if V/t is plotted against a series of pressures, a straight-line consistency curve should be formed intersecting the pressure axis at p (Figure 2b). Unfortunately this does not occur, but a non-linear curve is obtained as given in Figure 2c. This means that the assumption made in writing Equation 4 (that the same mechanism of flow exists here as for simple liquids) is not correct. The reason was not known at the time this fact was first discovered, but various "explanations" were suggested. For instance, the curvature was attributed to slippage, to seepage, and to a change in consistency under low rates of shear. There still are rheologists who hold to the last explanation, and, as a matter of fact, it is possible that that idea is partly true. The fact that the plastic-flow curve for capillary tubes was not found to be linear did more to hinder the development of a scientific non-Newtonian rheology than anything else.

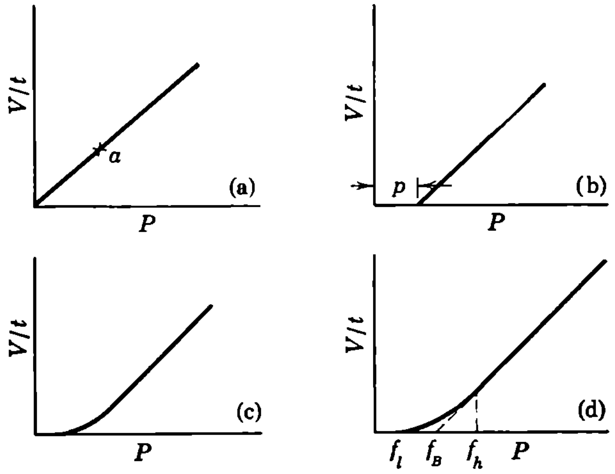


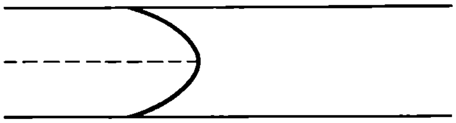
Fig. 2. Consistency Curves

The Microscopical Examination of Flow

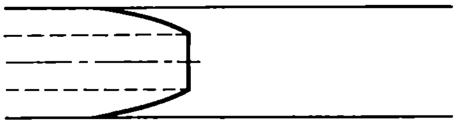
In order to find a possible explanation for the unexpected curvature, Green[5] in 1920 examined microscopically the flow of plastic suspensions in fine capillary tubes. This work was repeated in a more detailed manner by Green and Haslam in 1925.[7] Apparently nothing further was undertaken in that line until 1941 when Mukherjee, Sen Gupta, and Sen,[8, 9] evidently unaware of the earlier work, repeated it, but used flat cells instead of capillary tubes.

The microscopical technique for the study of flow is simple. An ordinary glass tube is drawn down until it becomes a fine capillary of sufficiently small diameter so that it can be placed under a 4-mm objective. The tube is then mounted on a microscope slide in a liquid with the same refractive index as that of the glass from which the capillary is made. When such a mount is examined through a microscope, no glass walls are visible so long as the tube is filled with the material under examination. If the material is transparent, like a simple liquid, it is necessary to mix into it some pigment particles coarse enough to be visible. The examination can be made with transmitted light. If the substance is an opaque plastic like paint or printing ink, this procedure is not necessary, and the material must be examined by reflected light. This is done by allowing the light to enter from the side.[7] When air pressure is applied to the end of the capillary, flow commences.

If one examines first a simple liquid, it will be found that the incorporated pigment particles make the flow lines visible. The particles in the center of the tube move the fastest with respect to the tube wall. The particles at the edge show the least flow. A cross section through the tube gives a parabola (Figure 3a) for the distances traveled in unit time instead of a straight line as in the Newton model of flow. This can be ascertained by measuring with a ruled eyepiece the velocity of the various pigment particles in the different telescopic layers of flow (laminar flow). The velocity v at radius r is



(a) Newtonian Liquid



(b) Plastic Material, Bingham Body

Fig. 3. Flow through Capillary

$$v = \frac{PgR^2}{4l\eta} - \frac{pgr^2}{4l\eta} \tag{5}$$

If we return now to a plastic of pigment suspension type, microscopical examination reveals at once that, when sufficiently low pressure is applied, the material does not move in telescopic layers.

It moves as a solig plug lubricated with a thin layer of vehicle between itself and the capillary wall. This type of flow has been called "slippage flow," a term that is probably confusing. There is no slippage of the vehicle against the tube wall. However, the pigment particles are too large to adhere to the wall (in ordinary cases), and so they appear to slip. Actually they are being carried along with the flowing vehicle. Slippage flow should give a linear consistency curve intersecting the origin. Whether it does or not is still a debatable question.

If the pressure is increased gradually, there comes a time when the particles in the outer layer of the plug become detached and move independently of and slower than the rest of the material. This is the beginning of laminar flow. All the other layers of the plug are held together in a solid piece. The reason they are held together is that the lateral shearing force per unit area gets smaller as the distance toward the tube axis is traversed. Eventually it gets smaller than the force required to start flow within the plug. This force can be calculated by equating the total lateral shearing force on the side of the cylinder, with the total applied pressure thus:

$$2\pi r l f = \pi r^2 p g$$

or

$$f = \frac{rpg}{2l} \tag{6}$$

When r, the cylinder radius (not necessarily the radius R of the capillary tube) becomes sufficiently small so that $rpg/2l$ is less than f, the rate of shear between the two adjacent layers at r becomes zero.

As the pressure is raised, more layers begin to shear. If the plastic is very opaque, it will be impossible to see what takes place in the interior of the material during flow. In order to satisfy one's curiosity, however, a "pigment" can be made of ground glass or of microscopic glass spheres[7,3] and incorporated in a vehicle whose refractive index approximately matches that of the glass. Such a mixture is sufficiently transparent to permit microscopical observation all the way through it. When a cross section of the velocities of the various layers is made, it will be found to follow a pattern as shown in Figure 3b. This is not a truncated parabola, but a parabola that has been cut in half and the two halves pushed apart. Between these two halves is the remains of the unsheared plug. As the pressure is further increased, the parts of the parabola increase, and the radius of the plug decreases. This type of flow is a mixed regime where laminar flow and plug flow exist side by side. As can be readily understood, this does not duplicate the model of flow shown in Figure 3a for a simple liquid. Consequently it is evident that Equation 4 cannot be correct, for the equation was based on the assumption that the model of flow for a plastic did not differ from that of a liquid in Equation 3. Consequently, no mystery exists as to why Equation 4 did not meet with the expectations of investigators in the 1916 period of rheology.

Erroneous Conceptions of Flow

It was desirable to dwell on these facts at some length, for the student who can clearly see that there is no necessity to adopt speculative ideas in regard to nonlinearity is, at least, started in the right direction. This viewpoint constitutes an important part of the rheological system that we are endeavoring to develop here. Hence, the advantage of commencing with the microscope; for if the microscopical picture of flow is firmly implanted in the mind, no conjectural ideas of contrary type will cause doubt or mental confusion. For instance, it is obvious that an empirical equation of flow such as

$$\frac{V}{t} = ap^n \tag{7}$$

is not acceptable, no matter how perfectly it might fit the laboratory data; for there is no reason to believe that Equation 7 can express a change in the model from plug to complete laminar flow. All such equations as 7 can be discarded, for almost any one of them can be made to fit a non-Newtonian consistency curve by suitable adjustment of the parameters. When this happens, no particular significance should be attributed to it, for the meaning of a and n are unknown, being empirical constants only. Furthermore the dimensions of a will depend on the magnitude of n. This means that a has no fixed significance or counterpart in nature.

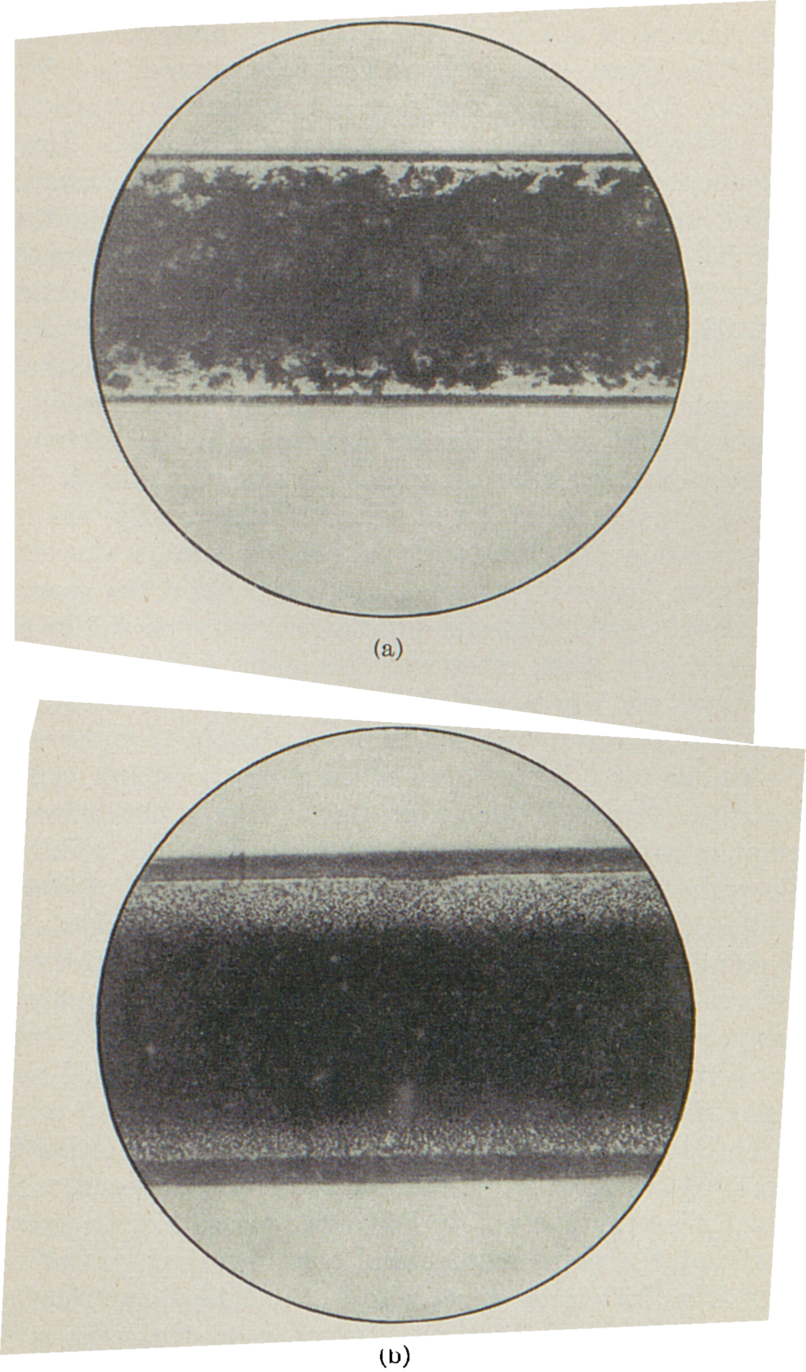
The Concept of Yield Value

When Bingham first recognized the significance of an intercept on the pressure axis, in deriving his consistency curve for clay and water mixtures, he attributed it to friction. This friction existed between the particles of clay and resisted flow to the extent of the pressure designated by the intercept. The letter f was used to symbolize friction. This letter has been retained by many rheologists, even though the name "friction" is no longer employed. It seemed highly probable that friction might not be the only factor involved in producing the intercept. It was, therefore, decided to change the name to something noncommittal. The term "yield value" was suggested as a temporary expedient until something more appropriate could be found. The term *yield value* appeared for the first time in a joint publication by Bingham and Green in 1918.[2] Several years later yield value was definitely adopted by them, though it was realized that the term was not entirely satisfactory.

In the preceding paragraph it was stated that friction might not be the only force producing an intercept. The force of pigment flocculation can also prevent flow unless it is exceeded by the applied force. If a pigment vehicle mixture be sufficiently diluted so that examination can be made microscopically by transmitted light, the pigment will most likely show flocculation. This experiment can be carried out easily in the microplastometer.[7] In Figure 4a (showing the tube of the microplastometer) the pigment is flocculated and held together by a force that must be overcome before shearing can take place. In Figure 4b such a force is being applied and has resulted in laminar flow.

Yield value is the factor that distinguishes plastics from liquids. (The term *plastic* used throughout this book refers to *Bingham bodies* [11] and not to synthetic plastics). When the yield value of a material is sufficiently high, it becomes manifest by imparting to it a shortness or butter-like consistency, a fact well known to investigators who are familiar with paints and printing inks. Yield value makes plasticity possible. Plasticity also includes the concept of flow without rupture; that is, the material must not be brittle. Putty and molding clays are two common examples of materials possessing yield value. Heavy oils, tars, and pitches, though highly viscous, have no yield values normally, and, consequently, they are not plastic. They will even flow under their own weight, although it might take some time before the quantity of flow becomes observable.

The reader might well ask at this stage how an intercept can be obtained from a plastic-flow curve, if that curve is not linear such as that shown in Figure 2c. For a long time it was believed that the



(a)

(b)

Fig. 4. Photomicrographs of Flow through a Capillary. (a) Plug Flow. (b) Laminar Flow

plastic-flow curve obtained with a capillary viscometer was composed of two parts—the upper part being linear and the lower part nonlinear. The intercept was then obtained by extrapolating the upper part of the pressure axis as shown in Figure 2d. This gave the intercept f_B, which Houwink [10] calls the "Bingham yield value." Houwink also conceived of two other yield values, f_l and f_h; the former he called the "lower yield value." It is apparently the pressure just necessary to start laminar flow in the outermost layer. The last yield value f_h Houwink called the "top yield value." This, as will appear, is approximately the force that produces laminar flow fairly completely throughout the tube. It is now known that the consistency curve of a plastic taken with a capillary viscometer cannot be linear in any part of it, if there is such a thing as a constant yield value.[4] Consequently, the process of extrapolation from the upper part of the curve is very inaccurate. Nevertheless it is used extensively. Also the concept of three different yield values is quite unnecessary, as will be shown in the discussion of the rotational viscometer.

As a result of these misconceptions, rheologists lost most of their faith in the objectivity of yield value. It became a purely subjective phenomenon. It was even called a "mythical intercept on a hypothetical line." To make matters worse various rheologists attempt to prove by experiment the nonexistence of yield value. Their methods for doing this were not always fair. They used non-Newtonians without yield values (pseudoplastics) to demonstrate their point. The term yield value fell into disrepute. However, it was never completely abandoned and is used now probably more extensively than ever. The reason is perhaps twofold. First, the work of Reiner and Riwlin [13,12] showed that the rotational viscometer should produce a consistency curve, the upper part of which must be linear for plastics. This made the extrapolation to an intercept on the force axis a rational procedure. Second, whether yield value is a myth or not, it does give a measure of a property of matter that the manufacturer and consumer find desirable and useful. This fact leads directly to a principle of our rheological system: It is not so important either to know the cause of yield value or to possess complete faith in its reality. It *is* necessary to be able to measure it by some reasonable and acceptable method. At the moment this might seem incompatible with scientific integrity. That it contains a basic truth, however, becomes continuously more evident when the investigator gains experience and knowledge of industrial rheology.

Viscosity

A Newtonian liquid is defined rheologically by only one constant. That constant is the coefficient of viscosity, commonly abbreviated to the single word, *viscosity*. Viscosity is directly proportional to the cotangent of the angle made by the consistency curve and the force axis (Figure 2a). Numerically it is equal to the number of dynes that will induce a unit rate of shear. This number varies with the temperature of the material; so the temperature at the time of measurement should be given with it. The unit of viscosity is the *poise*. When a shearing force of one dyne induces a unit rate of shear, the material has a coefficient of viscosity of one poise.

The coefficient of viscosity for a Newtonian can be obtained by a "one-point" method. The measurement is made for any point *a*. A straight line is drawn through *a* to the origin *o*. This gives the consistency curve (Figure 2a). Such a procedure is valid because the rate of flow is directly proportional to the pressure. The coefficient of viscosity is determined from the cotangent of the angle as stated before, and the calculation made by Equation 3.

Apparent Viscosity. Unfortunately the single-point method is invalid for non-Newtonians. Nevertheless many rheologists use such a procedure for non-Newtonians. They attempt to make their measurement valid by calling it "apparent viscosity." Now apparent viscosity is *the viscosity a material would have if it were a Newtonian;* but a non-Newtonian is never Newtonian. Therefore, *apparent viscosity* is, in truth, a myth derived from an entirely hypothetical consistency curve. Apparent viscosity, however, is found acceptable to the majority of rheologists, even to some of those who cannot accept the "yield value myth."

Retention of the apparent-viscosity concept has probably done more to create confusion in the minds of plant technologists and to delay rheological progress in industrial laboratories than any other factor, except the unfortunate nonlinearity of the plastic-flow curve. In the rheological system described in this book apparent viscosity plays no part. In the chapter which discussed thixotropy it will be shown how the beginner can confuse the decrease in apparent viscosity, resulting when the rate of shear is lowered (a matter of simple geometry), with thixotropic breakdown (arising from structural change). These two phenomena are not even related, and any system that cannot keep them clearly separated is misleading.

Plastic Viscosity. The type of material that gives a consistency curve like that shown in Figure 2b has been called by Reiner[11] a "Bingham body." A Bingham body can be defined as one that would comply with Equation 2, if a Newtonian model of flow could be had. In the Newtonian model, the tangential shearing force per unit area is the same on each layer. Consequently, when the yield value is exceeded by the applied force on any one layer it is exceeded on all of them. All the layers will start to move then at the same time; and as long as the applied force remains constant dv/dr will be constant throughout the body of the material. If the force in excess of the yield value is doubled, dv/dr is doubled; if tripled, dv/dr is tripled, and so forth. In other words dv/dr is proportional to $F - f$, and the relationship as given in Equation 2 is being followed. According to Equation 2,

$$U = \frac{F - f}{\frac{dv}{dr}} \tag{8}$$

where U is the *coefficient of plastic viscosity*[6] and f is the Bingham yield value (not Houwink's f_B, which is not yield value but a function of yield value). It is necessary to qualify U by calling it the coefficient of "plastic viscosity" in order to distinguish it from the coefficient of viscosity of liquids. *Plastic viscosity is the number of dynes per square centimeter of tangential shearing force in excess of the Bingham yield value that will induce a unit rate of shear.*

It should be evident by now that plastic viscosity cannot be determined experimentally from a one-point method. It takes at least two points to obtain a consistency curve of a plastic material, if it is assumed that a viscometer can be constructed capable of giving a straight-line relationship. In actual practice it is safer to use many points, not just two. To prove that the substitution of a multipoint for a single-point method can be accomplished in an easy and practical manner is one of the main purposes of this book; in fact, it is the keynote of our system.

Common Arguments Against the Multipoint Method

Opposition to the multipoint method rests on two arguments. One of these is valid, but not insurmountable; the other is incorrect. The first states that there are no entirely satisfactory viscometers manufactured that can be used for making consistency curves and that the investigator is, therefore, compelled to build his own instrument. That is true; but the investigator who is unable to build his own apparatus is out of place in a chemical or physical laboratory. Suitable viscometers can and have been constructed.

The other argument in opposition to the multipoint method is that such a laborious process is *unnecessary*. This argument is based on the hypothesis that, if two different non-Newtonians are measured in exactly the same manner by a one-point method, the results are at least comparable, even though they might not be accurate. The question of accuracy is of no importance for the moment. Do not let it confuse the issue. The serious fault of the argument lies in the fact that one-point measurements are not generally comparable, no matter how nearly alike they might be run. This point has been mentioned in the introduction, but it is such an important one that it cannot be emphasized too much.

Apparent Viscosities Are Not Comparable

Figure 5 will help to visualize the point involved. Suppose that a one-point measurement is made on the non-Newtonian marked A.

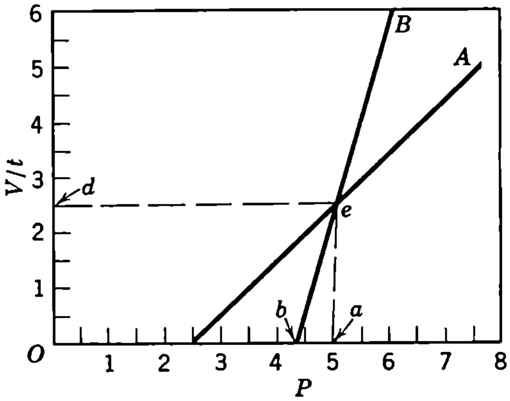


Fig. 5

If a pressure head of 50 g per square centimeter is employed, a flow of 0.25 cc per second will result. The so-called apparent viscosity would be $(50/0.25)K$ where K is the instrumental constant. For simplicity let $K = 1$. Then the apparent viscosity is equal to 200 poises. (The acceleration g is contained in K.) Now measure the non-Newtonian B in exactly the same manner, and see if the results are really comparable. Sample A was subjected to a pressure of 50 g per square centimeter. Exact duplication of the method necessitates that sample B is also subjected to 50 g per square centimeter. From Figure 5 it can be seen that a flow of 0.25 g per second is again induced. The apparent viscosity for B is, then, $(50/0.25)K$ or 200 poises. The advocates of the one-point method claim that the measurements for A and B are comparable because they were made in the same manner. Comparing the apparent viscosity of 200 poises for A with the apparent viscosity of 200 poises for B indicates no difference in them, and so they should be rheologically identical. A glance at Figure 5 shows this is not so. Any one familiar with consistency curves can see that sample A is "long" and viscous while sample B, by comparison, is "short" and much less viscous. The apparent viscosities, therefore, are not comparable, being in disagreement with the facts.

The argument will now be advanced that the example used was not quite fair because the chances of selecting a pressure that would correspond to the crossing point of the two curves would not be very great. In reply it can be stated that, if any pressure between the points a and b had been chosen, the results still would not be comparable for they would show that A is less viscous than B. The conclusion is that, if apparent viscosities fail to be comparable in any part of the consistency curves, there is no reason to believe that they are ever comparable except at infinitely high (and impractical) pressures.

A comparison of the *plastic viscosities* will now be made. In order to do this it is necessary to introduce the yield-value intercepts.

For sample A, $$U = \frac{50 - 25}{0.25} K = 100 \tag{9}$$

For sample B, $$U = \frac{50 - 44}{0.25} K = 24 \tag{10}$$

From Equations 9 and 10 it is seen that sample A is a little more than four times as viscous as sample B. That is as it should be.

Discussion and Summary of Chapter 2

So far quite a few ideas have been presented. They might seem at first to be more or less disconnected. Actually they all fit into the pattern that constitutes our rheological system. This should become apparent in the next chapter.

Three models of flow have been described. The first, in order to give it a name, has been called Newtonian. It is characterized by having the same shearing force on each layer, thus resulting in a constant dv/dr across the direction of flow. Experimentally it is difficult or impossible to produce a Newtonian model. Two other models have been described. These occur in flow through capillaries. One kind happens when a Newtonian liquid is flowing. In this case dv/dr is not constant, but varies with r, the distance from the axis to the point under consideration. The other model occurs when a Bingham body is employed. Here dv/dr varies the same as it does for a Newtonian in a capillary, but becomes equal to zero as soon as $Pr/2l$ becomes less than f. This gives a model containing simultaneously both laminar and plug flow.

The Newtonian and Bingham concepts have been given in Equations 1 and 2. Because the Newtonian model of flow cannot be produced in the laboratory, neither equation is subject to direct proof. After Poiseuille determined by experiment that the volume of flow discharged by a capillary tube in unit time is directly proportional to the activating force, mathematicians developed the theoretical equation of flow for capillaries. In making their deduction they used the Newtonian hypothesis in regard to the rate of flow being proportional to the shearing force. This procedure led to Equation 3, which checked with Poiseuille's discovery, thus proving indirectly (without the aid of the Newtonian model) that Equation 1 is valid.

When it was attempted to obtain the capillary-tube-flow equation for Bingham bodies by the simple expedient of inserting a "friction" factor in Equation 3, it gave Equation 4, which was found not to be in accord with experiment. This equation predicts a linear curve for V/t versus P. Experimental results give a nonlinear one. The reason for this discrepancy was not understood until the microscope revealed the fact that in capillary tubes Bingham bodies give a model of flow quite different from that of Newtonians. This was sufficient to account for a large part if not all of the nonlinearity in the consistency curve of plastic materials.

Apparent viscosity and the one-point method are compared with plastic viscosity and the multipoint method. Apparent viscosities are seen not to be comparable even when run exactly alike. Plastic viscosities are comparable.

Various kinds of yield values have been discussed. The Bingham yield value is the only one that is used in the system described here. It can be defined from Equation 2. It is the minimum tangential shearing force that will just cause flow. In the Newton model of flow each layer has the same shearing force. Therefore, shearing starts in all layers simultaneously. In the capillary model of flow the outer layer next to the wall of the capillary has the greatest shearing force. A material with a Bingham yield value, consequently, undergoes its initial shear at that place.

Houwink describes two other yield values besides the Bingham yield value. It is shown in Chapter 3 that the Houwink yield values, which he symbolizes f_l and f_h are known functions of the Bingham yield value and are, therefore, unnecessary.

Questions and Problems

1. Define (*a*) coefficient of viscosity, (*b*) coefficient of plastic viscosity, (*c*) apparent viscosity.
2. (*a*) What is a poise? (*b*) From where did the name come? (*c*) Has a unit of plastic viscosity been given a name?
3. (*a*) What is K? (*b*) Can you determine its dimensions? (*c*) Can you determine the dimensions of the coefficient of plastic viscosity? (*d*) Do they differ from the dimensions of the coefficient of viscosity?
4. If the radius of a capillary is 0.04 cm and its length is 4.0 cm, what is the instrumental constant?
5. Using the capillary in problem 4, the V/t was found to be 2.5 cc per second under an end pressure of 100 g per square centimeter in excess of the atmospheric pressure. What is the viscosity of the material? The exit end of the capillary is at atmospheric pressure.
6. In problem 5, what is the tangential shearing force at (*a*) $r = R$? At (*b*) $r = R/2$? At (*c*) $r = R/10$? At (*d*) $r = 0$? (*e*) What are the velocities at these four places with respect to the wall?
7. If an intercept of 35 g per square centimeter is produced from a plastic using a tube with $l = 6.5$ cm and $R = 0.05$ cm, what is the tangential shearing force in dynes that will cause flow? Has it got a name?
8. In what ways has the microscope proved itself of value in the study of flow?

9. If, when using a microplastometer, it can be seen that the outer layer of particles in a plastic become detached from the plug at 75 g per square centimeter end pressure, what is the yield value if $l = 3.0$ cm and $R = 0.015$ cm?
10. What expedient can be used to study the mechanism of flow inside the plug?

CHAPTER

3

An important question has probably arisen in the reader's mind. If the Newtonian model of flow cannot be produced in practice and Equation 4 is not in agreement with experimental facts, how can the investigator measure either yield value or plastic viscosity? In order to obtain an answer, a study of the works of Buckingham and of Reiner and Riwlin must be made.

The Buckingham Equation

In 1921 Buckingham[2] published a paper in which he derived a theoretical equation of flow through a capillary tube for plastic materials. He based his deduction on several concepts. The first one is expressed in Equation 2, which states that shear will not take place unless $F > f$. It should be understood that Buckingham made no claim as to the validity of Equation 2 and, therefore, realized that the correctness of his own deduction would be in doubt until Equation 2 could be experimentally justified. He also introduced a hypothesis of his own in regard to the constancy of ϵ, the thickness of the lubricating layer of vehicle which causes slip. He felt no great certainty that ϵ remained constant during increasing rate of flow and even pointed out that, if ϵ becomes larger, his equation, modified accordingly, would fit more nearly the available laboratory data.

Before describing Buckingham's work in what might seem an unusually detailed manner, the necessity for doing so must be explained. During the last hundred years or so, investigators have employed both capillary and rotational viscometers for careful scientific work. Other means like the falling-ball and the oscillating-disk methods have been used, but the greater part of the work seems to have been confined to the two methods first mentioned. Of these, the capillary-tube viscometer has had the more important part. In due course the capillary viscometer has become almost synonymous with the idea of precision and accuracy in scientific rheology. Furthermore, capillary viscometers have become firmly established in most plant laboratories as the principal instrument for rheological measurements. If Newtonians were the only materials subject to investigation, that situation would be sound enough, but non-Newtonians of the Bingham type play an important role in the rheology of today, and what constitutes the most suitable method for measuring them must be given full consideration. If the investigator is using a capillary viscometer for plastics, he will have to substitute a rotational instrument in its place in order to follow the present plan. Naturally, he will wish to have this change fully justified before making it; for the change involves expense, work, and time. A fairly comprehensive analysis of Buckingham's work is, therefore, in order.

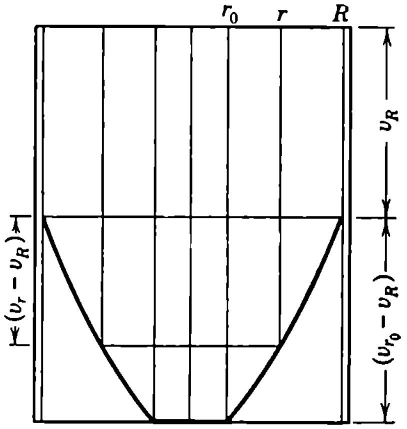


Fig. 6. Buckingham Model of Plastic Flow in Capillary.

For simplicity, Buckingham assumed that the end and kinetic energy corrections are negligible. (See Appendix B for these corrections.) This simplification in no way invalidates his deduction. In Equation 2, he substitutes $Pr/2l$ for F giving

$$-\frac{dv}{dr} = \mu\left(\frac{Pr}{2l} - f\right) \tag{11}$$

Then, for two different velocities at $r = r$ and $r = R$,

$$v_r = -\mu\left(\frac{Pr^2}{4l} - fr\right) + \text{constant} \tag{12}$$

$$v_R = -\mu\left(\frac{PR^2}{4l} - fR\right) + \text{constant} \tag{13}$$

Subtracting gives the relative velocity between the cylinder with radius r and the slippage velocity at the wall where $r = R$. (See Figure 6.)

$$v_r - v_R = \mu\frac{P(R^2 - r^2)}{4l} - f(R - r) \tag{14}$$

It is now necessary to determine the speed of the solid plug. Buckingham does this by letting $r = r_o$ and then substituting its value $2lf/P$ in Equation 14. Then,

$$v_{r_o} - v_R = \mu\left(\frac{PR^2}{4l} + \frac{lf^2}{P} - fR\right) \tag{15}$$

Determining the volume of flow per second V/t is a somewhat lengthy procedure, and only the important steps will be indicated. It is evident that the volume of flow is the sum of the volume of the central plug plus the volume around it undergoing laminar flow. Hence,

$$\frac{V}{t} = \pi r_o^2 v_{r_o} + \int_{r_o}^{R} 2\pi r v_r \, dr \tag{16}$$

Substituting the values already given for r_o, v_{r_o} (from Equation 15), and v_r (from Equation 14), integrating, and letting $2lf/R = p$, gives

$$\frac{V}{t} = \frac{\pi R^4 \mu}{8l}\left(P - \frac{4}{3}p + \frac{p^4}{3P^3}\right) + \pi R^2 v_R \tag{17}$$

When $P = p$, the first term in Equation 17 becomes zero, and the flow then is caused entirely by slippage. When $P < p$, the first term is omitted. When there is no slippage, the last term vanishes. Equation 17 takes into full consideration the change in regime from plug to laminar flow. After studying it, it is difficult to understand how rheologists can trust a purely empirical equation to give a true mathematical representation of plastic flow in a capillary tube.

The final step in the development of the Buckingham equation is the elimination of v_R in the last term. If it is assumed that the lubricating layer next to the capillary wall is very thin, then,

$$-\frac{dv}{dr} = \frac{v_R}{\epsilon} \tag{18}$$

The lubricating layer being a Newtonian with viscosity η,

$$-\frac{dv}{dr} = \frac{Pr}{\eta(2l)} \tag{19}$$

Then,

$$v_r = \frac{\epsilon PR}{2\eta l} \tag{20}$$

and, on substitution, the final equation becomes

$$\frac{V}{t} = \frac{\pi R^4 \mu}{8l}\left(P - \frac{4}{3}p + \frac{p^4}{3P^3}\right) + \frac{\pi R^3 \epsilon P}{2\eta l} \tag{21}$$

The development of Equation 21 is one of the most important milestones in the history of modern rheology, but not because it became a means for determining plastic viscosity and yield value, for, unfortunately, the equation could not be solved satisfactorily. The importance of Equation 11 lies in the fact it proves the plastic-flow curve for a capillary tube cannot be linear; and, hence, it succeeded in stopping students of rheology from attempting to obtain U or f by extrapolating a nonexisting straight part of the curve to the pressure axis. This left rheology, as far as plastics were concerned, in an awkward position, for there seemed to be no possible method of obtaining correct measurements of yield value and plastic viscosity. This condition existed for a number of years until Reiner and Riwlin discovered a way out. This is explained in the latter part of the chapter. In the meantime, the difficulties of solving the Buckingham equation must be investigated.

The equation gives a curve composed of two parts. The first part OA (Figure 7) is where the entire flow is the result of slippage. The second part is a hyperbola AF. At point A the outer layer begins to shear; consequently the abscissa of A is the pressure p, from which the yield value is calculated. From A upward the laminar flow increases while the volume of plug flow decreases. An important observation must now be made: *Plug flow is not eliminated completely until* V/t *is infinite.* It is for this reason that the plastic-flow curve for capillaries never becomes linear. The entire curve from point A to infinity is theoretically a mixed regime consisting of both laminar and plug flow in changing proportions. Superimposed on that flow is slippage flow. The plastic flow (which here includes plug flow) can be found by subtracting the ordinates of the slippage curve from the ordinates of the hyperbola AF.

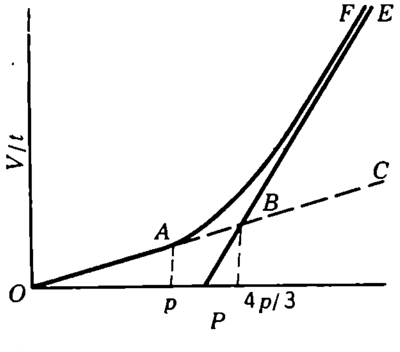


Fig. 7. The Buckingham Curve

Equation 11 contains four unknown quantities: U, p, ϵ, and η. However, there is no particular reason for determining the individual values of ϵ and η; so they can be combined as ϵ/η, which will reduce the number of simultaneous equations that must be solved from 4 to 3. Equation 21 can then be written in the form,

$$\frac{V}{t} = AP + \frac{R}{P^3} - C \tag{22}$$

where

$$A = \frac{\eta\pi R^4\mu + 4\pi R^3\epsilon}{8l\eta} \tag{23}$$

$$B = \frac{\pi R^4 \mu p^4}{24l} \tag{24}$$

$$C = \frac{4p\pi R^4\mu}{24l} \tag{25}$$

Then

$$p = \sqrt[3]{\frac{4B}{C}} \tag{26}$$

and

$$f = \frac{R}{2l}\sqrt[3]{\frac{4B}{C}} \tag{27}$$

From Equations 24, 26, and 27,

$$\mu = \frac{3C}{\pi R^3 f} \tag{28}$$

Equations 27 and 28 are simple enough for practical purposes; but they cannot be solved without knowledge of the value of the constants B and C. The value of these constants cannot be obtained unless A is also determined. Even if p could be found by graphical means (which it cannot), only the ratio B/C could be had; and, although this ratio can be substituted in Equation 27, it would be useless for the solution of Equation 28. This means that there is no escape from the task of solving three simultaneous equations.

In order to give the student some idea of the great difficulty involved in obtaining a solution to Equation 21, the three simultaneous equations will be written down. Compare these with the relatively simple equations of the rotational viscometer when that instrument is described.

$$A = \frac{\left[\left(\frac{V}{t}\right)_1 (P_3^{-3} - P_2^{-3}) + \left(\frac{V}{t}\right)_2 (P_1^{-3} - P_3^{-3}) + \left(\frac{V}{t}\right)_3 (P_2^{-3} - P_1^{-3})\right]}{P_1(P_3^{-3} - P_2^{-3}) + P_2(P_1^{-3} - P_3^{-3}) + P_3(P_2^{-3} - P_1^{-3})} \tag{29}$$

$$B = \frac{\left(\frac{V}{t}\right)_1 - \left(\frac{V}{t}\right)_2 - A(P_1 - P_2)}{P_1^{-3} - P_2^{-3}} \tag{30}$$

$$C = A + BP_1^{-3} - \left(\frac{V}{t}\right)_1 \tag{31}$$

P_1, $(V/t)_1$; P_2, $(V/t)_2$; and P_3, $(V/t)_3$ are three different points on the experimentally determined curve. These must be spread as far apart as possible. Various schemes can be devised for reducing somewhat the labor of computing Equations 29, 30, and 31; but it hardly pays to do so. Plastic viscosity can be obtained probably with a fair degree of accuracy from these equations; but the yield-value determination will be far from correct. The reason for this is lack of close agreement between Equation 21 and the lower end of the experimental curve (up to point *A*, Figure 7). It is unfortunate that the disagreement should be at that place, for otherwise Equation 21 could be used, if the labor in solving it was not considered too great.

In his paper, Buckingham was unable to compare his equation with sufficient experimental data to see how close an agreement might exist. Indeed, no one seems to have published data showing such a comparison. Data are given here for that purpose. They were obtained from pigment–vehicle mixtures with a Bingham and Green Plastometer.[1]

The Capillary-Tube Plastometer

This instrument is shown diagrammatically in Figure 8. It is composed of a container *A* for holding the plastic, a capillary *G*, an air-pressure tank *E*, and a manometer *C*. *B* is a gas flowmeter for measuring the rate of flow of material extruded from G, and D is a comparator for reading the flowmeter. The parts A and B are in a constant-temperature bath F. When the plastic passes through the capillary G into I, a volume of air is forced through B equal to the volume of plastic extruded. A back pressure is built up in the flowmeter because the displaced air must pass through the capillary B.

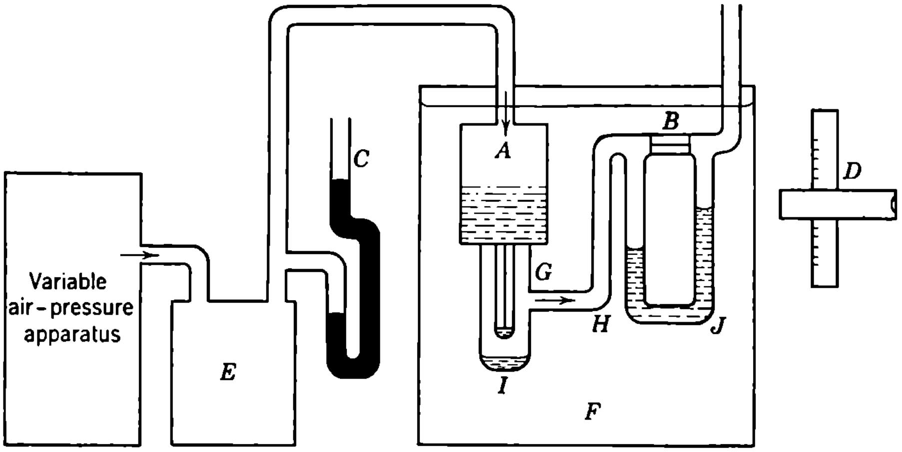


Fig. 8. The Capillary Tube Plastometer

This pressure depresses the manometer J, and the amount of depression, read with D, gives the rate of flow, V/t. The pressure causing flow through G is read on the manometer C. The consistency curve is obtained by plotting V/t for a series of different pres-

TABLE 1

DATA FOR FIGURE 9

Experimental Points		* Points Taken on Experimental Curve for Calculating f and U		
P (g)	V/t (cc/sec)	P	V/t	
160.1	0.00230	100 calculated	0.00443	
307.9	0.00652	174 calculated	0.00279	$f = 847$ dynes/cm^2
450.1	0.01084	* 200	0.00320	$U = 7.25$ poises
588.2	0.01513	* 300	0.00609	$p = 174$ g/cm^2
729.6	0.01963	* 500	0.01239	$(V/t)p = 0.00279$

Radius of capillary, 0.031365 cm.
Length of capillary, 3.162 cm.

$A = 0.00003225$
$B = 4983$
$C = 0.00377$

sures. Three points on the curve can be taken for determining the constants A, B, C. Their values are substituted in Equation 22, which is then plotted. As can be seen from Figures 9 and 10, agreement with the experimental data is satisfactory except at the lower part of the theoretical curve. The plastic viscosity and yield value are determined from Equations 27 and 28, the calculated values of B and C being used.

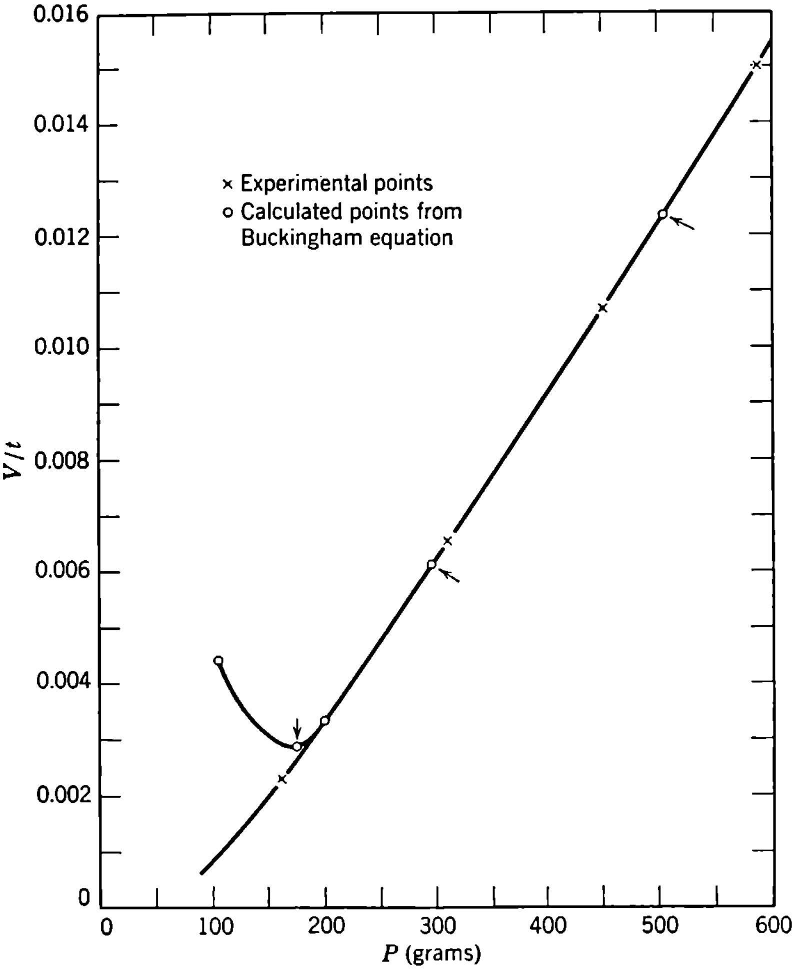


Fig. 9

In order to determine yield value with any degree of certainty, it is necessary that the lower end of the theoretical curve should coincide with the experimental one. Unfortunately, this is just where Equation 21 fails. In Figure 10 the three points used for the simultaneous equations were chosen in a way to favor the lower end of the curve. This was done by selecting two of the points in the neighborhood of the yield value. In this case, neither the upper nor lower parts of the theoretical curve were in agreement with the data.

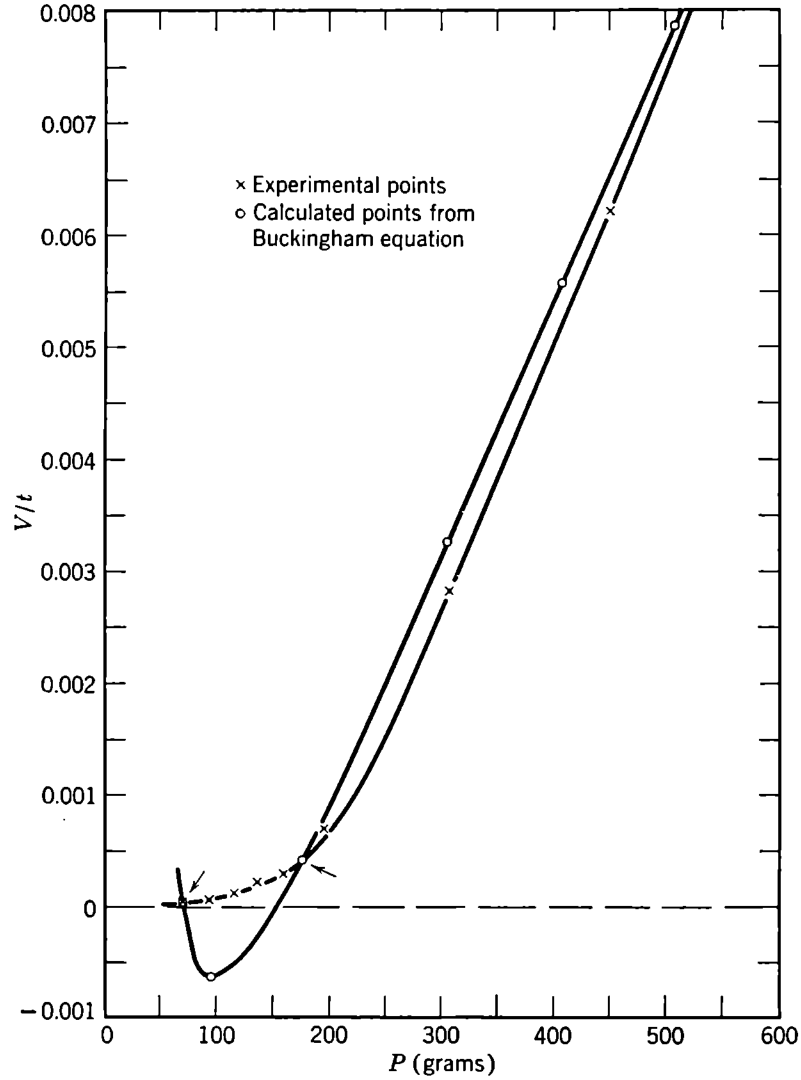


Fig. 10

Because of the time and labor required for solving Equation 21 and because that equation lacks sufficiently close agreement with the experimental curve, it has not been employed by either scientists or by technologists for rheological determinations.

TABLE 2

DATA FOR FIGURE 10

Experimental Points		* Points Taken on Experimental Curve for Calculating f and U		
P (g)	V/t (cc/sec)	P	V/t	
70.1	0.000048	* 70.1	0.000048	
91.5	0.000063	92.0 calculated	0.00064	
110.5	0.000119	* 175.	0.00047	f = 302 dynes/cm^2
138.8	0.000228	300. calculated	0.00326	U = 2.75 poises
157.3	0.000316	400. calculated	0.00551	p = 92.0 g/cm^2
193.3	0.000715	500. calculated	0.00778	$(V/t)p$ = 0.00064
301.5	0.002700	* 560.	0.00907	
447.5	0.006184			
595.2	0.01007			

Radius of capillary, 0.031383 cm.
Length of capillary, 4.681 cm.

$A = 0.00002207$
$B = 693.4$
$C = 0.00356$

The Slippage Curve

The lower part of the consistency curve of plastics is important only because of the confusion it has created in regard to the reality of yield value. All rheological consistency curves bend toward the origin. It can never be determined experimentally whether these curves meet the origin or not, for no matter how small the flow is, it is always greater than zero. This fact makes it impossible to determine whether the material yields under infinitesimally small pressure or not. If it does yield under such pressure, then there would be no yield value. The curvature toward the origin indicates such a possibility. It is, therefore, necessary to understand how this curvature is produced.

One of the reasons for the bend has been given, that is, the change (on the downcurve) from laminar to plug flow. A second reason is slippage. According to Buckingham's equation, the volume of slippage flow is $\epsilon RP/2$. There is no factor in this term like a yield value. Flow is finite as long as P is finite. Hence, the slippage portion of the curve must intersect the origin. This gives a second reason why the consistency curve bends as it does; and neither reason is based on the concept of zero yield value.

There are two ways of studying very minute rates of flow. One is with the microplastometer, which has already been described. Magnifications as high as 400 diameters can be used; and under such conditions exceedingly small shearing action can be detected when it exists. Plastics with consistency curves that bend toward the origin have been examined, and no detectable shear has been observed though the applied pressure has been sufficient to cause a substantial slippage flow. The plug can be seen to remain solid and intact during this kind of flow.

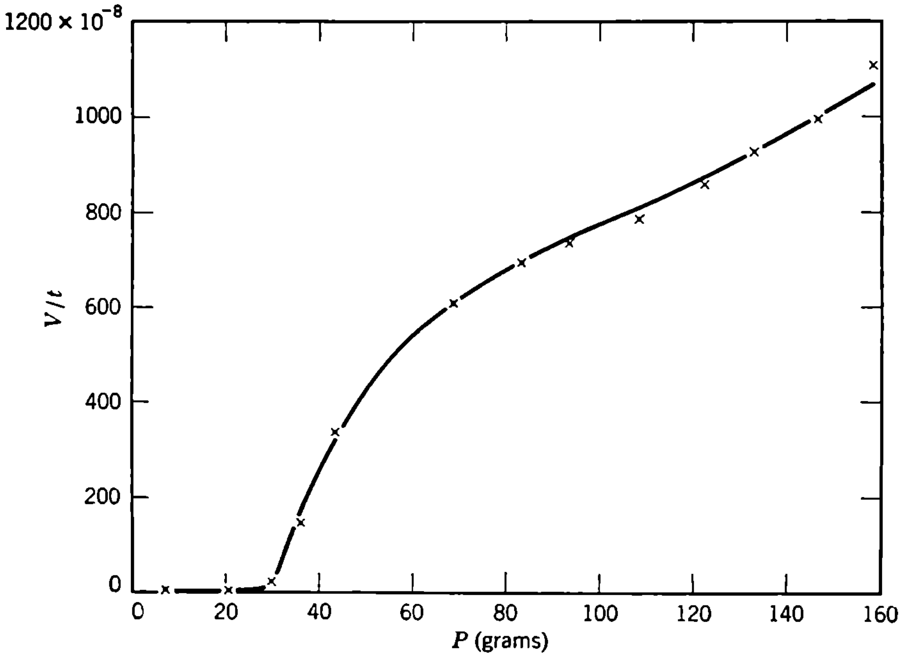


Fig. 11. Slippage Flow in a Capillary Tube

The second method is by means of the gas flowmeter attached to the plastometer shown in Figure 8. By inserting a fine wire in capillary B and so nearly closing it, rates of flow as low as 1 cc per hundred years can be detected. The microplastometer was used for obtaining the data for Figures 11 and 12. From these curves there seems to be no justification for assuming that slippage flow (very near the origin) is necessarily linear. It should be noted that the curves shown here are highly magnified portions of a very small spot at the lower end of the consistency curve. Normally, this spot would hardly be visible. The low flat part of the curve running along the pressure axis in Figure 11 is given in a magnified form in Figure 12. Though the curve is not linear, it seems to be headed for the origin. Since it is all slippage flow in this region (as far as the microscope can show) the direction of the curve hardly proves the nonexistence of yield value.

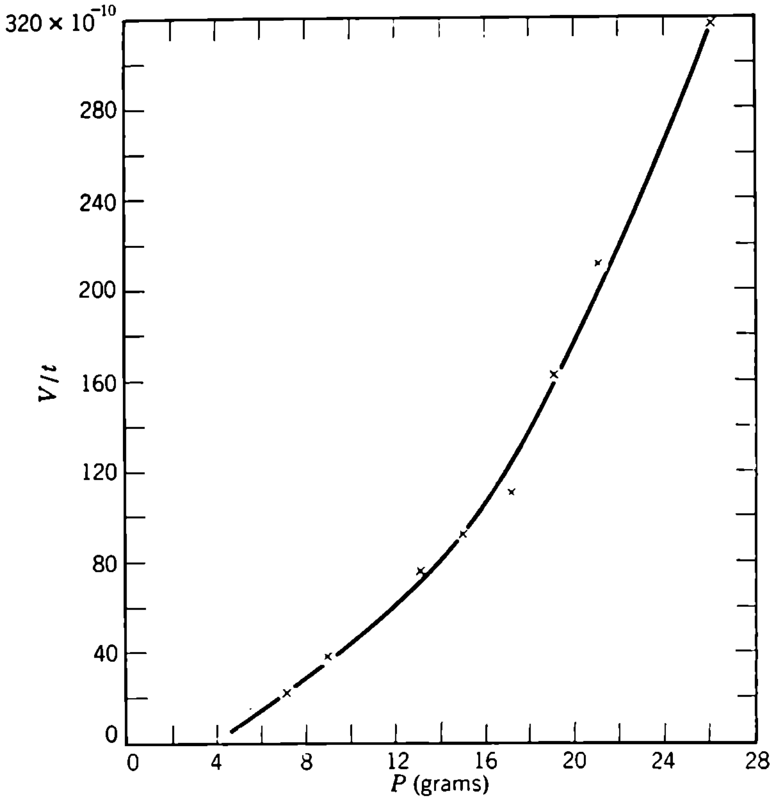


Fig. 12. Slippage Flow in a Capillary Tube

Reiner and Riwlin Equation for the Rotational Viscometer

The lack of agreement of the Buckingham equation with experiment, together with the considerable labor needed in solving it, barred it as a method of approach to the problems of industrial rheology. Furthermore, it made indefensible the simple expedient of extrapolating the consistency curve to the pressure axis as a means of determining f and U. As a result, there remained for the time being no logical method for resolving the consistency curve of a plastic into its two rheological factors—yield value and plastic viscosity. This situation remained unchanged until Reiner and Riwlin [3] in 1927 published their equation of plastic flow in rotational viscometers. In this work they pointed out the important fundamental difference given (in the following) that exists between the capillary and rotational viscometers when the material being tested is a plastic of the Bingham-body type.

The rotational viscometer is shown diagrammatically in Figure 13. The material A is placed in the cup C. A bob B is immersed in A and suspended by a torsion wire E from a fixed support F. A scale D with a pointer G is attached to read the torque induced when the cup is rotated. The rotation of the cup is given either in rpm or in angular velocity ω. The torque is equal to the scale reading multiplied by the wire constant K. A detailed description of a rotational viscometer built for industrial use is given in Part 2, Chapter 8.

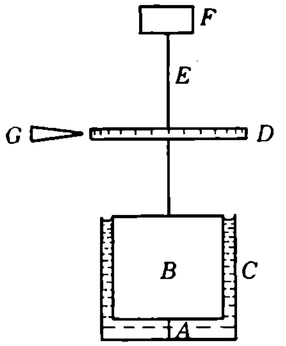


Fig. 13. Diagram of the Rotational Viscometer. The Cup Rotates

In 1929 Reiner and Riwlin published an English version of their original work. That paper appeared in the *Journal of Rheology*, volume 1, 1929. The reader is cautioned that there exists an unfortunate typographical error in which R^2 appears as R^4 from their equation 12 to the end of the article. However, the paper is easy to follow. An outline of their procedure is presented:

Bingham has stated (in regard to a discussion on Buckingham's equation) that "Rather than complicate our formula, it would seem to me a much better plan to so change the conditions of flow that the formula will be linear." Reiner then states, "This plan has been followed by me in collaboration with Miss Riwlin from the Hebrew University in Jerusalem." From the present paper (Reiner and Riwlin, 1929) it will be seen that it is possible to choose the conditions of flow so that the formula based on Bingham's law of plastic flow remains linear. This is realized in the rotational viscometer.

Reiner and Riwlin's development of the equation of flow in the rotational viscometer follows:

Let R_b = the radius of the bob
R_c = the radius of the cup
h = the depth of immersion of the bob
T = the moment due to the external forces (Torque)

At equilibrium, for a cylinder of radius r (between R_b and R_c), the moment of internal forces must be equal to T. Then, if F is the shearing force per unit area,

$$F \times 2\pi r \times r = T \tag{32}$$

or

$$F = \frac{T}{2\pi r^2 h} \tag{33}$$

Bingham's assumption is that there can be no plastic flow if F is less than the yield value f. From Equation 33 it may be seen that the maximum shearing stress is at $r = R_b$. Then,

$$F_{\text{max}} = \frac{T}{2\pi R_b^2 h} \tag{34}$$

If

$$\frac{T}{2\pi R_b^2 h} < f \quad \text{or} \quad T < 2\pi R_b^2 hf = T_0 \tag{35}$$

the material will not flow. When T exceeds T_0 (Figure 14), the material will start to flow where the stress is the largest. From Equation 34, this is seen to be at the surface of the bob. However, if the stress at the surface of the cup is still below f, laminar shearing will not take place there, and a shell of solid material existing at that surface will move along with the cup as a whole. The stress at the wall of the cup is the minimum shearing force and is equal to

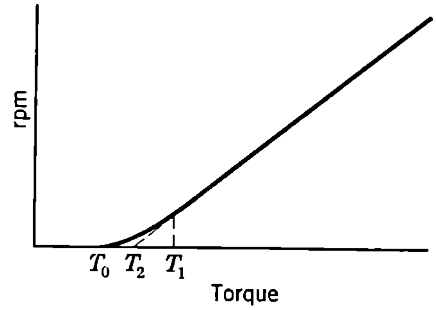


Fig. 14. Consistency Curve of a Bingham Body Made with a Rotational Viscometer

$$F_{\text{min}} = \frac{T}{2\pi R_c^2 h} \tag{36}$$

If

$$\frac{T}{2\pi R_c^2 h} \geqq f$$

or

$$T \geqq 2\pi R_c^2 hf = T_1 \tag{37}$$

then all the material between the cup and bob walls will be in laminar flow. This, as Reiner points out, is the "essential difference between the plastic flow in the rotating cylinder and the plastic flow in the capillary. As is well known, there exists *always* a 'solid cylinder' near the axis of the capillary, no matter how great the velocity is, and from this it follows that the consistency curve of plastic flow in the capillary is not linear."

If the reader will turn back to Equation 11, he will observe that the shearing stress F, which is equal to $Pr/2l$, cannot equal or exceed the yield value f at the axis, where $r = 0$, unless P becomes infinite. It is for that reason that, at any finite value of r, there will always be a solid cylinder of the material near the axis of the capillary; and so the consistency curve can never be linear, because there will always be a transition from solid to laminar flow as P increases. This is probably the most important of the various reasons for abandoning the capillary viscometer and replacing it with the rotational viscometer when measuring plastics of the Bingham-body type. This step also constitutes a very important one in the development of our rheological system.

The velocity gradient is now introduced for a rotational movement. The angular velocity is ω. Then the velocity at a distance r from the axis is $r\omega$. Quoting Reiner further, "The velocity at a distance dr beyond that point is

$$(r + dr)(\omega + d\omega) = r\omega + \omega\, dr + r\, d\omega + (dr)\,(d\omega) \qquad (38)$$

The last term can be neglected, being of the second order." The increase in velocity in passing from r to $r + dr$ is

$$dv = \omega\, dr + r\, d\omega \qquad (39)$$

and the velocity gradient is

$$\frac{dv}{dr} = \omega + r\frac{d\omega}{dr} \qquad (40)$$

The first term ω is the angular velocity all the cylinders would have, if no internal shearing of the material took place, that is, if the cylinder, bob, and material rotated as a solid piece. The internal stresses, therefore, arise only from the second term

$r\,d\omega/dr$. Introducing this velocity gradient into Bingham's law of plastic flow gives

$$r\frac{d\omega}{dr} = \mu(F - f) \tag{41}$$

But

$$F = \frac{T}{2\pi r^2 h} \tag{42}$$

Substituting 42 in Equation 41 gives

$$r\frac{d\omega}{dr} = \mu\frac{T}{2\pi r^2 h} - \mu f \tag{43}$$

Then,

$$\frac{d\omega}{dr} = \mu\frac{T}{2\pi r^3 h} - \frac{\mu f}{r} \tag{44}$$

which gives, on integration,

$$\omega = -\mu\frac{T}{4\pi r^2 h} - \mu f \ln r + \text{constant} \tag{45}$$

When $r = R_b$, $\omega = 0$; then,

$$0 = -\mu\frac{T}{4\pi R_b{}^2 h} - \mu f \ln R_b + \text{constant} \tag{46}$$

or

$$\text{Constant of integration} = \mu\frac{T}{4\pi R_b{}^2 h} + \mu f \ln R_b \tag{47}$$

Substituting in 45 gives

$$\omega = \mu\frac{T}{4\pi h}\left(\frac{1}{R_b{}^2} - \frac{1}{r^2}\right) - \mu f \ln\frac{r}{R_b} \tag{48}$$

Let the angular velocity ω equal Ω when T becomes sufficiently large so that all the material between the walls of the cup and the bob is in laminar flow. Then,

$$\Omega = \mu\frac{T}{4\pi h}\left(\frac{1}{R_b{}^2} - \frac{1}{R_c{}^2}\right) - \mu f \ln\frac{R_c}{R_b} \tag{49}$$

This is the Reiner and Riwlin equation of plastic flow in a rotational viscometer. It is the equation of the linear part of the curve only, that is, from T_1 upwards (see Figure 14). It is not necessary, as will be shown, to know the equation for the lower end of the curve where transition from plug to laminar flow takes place. In that respect it differs from the Buckingham equation. The curve of Equation 49, on extrapolation to the torque axis, cuts it at the point $\omega = 0$ and $T = T_2$. Then,

$$\frac{T_2}{4\pi h}\left(\frac{1}{R_b^2} - \frac{1}{R_c^2}\right) = f \ln \frac{R_c}{R_b} \tag{50}$$

Letting

$$\frac{\dfrac{1}{R_b^2} - \dfrac{1}{R_c^2}}{4\pi h} = S \tag{51}$$

and

$$\frac{S}{\ln \dfrac{R_c}{R_b}} = C \tag{52}$$

gives

$$f = CT_2 \tag{53}$$

Substituting Equations 51, 52, and 53 in Equation 49 and writing U for $1/\mu$ give

$$U = \frac{(T - T_2)S}{\Omega} \tag{54}$$

Equations 53 and 54 are the two most important flow equations for plastics of the Bingham-body type where the rotational viscometer is used in making the rheological measurements. They are the foundation on which the rheological system presented in this book is constructed.

The amount of torque T is calculated from the number of degrees through which the bob (and the wire) have been deflected multiplied by the wire constant K. Obviously, this constant is the torque per degree. Reiner and Riwlin outlined a theoretical method for determining the wire constant but state that its computation requires a knowledge of the moment of inertia of the bob. As this factor is not always known and is somewhat difficult to obtain, they suggest that the simplest procedure is to calibrate the wire with a liquid of known viscosity. Care should be taken that this liquid is a Newtonian. The equation for K is

$$K = \frac{\eta\omega}{\theta S} \tag{55}$$

and

$$T = K\theta \tag{56}$$

where θ is the deflection. This method is practical enough if the calibrating liquid is not too high in viscosity and if the rate of shear is not maintained above that critical value where the material ceases to act as a Newtonian.[4]

If the investigator constructs a viscometer such as described in Part II of this book, then the wire constant can be obtained directly without recourse to a standard calibrating liquid. This is a decided advantage because the rate of shear at which the viscosity determination was made is never available to the purchaser of such a standard material. Consequently, the figure given for the viscosity coefficient is just as useless as it would be if the temperature at which the determination was made was omitted. Few rheologists realize the importance of this fact.

In concluding their paper, Reiner and Riwlin make a statement which might be subject to misinterpretation. They say: "This, therefore, proves that in a rotation viscometer the consistency curve is a straight line. It is true that this straight line does not start at the torque axis. According to Equation 35 the consistency curve starts at the point T_0 and is curved to a point T_1. This part, however, is quite negligible. . . ." This last statement might seem to imply that, if the lower part of the curve were not negligible, the usefulness or perhaps even the validity of Equation 49 might be impaired. This of course is not so. The length of the lower part of the curve is immaterial. It is kept small simply for convenience and not for increasing the accuracy or usefulness of the equation. It is necessary to be able to distinguish only between the straight and curvilinear parts of the curve in order to make accurate use of Equation 49.

From Equations 35, 37, and 49, it is possible to determine what must be done in order to decrease the size of the lower portion of the curve. There are two ways of carrying this out. One is by decreasing the difference between T_1 and T_0, and the other, by decreasing the Ω for T_1.

$$\begin{array}{rl} T_1 &= 2\pi R_c^2hf \\ T_0 &= 2\pi R_b^2hf \\ \hline T_1 - T_0 &= 2\pi hf(R_c^2 - R_b^2) \end{array} \tag{57}$$

From Equation 57 it is seen that $T_1 - T_0$ becomes smaller, the nearer the radii of the bob and cup approach each other, h remaining constant.

Substituting the value of T_1 given in Equation 37 in Equation 49 gives

$$\Omega = \mu f\left(\frac{R_c^2}{2R_b^2} - \frac{1}{2} - \ln\frac{R_c}{R_b}\right) \tag{58}$$

Here again it is seen that decreasing the Ω for T_1 depends on R_b and R_c approaching each other. The conclusion is that, in order to have a narrow curvilinear portion, $R_c - R_b$ must be as small as practical. What happens when h increases, R_c and R_b remaining constant? From Equation 57, it can be observed that this results in increasing the length of the curvilinear portion. On the other hand, h has been canceled out of Equation 58; so any change in h does not affect the Ω of T_1.

It has been stated in Chapter 1 that the concept of three different yield values is unnecessary. These "yield values" are not yield values but three different intercepts on the force axis. They are shown in Figure 2d. From Reiner and Riwlin's work it is evident that these intercepts are three different functions of one and the same yield value f. They are:

$$T_0 = 2\pi R_b^2hf \tag{59}$$

$$T_2 = \frac{f}{S}\ln\frac{R_c}{R_b} \tag{60}$$

$$T_1 = 2\pi R_c^2hf \tag{61}$$

This fact greatly simplifies the application of scientific rheology to industrial rheology. It is necessary to know only the experimental measurement T_1 and the instrumental dimensions R_b, R_c, and h. The real yield value is calculated, then, from Equation 53.

The investigator should now compare the equations of plastic flow, 29, 30, and 31, for a capillary-tube viscometer, with the relatively simple Equations 53 and 54, for the rotational viscometer. The difference is striking. Which set the laboratory investigator will prefer is, no doubt, self-evident. The simplicity and solvability of Equations 53 and 54 constitute an important reason why the rotational viscometer has been selected in this book for measuring plastics of the Bingham-body type. There are also other reasons, which will appear under the subject of thixotropy. It must not be assumed that the rotational viscometer is universal in its application. The instrument is impractical for very high viscous materials like pseudoplastics of the synthetic-resin type. In this case the parallel-plate viscometers are far more serviceable. They are described under the section on pseudoplasticity.

Discussion and Summary of Chapter 3

In Chapter 3 it was shown that the model of flow of a Bingham body in a capillary tube differs substantially from the model of flow of a Newtonian. This difference arises from the existence of a yield value which holds the material together in plug formation until it is exceeded by the shearing force. The shearing force increases with r; consequently, the first shear takes place in the outermost layer as the force is gradually raised. This always leaves a plug at the axis of the capillary, for the end pressure would have to be infinite in order to produce a shearing force at the axis (where $r = 0$) equal to f. This fact led to the Buckingham equation.

Chapter 3 shows the development of the Buckingham equation, and proves that, for capillary tubes with a material of constant yield value, a straight part of the consistency curve can never be attained. This discovery made the use of capillary-tube viscometers (for Bingham bodies) impractical, especially for industry. It was also pointed out that the Buckingham equation fails to check with experimentally determined curves, and, consequently, a satisfactory solution of that equation cannot be had. Data and graphs are presented demonstrating the lack of agreement between theoretical and experimental determinations. Also slippage curves are given showing an apparent disagreement with a linear concept of slippage flow.

Reiner and Riwlin developed the equations of flow for Bingham bodies in a rotational viscometer. This equation is a linear one, starting from a point on the experimental curve designated as $T_1 = 2\pi R_c^2 hf$. It was pointed out that it is not necessary to know the equation for the nonlinear lower portion of the curve. Unlike the capillary-tube equation, the Reiner and Riwlin equation becomes linear at finite values of the applied force. This makes the rotational viscometer the ideal instrument for the industrial rheologist who wishes to measure yield value and plastic viscosity. The effect that changing R_c and R_b has on the length of the curvilinear portion of the curve is shown.

Questions and Problems

1. If $R_c = 2.0$ cm, $R_b = 1.8$ cm, and $h = 5.0$ cm, what does S equal? What does C equal? $\ln x = 2.31 \log x$.
2. If $\theta = 40°$ and $K = 600$, what does T equal? If $T_2 = 62.6 \times 10^3$ and $C = 1.60 \times 10^{-2}$, how much is f?
3. $T = 1000 \times 10^3$ and $T_2 = 300 \times 10^3$. $S = 2.30 \times 10^{-3}$ and ω for T is 10. What does U equal?
4. What are the advantages of the rotational viscometer over the capillary-tube viscometer? Can you name an advantage that the capillary-tube viscometer might have, in certain cases, over the rotational viscometer?
5. Is the rotational viscometer suitable for a material with a high viscosity like that of rosin for instance? If not, can you suggest a type of viscometer that might be used for such a material?
6. What materials and what viscometers produce linear consistency curves?
7. Why is it necessary to have coincidence of the lower end of the experimental and theoretical curves for capillary viscometers? Why is this unnecessary for rotational viscometers?
8. Do you think that the theoretical equation for the nonlinear portion of the experimentally determined curve for a Bingham body in a rotational viscometer can be deduced? Would there be any particular use for it if this should be done?
9. Give all the important points in the development of the rheological system outlined so far.

CHAPTER

4

Thixotropy

The subject of thixotropy is not a particularly important one in itself, but it is highly necessary that the investigator should have a clear understanding of it because of the effect thixotropy has on his laboratory measurements.

There is prevalent a tendency to depart somewhat from the original concept of thixotropy. Many writers now make the term cover materials that in no way resemble those substances which were recognized as thixotropic by the pioneers in the field. This change of viewpoint is not an admitted one but an unconsciously adopted one. Unfortunately, it often leads to the conclusion that any non-Newtonian is thixotropic, except those materials that are known as dilatant. The procedure, here, will be to retain the original concept of thixotropy as nearly as possible.

The word "thixotropy" means to change by touch. It was coined by Peterfi [5] in 1927 with Freundlich's approval. The thing that is "changed" is the structure of the material. It breaks down when shaken or stirred. Thixotropic structure, however, has an attribute that distinguishes it from all other types of structure—in the course of time the broken thixotropic structure will rebuild itself, if not prevented from doing so by externally applied forces.

It is important to note that the complete reaction—unbroken to broken, and back again to the rebuilt structure—takes place isothermally. That is another characteristic feature of thixotropic structure. The reaction is quite effective when seen for the first time. Some of the materials originally described as thixotropic were blood plasma and colloidal suspensions of ferric oxide.

There are types of structure that will not rebuild when broken. These structures are associated with aging and must not be confused with thixotropy. For instance, reactive pigments like zinc oxide when suspended in linseed oil with a suitable acid number will form zinc soaps which crystallize out in the suspension, forming a firm structure. If such a structure is broken, it will not reform unless there is sufficient acid remaining to form more soap. That type of rebuilding is not thixotropic, however.

The term "aging" is in constant use in the paint and printing-ink industries. The technologists in these fields do not, as a rule, think of aging as being a thixotropic process. They usually (and correctly) associate it with a chemical reaction between pigment and vehicle or with changes in the state of dispersion or of flocculation arising from surface adsorption. Such changes are nonreversible and differ decidedly in that respect from thixotropy.

There is another type of material to which the term "thixotropy," unfortunately, has been applied and which has, as a consequence, unnecessarily complicated the subject. The type referred to is a Bingham-body plastic with a pronounced yield value. It is the kind found occasionally that shows no visible evidence of breakdown when stirred or shaken. The argument is that the broken structure rebuilds so quickly after shaking has stopped that thixotropic buildup cannot be detected. If there is no way (by visual observation or by experimental measurement) to detect the phenomenon, existence of the phenomenon must be purely conjectural. If it were a good conjecture leading to a rationalization of the subject, it would be welcome. Unfortunately, it is not; it leads (as will be shown, when the hysteresis loop is discussed) to a serious conflict of ideas. Because comparatively few investigators have studied the thixotropic hysteresis loop, this conflict has not been given much publicity; consequently, a plastic with a pronounced yield value and no thixotropy is generally believed to be a material so highly thixotropic that its breakdown and subsequent buildup take place too rapidly to be detected.

In reference to the previous paragraph, Freundlich[1] has described an experiment which is claimed to illustrate the point. Freundlich made a heavy suspension of ground quartz in carbon tetrachloride. This produced a typical Bingham plastic. When the material was put into a test tube and shaken (with the thumb over the opened end) the material flowed forward and backward. When the thumb was removed suddenly and the test tube inverted, the suspension did not flow out. The conclusion was that the material would not flow when shaken unless it had first undergone thixotropic breakdown; also, that it did not finally flow from the test tube because, the instant the shaking stopped, thixotropic buildup had taken place. A study of Freundlich's papers on thixotropy leaves one in doubt as to how firmly he believed that his quartz suspension was thixotropic. Many of his followers have taken it for granted that he considered such materials to be highly thixotropic.

The criterion of thixotropy used in this book is the hysteresis loop. If a material is run in a rotational viscometer and two curves are produced, an up- and a downcurve, the material is thixotropic if these curves do not coincide but form a loop. The quartz and carbon tetrachloride mixture gives no loop. It is, therefore, considered to be nonthixotropic. The confusion lies in the fact that Freundlich's material flows when the applied force is greater than the yield value. Many investigators cannot visualize plastic flow without the aid of an accompanying thixotropic breakdown. It is necessary to be able to have flow without breakdown if a rational understanding of yield value and thixotropy is desired. This aspect of rheology is discussed in Chapter 6.

Thixotropic Structure

There are many types of structure that can be explained. Thixotropic structure is not one of them. The nature of the mechanism of thixotropy is still unknown. Microscopical examination reveals the fact that thixotropic materials of the pigment–vehicle type are flocculated. There are also flocculated pigment systems that are not thixotropic. No definite conclusion can, therefore, be drawn from microscopical observation. This does not indicate that the microscope (or the electron microscope) will not reveal eventually the secret of thixotropy. It means that so far this revelation has not been forthcoming.

There are structures that are microscopically visible. Soap formation in paints produces one of them. The zinc and lead soaps that form during the aging process can be seen sometimes as definitely crystalline materials, if the microscopical mount is not too dense or overilluminated. The refractive index of metallic soap usually does not differ greatly from that of the oil vehicle, and the resulting contrast is consequently small. The substage diaphragm should be nearly closed. If soaps form an adsorbed layer on the pigment particles, they cannot be seen. The setting of Portland cement is another example of structure produced by a crystalline growth binding the material together. Both soap formation and the setting of cement are the result of chemical reactions which are not reversible under the conditions of the experiment. Such chemically formed structures should never be classified as thixotropic.

When metals like lead are drawn through a die, they flow plastically. It has been suggested that they actually melt from a local formation of heat and really flow viscously. Some investigators, who are unable to believe in plastic flow, accept that viewpoint and consider that type of flow to be the result of thixotropic breakdown. This conception is not justified because one of the criteria of thixotropy is that the reaction must be an isothermal one.

Are there any ways by which thixotropic structure can be explained? The answer is yes; but no proof exists that they are correct. They are purely speculative. First, assume that the thixotropic phenomenon arises from structure. Second, that this structure possesses rigidity. Then to produce flow the structure must be broken, at least temporarily. As long as flow continues, the broken structure will not reform even in part, unless the rate of shear is lessened. The applied shearing force used in a viscometric measurement will in this case be divided. That part of the force used in breaking the thixotropic bond does not produce flow; hence, it will appear as a point on the force axis, that is, where flow equals zero. This point is called the yield value intercept. This intercept can be made to increase, as will be shown, by introducing greater power when obtaining the consistency curve. The only interpretation of this fact seems to be that in the same material all thixotropic bonds are not of the same strength. A good model of thixotropy must show how bonds of different strength become possible. This can be accomplished by having bonds of different cross-sectional areas. In Figure 15a two particles are bonded with three different degrees of strength. This is done with contact areas of three different sizes. Obviously, bond 1 will be the weakest and bond 3, the strongest.

Thixotropic setup is not produced instantaneously. It requires a finite time, especially for a complete rebuilding of the structure. A satisfactory model of thixotropy must show what causes this time lag. Furthermore, it must show why the buildup is continuously progressive: in other words, why the time intervals are not all equal in the same material. This can be accomplished by assuming the thixotropic structure to be an oriented one. This would be the case if each particle acted like a magnet, each possessing a north and a south pole. Structure would form only when unlike poles came in contact. If two poles met, they would not cling; a time lag would result while Brownian motion or some other disturbance produced the necessary readjustment so that unlike poles could meet. This is shown in Figure 15b. Because some particles will always be nearer to a north- and south-pole alignment than others, the duration of the time lag will vary from particle to particle. As a result the buildup will not be instantaneous, as it probably is in the case of unoriented flocculation, but, instead, is continuously progressive until the process is completed.

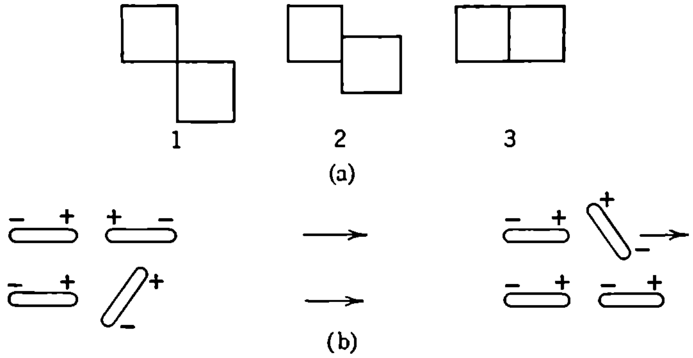


Fig. 15. (a) Schematic Drawing, Showing Thixotropic Bonds of Different Strength. (b) Schematic Drawing Illustrating the Possible Time Lag in a Thixotropic Setup

It has been suggested that thixotropy is simply a flocculated structure in which the force of flocculation is neither too weak nor too strong. This theory hardly accounts for the facts that have accumulated since the time it was originally proposed. Orientation having no part in the theory, it is difficult to understand how thixotropic breakdown can occur, for stirring a crowded pigmented system cannot cause deflocculation. If it did, it would be impossible to measure yield value, because yield value would be destroyed before a measurement could be made. Stirring induces plastic flow within the flocculated mass, but produces nothing simulating internal rupture. In addition, the flocculation theory of thixotropy cannot account for the time lag, for flocculation takes place as soon as particles touch. Orientation is not required.

There is another type of thixotropic structure where rigidity in the ordinary sense plays no part. This is the type of thixotropic breakdown shown by oils under high rates of shear as described by Weltmann.[6] Such materials as heavy-bodied linseed oils behave under low rates of shear like Newtonians. When submitted to sufficiently high rates, they produce a hysteresis loop indicating that a temporary structural breakdown has taken place. This case can be accounted for in the following manner. Under low shearing rates the molecules remain in a disorderly and tangled condition. At high rates of shear the molecules are straightened out and aligned. This reduces the viscous resistance between adjacent layers. As the shearing rate is decreased, the molecules require an appreciable time to regain their former state of entanglement. Hence, the time lag that is characteristic of thixotropic buildup is produced, and a hysteresis loop is produced.

How the Rotational Viscometer Is Used in the Study of Thixotropy

When opaque materials such as paints and printing inks are measured, it is necessary to use either a rotational viscometer or an *extrusion* viscometer of the capillary type. There is an important difference in the application of these instruments to thixotropy. This difference has not been mentioned previously. It is that thixotropic hysteresis loops can be formed with the rotational viscometers but not with viscometers of the capillary-extrusion type. The reason for this is quite evident. A loop forms because it consists of measurements made on material that is being continuously broken down until the point of highest shearing rate is attained. This is the top of the upcurve. (See Figure 16.) When the downcurve is run (immediately after the completion of the upcurve) no further breakdown occurs, and this curve, therefore, is linear (except at the lower end). As a consequence, the two curves cannot coincide, and a loop is created. In the capillary-tube viscometer the material under test

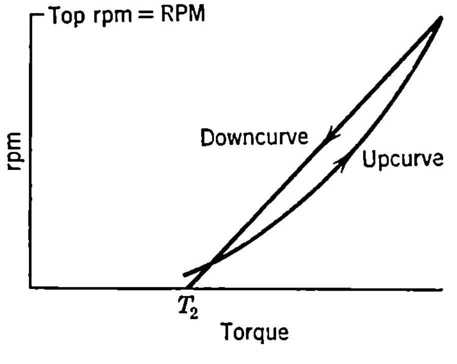


Fig. 16. Thixotropic Hysteresis Loop

is extruded and, therefore, cannot be remeasured in its broken-down state. This means that the up- and the downcurves are each made at the same thixotropic level, that is, in the same state of breakdown. Hence, the curves will coincide, and no evidence of thixotropy, so far as a hysteresis loop is concerned, will be evident. This fact, together with the one previously mentioned—that in a rotational viscometer any desired rate of shear within the instrumental limits can be had by the simple adjustment to the correct rpm—constitute the main reasons for using a rotational viscometer in our present rheological system.

It is difficult or perhaps even impossible to define *thixotropy* as a property possessing definite dimensions. For instance, viscosity has the dimensions M/LT, where M is mass, L is length, and T is time. Viscosity can, as a consequence, be measured. Thixotropy has not been defined in a manner that will make it measurable—unless Goodeve and Whitfield[2] have discovered the correct procedure. Their definition and method are discussed later. However, *thixotropic breakdown* is a reaction the extent of which can be determined. It can also be written dimensionally. The hysteresis loop makes such a measurement possible. This point can be visualized roughly in the following manner: Suppose there exists a series of printing inks which break down to noticeably different extents. Also, imagine that these materials can be arranged in the order of the magnitude of their thixotropic breakdown. If these inks are now run on a rotational viscometer and their hysteresis loops arranged so that the one with the largest area is at one end of the row and the ink with the smallest area is at the other, it will be found that the size of the area coincides with the extent of thixotropic breakdown. (See Figure 17.) In this figure, loop D has the largest area, and the material that produced it appears to break down the most. Material C breaks down less. Material B breaks down very little, and A not at all.

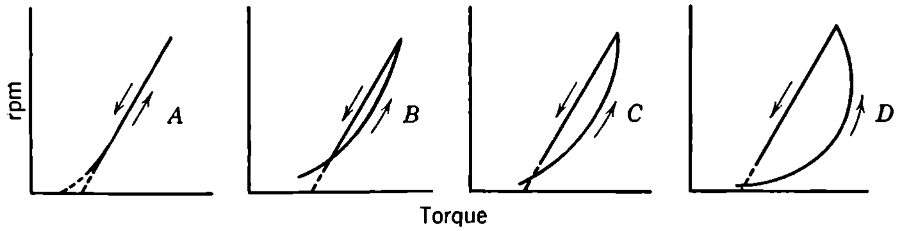


Fig. 17. Loop Showing Varying Amounts of Thixotropic Breakdown

The difficulty that arises when the Freundlich suspension is considered to be highly thixotropic can now be seen. If observation tells us that the material of loop D is the most thixotropic one in the series (and this idea checks with the size of the loop), it is hardly logical to claim that "loop" A is also highly thixotropic. The quartz–carbon tetrachloride suspension gives a curve like A.

No one can disprove the concept that material A is highly thixotropic. It simply seems to be an illogical way of looking at it. Furthermore, such an idea destroys any possibility of measuring thixotropic breakdown by means of the loop, for it implies that breakdown is not the cause of loop formation.

The Method of Making the Hysteresis Loop

The viscometer is first adjusted for its lowest practical rpm. The loop is always started at that point; assume that it is 10 rpm in this case. The degree deflection on the torque scale is noted but not written down. The rpm is next increased, say, to 20. The *first* scale reading is now written down. During the time required to do this, the bob has reached its next point. This new scale reading is noted, but again it is not written down. The rpm is next advanced to 30. The second point is written in during this interval. This process is repeated, the rpm always being increased by the same number at each step. The time interval between each two steps must be as nearly constant as the operator is able to make it.

After a sufficient number of points have been recorded to arrive at the desired top rpm (which should be decided beforehand), the downcurve is commenced immediately. It is assumed that the test material is thixotropic, and so no time must be lost. Descent on this curve is made by using the same intervals in rpm and in timing that were previously employed against the torque-scale reading, and a loop as shown in Figure 16 will result. The straight part of the downcurve is extrapolated to the torque axis and the intercept T_2 multiplied by the instrumental constant C to obtain the yield value in dynes per square centimeter. The easiest and most customary procedure is to plot scale deflection instead of torque and then multiply the intercept by the wire constant K to convert to torque. This also holds for any point T in calculating the plastic viscosity from the equation, $U = (T - T_2)S/\omega$.

In the symbols that follow, the "time of the upcurve" is given by t, the "time interval" by Δt, and the number of points in the upcurve by N. Then,

$$\Delta t = \frac{t}{N} \tag{62}$$

If a top rpm of 100 can be reached in time t, then, Δt being constant, a top rpm of 200 can be attained in the time $2t$. In other words, under the condition of the experiment t is proportional to ω. Let R be the proportionality constant, then,

$$t = R\omega \tag{63}$$

Equations 62 and 63 are of fundamental importance in the development of the time relationship to the coëfficients of thixotropic breakdown.

The Mathematical Development of the Equation of the Hysteresis Loop

The Two Methods of Breakdown. When a thixotropic material is subjected to a *constant* shearing rate over a period of time, it breaks down rapidly at first, and then more slowly, until finally it reaches an equilibrium point where the rate of buildup equals the rate of breakdown. This procedure is called *breakdown with time.* If further breakdown is now desired, it can be induced only by increasing the rate of energy input, which is accomplished by raising the rpm. This is called *breakdown with rate of shear.* Whether or not an equilibrium point exists in this case when no further breakdown can be obtained is not known.

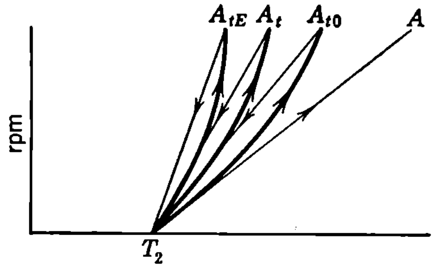


Fig. 18. Thixotropic Breakdown under Constant Shearing Rate

BREAKDOWN WITH TIME. When the time interval Δt is increased, N and the top rpm remaining constant, the upcurve is displaced toward the rpm axis.[3] (See Figure 18.) If no breakdown took place the upcurve would be straight (except at the lower end) and represented by the line T_2A.

If the material is thixotropic, it will continuously break down during the running of the upcurve. If it is assumed that the upcurve could be run in zero time, there would still be breakdown on account of the increasing rate of shear. The curve would, therefore, meet the top rpm at some point, A_{t_0}, which would have a smaller torque than that of A, but greater than a torque for a *real* curve run in finite time. In practice the time, obviously, cannot be zero; hence, the curve will fall to the left of At_0 and meet the top rpm at a point A_t. If the cup is allowed to continue rotation at this point without changing its speed, the material will continue to break down with time until the equilibrium point is reached at A_{t_E}.

The equation of thixotropic breakdown with time has been determined experimentally by Weltmann.[7] It gives the relation between the rate of decrease in plastic viscosity and the time of application of the constant shear:

$$B = -\frac{dU}{dt}t \qquad (64)$$

where B is the *coefficient of thixotropic breakdown with time.*

Weltmann carried out her experimental work in the following manner. The viscometer was started at the desired top rpm. As soon as the bob reached maximum deflection, the measurement of the time factor was commenced. After a suitable time interval had elapsed, a downcurve was run. The instrument was next reset for the original top rpm. Because of a slight thixotropic buildup, which took place during this interval, the bob registered a maximum torque somewhat higher than the top torque of the previous downcurve. Breakdown, however, recurs, and, as soon as the former top torque had been regained (through breakdown), the time was again measured until the next downcurve was commenced. The time of breakdown for this second curve is the sum of the two time intervals so far measured. This process of extending the time of application of shear was continued until equilibrium was finally reached, and no further breakdown could be obtained at that particular top rpm.

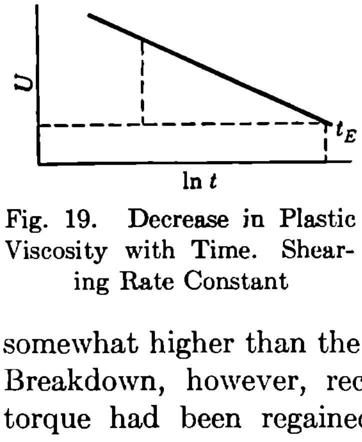


Fig. 19. Decrease in Plastic Viscosity with Time. Shearing Rate Constant

The plastic viscosity for each downcurve was then plotted against the logarithm of the time of the application of shear. A straight line relation as far as t_E, the equilibrium time, was obtained. (See Figure 19.) The slope of the curve is the coefficient B. From two points (U_1t_1) and (U_2t_2) it is readily shown that

$$B = \frac{U_1 - U_2}{\ln \frac{t_2}{t_1}} \tag{65}$$

which gives the experimental method for obtaining B. By differentiating Equation 65 Equation 64 was obtained.

Weltmann arrived at three important conclusions as the result of her work on the time coefficient:

1. Yield value is independent of the time of the application of the shearing stress, provided the top rpm remains constant. This follows from the fact that all the downcurves, Figure 18, meet at the same point on the torque axis for any single substance.
2. The rate of breakdown is independent of the top rpm.
3. The time t for making an upcurve is the same as the time t in Equation 64. In other words the time required to reach a certain point like A_t, Figure 18, is the same whether the measurements commence at T_2 and proceed to A_t, or starts at the point of maximum torque (when the top rpm is applied suddenly) and proceeds to A_t by a horizontal path.

Breakdown with Rate of Shear. As stated previously, after equilibrium is established with a constant rate of shear, further breakdown can be had by increasing the rate of energy input, or power. It should be noted that the product, torque times rpm, has the dimensions of power. Therefore, the area of the rectangle $OGAF$, Figure 20, is a measure of the power necessary to attain the state of breakdown at A and the rate of shear for RPM_1. If RPM_1 is maintained until equilibrium is reached, the torque at A drops to the torque at B. The power has fallen also. It is now equal to the area $OFBM$. To increase the size of the power rectangle, it is necessary to increase the rpm to, say, RPM_2. This causes further breakdown as can be seen by the shift in the downcurve from the position BT_2 to CT_2. Again, if RPM_2 is maintained over a sufficient period, C moves to the equilibrium position D, and further breakdown can be had only by another increase in the power.

It should be noted that the upcurve for any given material can reach a point of maximum torque beyond which the torque diminishes as rpm is increased. The reason is that breakdown has continued so far that the structural resistance cannot induce higher torques without changing the instrumental dimensions. Hence, it follows that there exists a limit to the process of power increase by the simple procedure of raising the rpm. In other words, the area of the power rectangle passes through a maximum as the rpm is increased. There are no experimental data available to show what happens to thixotropic breakdown beyond that point. Fortunately, it is not necessary to go that far for ordinary laboratory measurements.

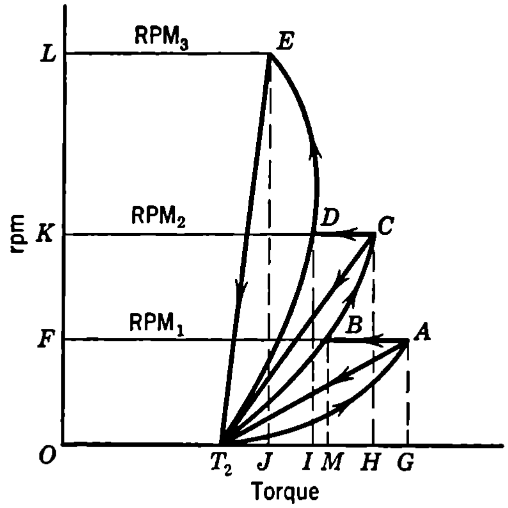


Fig. 20. Thixotropic Breakdown with Increasing Rate of Shear

Thixotropic Levels. The upcurve is the experimental record of increasing breakdown. If no breakdown should take place, the curve would be straight. Its bow shape, however, indicates that the structure is breaking and so cannot induce a torque sufficient to give a linear relationship with the rpm. Because no action can take place in zero time, the breakdown is the combined result of an increasing rate of shear and its time of application. When the rate of shear is decreased (after the top rpm has been reached), no further breakdown from rate of shear can take place. Any further breakdown would now be the result of time of application. However, this possibility is apparently nullified by the fact that buildup can also take place under the decreased rpm. Whatever happens during the period in which the downcurve is recorded, this part of the hysteresis loop is invariably linear, if made within a reasonable short period of time. The time required with the viscometer described in Part II is about 30 seconds to one minute for 15 points. The downcurve remains linear until it reaches the lower end where plug flow commences.

Whatever the cause is for the linearity of the downcurve, it seems reasonable to assume that it is an indication that the thixotropic structure is neither breaking down nor building up. The downcurve, then, represents a condition of temporary stability and is referred to hereafter as a *thixotropic level.* It is possible to have an infinite number of such levels for any thixotropic material.

The Empirical Equations of the Loop. Green and Weltmann [3] showed experimentally that the area of the hysteresis loop is proportional to the square of the top angular velocity ω. (The relation between ω and rpm is $\omega = \text{rpm}/9.55$). Hence,

$$\text{(Area) } A = Q(\text{RPM})^2 \tag{66}$$

where RPM is the top rpm and Q is the proportionality constant. The same investigators also showed when U was plotted against $\ln (1/\text{RPM})^2$, Δt remaining constant for all parts of the curve, that a linear relation was obtained.[3,4] Then, if m is the slope of the resulting curve,

$$m = \frac{d \ln \dfrac{1}{\text{rpm}^2}}{dU} \tag{67}$$

Calling the constant of integration $\ln k$ (for it must be dimensionless) gives,

$$e^{mU} = \frac{k}{\text{rpm}^2} \quad \text{or} \quad \frac{k}{\omega^2} \tag{68}$$

If it be assumed that U can break down until it has a value of zero, then it can be seen that k is the square of the top rpm when $U = 0$. Both Equations 67 and 68 were then derived theoretically.[3] This was important for it led to the second coefficient of thixotropic breakdown M. Before deriving M it is necessary to determine the value of the rate of shear at any radius r in the rotational viscometer.

The Rate of Shear, or the Velocity Gradient. It will be recalled that the rate of shear is the distance traveled per second by one plane with respect to a parallel plane, divided by the distance between them. If the radius of the cup and bob were infinite, the model of flow would be Newtonian, and the rate of shear would be

$$\frac{dv}{dr} = \frac{\omega r}{R_c - R_b} \tag{69}$$

where ωr is the distance traveled per second. Actually, Equation 69 gives only a rough approximation of the correct value because R_c and R_b are finite.

The rate of shear for the rotational viscometer has been shown to be $r(d\omega/dr)$. The present problem is to convert the derivative into usable form. Starting with $dv/dr = \varphi F$, where φ is the fluidity and F the shearing force per square centimeter, it can be shown, by substituting $r(d\omega/dr)$ for dv/dr and $T/2\pi r^2 h$ for F and integrating, that

$$\eta = \frac{TS}{\omega} \tag{70}$$

but

$$\eta = \frac{F}{\dfrac{dv}{dr}} \tag{71}$$

Equating gives

$$\frac{dv}{dr} = \frac{F\omega}{TS} \tag{72}$$

and, since $F/T = 1/2\pi r^2 h$,

$$\frac{dv}{dr} = \frac{\omega}{2\pi r^2 hS} \tag{73}$$

where ω is the angular velocity of the cup and dv/dr is rate of shear for any radius r. The rate of shear varies from the cup to the bob. If $R_c - R_b$ is small, the average radius $(R_c + R_b)/2$ will give a close approximation to the average rate of shear.

The Theoretical Equations of the Loop. In the development of the theoretical equations, Green and Weltmann [3] made the basic assumption that the loss in torque due to breakdown is proportional to the rate of shear. Figure 21 shows what is meant by loss in torque. At any point a on the upcurve the plastic viscosity is given by the cotangent of the angle aT_2T. If raising ω to $\omega + d\omega$ caused no further breakdown (in plastic viscosity), the angle

aT_2T would not change, and the next point on the upcurve would be b. Actually there is breakdown and the next point, instead of being b, is c. The loss in torque is cb or de. Without breakdown the total increase in torque would have been ae. Therefore, there is a net gain in torque equal to ad.

In going from $\omega = 0$ to $\omega = \omega$ let the total loss in torque be $T' - T_2$, where T' has a value greater than T_2. T' is not marked in Figure 21 for its value is not known at the moment. Using the basic proportionality assumption previously stated gives

$$T' - T_2 = \frac{Z\omega}{2\pi r^2 hS} \tag{74}$$

where z is the proportionality factor. Since the torque is the same for each cylinder, it is immaterial what value between R_c and R_b is given to r. The value taken by Z will depend on r so that the ratio Z/r is constant for all cylinders. Z can be defined as the loss in torque per unit increase in rate of shear.

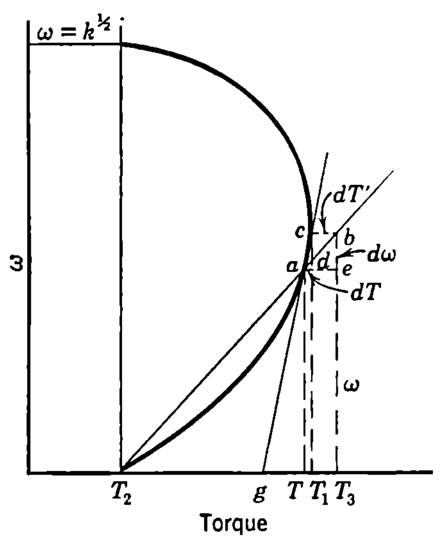


Fig. 21

Differentiating Equation 74 gives

$$\frac{dT'}{d\omega} = \frac{Z}{2\pi r^2 hS} \tag{75}$$

where dT' is obviously the loss in torque due to the increment $d\omega$. However, from similar triangles abc and aT_2g with their respective altitudes, $d\omega$ and ω, it follows that

$$\frac{dT'}{d\omega} = \frac{g - T_2}{\omega} \tag{76}$$

Then,

$$g - T_2 = \frac{Z\omega}{2\pi r^2 hS} \tag{77}$$

and, if we compare Equations 74 and 77, it is evident that

$$T' = g \tag{78}$$

Briefly, the total loss in torque from $\omega = 0$ to $\omega = \omega$ is equal to the intercept on the torque axis made by the tangent to the curve at point a.

From the similar triangles bae and aT_2T,

$$\frac{dT'}{d\omega} + \frac{dT}{d\omega} = (T - T_2)\omega \tag{79}$$

Substituting from Equations 76 and 77 and making the constant $Z/2\pi r^2 h$ equal to a constant which will be designated $2/m$ give

$$\frac{dT}{d\omega} - \frac{T}{\omega} + \frac{T_2}{\omega} = \frac{-2}{mS} \tag{80}$$

(The fact that m in Equation 80 is the same m that appears in Equation 67 cannot be seen here. That relationship becomes evident later.)

Multiplying Equation 80 by $\omega\, d\omega/\omega^2$ gives

$$\frac{\omega\, dT}{\omega^2} - \frac{T\, d\omega}{\omega^2} + \frac{T_2\, d\omega}{\omega^2} = \frac{-2\, d\omega}{mS\omega} \tag{81}$$

Making use of the fact that the left-hand side of Equation 81 can be written

$$\frac{\omega\, dT - T\, d\omega}{\omega^2} - \frac{\omega\, dT_2 - T_2\, d\omega}{\omega^2} \tag{82}$$

which is

$$d\,\frac{T - T_2}{\omega} = \frac{dU}{S} \tag{83}$$

gives

$$dU = \frac{-2\, d\omega}{m\omega} \tag{84}$$

On integration and multiplying by $m/2$, we have

$$\frac{mU}{2} = -\ln \omega + \text{constant} \tag{85}$$

The constant of integration must be dimensionless like the other terms in Equation 85. It will be written $k^{1/2}$. Then

$$\frac{mU}{2} = \ln \frac{k^{1/2}}{\omega} \tag{86}$$

which becomes

$$e^{mU} = \frac{k}{\omega^2} \tag{87}$$

where ω is the top angular velocity employed in measuring U.

The laboratory investigator will find Equation 86 an exceedingly valuable tool if he is in the printing-ink field. Process printing inks are usually thixotropic. They break down during printing to lower thixotropic levels than those measured in the rotational viscometer. By plotting U versus $\ln (1/\omega^2)$ a linear relation is obtained from which it is possible to extrapolate values for U at any desired ω. The necessity for being able to do this is explained in Chapter 9.

The equation of the upcurve is easily obtained by substituting $(T - T_2)S/\omega$ for U. It is

$$T = \omega \frac{\ln\left(\frac{k}{\omega^2}\right)}{mS} + T_2 \tag{88}$$

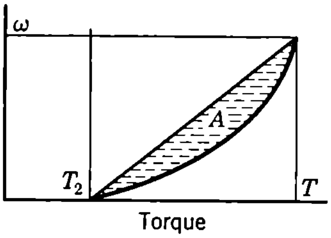


Fig. 22

The area of the hysteresis loop can be seen from Figure 22 to be

$$A = \int_0^{\omega} T\, d\omega - T_2\omega - (T - T_2)\frac{\omega}{2} \tag{89}$$

Substituting from Equation 88 and integrating give

$$A = \omega^2 \frac{\ln k}{2mS} - \omega^2 \frac{\ln \omega}{mS} + \frac{\omega^2}{2mS} - (T - T_2)\frac{\omega}{2} \tag{90}$$

Equation 88 shows that

$$\omega^2 \frac{\ln k}{2mS} = \omega^2 \frac{\ln \omega}{mS} + (T - T_2)\frac{\omega}{2} \tag{91}$$

Therefore,

$$A = \frac{\omega^2}{2mS} \tag{92}$$

If Equations 66 and 68 are compared with Equations 92 and 87, it will be seen that the theoretical Equation 87 is identical with the empirical Equation 68 in every respect and also that the theoretical Equation 92 is the same in form as the empirical Equation 66. Since the theoretical equations are checked by the empirical ones, the assumption from which the theoretical equations were derived is evidently correct. In other words, the law of breakdown in the rotational viscometer is that *the loss in torque is proportional to the rate of shear.* It should be pointed out in this connection that Goodeve and Whitfield[2] use a somewhat similar hypothesis for the basis of computing their coefficient of thixotropy. They state that "the rate of breakdown is proportional to the shear." The rate of breakdown involves time and is not the same as "loss in torque," which, it will be shown, is independent of time. Goodeve and Whitfield do not deduce any of the equations of the hysteresis loop as developed and presented here. Their work applies to single consistency curves and not to loops.

Torque induced at a given ω not only is a function of the test material but also depends on the instrumental dimensions. In order to have a measure of thixotropic breakdown that is related to the test material only, the instrumental constants must be removed. In deriving Equation 80, the constant $Z/2\pi r^2 h$ was made equal to $2/m$. From Equation 87 it can be shown that m is the slope of the U versus $\ln (1/\omega^2)$ curve. The term, $2/m$ will be written M so that

$$Z = M \times 2\pi r^2 h \tag{93}$$

If Z were torque, M would be shearing force per unit area. Z, however, is loss in torque per unit increase in rate of shear. Therefore, *M is the loss in shearing force per unit area per unit increase in rate of shear.* This is the second coefficient of thixotropic breakdown described so far. The first was B, which gives the rate of breakdown with time. Since the act of increasing the rate of shear requires a certain time to perform, M contains a time element. It will be shown in the next chapter that the time element is B, which is a constant for a given material and independent of Δt. Therefore, the value of M is not influenced by the speed at which the investigator makes the upcurve. By the use of Equation 87 and two points, $(U_1\omega_1)$ and $(U_2\omega_2)$, it can be shown that

$$M = \frac{2(U_1 - U_2)}{\ln \dfrac{\omega_2^{\,2}}{\omega_1^{\,2}}} \tag{94}$$

Equation 94 gives the means for determining M from laboratory measurements.

Review and Summary of Chapter 4

In Chapter 4 the subject of thixotropy was introduced. A thixotropic material was described as one possessing a certain kind of structure. The characteristics of this structure are that, after breaking *it will rebuild itself*, if not prevented by external forces. The breaking down and rebuilding are always an isothermal reaction.

It was pointed out that the modern tendency is to depart from this original conception and include many materials that give non-Newtonian curves on the supposition that such curves could not exist if they did not have a changing structure. This conclusion, as noted, is an unfortunate one.

It was shown that thixotropic materials always give a hysteresis loop when run in a rotational viscometer. Other things being equal, the larger the loop the greater the thixotropic breakdown. A description was given of how to operate the rotational viscometer and how to produce the loop. Pictures were given illustrating various possibilities as to how thixotropic structures could form and how the necessary "time lag" could arise, thus making possible the existence of the loop.

The subject of the time element Δt, which is an important one, was discussed in some detail.

The two methods of thixotropic breakdown were described. The first, "breakdown by time," was shown to give a coefficient of thixotropic breakdown B, which indicates the rate of breakdown with the time for which a constant shearing rate is applied.

The second method was called the breakdown with rate of shear. This led to a coefficient M, which is the loss in shearing force per unit area per unit increase of rate of shear.

Empirical equations giving the area of the loop and the relation between U and rpm were presented. The supposition was then made that the loss of torque in the viscometer, due to breakdown, is directly proportional to the rate of shear. With this supposition it becomes possible to develop a set of equations that match the previously mentioned empirical equations exactly. This indicates the correctness of the proportionality supposition.

Chapter 4 does not cover that part of the subject of measuring thixotropic breakdown that relates to the effect Δt might possibly have on B and M. Nor does it take into consideration what happens when the yield-value intercept changes with breakdown. These facts are discussed in Chapter 5.

Reviewing our rheological system up to the present point shows the following facts have been covered.

1. The microscope reveals two models of flow in capillary tubes. One for Newtonians; and the other for Bingham bodies. Newtonians show no plug flow; Bingham bodies do.
2. The transition from plug to laminar flow is sufficient to cause most if not all the curvature in the lower end of the consistency curve for Bingham bodies. This is true for rotational as well as for capillary viscometers.
3. The concepts of apparent viscosity and of the lower and upper yield values of Houwink have not been accepted here. Plastic viscosity and the Bingham yield value are used in their place.
4. The Buckingham equation for capillary viscometers is not considered practical for routine industrial rheology. The Reiner and Riwlin equation for the rotational viscometer is. The reasons are given.
5. The measurements of the coefficients of thixotropic breakdown B and M by means of the rotational viscometer and hysteresis loop are described.

Questions and Problems

1. Name a thixotropic plastic. A nonthixotropic plastic. What will be the difference in their consistency curves?
2. How is a thixotropic structure distinguished from a nonthixotropic one?
3. Name examples of aging that do not necessarily involve any thixotropic change.
4. Can thixotropy be detected by means of the microscope?
5. Name and explain the two types of thixotropic breakdown.
6. Calculate the power to reach the point $T = a$, $\omega = b$.
7. How is the power increased to get increased breakdown? Is there a limit to the method?
8. If $U = 250$ at rpm 100 and $U = 150$ at rpm 200, what is the rpm for $U = 125$?
9. If $U_A = 400$ at rpm 100 and $U_A = 100$ at rpm 400, and $U_B = 200$ at rpm 100 and $U_B = 150$ at rpm 300, at what rpm does $U_1 = U_2$?
10. At constant ω, 10 seconds application breaks the material down to $U = 90$; at 25 seconds down to $U = 75$. What is the time coefficient of thixotropic breakdown?
11. If $U_1 = 300$ at $\omega_1 = 10$, $U_2 = 225$ at $\omega_2 = 30$, what is the loss in shearing force per unit increase in rate of sheer?

CHAPTER

5

In the preceding chapter the subject of thixotropic breakdown in rotational viscometers was discussed and developed as far as the coefficients B and M. Simple cases were taken where it was assumed that the up- and downcurves start at a point T_2 on the torque axis; also it was assumed that the yield-value intercept remains constant when the top rpm is varied. Furthermore, no attempt was made to prove that B and M are independent of Δt. These points are studied in this chapter. If the laboratory investigator has acquired from Chapter 4 sufficient information to enable him to obtain a hysteresis loop and to calculate B and M by the methods indicated, he may omit this chapter for the time being. If desired, he need not study Chapter 5 until he is actually confronted with the problems presented here.

The Effect of Δt on M. It has been noted that a change in Δt will displace the position of the loop. It is natural to ask, Will such displacement have any effect on the value of M? In order to answer this question it must be seen how "time" can enter, for Δt was not obviously employed in deriving Equation 87 (if we remember that $M = 2/m$.) Because no action can take place in zero time, a time element dt must be involved in changing from ω to $\omega + d\omega$. Laboratory measurements are not theoretical but real, and time cannot be dissociated from the measurement of M. What effect, if any, does this involvement with time have on the experimentally determined value of M. If Δt should produce a variation in M, then M is not a coefficient of thixotropic breakdown independent of everything except the material under test. Expressed otherwise, will the investigator obtain the same value for M whether he produces his loop rapidly or slowly?

The solution of this problem has been developed by Green and Weltmann.[1] They assume that $M = M_0 + X$ where M_0 is that part of M dependent only on ω, and X is the unknown factor associated only with time. Then assuming as before that the loss in torque is proportional to the rate of shear gives

$$\frac{2U_\omega}{e^{M_0}} = \frac{k_0}{\omega^2} \tag{95}$$

where U_ω, k_0, and M_0 naturally have values that differ from the normal values of U, k, and M of Equation 87. Equation 95 can be written

$$dU_\omega = -M_0 d \ln \omega \tag{96}$$

and Equation 64,

$$dU_t = -Bd \ln t \tag{97}$$

where U_t is the change in plastic viscosity due to time of application of the shearing rate. Adding Equations 96 and 97 gives

$$dU_\omega + dU_t = dU = -M_0 d \ln \omega - Bd \ln t \tag{98}$$

which on integration and symbolizing the constant of integration as $\ln K^{M_0/2}$ gives

$$e^{2U/M_0} = \frac{K}{\omega^2} t^{2B/M_0} \tag{99}$$

In Equation 99, M_0 is impossible to determine by direct measurement. M_0 is, however, equal to $M - X$. The next step is, then, to determine X. Using two different points $(U_1\omega_1)$ and $(U_2\omega_2)$ in Equation 99 gives

$$M_0 = \frac{2\,(U_1 - U_2)}{\ln \frac{\omega_2{}^2}{\omega_1{}^2}} - B\,\frac{\ln \frac{t_2{}^2}{t_1{}^2}}{\ln \frac{\omega_2{}^2}{\omega_1{}^2}} \tag{100}$$

If we substitute the value of M from Equation 94 in Equation 100 and remember that $t = R\omega$, we have

$$M_0 = M - B \tag{101}$$

The unknown factor X is, therefore, the Weltmann coefficient of thixotropic breakdown with time;[3] B is a constant for a given material and is not affected by the rate of breakdown. M_0 is not related to time; hence, M is independent of Δt.

Substituting Equation 101 in Equation 99 shows that

$$e^{2U/M} = \frac{K^{(M-B)/M}}{\omega^{2(M-B)/M}t^{2B/M}} \tag{102}$$

where t is the total time for the upcurve. Equation 102 shows how t is associated with U and ω. Any change in Δt affects t and does not change the values of M, B, and K. Substituting $t = R\omega$ in Equation 102 gives

$$e^{2U/M} = \frac{K^{(M-B)/M}}{R^{2B/M}} \frac{1}{\omega^2} \tag{103}$$

which, when compared with Equation 87, shows that

$$k = \frac{K^{(M-B)/M}}{R^{2B/M}} \tag{104}$$

Since R is a function of t, it follows that the value of k will vary with a change in Δt. This means that, the greater the time of the upcurve, the smaller will be the theoretical top ω for producing complete breakdown to $U = 0$.

The Effect of Δt on the Equation of the Upcurve. It has been pointed out that Δt affects the position of the loop. The equation involves time. This effect produces a change in k. In order to see how time enters the equation of the upcurve, k is eliminated and replaced by K and t. This is easily carried out. $U = (T - T_2)S/\omega$. Substituting in Equation 102 gives

$$T = \frac{(M - B)\omega \ln K}{2S} - \frac{(M - B)\omega \ln \omega}{S} - \frac{B\omega \ln t}{S} + T_2 \tag{105}$$

The Effect of Δt on the Area of the Loop. In Equation 92 it is shown that the area of the loop depends only on ω, m, and S. Since all these factors are independent of Δt, it follows that the area of the loop is also independent of Δt.

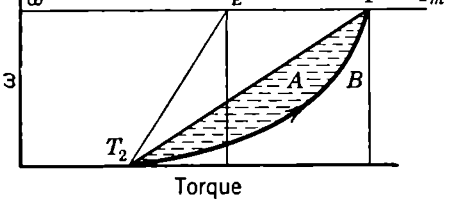


Fig. 23

There is another type of loop called by Green and Weltmann[2] the *equilibrium hysteresis loop.* If after the upcurve has attained its top ω at T (Figure 23) the rate of shear is maintained until equilibrium is reached, the torque will drop from T to some smaller torque T_E. This is called the equilibrium torque and the area BTT_ET_2 is the equilibrium area A_E. The time required in going from the maximum torque T_m (that is, when the top ω is applied suddenly) to the equilibrium torque T_E is the equilibrium time t_E. This is equal to the time of the upcurve plus the time in going from T to T_E. Weltmann[3] has shown that t_E is independent of the top ω. Green and Weltmann[1] have shown that A_E is not independent of Δt. Their solution is as follows:

$$A_E = A + (T - T_E)\frac{\omega}{2} \tag{106}$$

Substituting T_E for T in Equation 105 gives

$$T_E = \frac{(M - B)\omega \ln K}{2S} - \frac{(M - B)\omega \ln \omega}{S} - \frac{B\omega \ln t_E}{S} + T_2 \tag{107}$$

Subtracting 107 from 105 gives

$$T - T_E = \frac{B\omega}{S} \ln \frac{t_E}{t} \tag{108}$$

Substituting Equations 92 and 108 in Equation 106 gives

$$A_E = \frac{M\omega^2}{4S}\left(1 + 2B \ln \frac{t_E}{t}\right) \tag{109}$$

Since t_E is independent of both Δt and ω, it follows that the ratio t_E/t is not independent of Δt. Therefore, A_E is not independent of Δt. Equation 109 is of the form,

$$A_E = a - b \ln t \tag{110}$$

Plotting A_E against $\ln t$ gives a straight line with a negative slope. Plotting A against $\ln t$ gives a straight line parallel to the $\ln t$ axis.

The Change in Yield Value with Breakdown. In order to operate a viscometer, energy must be put into the system. In the rotational viscometer the energy input per revolution is $2\pi T$. The rate at which this energy is consumed, or the power, is ωT. The energy is divided; that part which is used in producing flow is equal to $2\pi(T - T_2)$; the remainder, $2\pi T_2$, is consumed in performing various kinds of internal work and does not appear as flow.

One type of internal work is the maintaining of the state of thixotropic breakdown existing at the particular thixotropic level involved. The energy consumed does work against the force of rebuilding. This energy appears in the consistency curve as part of the yield-value intercept T_2. When a greater state of breakdown is induced by raising the top ω, more energy is required to maintain the new state of thixotropic equilibrium; hence, the yield-value intercept should show an increase. This actually happens. The intercept does become larger with each increase in the top ω.

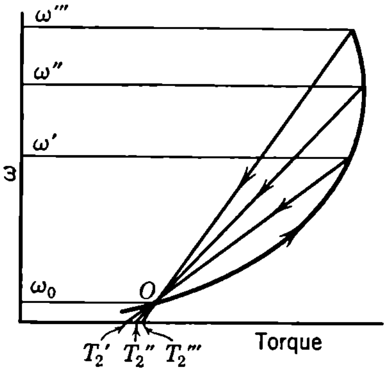


Fig. 24. Showing the Crossing Point of the Downcurves

An increase of T_2 with a breakdown in thixotropic structure seems at first like a contradiction of ideas. It is not structure *per se* that causes yield value, but the force that induces structure. Because the breaking of structure does not destroy this force, there is no decrease in T_2. This is one of the cardinal principles of plastic flow and one that is least appreciated by the average investigator. There is one exception to this rule, however, and that occurs in the drop in T_2 when passing from a static to a dynamically determined yield value (in the case of thixotropic materials). Of course where the destruction of structure is permanent (that is, where no rebuilding force exists) there will naturally be a drop in T_2. Such cases are not considered here. The structure from which static yield value is derived usually is broken with a force far greater than that necessary to establish thixotropic equilibrium; hence, a very rapid and real decrease in T_2 takes place before equilibrium is attained. This reaction takes place so rapidly that an automatic recorder must be used in connection with the viscometer in order to prove its existence. This is discussed further in Chapter 8, Part II.

In Chapter 4 no mention of a possible change in T_2 was made. This was done to keep the subject as uncomplicated as possible. Figure 24 will give a better idea of what actually happens. The upcurve and all the downcurves made from various top angular velocities meet approximately at a common point O. This picture is sufficiently accurate; it will not introduce any serious discrepancies in the calculation of the various coefficients of thixotropic breakdown. Figure 24 can, therefore, be used as a model from which to derive the equations of the loop when T_2 increases with an increase in ω. It should be noted at this point that, when breakdown is accomplished by "time of application of the rate of shear," the power is not raised, and there is no increase in T_2 as a result. Actually there is a falling off in power, but there is no decrease in T_2. This indicates that there is an increase in the number of bonds being broken, but no new bonds are being broken that require an increase in power. Apparently it takes the same energy input to maintain a given state of breakdown that it does to produce it.

In deriving a new set of equations to fit the loop shown in Figure 24, the differential equation is set up in the manner employed in Chapter 4 except $\omega - \omega_0$ is substituted for ω. This gives

$$\frac{2U}{e^M} = \frac{k'}{(\omega - \omega_0)^2} \tag{111}$$

where k' is a constant resulting from integration and is equal to $(\omega - \omega_0)^2$ when $U = 0$.

If we assume the correctness of a common crossing point O, Figure 24, then, $U = (T_{\omega_0} - T_2)S/\omega_0$ and $dU = -(S/\omega_0)\,dT_2$. Differentiating Equation 111, making the substitution for dU, integrating, and condensing the constants give

$$Jf = \ln k'' + \ln (\omega - \omega_0)^2 \tag{112}$$

where $J = 2S/MC\omega_0$, and k'' is a constant resulting from the integration. Differentiating Equations 111 and 112 and adding, and letting $2/MJ = V$ give

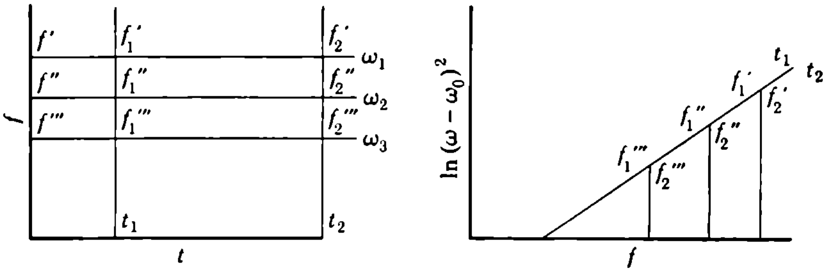
$$V = -\frac{df}{dU}$$

or

$$V = \frac{f_2 - f_1}{U_1 - U_2} \tag{113}$$

V is the third coefficient of thixotropic breakdown. V *gives the increase in yield value per unit decrease in plastic viscosity.*

***V* Is Independent of Δt.** It is known from experiment that, when the rate of shear is constant, the yield-value intercept does not change with time. Consequently, when f is plotted against time for different top ω, a series of straight-line curves is produced parallel to the t axis (Figure 25a). Then for any two times t_1 and t_2 at ω' the yield values will be f', so that $f_1' - f_2' = 0$; and similarly, $f_1'' - f_2'' = 0$; $f_1''' - f_2''' = 0$, etc. When f is plotted against $\ln(\omega - \omega_0)^2$, it follows from Equation 112 that the resulting curve will be linear. If two such curves are plotted for t_1 and t_2, these curves must coincide because of the foregoing relation $f_1' - f_2' = 0$, etc. (Figure 25b.) The slope of the curve for t_1 will then be the same as the slope of the curve for t_2. The slope of these curves is J, as can be seen from Equation 112. J, then, is independent of time. It has already been shown that M is independent of time; therefore V, which is $2/MJ$, must also be independent of time or Δt. None of the three coefficients of thixotropic breakdown is affected by the speed at which the operator produces the upcurve.



(a) (b)

Fig. 25

The Equations of the Upcurve and the Area. By substituting $U = (T - T_{\omega_0})S/(\omega - \omega_0)$ in Equation 111 gives the equation of the upcurve.

$$T = \frac{M(\omega - \omega_0)}{2S} \ln \frac{k'}{(\omega - \omega_0)^2} + T_{\omega 0} \tag{114}$$

Substituting $\omega - \omega_0$ for ω in the equation for the area of the loop gives

$$A = \frac{M(\omega - \omega_0)^2}{4S} \tag{115}$$

where A is the area of the loop above the point $(\omega_0 T_{\omega_0})$. Equations 114 and 115 can be obtained with time in the same manner in which the two similar equations were treated in Chapter 4. The constant k' then becomes a function of time.

Review and Summary of Chapter 5

This chapter is a continuation of the preceding one. It develop a third coefficient of thixotropic breakdown, V. It also shows tha M and V are independent of Δt. It is highly desirable that th operator realizes this fact of the time independence of the coefficients; but it is not so essential, from a practical viewpoint, fo him to study the details of the mathematical development. N problems, therefore, are included in this chapter. The main valu of Chapter 5 is to develop the equations of Chapter 4 to thei logical conclusion, thus completing, for the present, the mathematics of the hysteresis loop as used in this system.

CHAPTER

6

Plastic Flow

This term, as used here, refers to the flow of Bingham bodies only. Such materials can be suspensions in which the dispersed phase is either solid or liquid. Bingham's original conception was that yield value results from frictional resistance between the suspended particles. This idea was broadened later to include the force of flocculation, which holds the particles together, forming a structural resistance to flow.

The conception of flocculation is an important one in its relation to our present rheological system. It is necessary to have a correct visualization of what the term means. There are various types of particle aggregation, only one of which is used to designate flocculation. Flocculation implies softness, wooliness. The term, therefore, is not used in reference to any form of hard aggregation where the particles are cemented or sintered together. Such hard lumps can exist by themselves, that is, without the aid of a suspending medium or vehicle. The particles of a flocculate, on the other hand, must always be in contact with a liquid; otherwise the flocculate would fall apart. A flocculate is formed *after* the particles have been dispersed in the vehicle; never before. *Hard* aggregates are usually (but not necessarily) formed before they are incorporated in the suspending medium. There is no indication that the particles of a flocculate are oriented. The supposition is, that the particles adhere as soon as they touch each other. This adherence takes place regardless of which faces or spots on the particles come in contact. What causes the particles to cling together after contact is made is not entirely understood, except that there must be a decrease in the free energy of the system before flocculation will take place. The force of adherence will be called the *force of flocculation*. The fact cannot be denied that it would be of great interest to know the exact mechanism of flocculation; but it is not essential to have this knowledge for the construction of a rheological system. In the final analysis the forces of flocculation are probably van der Waals forces.

Particles that are poorly wet by the vehicle give rise to the strong forces of flocculation; those that are completely wet, to deflocculation. Strong forces of flocculation produce high yield values. This is one of the cardinal principles of the rheology of Bingham bodies. The term "wet" is not defined. When used here, it will mean that the force of adhesion between the particles and vehicles is finite. This includes contact angles greater than 90°. Wetting, thereby, becomes a comparable term; it exists in all degrees. Every kind of particle, then, is wet to a certain extent by every kind of vehicle. Only materials giving a contact angle of 180° would be completely unwet. No such materials are known, however.

Surface-active agents can alter the degree or extent of wetting. They do so by changing the force of adhesion. Deflocculating agents increase the wetting; flocculating materials decrease it. An agent that increases the interfacial tension decreases the wetting. Other factors remaining unchanged, this procedure increases the yield value. Summarizing these statements gives the following:

Poor adhesion gives:	Good adhesion gives:
Poor wetting.	Good wetting.
High interfacial tension.	Low interfacial tension.
High yield value.	Low yield value.

In attempting to use any of the foregoing facts, it should be borne in mind that the magnitude of the yield value depends on factors other than poor wetting. In the case of pigment suspension, it depends on the pigment–vehicle ratio, the specific surface of the pigment, and on the amount of surface "lost" when pigment surfaces come in contact with one another. Then there is always the possibility of a frictional factor entering, especially in crowded systems. Consequently, any statement in regard to yield value should be qualified as follows: *All other factors remaining unchanged, the yield value increases with the interfacial tension.* It should be apparent that by increasing the interfacial tension and at the same time decreasing the pigment–vehicle ratio sufficiently, yield value could be eliminated entirely.

It would seem advantageous to have an equation showing the relationship among all the factors which give rise to yield value. It is possible that such an equation can be derived, but there would be no way to prove its correctness experimentally, for there is no way to determine the amount of surface "lost" on flocculation. The fact that surface is lost is apparent, for, if it were not, there would be no drop in the free energy of the system, and flocculation would not occur. If all the areas of surface contacts were mathematical points, the sum of their areas would be zero. The contact areas must, therefore, be finite, and their magnitude must depend on particle size, shape, and flatness or smoothness of the surface. Unfortunately, there is no known way of determining these factors. Therefore, any relationship such as the one previously mentioned can have no great practical value.

If yield value depends on flocculation, why does it not disappear on stirring? This is a question that confuses many beginners in rheology. The answer constitutes one of the basic concepts of plastic flow. If there exists a flocculated suspension in which the flocculates are comparatively large distances apart, then stirring will mechanically deflocculate such material as long as stirring continues. In such a case there will be no yield value either before stirring or during stirring. There will be no yield value before stirring because the structure is not continuous, and shearing will take place between the flocculates. In a crowded system, conditions are quite different. Stirring cannot separate the particles, because there are no empty spaces into which the particles can be moved. If stirring did separate the particles, then the forces of flocculation would be lessened, and the yield value would drop or disappear. In other words there would be no way to measure yield value. It should be noted that structure *per se* is not the cause of yield value. The real cause is the force that holds the structure together. If the particles become separated, this force would decrease; but, if there is no room for the particles to expand into (on stirring), there can be no decrease in the force of flocculation, and, consequently, no drop in yield value will occur. This is the case for materials such as paints and printing inks; hence, their yield values can be measured.

The mechanism of plastic flow can be visualized roughly in the manner shown in Figure 26. Three stages are given in the motion of layer *a* past layer *b*. At first, particle *c* contacts the middle of particle *d*. As flow continues *c* leaves *d* gradually without rupture (separation) and contacts particle *e*. Further continuation of flow brings *c* in contact with the middle of *e*, in which position it is no longer touching particle *d*. Particle *c* has gone through this motion without increasing the distance between any particles. The force of flocculation, therefore, has not decreased, and the yield value which is a force acting against the force of flocculation remains measurable. Presumably, the force of flocculation tends to hold the particles rigidly in their structural position. It is not until the applied shearing force becomes great enough to overcome the force of flocculation (plus frictional resistance) that flow can take place. The amount of the applied force in dynes per square centimeter is the yield value of the material. After flow has started, the rate of shear becomes directly proportional to the applied force in excess of the yield value. Such a material is a Bingham body. It should be evident by now that yield value and thixotropy are two entirely different phenomena.

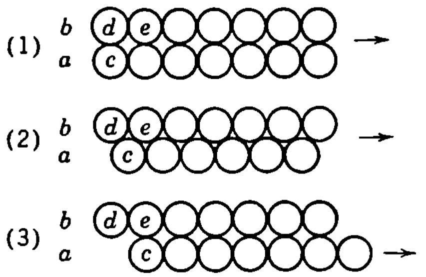


Fig. 26. Schematic of Plastic Flow in a Crowded Particle System

Pseudoplastic Flow

There is a very large class of materials that flow neither like Newtonians nor like Bingham bodies. This class includes practically all resinous materials and solutions of these materials at sufficiently high concentrations. As a class they are called pseudoplastics. Their method of flow does not follow the Newtonian concept—that the rate of shear is directly proportional to the shearing stress.

This is evident from the fact that their consistency curve, as determined with either a capillary or rotational viscometer, is not linear and is convex toward the force axis. The lower part of the curve extrapolates to the origin and resembles Newtonian flow. The up- and downcurves coincide except at comparatively high rates of shear where a hysteresis-like loop can form. This fact was pointed out by Weltmann.[3] The shape of the pseudoplastic consistency curve has been explained in several ways; but the one most generally accepted is as follows: the material is composed of long chain molecules. Under low rates of shear the tendency of such molecules to align in the direction of flow is negligible. They remain, therefore, in a disorganized state in which case their rate of shear will remain practically proportional to the shearing stress. As the rate of shear increases, however, molecular alignment increases. This reduces the frictional resistance between adjacent layers and the result is a greater rate of shear for a given stress than would occur otherwise. This causes the curve to leave its linear course and bend upward.

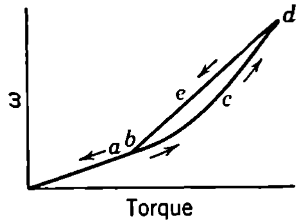


Fig. 27

If the curve has been experimentally obtained up to a sufficiently high rate of shear, there can be an appreciable time lag in the return of the molecules to their normal position. This will result in the material behaving like a thixotropic substance, and a hysteresis loop will form (Figure 27, *bcde*). Heavy-bodied oils as well as resinous materials give such consistency curves.

The pseudoplastics form a large and important class of industrial products. Though empirical equations have been suggested for their flow in capillary and rotational viscometers, no satisfactory equation has been theoretically deduced. The next important step in advance in industrial rheology will probably be in that direction. At present measurements can be recorded only as consistency curves. When two such curves coincide, the materials may be said to be rheologically identical. The initial viscosity can also be recorded. This is carried out at low rates of shear where the material for all practical purposes behaves like a Newtonian. The cotangent of the angle the curve makes with the force axis is multiplied by the proper instrumental constant necessary to give the coefficient of viscosity in poises. This can be done with either capillary or rotational viscometers.

Dilatant Flow

There is another type of flow that does not follow the Newtonian concept. The materials belonging to this class are called *dilatant.* Their consistency curve is concave toward the force axis. In most cases the curve appears to start from the origin.

Dilatant materials were first recognized and named by Osborn Reynolds in 1885.[2] He gives as a typical example wet sand in which the water-to-sand ratio is such that there is just enough water to fill the voids when the voids are at their minimum volume. Any disturbance, like shear, will expand or dilate the voids, giving them a total volume greater than the volume of water present. This procedure results in producing a state of partial dryness, and the material increases its resistance to shearing stress more rapidly than it would otherwise. Hence the flow curve flattens out as shown in Figure 28. In the region of low stresses, *O* to *a*, the curve resembles Newtonian flow. From *a* to *b*, a pronounced curvature arises. The up- and downcurves coincide (unless thixotropy is also present).

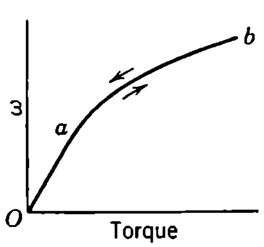


Fig. 28

It has been stated that dilatancy is the opposite of thixotropy because not only does a dilatant material increase its resistance to flow in a nonlinear way as the rate of shear increases, but also the suspended particles, unlike those in thixotropic materials, are dispersed (usually possessing vigorous Brownian motion), showing no sign of flocculation. This viewpoint is one of convenience, not one of necessity. Actually there is no known relation between the two totally different phenomena—thixotropic structure and void dilation. It is best not to get accustomed to thinking of thixotropy as representing one extreme and dilatancy the other of a hypothetical series of rheological specimens. There are frequent cases where thixotropy and dilatancy occur in the same material. Certain types of clay suspensions in water will produce dilatant materials that form a thixotropic structure on standing. Stirring breaks down this structure, leaving a highly dilatant product.

Dilatancy is quite frequently encountered in pigment–vehicle suspensions such as paints and printing inks. Paints and especially enamels that have been settling over a long period of time often have a layer of dilatant pigment in the bottom of the container. If the supernatant liquid is poured off, the settled layer can be examined with a spatula. This layer is usually tough and takes on a dry appearance when the surface is scraped. The end of the spatula will sink into the layer easily enough, under its own weight;

but, if one tries to pull the spatula out suddenly, there is set up considerable resistance to such action, sometimes causing the layer to fracture. The investigator should examine carefully all materials that show evidence of dilatancy until he is able to recognize the phenomenon with ease. It is important to be able to do this in order to avoid confusion and misinterpretation of laboratory data.

Turbulent Flow

When liquids flow through capillary openings at relatively small shearing rates, the type of flow tends to be laminar. This ideal condition is affected by increasing the size of the opening, increasing the rate of flow, or what amounts to the same thing in the latter case by decreasing the viscosity. This type of flow is referred to as turbulent or hydraulic flow and has been studied by various investigators such as Darcy, Hagen, Brillouin, and Reynolds.

In the case of laminar flow the viscous resistance is directly proportional to the rate of shear; in hydraulic flow the resistance is proportional approximately to the second power of the rate of shear.

Hydraulic flow is the type associated with the flow in pipes and is of more interest to the engineer than to the rheologist. Couette, however, confirmed the work of Reynolds proving the existence of turbulence in rotational viscometers under conditions suitable for it. Since the resistance increases more rapidly than it does under normal streamlined flow, the consistency curve of a turbulent material run on a rotational viscometer such as described in this book will be nonlinear and convex toward the torque axis. In appearance the curve will be similar to that of a dilatant material. It will sometimes be difficult for the beginner to know whether the material he is measuring is dilatant or undergoing turbulent flow. With a little practice, however, he will soon be able to distinguish between the two types. If the distance between the cup and bob is in the order of magnitude of 1 mm it is surprising how great the rpm can be without producing the turbulence. If turbulence does occur the results should be rejected. Reynolds found in the case of capillary tubes that when the quantity $\rho RI\varphi$ exceeds 1000 nonlinear flow can be expected. R is the radius of the capillary, and I is the mean velocity.

Flow Classifications

In our rheological system, nonturbulent-flow types are classified as follows:

Newtonian flow: Rate of shear is proportional to shearing stress.

Plastic flow: Rate of shear is proportional to the shearing stress in excess of yield value.

Pseudoplastic flow: Rate of shear increases faster than linearly with shearing stress.

Dilatant flow: Shearing stress increases faster than linearly with rate of shear.

In the cases of Newtonian and plastic flow, no structural change takes place. Their flow curves are, therefore, linear. With pseudoplastics, molecular alignment seems to occur. This procedure does not involve rupture, if no measurable time lag is involved in returning to random distribution, and up- and downcurves coincide. These curves cannot be linear, however, because of the internal change resulting from alignment. In the case of dilatants, an internal change also takes place when the voids dilate; but again no rupture is involved, and the up- and downcurves will coincide and be nonlinear.

If structural change can take place without producing a detectable time lag, then why is it not desirable to classify Bingham bodies that show no loop as thixotropic but having no measurable time lag? The answer is that thixotropic breakdown involves a structural change, and this must produce a nonlinear upcurve. A linear upcurve indicates no structural breakdown, and, consequently, a material giving such a curve cannot be thixotropic. That is the case of the Bingham body showing no hysteresis loop.

Reiner's Rheological Systematics

In 1931 and 1932 Reiner[1] devised a system for classifying substances rheologically, based on the concept of three ideal bodies:

1. The Hooke solid.
2. The Newtonian liquid.
3. The St. Venant body.

Reiner's claim is that all real bodies can be pictured as combinations of these three elementary models. In the Hooke solid, stress is directly proportional to strain; in the Newtonian liquid, stress is directly proportional to rate of shear; and, in the St. Venant body, the stress is never greater than the yield value (frictional resistance to motion). In other words, if a lateral force applied to a block of wood lying on a tabletop is enough to overcome the frictional resistance, then, no greater force can be applied (if the friction is assumed to remain constant). Any attempt to increase the force will simply increase the speed at which the block is moving.

The mathematical expressions of the ideal bodies and all the complex bodies built from them Reiner calls "rheological equations." For the ideal bodies

$$(1)\quad P = \eta\dot{e} \quad \text{(Newtonian)}$$

$$(2)\quad P = \gamma e \quad \text{(Hooke)}$$

$$(3)\quad P = \vartheta \quad \text{(St. Venant)}$$

where P is the stress; e, the shearing strain; $\dot{e}$, the time derivative of e; and η and γ are the viscosity coefficient and elastic modulus, respectively. The equations built of two elements are:

$$(4)\qquad \dot{e} = \frac{P}{\eta} + \frac{\dot{P}}{\gamma} \quad \text{(Maxwell liquid)}$$

$$(5)\qquad P = \gamma e + \eta_s\dot{e} \quad \text{(Kelvin solid)}$$

$$(6)\quad P - \vartheta = \eta_{Pl}\dot{e} \quad \text{(Bingham body)}$$

where $\dot{P}$ is the time derivative of P; η_s is the solid viscosity of Kelvin; and η_{pl} is plastic viscosity.

From (2), $\dot{P} = \gamma\dot{e}$. Combining this with (1) in order to get the total shear gives (4). A Maxwell liquid, then, can be pictured as a combination of a Hooke solid and a Newtonian liquid. Its properties are instantaneous elastic elongation together with a steady Newtonian flow. A model of such flow is represented by a "dashpot" in series with a "spring" (Figure 29a).

In (5) the total stress is obtained from adding the right-hand terms of (1) and (2). This gives a Hooke solid "in parallel" with a Newtonian liquid (Figure 29b). Its properties are: Full elastic effect is not instantaneous; and there is a time lag in the appearance and disappearance of the elastic strain.

(6) is derived by adding (1) and (3) to give the total stress. A Bingham body, therefore, is composed of a Newtonian liquid and a St. Venant body. Its properties are an elastic effect followed by viscous flow, the latter taking place after the stress has exceeded the yield value (Figure 29c).

The rheological equations (1) and (6) are not instrumental equations of flow. Instrumental equations can be obtained by substituting in the rheological equations the equivalent values for rate of shear and shearing stress. This was done when Reiner, for instance, developed his equation of plastic flow for the rotational viscometer. It will be recalled that in this instrument the rate of shear is $r(d\omega/dr)$, and the shearing stress is $T/4\pi r^2 l$. By substituting these values in (6) the instrumental equation was obtained. A similar plan was carried out when mathematicians developed the equation of flow for Newtonians in the capillary-tube viscometer.

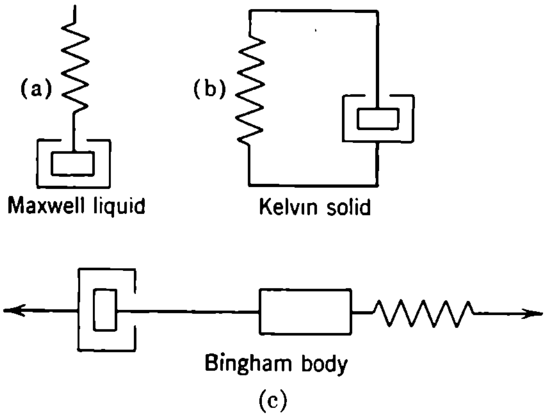


Fig. 29 Systematic Plan Models

Likewise, any rheological equation can be developed for the rotational and capillary-tube viscometers, provided it does not lead to an equation that cannot be integrated. For instance, let it be assumed that the rheological equation of flow for a pseudoplastic is

$$\dot{e} = ap^b \tag{116}$$

where $b > 1$. Such an equation means that the rate of shear is increasing nonlinearly with the shearing stress, and the flow curve will be convex toward the force axis. The equation also shows that the curve starts from the origin. By making the previously mentioned substitutions for the rotational viscometer and integrating, the following equation is obtained:

$$\omega = \frac{aT^b}{2b(2\pi h)^b}\left(\frac{1}{R_b{}^{2b}} - \frac{1}{R_c{}^{2b}}\right) \tag{117}$$

When $b = 1$, this equation reduces to the well-known equation for Newtonians in rotational viscometers. When $b = 1$, it can be seen that a is the factor that corresponds to the coefficient of fluidity. The exponent b, therefore, must state how viscous resistances change with rate of shear. In a true pseudoplastic, however, b is not likely to be a simple constant.

The inadequacy of Equation 117 becomes apparent as soon as it is studied dimensionally. If b is a parameter and can take on an unlimited number of values, depending on the material to which it belongs, then, when $b = 1$, a will not have the dimensions of fluidity. As a matter of fact, the dimensions of both a and b can be practically anything. There is a tendency amongst certain rheologists to create a school of thought that is willing to ignore the fluctuating dimensional nature of such factors as a and b. They argue that, if a is not called anything definite like a "coefficient of fluidity," then, a can be accepted logically as a useful indication of some unknown property of the material. Be that as it may, such a conception is not compatible with the development of a practical rheological system intended for industrial use.

Summary and Review of Chapter 6

It would be difficult, perhaps, at this stage to arrange the first six chapters of this book in the order of their ultimate importance to the laboratory investigator. In the course of time, however, it will become apparent that the subject matter in this chapter will be the most far-reaching in its effect on formulating the investigator's rheological viewpoints. The ideas presented here are basic and accepted by a large percentage of the theoretical rheologists.

The important points discussed are:

(*a*) The relationship of yield value to the force of flocculation. In this connection it has been shown why stirring a crowded pigmented system does not destroy flocculation, which would eliminate yield value from laboratory measurements. This is one of the most important facts in the development of our rheological system. If the student has not understood it, he is advised to review the subject until he has a clear understanding of it.

(*b*) From what has been said in this chapter, it should be obvious that yield value and thixotropy are two entirely different phenomena.

(*c*) The important relationship among adhesion, wetting, interfacial tension, flocculation, and yield value has been explained.

(*d*) The nature of pseudoplastic and of dilatant flow has been described.

Finally, the rheological systematics of Reiner has been given a brief (unfortunately, much too brief) discussion. Reiner has shown how all real rheological objects can be considered as composed in various combinations of three elementary ideal bodies—the Newtonian liquid, the Hooke solid, and the St. Venant body. This distinction between real and ideal bodies is an important concept which must be included in our rheological system. The method of developing instrumental equations of flow from rheological equations has been described.

Questions and Problems

1. (*a*) In two adjacent layers of a thixotropic material, is there an internal rupture during shear? (*b*) In a Bingham body free from thixotropy, is there any internal rupture during shear? (*c*) Can you draw models illustrating the two cases?
2. (*a*) Other things remaining unchanged, increasing the pigment–vehicle ratio does what to the yield value? (*b*) Increasing the interfacial tension does what? (*c*) Increasing the adhesion of the vehicle to pigment does what?
3. (*a*) How is a flocculate formed? (*b*) How does it differ in its formation from a cemented aggregate? (*c*) Do you think that a flocculate would act rheologically as a large particle? (*d*) Do you think that the "size" of a flocculate has any rheological significance?

CHAPTER

7

A Rheological System

The theoretical background for a rheological system has now been covered, and the time has arrived when it becomes necessary to answer certain questions. Why has so much theoretical rheology been omitted? If the investigator reads, for instance, Scott-Blair's *A Survey of General and Applied Rheology*, Chapters XI, XII, and XIII, he will become impressed by the extent and scope of the theoretical rheology discussed there. Hardly any of that work could be touched on in a book of this kind. And again the question arises, Why?

Before answering, let it be stated once more what our present aim is. The ultimate desire is to introduce rheology into industries where it is needed. The immediate problem is to induce Bill (as Scott-Blair calls the investigator) to become an industrial rheologist. Bill's problem is this: He has a laboratory. He has been granted money to build the rheological instruments he needs. When he has accomplished this, he must use his instruments to secure rheological measurements on the products manufactured by his company. Then comes the laboratory reports, which must be understandable at least by the technical director. The director must then be able to prove to the company's officers that Bill's measurements are useful and capable of increasing the company's income. If Bill is to do this, nothing must be allowed to discourage him; and discouragement is exactly what would occur if Bill studied many of the theoretical subjects published on rheology.

Can a practical laboratory system be constructed without including all the theoretical aspects of rheology? Yes. It is being done constantly. Bill's job is to produce a measurement. This he can do, if he has suitable instruments for his purpose. His measurements result in consistency curves. A dozen theoretical rheologists can give a dozen different explanations as to why Bill's measurements produce the kind of curves they do. Not a single explanation will alter Bill's curves in any visible way. As far as Bill is concerned, the dozen different theoretical explanations might just as well not exist. Bill can, if necessary, get along without them. Bill will find it more desirable, however, to convert his curves into numbers like U, f, and M. Such numbers are convenient to enter into reports and are much easier to interpret when making comparisons of different materials. It is here (where the curves are to be converted) that Bill needs guidance, for presumably he has no previous rheological training that will tell him what to do. There are many ways for converting consistency curves into numbers. Which method should he choose? The selection of a suitable method is one of the main purposes of a rheological system. The author of a system not only selects what he considers to be the best method for making the conversion, but, in addition, shows how that method came into existence and why it is given preference to all others.

An imaginary critic might say: "Do you think it is fair to Bill to present him with only one system? Why not explain many systems to him, in an absolutely unbiased manner, and then let him do his own selecting?" The answer is that such a procedure would result in a stalemate. In order for Bill to be able to make an intelligent choice, he needs a rheological background and training, and that is contrary to our hypothesis. Given his own freedom in the matter, Bill would probably do exactly nothing—like the hungry donkey who starved to death standing between two equally tempting haystacks. Bill realizes more fully than anyone his own inability to make a selection and rightfully should refuse to do it. Equally so, the author of a system should refrain from giving Bill too much leeway in making a choice. Of course, if the author is not convincing in presenting his own system, Bill rightfully should look elsewhere for guidance.

The question should never arise as to whether a system is the only way of producing a rheological measurement and of converting it to figures or not; but rather the question should be: How nearly does the system give answers that approach the truth? (The word "truth" will not be defined here.) In order to make a decision in such matters, it is necessary to have no confused picture of what might be called the grosser aspects of flow. (As far as the finer or molecular aspects are concerned, one can only reason about them and try to arrive at some kind of mental picture of what probably takes place.) Hence, the application of the microscope to the study of flow in capillary tubes has been recommended as the proper starting point for the beginner in rheology. With a clear picture of the mechanism of flow (particularly of Bingham bodies) in mind, the direction that the rheologist must take, in developing a system, is almost forced on him; for he cannot digress too far to the right nor to the left without coming into conflict with the facts—revealed by the microscope. The next step is inevitably the elimination of all rheological equations that are unable to account for those facts. Then the elimination of rheological instruments that give results that cannot be satisfactorily correlated with the same facts. And, finally, the development of suitable instruments and the deduction of satisfactory rheological equations that can be applied to them.

This is an outline of what will be called a "complete system," that is, one that starts with a model of flow and then by a series of logical steps leads to the development of a viscometer, and, finally, to the conversion of the viscometric measurements to usable figures like U, f, and M. Such a system is needed by every practical laboratory investigator who works in the field of rheology. Part of the system, of course, includes the knowledge of the theory on which the system has been developed. How many complete systems there are in existence, it is impossible to say; for the practical rheologist seldom if ever publishes anything that would require the time and effort such an undertaking would demand. There are a number of "fragmentary systems" in existence, and these will now be described. By "fragmentary" is meant that the published parts known to the present author do not cover the complete outline as described in the foregoing. It is suggested that the reader strictly refrain from forming any opinion about these systems without first making a careful study of the original papers. It is practically impossible to describe another man's work in a way that will be satisfactory to all concerned. The descriptions must, of necessity, be brief.

Bingham's System

This is one of the pioneer systems. It is based on the concept that the rate of shear of a true plastic is directly proportional to the shearing stress in excess of the yield value. Bingham did not deduce by any mathematical process an instrumental equation from his assumption, but introduced the yield value directly into the Poiseuille equation and obtained, naturally, a linear equation of flow. He extrapolated his curve to the force axis. The intercept he called the "friction" and later the "yield value." This was given in grams of pressure head at first and later converted to shearing stress in dynes per square centimeter by multiplying by $Pr/2l$. The proportionality constant Bingham called the "mobility" and obtained it by multiplying the tangent of the curve by the same instrumental constant used in the Poiseuille equation, $\pi R^4 g/8l$.

Actually the experimental curve is not linear, and the Bingham method of treating it as if it were and extrapolating it to the force axis gives only approximate values. It is the method, however, which is used practically universally today. Where the yield value is small (a few dynes per square centimeter), such a method is accurate enough for most industrial work.

Bingham recognized fully the part played by flocculation; but his system does not include the microscopy of flow in capillaries. It contains nothing about thixotropy and rotational viscometers. Originally it included nothing about plug flow. It explained the nonlinearity at the lower end of the consistency curve as due to seepage and slippage.[1]

The Goodeve and Whitfield System

Next to the Bingham system, this one is probably the most popular. It would be dangerous to attempt to condense it into a few paragraphs, as the work of these investigators covers considerable territory. It contains several important features: (*a*) a mechanical model of thixotropy, (*b*) a mathematical definition of thixotropy, and (*c*) a rotational viscometer. The characteristic feature of their instrument is the fact that it possesses a cone-shaped cup and bob. The rate of shear is increased by lowering the bob farther into the cup, thus decreasing the distance between the walls. In order to develop their equation of thixotropy (thixotropy as a phenomenon, not as thixotropic breakdown), Goodeve and Whitfield[2] first assume that the rate of structural increase dx/dt is proportional to the structural concentration x. Then, if the maximum concentration is x_m and a is the order of the reaction,

$$\frac{dx}{dt} = k''(x_m - x)^a \tag{118}$$

Their next assumption is that the rate of structural breakdown $-dx/dt$ is proportional to the shear s. (Note: They use *rate* of structural breakdown, not *amount* of torque lost.)

$$-\frac{dx}{dt} = Ksx \tag{119}$$

At equilibrium the rate of buildup is equal to the rate of breakdown. Then by equating Equations 118 and 119 and assuming x to be negligible when compared to x_m, they get

$$x = \frac{k''x_m{}^a}{ks} \tag{120}$$

Another assumption is now made, that the concentration x is proportional to the difference between the apparent viscosity and the residual viscosity η_0. The "residual viscosity" is that which would be obtained at infinite shearing force—where the intercept is negligible in comparison with the force employed. Expressing the third assumption in the form of an equation gives

$$\eta - \eta_0 = k'x \tag{121}$$

Equation 121 is next substituted in Equation 120, giving

$$\eta - \eta_0 = \frac{k'k''x_m{}^a}{K} \cdot \frac{1}{s} \tag{122}$$

This is condensed to

$$\eta - \eta_0 = \frac{\theta}{s} \tag{123}$$

and the constant θ is called the "coefficient of thixotropy." An inspection of the development of θ shows that it is the rate of viscosity increase when the material is undisturbed, divided by the rate of structural decrease when a unit structure is subjected to unit shearing stress. According to Goodeve and Whitfield, θ includes a time factor and a factor indicating the strength of the structure. θ and η_0 are obtained experimentally by plotting η_0

against $1/s$. The intercept on the η axis is η; the tangent of the curve is θ.

Equation 123 is a "rheological equation." It can be used, however, only in connection with an "instrumental equation of flow." η is determined in the usual manner.

$$\eta = K\frac{F}{s} \tag{124}$$

where K is the instrumental constant.

Substituting Equation 124 in Equation 123 gives

$$KF = \eta_0 s + \theta \tag{125}$$

If in Equation 125, s is plotted against F, a normal Bingham-body curve is produced in which the yield-value intercept is θ. Goodeve and Whitfield state that f and θ are identical, but say that θ cannot be a yield value, for a yield value of a thixotropic material must decrease on stirring, whereas their θ remains unaffected.

It has been pointed out that stirring does not decrease the yield value of a thixotropic material *after the dynamic yield value has been reached.* The drop from the static to the dynamic yield value takes place almost instantaneously (as is shown in Part II under results obtained with the automatic recorder). No recorder was used by Goodeve and Whitfield, and no drop in yield value was detected by their method. It is at this point that confusion arises in regard to the relation between yield value and thixotropy. There are many statements in the literature that no difference exists between yield value and thixotropy. This situation has been in existence so long that it will probably never become clarified. Thixotropic materials break down in accordance with clear-cut laws—laws that are never associated with yield value. Thixotropy can produce yield value; but there is no evidence or known reason why yield value cannot exist without the presence of thixotropy.

For a detailed description of their viscometer and their conception of thixotropic structure, the reader should refer to the original papers.[2]

The Pryce-Jones System [5]

This system comprises a specially constructed rotational viscometer and a method of measuring thixotropy. Pryce-Jones laid down as a cardinal principle the fact that it takes at least two consistency curves obtained from a single material in order to obtain a measurement of its thixotropic nature. Although this might seem self-evident at present, at the time the statement was made there was a real necessity for it. There were many, and still are many, investigators using one-point measurements and single consistency-curve methods in an attempt to determine thixotropy. Pryce-Jones emphasized the fact that it is necessary to have measurements made both before and after thixotropic change is induced. The idea was not new by any means; but neither had it been given the full consideration it demanded.

Pryce-Jones' viscometer or "thixotrometer" gives deflection (stress) versus time curves. After the material is stirred, the cylinder is set under high stress by being twisted through a given angle. The stress is then allowed to act on the material. If the stress decreases logarithmically with the time, the substance is Newtonian. If the stress is plotted against various "times" and the curve is not logarithmic, then, the material is non-Newtonian. If the curve is rerun after a longer rest period and it is found to fall higher on the scale than the first curve, then thixotropic buildup is indicated.

Pryce-Jones emphasizes his concept of what he calls "false-body" and goes to considerable effort to explain the difference between false body and thixotropy. The present author has made various attempts to get a clear understanding of this subject, but so far without success. There are times when it seems that by "false-body" is meant a Bingham body with little or no thixotropic structure (a material that will give a very small loop, or none at all). By "thixotropic material" is probably meant one that gives a relatively large loop. However, there is much that has been written and much that has been said in explaining Pryce-Jones' work that does not seem to agree with that conclusion. The real difficulty is probably the inability to understand the meaning of rheological terms as used by different rheologists.

The Reed System

The Reed system is for the study of the consistency of lithographic and printing inks. It consists of a rheological instrument called an "Inkometer" and of a method of recording the results. Its characteristic features are:

1. It is an instrument so constructed that it tends to duplicate the conditions of the printing press by duplicating film thickness, and by duplicating the rate of shear to which the ink is subjected in the printing operation.

2. The system is based on two principal ideas: first, that "the conventional methods of plastometry that have been more or less successfully applied to special materials such as clays, tars, asphalts, paints, and lacquers were found altogether unsatisfactory"; and, second, "since inks are thixotropic plastic materials subject to reversible changes in consistency with mechanical agitation, consistency measurements should be taken while the inks are in a state of agitation comparable to that which takes place during actual printing." [4]

At the time Reed wrote these statements, they were undoubtedly justified. The question remains: Have the conditions changed since then? At that time the laws governing thixotropic breakdown of inks were not known, and, consequently, U and f could not be calculated for high rpm from ones obtained lower down in the scale. In addition, suitable rotational viscometers for plastics like printing inks had not been developed, and so "the conventional methods of plastometry" could not be at all satisfactory.

The Inkometer is composed essentially of two rollers of the type used on printing presses. These rollers are in contact with each other with the ink between them. The top roller is composition-covered. The lower roller is metal. A measured amount of ink is always used. The lower roller is set in motion. The viscous drag created by the ink exerts a torque on the upper roller, which is supported at each end by arms pivoted on the axis of the metal roller. This drag brings the upper roller forward. The torque thus produced is then counterbalanced by a weight, which pushes the two rollers back again into their vertical alignment. This counterbalancing is carried out at three different speeds—200, 400, and 600 rpm.

The three different rpm are plotted against the three torques, and a three-point consistency curve is obtained. "Tack" is defined as pull of the ink on the paper and is recorded as the torques at the two opposite ends of the curves. This difference is proportional to the slope of Reed's curve (if the curve is considered to be linear) which would make it roughly proportional to plastic viscosity. It would seem far more logical, therefore, to call Reed's "length" tack. The torque at 400 rpm constitutes a one-point curve, which should be used with that understanding. Summarized briefly, the Reed system consists of an apparatus specially designed for measuring lithographic and printing inks. It has an appeal to the ink manufacturer because of its resemblance to a printing press. Unfortunately Reed does not employ the generally accepted rheological concept and, as a consequence, places an interpretation on his measurements that is difficult to understand. This condition is by no means uncommon in rheological laboratories where it is desired to avoid the difficulties of rheology as much as possible and at the same time to secure a method that will be "accurate enough for all practical purposes." The investigator should note that the foregoing criticism is directed entirely toward the *interpretation* of Reed's consistency curves. It seems that a better method of interpretation could be devised.

Other Fragmentary Systems

Houwink[3] has developed a rheological system that pertains to the lower end of the consistency curve. It is somewhat difficult to give a simple explanation of his conception of flow in this region for it is not always explained how the curves are obtained, that is, by deduction or by experiment. Houwink makes little use of the idea of plug flow. He plots measurements (dv/dr versus stress) for materials that are not Bingham bodies, giving curves of the kind that result from a transition of plug to laminar flow. The curvature thus produced at the lower end of the curve is explained by the concept that stronger bonds are broken as the stress is increased. When all the bonds are broken, the "straight" part of the consistency curve is attained. This picture necessitates the ultimate adoption of three different yield values. The lower yield value f_l is where the weakest bonds are broken. Houwink's description does not say whether the flow is obtained with a capillary viscometer or not. If it were, and the material were a Bingham body, it would not be necessary to have three different yield values, as already pointed out in Chapter 2.

Houwink then states that the upper yield value f_m is at the point where all the bonds are broken. The Bingham yield value f_B is not introduced at this place but is discussed under the subject of paints (true Bingham bodies) and is obtained by extrapolating the curve to the stress axis.

There are many investigators who have developed what might be called rheological "schools" of thought whose work is too expansive to include in a book on applied rheology. Outstanding amongst these should be mentioned Mark, Eyring, Flory, Scott-Blair, and Simha. In the practical fields are such well-known investigators as Mooney, Traxler, de Waele, Bowles, and Bekk. Every rheologist should eventually become acquainted with the works of all these investigators.

Summary of Our System

Two concepts are given that form the foundation of the system. These are expressed in the form of two rheological equations:

Newton's concept: $$F = \eta \frac{dv}{dr} \quad \text{(for liquids)}$$

Bingham's concept: $$F - f = U \frac{dv}{dr} \quad \text{(for Bingham bodies)}$$

The Newton concept was used to deduce the Poiseuille equation. This theoretical equation (based on the Newton concept) checked with Poiseuille's experimental work, thus proving the correctness of the concept. The Bingham hypothesis was employed by Reiner and Riwlin in deriving their equation of flow for Bingham bodies in a rotational viscometer. This equation also checked with experiment.

The present system does not include in it any generalized or nonlinear equations of flow, for such equations have not been sufficiently established experimentally to warrant their use in an industrial laboratory. In addition, some of them are dimensionally unimaginable. This is particularly true for power equations where the dimensions of the "viscosity parameter" change with every different material.

The system given here makes a point of associating rheology with the study of flow by means of the microscope. It also includes the study of flocculation and its relationship to the formation of yield value.

The reasons for the curvature of the lower end of the plastic flow curve are explained. These are the change from plug to laminar flow and slippage flow.

The impossibility of obtaining a linear consistency curve with the capillary viscometer is noted, and a comparison with the rotational viscometer is made. The fact that a large part of the rotational-viscometer curve is linear for Bingham bodies led to its selection in preference to capillary viscometers.

The Reiner and Riwlin equation for calculating the plastic viscosity and the yield value is employed. The laws of thixotropic breakdown are developed and the requirements of a thixotropic model are explained.

In Part II descriptions of the viscometers used in the system are given. In Part III the relation between structure and the consistency curve are analyzed. Both Part II and Part III form essential divisions of our rheological system.

PART II

The System Applied to Laboratory Measurements

CHAPTER

8

The Rotational Viscometer

In this system the rotational viscometer plays a dominant part. It will not be the only instrument described, however. For certain materials, capillary-tube viscometers are preferable; for others, parallel-plate instruments are the only kind that can give satisfactory results.

By the expression "satisfactory results" is not meant simply a measurement that can be duplicated with the desired degree of precision. The expression is far more comprehensive. A "satisfactory result" must be one that not only is easy to duplicate but also bears a known fundamental relationship to the physical properties of the material tested. For instance, the time of rise of an air bubble in a material with a yield value is not proportional to the plastic viscosity. Time, then, cannot be used as a measure of plastic viscosity. Again, the time of thixotropic setup cannot be a measure of the "coefficient of thixotropy." Here the problem is too vague to be analyzed. If the student has followed the analysis of thixotropic breakdown given previously, he will understand that there are factors involved in thixotropic buildup that cannot be included in a single simple measurement of time. In general, any instrumental measurement of the single-point type is of little use for materials other than Newtonians (Reiner would say "simple Newtonians").

Our industrial laboratories are crowded with single-point-method viscometers. Because they can duplicate measurements on Newtonians, such instruments are erroneously assumed to be satisfactory for pseudoplastics and Bingham bodies. As long as that condition prevails, industrial rheology cannot advance very rapidly. As a rule, each rheologist will find that the instrument he ultimately uses must be constructed, or at least modified, to fit the special kind of work he is required to do. This usually results in building one's own instrument. Whether an instrument gives measurements in cgs units or employs some other standard unit is not so important. It is simply convenient to use the cgs system because of its universal acceptance by rheologists. It is the system that is employed here.

The rotational viscometer described in this chapter is useful for the measurement of Newtonians, pseudoplastics, and Bingham bodies. When Newtonians are measured, the results are given in poises. The range, here, is from 1 poise to 2500 poises. When pseudoplastics are measured, the results are given as a consistency curve. No attempt is made to convert such a curve into plastic viscosity (poises) and yield value (dynes per square centimeter). The range again is for $U = 1$ poise to $U = 2500$ poises and $f = 50$ dynes per square centimeter to $f = 180{,}000$ dynes per square centimeter. Modifications of this instrument are also described that will give measurements as low as $U = 0.005$ poise and $f = 3.0$ dynes per square centimeter.

Dimensions of the Rotational Viscometer

The viscometer[1] is built on a cast aluminum base 100 x 30 x 2.5 cm. This base is fitted with leveling screws. In order to minimize the noise of vibration arising from the motor, the base may be placed on rubber padding of the kind that is made for such purposes. (Refer to Figure 30, *a*, *b*, and *c*.)

There are three sections to the viscometer: *d*, the motor (¼ horsepower); *e*, the rpm regulator; and *f*, the viscometer proper. Commercial rotational viscometers are usually inadequate as far as their power supply is concerned. In the instrument used here, the motor is ¼ horsepower. This is sufficient to produce high shearing rates for materials like stiff base paints and base inks. High shearing rates are always necessary when the materials are thixotropic; therefore, the investigator should not try to economize by equipping his viscometer with an inadequate motor. Rather too much than too little power should be available. In addition to sufficient power, it is necessary that the motor be of the synchronous type. The rpm of the motor shaft remains constant (1800 rpm). The speed of the rotating cup is varied by the rpm regulator *e*.

The rpm regulator is of the continuously variable-speed transmission type. Its useful range is 5 to 200 (some instruments 400 rpm). The rpm is changed by moving the handle *g*. The change is smooth and continuous and *takes place while the cup* h *is rotating.* This is an exceedingly important point in making hysteresis loops in the study and measurement of thixotropic breakdown. Those instruments where the rpm cannot be changed without first stopping the motor (in order to make the gear shift) allow thixotropic buildup to take place during the interval employed in making the change. This always is detrimental to the measurement.

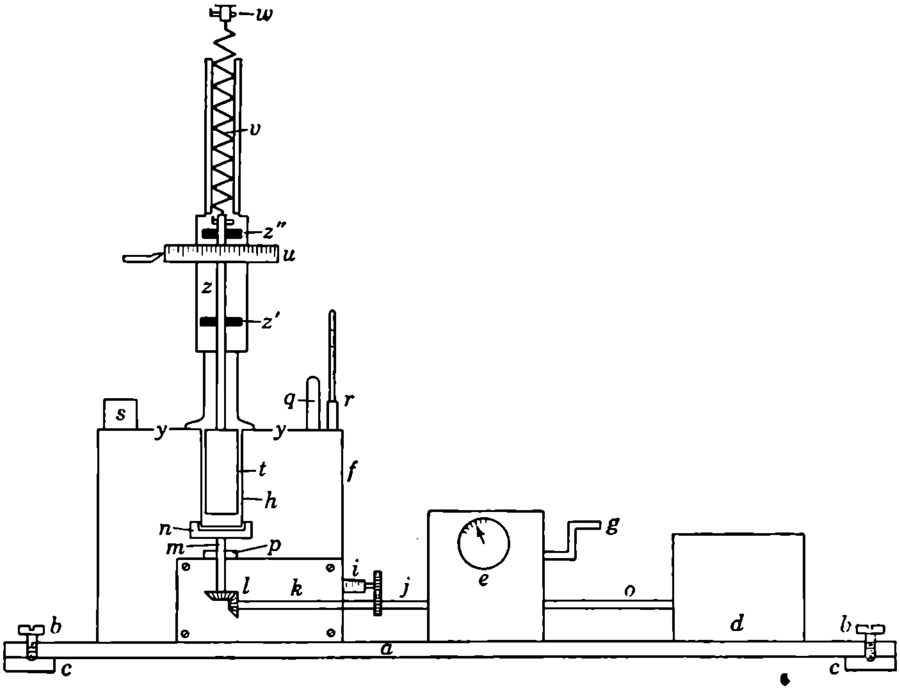


Fig. 30. Sketch of the Rotational Viscometer. Not Drawn to Scale

The gear regulator used by the author was made by the Briggs and Stratton Corporation. An extra dial was attached so as to give it a finer scale reading than that furnished (at that time) by the manufacturers. The scale is calibrated in rpm by the use of a stopwatch and a revolution counter *i*, which can be geared to the shaft *j* when desired. The calibration curve (between rpm and scale reading) is quite linear.

The shaft *j*, which is moving at a different velocity from the motor shaft *o*, enters the water-tight compartment *k* where it is geared to the upright shaft *m*. Shaft *m* leaves the compartment *k* and enters the water bath *f* through a stuffing box *p*. This stuffing in building one's own instrument. Whether an instrument gives measurements in cgs units or employs some other standard unit is not so important. It is simply convenient to use the cgs system because of its universal acceptance by rheologists. It is the system that is employed here.

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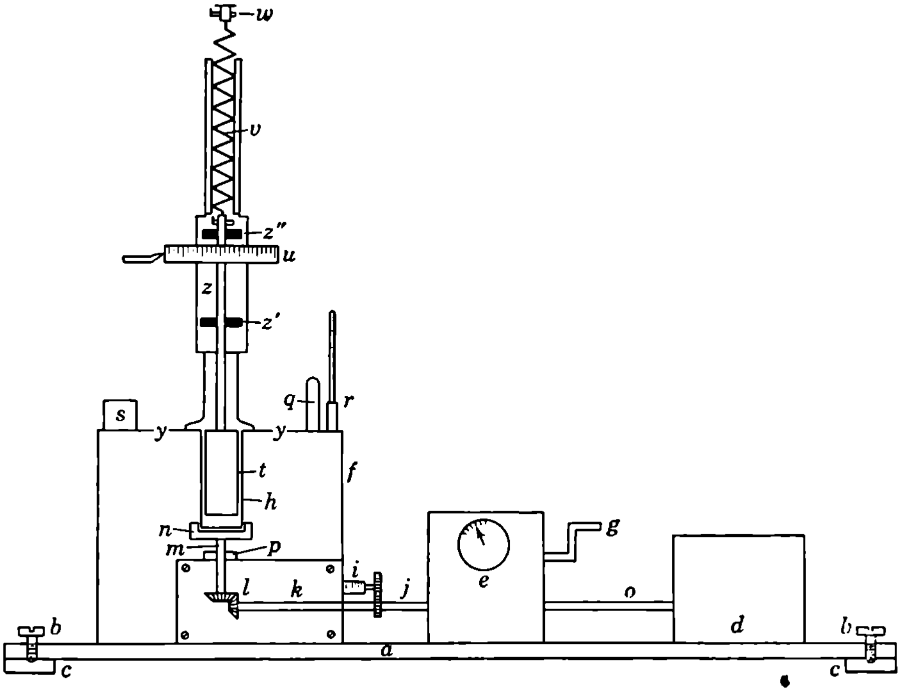

Fig. 30. Sketch of the Rotational Viscometer. Not Drawn to Scale

buildup to take place during the interval employed in making the change. This always is detrimental to the measurement.

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The shaft *j*, which is moving at a different velocity from the motor shaft *o*, enters the water-tight compartment *k* where it is geared to the upright shaft *m*. Shaft *m* leaves the compartment *k* and enters the water bath *f* through a stuffing box *p*. This stuffing box is not tight to high bath temperatures and is best operated below 60°C.

Normally 30°C is probably the most convenient all-year-round temperature at which to make measurements. It is better than the usual 25°C, because during the summer months the bath would have to have its temperature lowered to meet that requirement. This can be done if a source of cool running water can be had. A coil of pipe (not shown in the diagram) runs from one end of the bath to the other. Through this pipe the water is passed. The temperature of the bath does not drop to the temperature of the running water, because the bath is thermostatically controlled. The apparatus for the temperature control is of a standard make and maintains the bath at 25.0 ± 0.2°C. The mercury control is inserted at *q*. The relay is fastened to the back of the water bath and is not shown in the figure. More accurate control can be used if desired, but for ordinary industrial work ±0.2°C has been found satisfactory.

The construction of the cup *h* and the bob *t* demands some thought. The work of Reiner and Riwlin [4] shows that, the smaller the clearance between the bob and cup wall, the shorter will be the lower curvilinear end of the consistency curve. By actual trial and error the present author and his collaborators have found that the most practical clearance is in the neighborhood of 1.0 to 2.00 mm. This means that the bob must be held in center with no chance of moving out during a consistency measurement. This is a new departure in rotational viscometers. The usual method of mounting the bob is to suspend it at the end of a torsion wire. This is no better than making a pendulum of the bob. It leaves the bob free to swing over toward the wall of the cup, in which position it is no longer centered. Furthermore, Reiner's mathematics would no longer apply, and the material would ride out of the cup. It is, therefore, necessary to fasten the bob to the end of a strong shaft *z*, which in turn is guided and held centered by two ball bearings z' and z''. The ball bearings must be of the best quality and thoroughly cleaned. The resistance they offer to the twisting of the bob is negligible. The torsion wire *v* is fastened to the other end of the bob shaft and suspended from a holder *w*.

The cup should be made with a removable bottom *a*. (See Figure 31.) The bottom is screwed on the cup, which is threaded on the outside. This gives a smooth inner wall the entire length of the cup. In order to clean the cup, the bottom is removed and a tight-fitting cleaning cloth forced through.

The bob has a flat bottom which is capable of producing an end effect from the viscous drag exerted on it. In the MacMichael rotating viscometer the end is hollowed out so as to entrap an air bubble, thus eliminating the viscous drag. Mooney and Ewart[2] have shown that, if the end is not flat but cone-shaped with a known angle at the base of the cone, an end correction can be calculated. (See Appendix C.) In our present instrument where $R_c = 1.5$ cm, $R_b = 1.3$ cm, $h = 5.1$ cm, and the distance between the end of the bob and the bottom of the cup is 1.0 cm, neglect of the end effect decreases the values of S and C about 2.0%. (See Appendix C.) For most industrial purposes 2.0% is negligible.

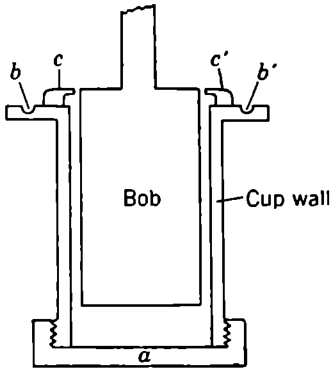


Fig. 31. Sketch of the Bob and Cup

The cup has a grooved channel (Figure 31, *b*) around its edge for the purpose of catching any overflow of the material squeezed out during the insertion of the bob. The material is leveled off with a spatula at the top of the cup, which should be rotating. Sometimes it is necessary to use a cover ring *cc'* to prevent the material from riding out. The inner edge of the ring does not touch the bob, although the clearance is quite small.

The upright support, which holds the spring *v*, the scale *u*, the shaft *z* (Figure 30), and the bob, can be raised until the bob is clear of the cup. The support can be clamped in this elevated position. The clearance is great enough to permit easy removal of the cup from the water bath. The material to be measured is poured into the cup until the cup is about one-third full (Figure 32). The support *b* is then slowly lowered until the bob enters the cup the correct distance. This distance is controlled by means of a metal stop *d* which is screwed into the lower end of the support so that, when the support is down, the stop rests on the top plate of the bath. The bottom of the bob should then be 1 cm from the bottom of the cup. It will be found advantageous to have the cup slowly rotating while the bob is being lowered into the material. The support slides in the support holder *a* which is screwed on to the top plate of the bath.

If the material rides out at one side of the cup, then, the bob is off center in the direction of the spot where the overflow takes place. The support holder must be moved in the opposite direction. This moving should be done while the cup is rotating. It is carried out by first loosening the screws *e* that fasten the holder to the bath. These screws are in holes that are large enough to permit sufficient motion of the holder in any direction. By tapping the base of the holder with a hammer while the cup is in motion very fine adjustments can be made so that the bob can be accurately centered. When centering is achieved, the holder screws are tightened.

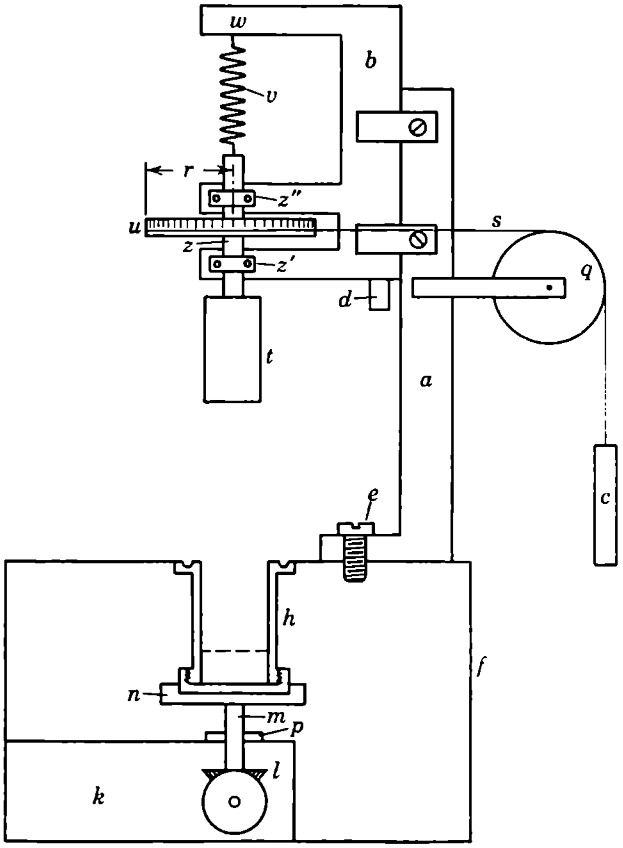


Fig. 32. Sketch of Side View of the Viscometer

The Torsion Wires or Springs

The torsion wires in the viscometer are not the customary straight wires but helical springs. It is convenient to have a set of about six such wires, giving different degrees of torsion. The lightest wire is thin and very easy to twist. The heaviest one can be twisted by hand with difficulty, and then only through a few degrees. Each wire must be calibrated so that the torque (in grams centimeter) is known per degree of twist. This gives the wire constant K. The total number of degrees of twist (read on the scale in Figure 32) multiplied by K gives the torque for the particular rpm at which the viscometer happens to be running. This torque when plotted against its rpm gives a point on the consistency curve. The method for obtaining the curve (and hysteresis loop) has been explained in detail in Part I.

The springs must be mounted securely so that there is no loose motion at the points a, a' (Figure 33). If such motion is allowed, it will increase the yield-value intercept, thereby giving erroneous results. In order to avoid this possibility, set screws b, b' are employed. This precaution is particularly necessary for the heavier springs. The springs are fastened to the support c' and the upper end of the bob shaft c by means of tapered pins, e, e'.

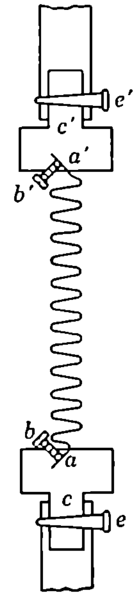


Fig. 33. Sketch of the Torsion Spring

Commercial rotational viscometers are calibrated with liquids of known viscosities. The present viscometer, however, cannot employ such a method, because the stiffest springs would require liquids of such high viscosities that they would be pseudoplastics and not Newtonians. The viscosity of a pseudoplastic has no particular significance, or rather no known significance, except at very low rates of shear. When the investigator buys a high-viscosity liquid, he has no way of knowing at what rate of shear the so-called "viscosity" has been determined. If the liquid is pseudoplastic the measurement obviously will be useless to him. If he knows definitely that the figure for the viscosity given to him has been determined at an equivalent rate of shear of, say, 10 rpm on his own viscometer, some use might be made of it; but, unfortunately, he does not know that. Another method for calibrating the springs had to be devised.

The Calibration of the Springs. The method of calibration employed is simple and direct. The torque that will twist the wire through a known number of degrees is measured. This is done by attaching a string *s* to the scale (Figure 32) and running it over a ball-bearing-mounted wheel, fastened to the back of the support holder *a* (Figure 32). A known weight *c* (or series of weights) is attached to the lower end of the string. This weight causes the spring to twist through a certain number of degrees. The torque produced is the radius *r* of the scale multiplied by the weight. This product when divided by the scale reading gives the wire constant *K* (the torque per degree of scale). The radius of the scale is 5 cm on the present instrument. The various *K* values are (approximately) as shown in Table 3:

TABLE 3

Spring Number	Dynes Centimeter per Degree
0	200
1	600
2	2,000
3	5,000
4	15,000
5	35,000

The bath (Figure 30, *f*) is made of cast bronze, except the top plate which is made of brass. The dimensions of the bath are 36 x 28 x 25 cm. A water-tight compartment *k* is made in the lower right-hand corner. This compartment is closed by a plate which can be removed if desired. The bath has a stirrer. The motor that operates the stirrer is shown at *s* (Figure 30). A thermometer is inserted in the bath at *r*. Holes *y* are put in the top plate to accommodate extra cups so that the material can come to temperature while the material in the central cup is being measured.

Modified Forms of the Viscometer

The viscometer as described has been modified in two ways. The first was accomplished by making a larger cup and bob than those that fit into the original model. The top plate of the water bath is cut with a larger hole to accommodate the new cup. Like the smaller cup, the larger one is keyed into the revolving platform *n* (Figure 30). The dimensions are: R_c = 5.21 cm, R_b = 5.01 cm, and the immersed height of the bob is 4.5 cm. The distance between the bottom of the bob and the bottom of the cup is 1 cm. These dimensions give an error of about 23% when the end effect is neglected. This error is too large to overlook and must be taken into consideration. How this is worked out is shown in Appendix C. The large cup and bob with spring no. 5 give (top rpm = 100) a maximum viscosity (where $f = 0$) of 50 poises; with spring no. 0, a minimum viscosity of 0.03 poise can be obtained.

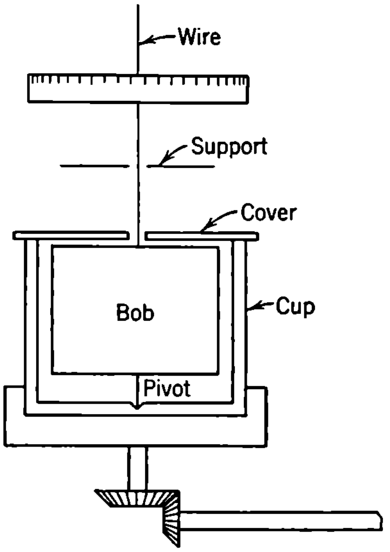


Fig. 34. Sketch of the Bob and Cup of the Microviscometer

The second modification of the viscometer was obtained by making the bob of aluminum, to secure lightness, and by replacing the torsion springs with the straight phosphor-bronze wires used in the MacMichael viscometer. The bob is not supported with ball bearings, and so the bottom of the bob has a sleeve bearing inserted at its center which pivots the bob in a hole in the center of the cup bottom (Figure 34). The dimensions are: R_c = 2.0 cm; R_b = 1.95 cm. The inside length of the bob is 4.0 cm. Using the lightest MacMichael wire no. 32, a viscosity as small as 0.005 poise and a yield value of 5.0 dynes per square centimeter can be measured.

The Weltmann Recorder

An automatic-recording device has been developed by Weltmann[5] that can be attached to the viscometer. In order that a recorder can be used successfully it must be constructed in a way that will not hinder the free motion of the bob by imposing friction on it. This means the elimination of gears of all types. Pryce-Jones[3] has succeeded in doing this with his thixotrometer by means of a narrow beam of light reflected from a mirror (attached to the bob shaft) onto photographic paper. This procedure necessitates two inconveniences—taking the measurement in a room illuminated only with red light, and development of the photographic paper.

These inconveniences are avoided in the Weltmann apparatus, which records the consistency curve by means of an electric spark. The spark causes no friction and, hence, no hindrance to the twisting of the bob. The reader should refer to the original paper on the recorder for an exact and detailed description. Briefly, the recorder is constructed in the following manner: On the bob shaft (Figure 30) between the two sets of ball bearings is fitted a solid cylinder composed of an electrical nonconductor. A metallic strip, making exactly one encirclement of the cylinder, is inserted in its surface starting from the top and ending at the bottom of the cylinder. This strip is one of the electrodes and is grounded to the viscometer.

The other electrode is a straight vertical metallic strip running parallel to the surface of the cylinder and firmly secured in a nonconducting block of material. This block is attached to the sliding support (Figure 32) that holds the spring, scale, and bob, and is inserted just back of the cylinder. Enough space is left between the two electrodes to allow the recording paper to pass between them. The vertical electrode is attached to one end of the high-voltage coil of a transformer. The other end of this coil is grounded. The electrodes are sufficiently close together so that, when the transformer is operating, sparks will pass at that point where the spiral electrode on the cylinder is in closest proximity to the straight electrode. The sparks pass through the recording paper and perforate it. These perforations draw the consistency curve. The apparatus sparks about 60 times a second.

When the position of the bob is changed by increasing the twist, a higher part of the spiral electrode moves opposite the straight electrode, and a perforation is made higher up on the recording paper. It should be noted that the recording paper is unwound from a roll on the right-hand side of the viscometer while being pulled by a drive cylinder operating on the left-hand side. Against the drive cylinder is pressed an idling cylinder, the paper passing between the two. The paper moves horizontally in a direction perpendicular to the straight electrode. If the position of the bob is changed by untwisting the spring (which happens in recording the downcurve), then the puncture mark is recorded lower down on the paper which is now in reverse motion, moving from left to right. The drive cylinder cannot push the paper backward in this direction; so the rewinding on the roll cylinder is done by means of a weight attached to a string wound around the roll cylinder. The winding is made in such a way that, as soon as the downcurve is started (and the pull from the drive cylinder stops), the weight drops and rewinds the roll cylinder.

The drive cylinder, which pulls the paper between the electrodes, is geared by means of a chain and shaft to the dial shaft of the variable-transmission box. Turning the transmission handle in the upcurve direction pulls the paper to the left. The paper moves only when the dial shaft is moving. When the dial shaft is moved until the top rpm is reached, the paper moves from right to left its maximum distance.

The rpm axis is the lower edge of the paper. A line drawn across the width of the paper and perpendicular to the edge is the torque axis. The act of adjusting the viscometer for any definite rpm, by turning the dial shaft, automatically pulls the paper into the correct position so that the point on the edge of the paper (corresponding to the definite rpm) will be opposite the spiral electrode. The cup can continue to rotate at this rpm, but the paper will not move until the operator turns the dial shaft.

If the dial shaft is turned in equal increments of x degrees, the paper will not be pulled through in equal steps of rpm. Below 200 rpm this nonlinear relationship is very slight and is not in evidence on casual inspection of the recorded downcurve of either a Bingham body or a Newtonian. This discrepancy is sufficient, however, to affect the calculated value of U. This difficulty has been overcome by Weltmann as follows:

A paper is inserted in the recorder and the sparker turned on. By careful adjustment of the dial shaft, the bob is deflected 0°, 10°, 20°, 30°, etc., dividing the vertical direction of the paper into equal divisions. At the same time that the rpm is being increased (by turning the dial shaft) the rpm axis is being marked off in distances that are not quite equal. The rpm for each distance, however, is known; and that is the important point. Vertical and horizontal co-ordinate lines are now drawn through the markings, and the chart thus obtained is photographed on a transparent glass plate. This plate is superimposed on any recorded consistency curve (top rpm not to exceed 200) and the co-ordinates on the plate used for making the rheological calculations. In order to secure the exact positioning of the plate, the paper on which the consistency curve is to be recorded is perforated with a spark at 0° and 360°, simultaneously. This is done at any arbitrarily chosen rpm. When the chart is superimposed, these two points must coincide with the same points on the chart.

Summary of Chapter 8

This chapter has been devoted entirely to a description of the rotational viscometer used in our rheological system. This viscometer is composed of a ¼-horsepower motor, a device for changing the rpm without stopping the rotation of the cup, a temperature-controlled water bath, a rotating cup, a bob, and a set of torsion springs. The dimensions of the important parts of the viscometer have been given. The viscosity and yield-value ranges have been touched on, but are summarized here in a more comprehensive form.

TABLE 4

APPROXIMATE VALUES

		Maximum Viscosities				Maximum Viscosities			
		$R_b = 1.3$ cm		$R_c = 1.5$ cm		$R_b = 5.01$ cm		$R_c = 5.21$ cm	
		$f = 0$–1000		$f = 80{,}000$		$f = 0$		$f = 5000$	
		rpm				rpm			
Spring No.	K (dynes × cm)	100	200	100	200	100	200	100	200
0	200								
1	600	100	50			1	0.5		
2	2,000	150	75			4	1		
3	5,000	400	200			8	4		
4	15,000	1,200	600	100	50	24	11	4	2
5	35,000	2,500	1,250	1,500	750	48	25	30	15

MINIMUM VALUES FOR VISCOSITY AND YIELD VALUE

R_c (cm)	R_b (cm)	h (cm)	U (poises)	f (dynes/cm^2)	S	C
1.5	1.3	5.1	1.0	50	2.30×10^{-3}	1.58×10^{-2}
5.21	5.0	4.5 (5.53) *	0.03	10	4.35×10^{-5}	1.10×10^{-3}
2.0	1.95	4.00	0.005	3	2.25×10^{-4}	8.89×10^{-3}

* Corrected for end effect.

Table 4 gives approximately the limitations of the several instruments described in this chapter. The figures indicate the springs to be used. When a torsion spring is twisted too far (beyond its strain point), it must be recalibrated. If the spring should be badly damaged, it must be discarded and replaced by a new one. In order to prevent such a possibility, the length of each spring should be so adjusted that it can withstand at least one complete revolution of the bob without being damaged. A stop should be attached to the bob to prevent it from making more than a single revolution.

A Weltmann automatic recorder has been described for plotting the consistency curve by means of a sparking device. The curve is a continuous series of small puncture marks. An up- and down-curve which can be recorded in 15 seconds shows facts in regard to thixotropic breakdown that cannot be detected when visual readings are taken. This is more fully discussed in the chapter on laboratory results.

Questions

1. In what ways does our rotational viscometer differ from the usual type of commercial rotating viscometer?
2. What is the primary advantage of being able to change rpm without stopping the rotation of the cup?
3. Name two of the principal advantages gained by the use of the automatic recorder.

CHAPTER

9

Parallel-Plate Viscometers

For materials possessing relatively high viscosities such as tars, pitches, rubbers, and resins, the parallel-plate type of viscometer is better suited, perhaps, than any other kind. In the case of the Tackmeter[3] described here, viscosities as high as 200,000,000 poises have been measured; and even this figure is not necessarily the upper limit.

Flow is induced in plate viscometers in several ways: by pulling the plates apart, in which case the material flows into the space between the plates as plate separation takes place; by squeezing the material between the plates; and by rotating one of the plates, thereby producing a shearing action. The Tackmeter is the first type and is described in detail. The compression and shearing viscometers are discussed briefly, but the reader should refer to the original papers for a complete account of them.[1,2,4,6]

The Tackmeter was developed for the purpose of analyzing the phenomenon called "tack," a term used by manufacturers and users of printing inks. The scope of the Tackmeter was found, however, to cover more territory than that for which it was originally intended. It was found, for instance, that the Tackmeter is a quick and easy viscometer to use for many industrial purposes. The instrument requires but a drop or two of material; and, because the material is spread out into a thin film, only a few minutes are needed for it to come to temperature. In addition, a few seconds are all that are necessary for cleaning and getting the instrument ready for the next sample.

Two different measurements are made in operating a plate viscometer; one is the force used in pulling the plates apart; the other is the time required in making this separation. It is not necessary that the separation be completed. In the case of the Tackmeter the material "necks down" until only a thin column extending from the bottom to the top plate remains. Sometimes this column breaks, but usually it does not. If the material is Newtonian, only one such set of measurements is needed; otherwise, a consistency curve must be obtained (by employing a series of weights) from which tack is calculated.

Tack

This is a phenomenon for which a simple definition that will cover all possible cases cannot be made. Tack from the printing-ink point of view does not include elasticity. Obviously, this is not so where rubbers are concerned. Adhesion is another property which may or may not be included in the concept of tack. Whether it is or not depends on the nature of the problem involved.

The simplest and most elementary form of tack probably is that found in the ink industry. The author feels that this type of tack can be defined. Objections have been raised on the grounds that cohesion must be included, but the arguments are debatable, to say the least.

The necessity for knowing the tack of an ink is mainly because of two important facts: First, if the tack is too great, the ink will "pick" or even tear the printing paper (stock). Second, if the tacks of process inks are not properly graded, faulty trapping will be the result. This can produce "pattern" and give false color values. In the case of process inks, the order of printing is usually yellow, red, blue, and black. The yellow must be the tackiest, and the black the least tacky in the graded series.

The Inkman's Method for Estimating Tack. This test is carried out as follows: A small amount of ink is rubbed out into a thin layer with the finger tip. This is done either on glass or on paper. When the film feels sufficiently thin, the finger tip is pressed firmly into it and then drawn away suddenly. This motion is repeated rapidly so that it results in a feeling that the ink is pulling on the finger tip. When this resistance to pulling feels great, the tack is considered to be large; when small, it is recorded as slight.

From an inkman's viewpoint, *tack is pull resistance.* The original object of the Tackmeter was to analyze pull resistance and express it in rheological terms. In order to do this the Tackmeter had to be built in such a way that its several parts could be varied—one at a time. These parts are the original film thickness, the finger-tip area, and the pulling force.

The Tackmeter [3]

The instrument is shown diagrammatically in Figure 35. It is essentially a mechanical finger. This finger is built on top of a constant-temperature bath *a*. The temperature is maintained constant by means of the control *b*, with relay attached in the back (not shown here). The bath contains a stirrer *c* and a thermometer *d*. The bath is mounted on an aluminum base *e* which can be leveled by means of screws *f*. The dimensions of the bath are the same as those given for the viscometer—36 x 28 x 25 cm. It is filled completely with water. No air space is left in it.

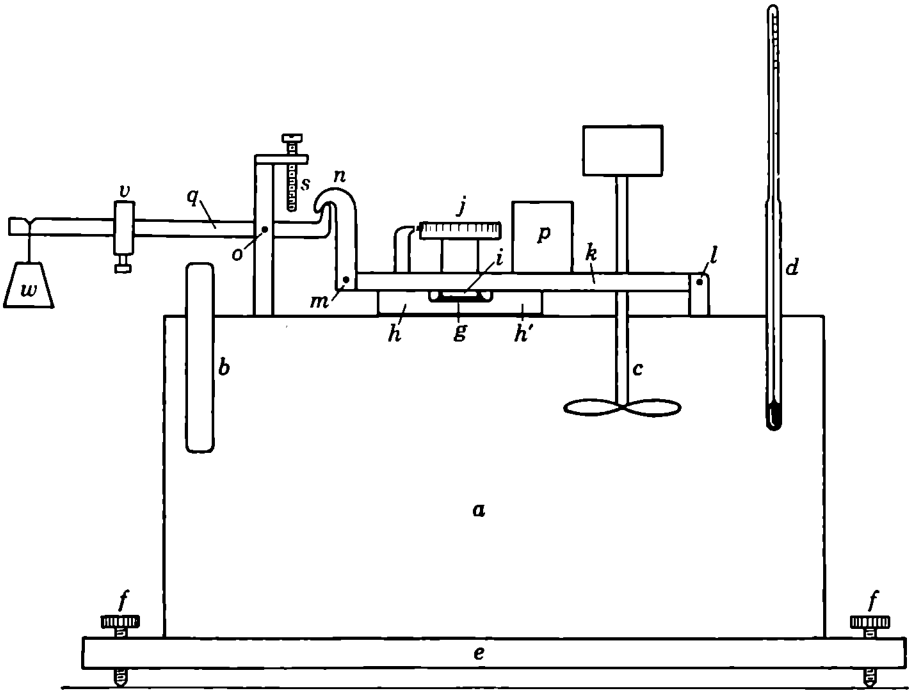


Fig. 35. Sketch of the Tackmeter

On top of the bath is firmly secured a brass plate *g*. On the center of this plate is placed a drop or two of the material to be tested. The finger tip *i* is pressed down on the material, forcing it out into the shape of a very thin disk. The supports *h* stop the tip from going down the entire distance, preventing it from touching the plate *g*. The finger proper is a threaded cylinder (40 threads per inch) which can be screwed up or down by means of the graduated head *j*. In this manner the original film thickness (symbolized hereafter as *D*) is controlled. The radius of this cylinder is R. The area of the finger tip is πR^2.

The cylinder is mounted in a hole through the bar *k*. This bar is pivoted at *l* and can be lifted up and swung backward. At *m* is another set of pivots which holds a connecting bar *n*. This bar is hooked over the horizontal bar *q*, which holds the pulling weight *w*; *q* is pivoted at *o*. There is a balancing weight *v* attached to *q*.

When there is no material under the finger tip and the weights *w* and *P* are removed, the weight *v* should be adjusted so that the instrument is in balance. When this condition is attained, the finger, together with the series of lever arms to which it is attached, can be pushed into any position (either up or down) and will remain there. If the balancing weight is too far out, the finger will rise until the right-hand end of the arm comes in contact with the adjustment set screw *s*. This screw is so fixed that the finger tip cannot rise more than 1 cm. If the weight *v* is too far to the right, then the finger arm *k* will fall down until it rests on the supports *h*, *h'*.

There are three sets of case-hardened pivots, *l*, *m*, and *o*. These are screws that have pointed ends. They must be adjusted so that the lever system can move freely with as little friction as possible. Screwing the pivots too tight stops this free motion. When the adjustment is properly made a 1-g weight placed on the arm *q* in the region of the pivot *o* will cause the lever system to move.

The Tackmeter is a viscometer made in the form of a balance. The weight *w* is the pull resistance and the motivating force. The rate of flow is proportional to the reciprocal of the time *t* it takes the arm *k* to rise until it is stopped by the arm *q* meeting the set screw *s*. The Tackmeter does, then, what all viscometers do—measure applied force and the resulting flow. By using a series of different weights *w*, a rheological consistency curve can be obtained. Can the Tackmeter make a rheological analysis of tack? Before answering that question let us first try to find what factors might play a part in the manifestation of tack.

The following items can be written down as possibilities: viscosity, yield value, surface tension, adhesion, and cohesion (tensile strength). Let us examine carefully what happens when the finger is pulled up until rupture of the ink film takes place. The first thing that occurs is the drawing in of any external ink lying around the periphery of the finger tip. When this is all under the tip, the ink commences necking down until it forms a long thin column extending between the plates. As the plates continue to separate, the column gets thinner until finally it breaks. An examination of the tip and plate will show that ink is firmly adhering to both. This observation is an important one, for it tells at once that no work was performed against the force of adhesion (that is, between the ink and the metal). The next observation is that the ink ruptured only when the column was drawn down to probably molecular dimensions. This means that the work done against the force of cohesion is negligible. The third fact noticed is that two new ink surfaces, equal to $2\pi R^2$, have been formed. The work of cohesion is equal to twice the surface tension of the ink; consequently, the work performed in creating $2\pi R^2$ sq cm of ink surface is negligible in comparison with the work expended in pulling the plates apart.

Summarized briefly, from the inkman's viewpoint, adhesion, cohesion, and surface tension can play, at the most, only a negligible part in creating pull resistance or tack. This leaves but two possibilities, viscosity (or plastic viscosity) and yield value.

The Tackmeter is a viscometer employing a capillary space through which the ink is compelled to flow. This space does not remain of capillary size after the plates are separated appreciably. However, at the beginning, the space (which is that occupied by the film of ink of thickness D) is of capillary size in one dimension, and the ink is forced to flow into it. Because the ink has flow-resisting properties (manifested by U and f) a resistance is set up when an attempt is made to draw the finger upward. It is this resistance to flow that the inkman feels when he makes his finger tap-out test. The only thing required of the Tackmeter, then, in order to measure tack is its ability to measure viscosity and yield value. This ability, however, will not state what function of U and f tack happens to be. In order to determine the nature of this function, the Tackmeter must have certain attributes. It must be able to vary separately the initial film thickness, the area of the finger tip, and the pulling weight.

It has already been explained how the initial film thickness is varied. This is accomplished by means of the micrometer screw j.

The area of the finger tip is varied by having a series of finger tips of different areas. These all fit into the same threaded hole in the arm *k*.

Method of Using the Tackmeter. The lever arm *k* is pulled back, exposing the plate *g*. On the center of *g* is placed the material to be measured. The arm *k* is now returned to its original position; this will press the finger tip *i* into the material, causing most of it to flow out and gather around the periphery of the finger. The initial film thickness is now adjusted by turning the head of the micrometer screw *j*. On *j* is engraved a scale divided into spaces corresponding to intervals of 0.001-inch film thickness. The lowest space is divided further, giving intervals of 0.0002 inch.

A 500-g weight *p* is placed on the arm *k* as close to *j* as possible. This presses the arm *k* down firmly on its supports *h*, *h'* and secures the exact initial film thickness. A suitable weight *w* is suspended from the notched end of arm *q*. After the material has acquired the temperature of the water bath (which takes but a few minutes because the bath is filled with water until it contacts the top plate), the weight *p* is lifted. The weight *w* now causes the finger to rise and will continue to do so until stopped by the set screw *s*.

The time interval elapsed from the moment *p* is removed until the upward motion is stopped by *s* is measured with a stopwatch. The reciprocal of this time interval, $1/t$, is plotted against the weight *w*. When a series of weights *w* is used, giving a series of time intervals *t*, a rheological consistency curve can be plotted. In order to determine the relation between tack, *R*, *D*, *U*, and *f*, the viscosity equation must be developed.

The Viscosity Equation. This equation can be developed empirically with the Tackmeter. The development requires three experiments: (*a*) finding the relation between *t* and *w* when *R* and *D* are constant; (*b*) finding the relation between *t* and *D* when *R* and *w* are constant; and (*c*) finding the relation between *t* and *R* when *D* and *w* are constant.

(*a*) FIRST EXPERIMENT. This experiment is carried out by using successively two or more weights *w*. For each *w* the time of break *t* is recorded; *w* is then plotted against $1/t$. The results of the plot show a straight-line relationship. For Newtonians, the curve intersects the origin; for Bingham bodies, it gives an intercept *k*, on the *w* axis. This intercept is at present an unknown function of yield value. The results of the first experiment can be expressed as follows:

Newtonians: $$\frac{1}{t} = Kw \quad (R \text{ and } D \text{ constant}) \tag{126}$$

Bingham bodies: $$\frac{1}{t} = K(w - k) \quad (R \text{ and } D \text{ constant}) \tag{127}$$

where K is a constant depending on three factors. These factors are R, D, and the viscosity of the material. Probably the easiest way to develop the viscosity equation is by letting $K = K'K''K'''$ where K' is a function of viscosity; K'', a function of R the radius of the finger tip; and K''', a function of the initial film thickness D. Then for

Newtonians: $$\frac{1}{t} = K'K''K'''w \tag{128}$$

Bingham bodies: $$\frac{1}{t} = K'K''K'''(w - k) \tag{129}$$

(*b*) Second Experiment. Here D is varied by means of the micrometer screw, and w and R remain constant. When D^2 is plotted against $1/t$, the relationship obtained is not quite linear (Figure 36*a*). When a small constant value d is added to the variable D, the curve can be rectified and on extrapolation will intersect the origin (Figure 36*b*). The exact value of d is found by trial and error. Its origin is probably the result of the fact that neither

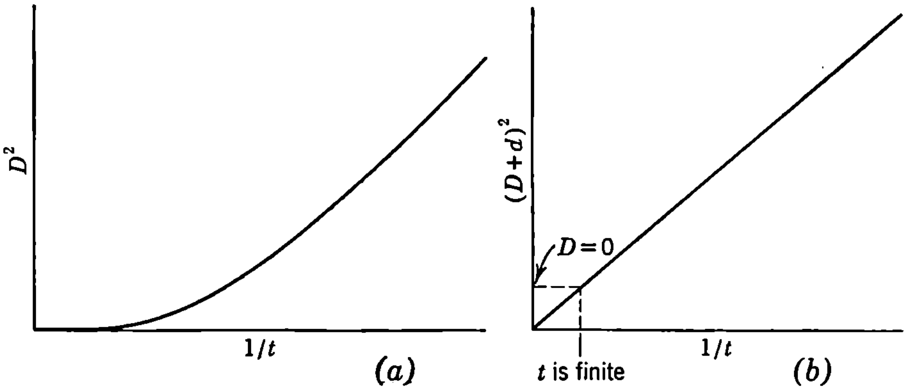


Fig. 36

the finger tip nor plate is optically flat and they always have a space between them; so the micrometer scale gives a reading that is a little too small. Note that the $(D - d)^2$ versus $1/t$ curve goes to the origin on extrapolation *only when* d *is finite.* Certain critics have missed this point entirely and have made statements to the effect that d cannot remain constant but must become zero if the $(D + d)^2$ curve is to intersect the origin.

From the results of the second experiment it is evident that $1/t$ varies directly as $(D + d)^2$. Then Equation 128 can be rewritten,

$$\frac{1}{t} = K'K''(D + d)^2 w \tag{130}$$

Unfortunately, there is no way to be sure that $(w - k)$ can be maintained constant, and so Equation 127 cannot be rewritten. This point is discussed in the following.

(*c*) THIRD EXPERIMENT. The area of the finger tip is the remaining factor to be varied. This can be done by having a series of finger tips with different areas. D and w are maintained constant. Plotting various powers of R against t shows that R^4 gives a linear curve intersecting the origin. Then,

$$\frac{1}{t} = K' \frac{1}{R^4} (D + d)^2 w \tag{131}$$

and, again, no equation for a Bingham body can be given.

This is as far as experiment can go. The ultimate viscosity equation must be obtained by trial and error. If $1/\eta$ is substituted for K', the results will not check with experiment. If, however, $1/\pi\eta$ is used, an equation is obtained which gives viscosities of known materials with satisfactory accuracy. The final equation can be written as follows:

$$\eta = \frac{(D + d)^2 w(4.6 \times 980)t}{\pi R^4} \tag{132}$$

where 4.6 is the lever factor of the Tackmeter.

In Equation 127, k is the intercept on the w axis and is obviously constant for different values of w. Then follows from the fact that f, R, and D have not varied. The situation is quite different for Equations 130 and 131. An increase in D will decrease k. An increase in R will increase k. Therefore, $w - k$ will not remain constant in these cases unless w is varied. Experimentally this would present almost unsurmountable difficulties. A practical solution can be found, however. It will be recalled that Bingham assumed the model of flow in a capillary tube to be the same for a material with a yield value as it is for a Newtonian. Consequently, he felt justified in substituting $F - f$ for F in the Poiseuille equation when he wrote his capillary-tube equation for plastics. For many purposes his equation has been found useful. If we are allowed to make the same mistake by assuming that there is no plug flow in the Tackmeter, then, the force causing flow $w - k$ can be introduced into Equation 132 without altering the instrumental constant. Hence, we can write, for plastics,

$$U = \frac{(D + d)^2(w - k)(4.6 \times 980)t}{\pi R^4} \tag{133}$$

It might be thought that Equation 133 could be checked against measurements made with the rotational viscometer. This is not so easy to do as appears, because Bingham bodies with a yield value sufficiently high to measure are as a rule thixotropic. Since there is no reason to believe that the Tackmeter and the viscometer will each reduce the Bingham body to the same thixotropic level, no basis for comparing measurements exists. The best course to take where Bingham bodies are involved is to use the rotational viscometer. This is especially true, if thixotropy is present.

Equation 132 can be written simply,

$$\eta = Kwt \tag{134}$$

where K is the instrumental constant. A table of Ks can be made, using various values of $D + d$ and of R. The simplicity of Equation 134, the speed of acquiring temperature, the ease of cleaning the instrument, and the smallness of the sample required make the Tackmeter one of the most convenient viscometers for many industrial purposes.

If a standard liquid of known viscosity is at hand, the viscosity of an unknown can be determined without the use of K. Let η_0, w_0, and t_0 pertain to the standard. Then it follows from Equation 134 that,

$$\eta = \eta_0 \frac{wt}{w_0 t_0} \tag{135}$$

In using Equation 135 it is advisable to choose a standard with a viscosity as nearly equal to that of the unknown as possible.

Definition of Tack

Tack, for Newtonian and Bingham bodies (like printing inks) has been defined as *pull resistance*. If we adopt this as our definition, it follows that tack is w or $w - k$. Let (T) symbolize tack. Then from Equations 128 and 129

Newtonians:
$$(T) = \frac{\eta}{Kt} \tag{136}$$

Bingham bodies:
$$(T) = \frac{\eta}{Kt} + k \tag{137}$$

where K is $K''K'''$. It can be seen that if η is constant then tack or pull resistance varies with the initial film thickness, the area of the finger tip, and the speed with which the finger is pulled up. Tack is not a material constant, but a quantity depending on the material, the instrumental dimensions, and the speed of operation. The tack of a single material, at a given temperature, can have an infinite number of values. Apparently, then, tack is not a valuable measurement. In order to make it valuable it must be put on a relative basis. Even then it will be valuable mainly to manufacturers and users of printing inks.

Relative Tack. Relative tack is the number of times a substance is tackier than the tack of a standard material. The standard should be a stable substance like a mineral oil. Its viscosity should be in the neighborhood of the unknown material. This sometimes necessitates a series of standards covering a wide range of viscosities. The advantages of relative tack should become evident in what follows. Let $(T)_{1/t}$ be the tack of a printing ink when the rate of plate separation is $1/t$. Then,

$$(T)_{1/t} = \frac{U}{Kt} + k \tag{138}$$

Also let the tack of the standard be

$$(T_0)_{1/t} = \frac{\eta_0}{Kt} \tag{139}$$

where the t in Equation 139 is the same as the t in Equation 138.

Dividing 138 by 139 gives relative tack,

$$\left(\frac{T}{T_0}\right)_{1/t} = \frac{U}{\eta_0} + \frac{Kkt}{\eta_0} \tag{140}$$

If the standard material should have a viscosity of 1 poise and the rate of the printing press is high enough to make t very small, then,

$$\text{Relative tack} = U \tag{141}$$

Equation 141 is invariably misquoted as follows,

$$\text{Tack} = U \tag{142}$$

which obviously is not true.

Relative tack is composed of a viscosity term and a yield-value term. At high speeds, relative tack approaches a value proportional to the plastic viscosity. The proportionality constant is the reciprocal of the viscosity of the standard. At very slow speeds the yield-value term can become the dominant factor, depending on how large t is in comparison with U.

DETERMINING RELATIVE TACK WITH THE VISCOMETER. Because no pulling force is used in the rotational viscometer, tack cannot be determined with such an instrument. The rotational viscometer pulls nothing apart; consequently, pull resistance is never measured. Viscosity is measured, however, and it has been shown that at high speeds relative tack tends to become proportional to viscosity. Therefore, as far as the inkman is concerned he need not measure relative tack but may use in its place "plastic viscosity." In making process inks the manufacturer must be sure that the first down ink has the highest viscosity; the second down, a lower viscosity; the third, still lower; and so on.

Other Parallel-Plate Viscometers

The Mooney Viscometer.[4] This instrument is used for the measurement of rubber. It can be classified either as a parallel-plate or as a rotational viscometer. In order to create a shearing action one of the parallel plates rotates. The other plate is stationary and is of pillbox formation. The rotating plate is in the center, that is, halfway between the top and bottom of the box.

The rubber (usually unvulcanized) is put into the box under a pressure of 400 to 800 lb per square inch. This insures its firm contact with the rotating plate, or rotor. The viscometer is maintained at a temperature of 100°C during operation. The thickness of the rotor plate is 0.218 inch, and it rotates at 2 rpm. The inside diameter of the box or stator is 2.0 inches, leaving a half-inch clearance on the side. The top and bottom clearances are 1 inch each. Since the rotor plate is quite thin (0.218 inch), the torque is produced mainly on the top and bottom of the plate. The torque is registered by means of a spring and deflection scale and calculated to viscosity.

The Williams Viscometer.[6] This is a true type of parallel-plate viscometer; the plates approach each other during the test. Like the Mooney viscometer, it is used for rubber. The test piece is cut in the form of a cube. The viscometer compresses it under a load of 5 kg for 3 minutes at 100°C. The results can be expressed by the empirical equation,

$$K = YX^n \tag{143}$$

where K is the material constant (firmness or stiffness), and Y is the thickness under the load X applied for time n. The instrument gives values for the viscosity of rubber of 1,150,000 poises.

The Bekk Viscometer.[1] This instrument is used in the measurement of printing inks. The parallel plates are not flat but hemispherical. Bekk uses both a compressing and a pulling action. The velocity is low enough so the action can be observed under a microscope. The compressing force Bekk calls "viscosity"; the pulling force, "tack." Since the ratio of these two factors is not unity, Bekk claims that tack and viscosity are not identical. Bekk also concludes from his investigations that films thicker than 10 microns neck down, but below that value the ink film splits by rupture (that is, by doing work against the force of cohesion).

In Bekk's apparatus no provision is made for changing the "finger tip" area; consequently, there is no possibility of developing an equation like 132. Bekk does not obtain any equations for tack or for relative tack such as those developed for the Tackmeter.

The Dienes and Klemm Viscometer.[2] This instrument is used for getting the absolute viscosity of high polymers in the range of 10^4 to 10^9 poises. The authors' claim that their viscometer offers promising possibilities for the empirical determination of weight average molecular weights of polyethylene resins and polyethylene resin–paraffine wax mixtures.

In this viscometer the plates approach each other, squeezing the material out between them. The authors develop: case I, where the viscous liquid completely fills the space between the plates; case II, where the plates are larger in radius than the test specimen. For the first case they deduce the Stefan [5] equation:

$$\frac{1}{h^2} = \frac{4wt}{3\pi\eta a^4} + C_1 \qquad (144)$$

where h is the distance between the plates at time t; a, the radius of the plate (and specimen), and C_1, the constant of integration. (Note the similarity of Equations 132 and 144.)

The authors point out that C_1 cannot be determined except by assuming that Stefan's equation holds down to $t = 0$, which is an assumption that is not true. They, therefore, calculate η from the slope of the $1/h^2$ versus t curve.

For their case II they deduce the following equation:

$$\frac{1}{h^4} = \frac{8\pi wt}{3\eta V^2} + C_2 \qquad (145)$$

where V is the volume of the test piece. Here viscosity is derived from the slope of the $1/h^4$ versus t curve.

Summary of Chapter 9

In this chapter various types of plate viscometers have been described with emphasis on the Tackmeter, because it constitutes part of the system presented in this book. The Tackmeter was developed for the purpose of analyzing the phenomenon that the manufacturers and users of printing inks call "tack." Tack or pull resistance is found to depend on both instrumental and material constants. By putting tack on a relative basis (that is, comparing it with a standard) the instrumental constants can be eliminated.

Relative tack is shown to be analogous to plastic viscosity *at high rates of shear*. Because printing inks are usually applied at high shearing rates, "plastic viscosity" can be employed by the inkman in place of relative tack. As a consequence of this simplification, tack (pull resistance) often is said to be analogous to plastic viscosity, which, naturally, is a misconception.

The rubber investigator has a different viewpoint on tack because his materials are elastic. Also there are those who are interested in materials like adhesive tapes. Both the nature and completeness of the adhesion of the material to the surface to which it must stick play a part that should be given careful thought. It is natural that the solution of the tack problem cannot be the same for the investigators in different fields of research.

Questions and Problems

1. (*a*) What instrumental variables are involved in carrying out an analysis of tack with the Tackmeter? (*b*) How is each one varied without changing any of the others?
2. Does the foregoing analysis lead to an empirical equation expressing viscosity?
3. Can the Bekk "viscometer" lead to an empirical equation expressing viscosity?
4. What is the probable significance of d? Why will the curve $1/t$ versus $(D + d)^2$ *not* pass through the origin, if d is made equal to zero?
5. (*a*) Given the following data, determine the tack at $1/t = 0.050$. (*b*) Find the relative tack, if $(T_0) = 1.0$ poise and t is very small.

$1/t$	w (grams)
0.100	25.0
0.067	20.0
0.047	17.0
0.033	15.0

$D = 0.01$ cm

$R = 0.788$ cm

CHAPTER

10

The Instrumental Constants for the Rotational Viscometer

Before the material constants can be calculated, it is necessary to determine the instrumental constants, K, S, and C.

The wire constant K is the torque per degree of arc through which the dial (Figure 30, u) has been rotated. As previously explained (Chapter 8), K is obtained from the known radius of the dial and the suspended weight (Figure 32). The radius of the dial is 5.0 cm. A weight of 100 g causes a rotation, for spring no. 3, of 80.3°. Then,

$$K = \frac{100 \times 980 \times 5.0}{80.3} = 6100 \tag{146}$$

In the case of helical springs where the twist is never allowed to exceed one revolution, K will be constant. In other words, if 50 g were used instead of 100, the twist would be 40.15°.

The instrumental constant S is determined from the dimensions of the cup and the bob. In the present case, $R_c = 1.5$ cm, $R_b = 1.3$ cm, and $h = 5.1$ cm. Then (see Equation 51),

$$S = \frac{\frac{1}{1.3^2} - \frac{1}{1.5^2}}{4 \times 5.1\pi} = 2.3 \times 10^{-3} \tag{147}$$

The instrumental constant C is determined from R_c, R_b, and S. In the present case it is (see Equation 52)

$$C = \frac{2.3 \times 10^{-3}}{\ln \frac{1.5}{1.3}} = 1.60 \times 10^{-2} \tag{148}$$

It should be noted that ln is the natural logarithm. Its relation to the common logarithm is, $\ln x = 2.303 \log x$.

Laboratory Measurements of a Thixotropic Bingham-Body

The method of operating the rotational viscometer has been described. The method of using the data for obtaining the material constants will now be explained. The data in Table 5 are those obtained from the viscometer during the running of an up- and downcurve. The dial reading on the transmission has (by means of a calibration curve) been converted to rpm. Notice that *two* loops have been obtained. The smaller loop has a top rpm of 100. When that point has been reached, the downcurve is run. The viscometer is then set for 100 rpm, and, as soon as the torque has fallen to the previous torque (requiring a few seconds to attain) at 100 rpm, the upcurve is continued where the old one left off. This new curve is continued (in this particular case) until a top speed of 215 rpm is obtained. At 215 rpm the second downcurve is started. The necessity for two loops is to make possible the determination of the coefficient of thixotropic breakdown M.

$$M = \frac{2(U_1 - U_2)}{\ln \dfrac{\omega_2^2}{\omega_1^2}} \tag{149}$$

where U_1 and ω_1 pertain to the smaller loop. It should be noted that $U_1 > U_2$, thus making M positive, as it should be. The calculations of U_1 and U_2 are made in the following.

The curves obtained from Table 5 and the rheological constants of the material are given in Figure 37.

The red printing ink, Table 5, is thixotropic. The two loops, then, will give two different yield values and two different plastic viscosities; but the two curves will both have the same coefficients of thixotropic breakdown, M and V.

In order to determine yield value, the intercept of the *downcurve* must be had. Since the downcurve is not straight at its lower end, the intercept is obtained by extrapolating the straight part of the downcurve to the torque axis. Why this procedure is not invalid as it is in the case of the capillary tube has been explained in Chapter 3. For the lower loop (Figure 37) the intercept is 21. Then (see Equation 53),

$$\begin{aligned} f_1 &= 21 \times 1.60 \times 10^{-2} \times 6100 \\ &= 2126 \text{ dynes per square centimeter} \end{aligned} \tag{150}$$

TABLE 5

RED PRINTING INK

Spring constant $K = 6100$ (dynes×centimeter)

$S = 2.3 \times 10^{-3}$ $C = 1.60 \times 10^{-2}$ $R_c = 1.5$ cm $R_b = 1.3$ cm $h = 5.1$ cm

rpm	Up-curve (T)	Down-curve (T)	rpm	Up-curve (T)	Down-curve (T)
10	39	29	10		25
16	47	39	16		32
23.5	58	47	30.5		47
30.5	68	55	44		62
37.5	76	62	58		73
44	83	72	72		87
52	91	78	86		97
58	98	86	100	131	110
66	104	93	112	137	121
72	111	101	126	148	130
74	116	107	140	158	141
86	121	115	153	168	151
92.5	128	120	172	176	168
100	131	130	192	193	183
			203	200	195
			215	207	204

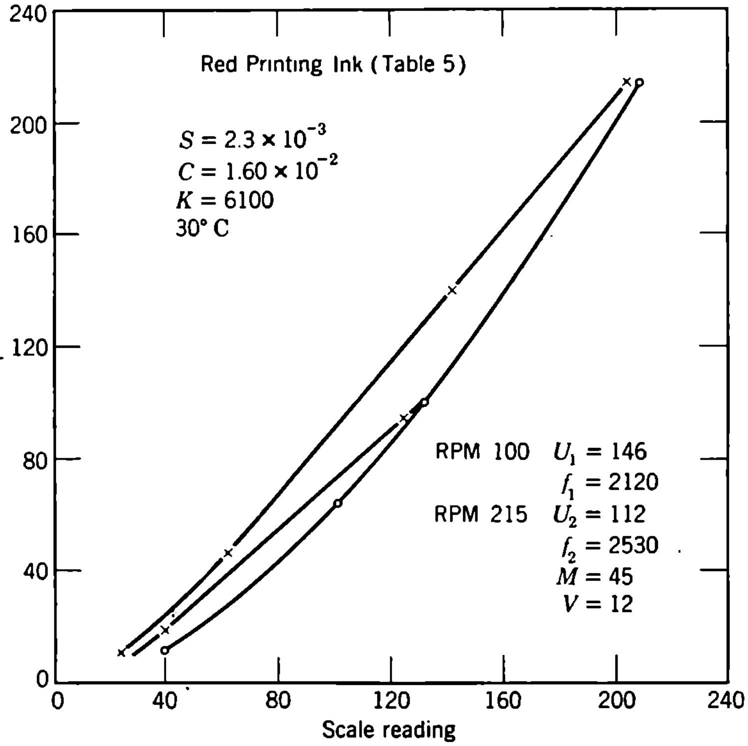


Fig. 37

The plastic viscosity U_1 for the lower loop is obtained from any convenient torque T on the straight part of the downcurve and its corresponding rpm. Let this be $T = 130$, and rpm $= 100$. Then (see Equation 54),

$$U_1 = \frac{(130 - 21)9.55 \times 2.3 \times 10^{-3} \times 6100}{100} = 146 \text{ poises} \qquad (151)$$

The factor 9.55 converts rpm to ω.

Similarly for the larger loop, the intercept is 25.

$$f_2 = 25 \times 1.60 \times 10^{-2} \times 6100$$

$$= 2531 \text{ dynes per square centimeter} \qquad (152)$$

and

$$U_2 = \frac{(192 - 25)9.55 \times 2.3 \times 10^{-3} \times 6100}{200} = 112 \text{ poises} \qquad (153)$$

The calculations of M and V are made from Equations 94 and 113.

$$M = \frac{2(146 - 112)}{\ln\left(\frac{215^2}{100^2}\right)}$$

$$= 45 \text{ dynes per square centimeter per } \frac{dv}{dr} \qquad (154)$$

and

$$V = \frac{2530 - 2120}{146 - 112}$$

$$= 12 \text{ dynes per square centimeter per poise} \qquad (155)$$

It should be noted in Equation 154 that only the top rpm can be used. That is, 215 instead of the 200 employed in determining the plastic viscosity. The time coefficient of thixotropic breakdown B is not calculated here, because that requires an entirely different set of experimental measurements. (See Equation 65.)

In Table 6 are given the laboratory measurements for a yellow printing ink. The data are plotted in Figure 38. It is seen that the intercept does not follow the customary procedure of increasing when the top rpm is raised. This is an exceptional case but is met with occasionally. It is likely to occur when the areas of the loops are small and the experimental error is approximately the same as the difference in yield values expected. It shows that, unless the

TABLE 6

Data for Light Chrome-Yellow Printing Ink

Spring constant $K = 16{,}900$

$S = 2.3 \times 10^{-3}$ $C = 1.60 \times 10^{-2}$ $R_c = 1.5$ cm $R_b = 1.3$ cm $h = 5.1$ cm

rpm	Up-curve (T)	Down-curve (T)	rpm	Up-curve (T)	Down-curve (T)
10	45	26	10		20
16	48	31	16		24
23.5	53	35	30.5		32
30.5	58	40	44		39
37.5	61	45	58		46
44	66	50	72		51
52	69	54	86		58
58	71	58	100	85	63
66	74	62	112	88	70
72	76	66	126	91	77
79	78	70	140	96	84
86	81	74	160	101	94
92.5	83	79	172	107	100
100	85	84	192	113	108
			203	116	114
			215	118	117

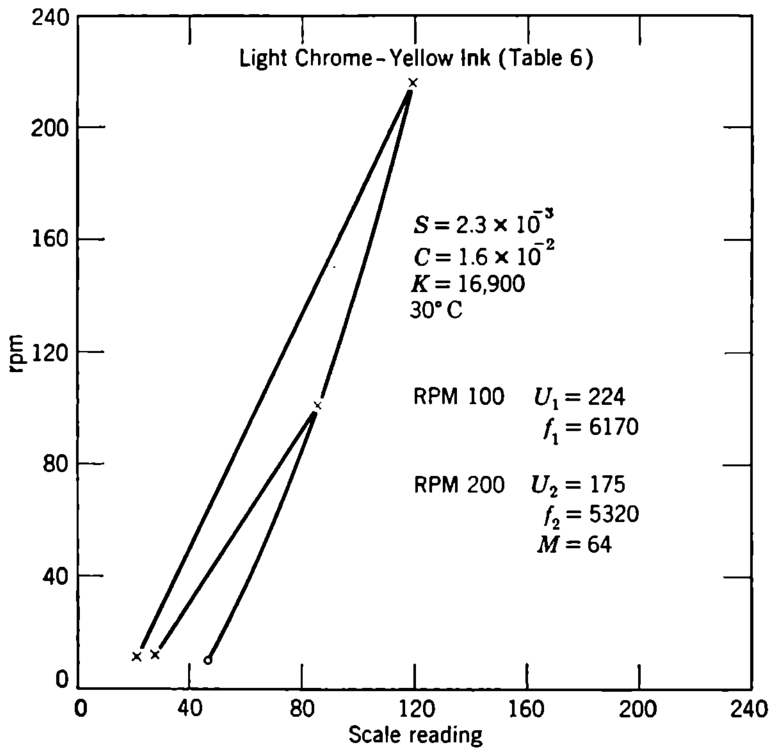


Fig. 38

thixotropic breakdown is substantial, V is of little importance in actual practice. The data for the curves are given in Table 6.

Data for two more printing inks are given in Tables 7 and 8 and plotted in Figures 39 and 40. These last inks are important examples of "crossing" inks and illustrate, as will be shown, how the tacks can reverse at high printing speeds.

TABLE 7

FIRST DOWN OIL YELLOW PRINTING INK

$K = 6100$. All Other Dimensions Same as in Table 6

rpm	Up-curve (T)	Down-curve (T)	rpm	Up-curve (T)	Down-curve (T)
10	68	37	10	63	32
16	99	56	16	87	47
23.5	113	72	23.5	107	61
30.5	135	90	30.5	125	75
37.5	140	107	37.5	135	86
44	154	122	44	150	98
52	171	138	52	165	110
58	184	155	58	177	120
66	195	170	66	181	130
72	210	185	72	191	139
79	223	200	79	205	150
86	234	215	86	212	160
92.5	244	235	92.5	225	168
100	254	250	100	228	179
			106	237	187
			112	244	199
			120	252	209
			126	260	215
			133	269	225
			140	272	235
			146	280	241
			153	285	250
			160	295	258
			166	300	268
			172	306	278
			178	307	289
			192	316	302
			203	329	327

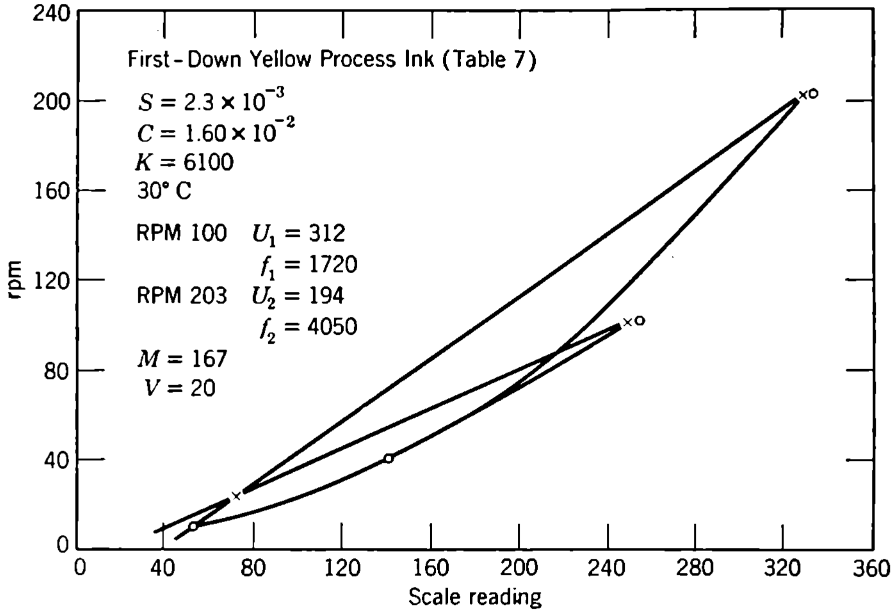

First-Down Yellow Process Ink (Table 7)
S = 2.3 × 10⁻³
C = 1.60 × 10⁻²
K = 6100
30° C
RPM 100 U₁ = 312
f₁ = 1720
RPM 203 U₂ = 194
f₂ = 4050
M = 167
V = 20
rpm
0
40
80
120
160
200
240
0
40
80
120
160
200
240
280
320
360
Scale reading

Fig. 39

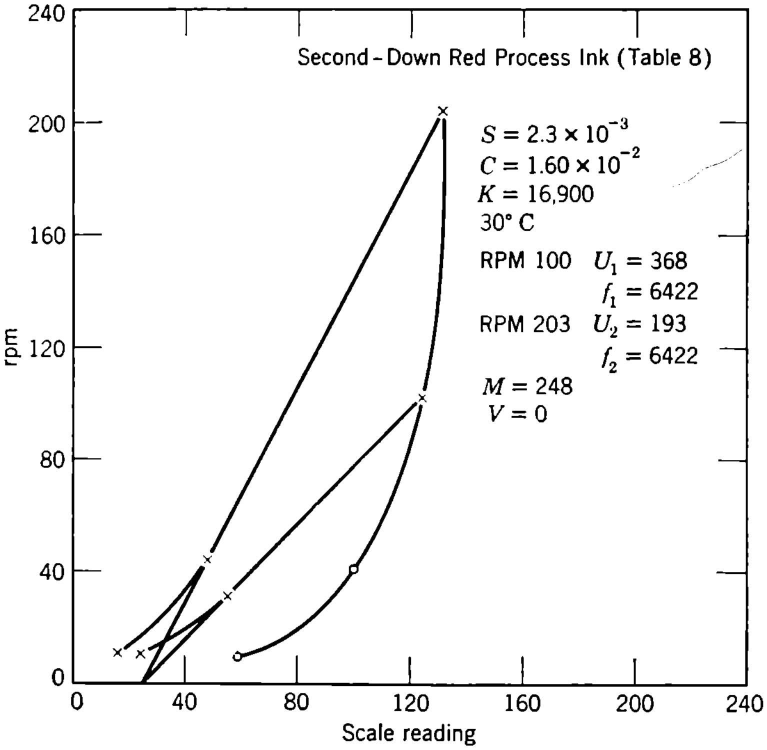

Second-Down Red Process Ink (Table 8)
S = 2.3 × 10⁻³
C = 1.60 × 10⁻²
K = 16,900
30° C
RPM 100 U₁ = 368
f₁ = 6422
RPM 203 U₂ = 193
f₂ = 6422
M = 248
V = 0
rpm
0
40
80
120
160
200
240
0
40
80
120
160
200
240
Scale reading

Fig. 40

TABLE 8

SECOND DOWN OIL RED PRINTING INK

$K = 16{,}900$. All Other Dimensions Same as in Table 7

rpm	Up-curve (T)	Down-curve (T)	rpm	Up-curve (T)	Down-curve (T)
10	59	23	10	52	14
16	75	35	16	67	23
23.5	85	43	23.5	75	29
30.5	92	53	30.5	83	35
37.5	96	61	37.5	89	40
44	102	69	44	92	45
52	106	75	52	98	49
58	111	81	58	102	54
66	114	89	66	105	57
72	118	95	72	109	61
79	119	101	79	115	64
86	120	108	86	117	68
92.5	123	115	92.5	119	71
100	125	122	100	122	75
			106	125	78
			112	127	81
			120	128	84
			126	129	88
			133	130	91
			140	130	95
			146.5	130	98
			153	130	102
			160	130	105
			166	131	109
			172	133	112
			178	132	116
			192	134	125
			203	133	132

Crossing Inks

This is a phenomenon pertinent to the subject of trapping of process inks. It has been mentioned that at *high* printing speeds the *relative* tack of printing inks should be in the order of their plastic viscosities. Because printing inks are thixotropic materials, there will be a decrease in their plastic viscosities as the rate of shear (speed of the press) is increased. What must be determined is this: Do all the inks used in making a print decrease with equal rapidity and so leave the order of trapping unchanged; or does one (or more) of the inks break down at a rate differing from the others, and so produce a combination of inks that do not trap properly at the high speed desired?

The answer to this important question can be found from the equation of thixotropic breakdown:[3]

$$e^{mU} = \frac{k}{\text{RPM}^2} \tag{156}$$

Then,

$$mU = \log k + \log \frac{1}{\text{RPM}^2} \tag{157}$$

From Equation 157 it follows that U plotted versus log $(1/\text{RPM}^2)$ gives a straight-line relation. In Figure 41 such a plot has been

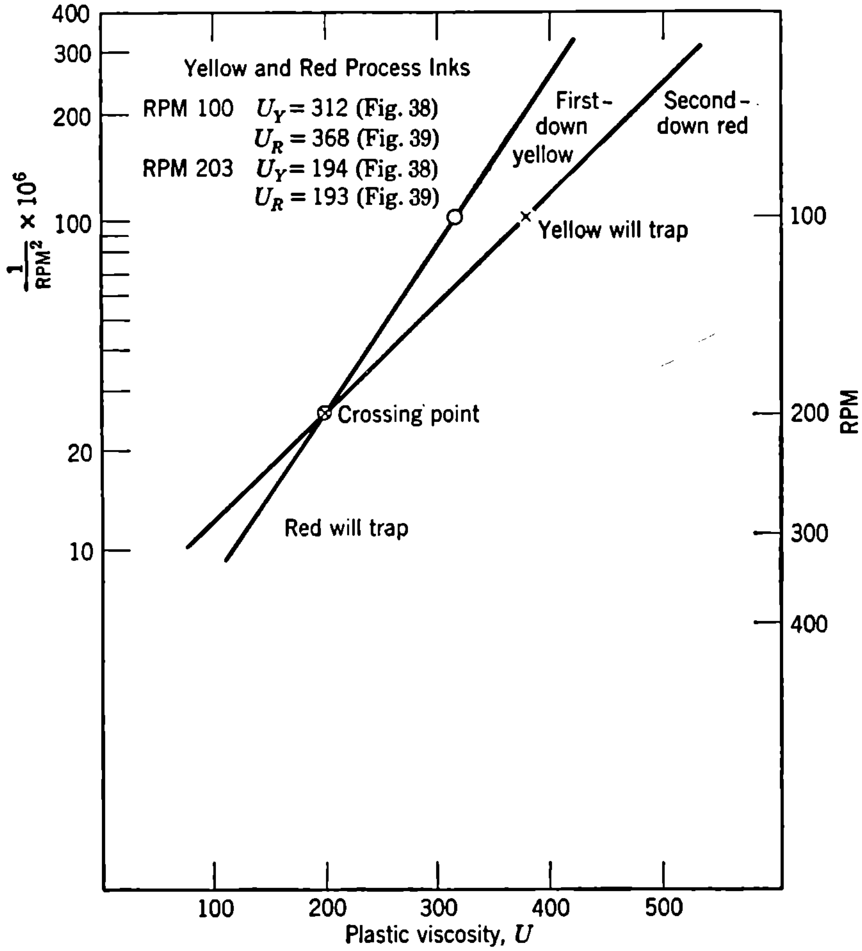


Fig. 41

made of a first-down yellow (in process printing) and a second-down red. The data are taken from the two printing inks shown in Figures 39 and 40. The curves plotted in Figure 41 are interpreted as follows: When the speed of the press is such that the rate of shear to which the ink is subjected corresponds to the rate of shear of the viscometer when operating at less than 200 rpm, then the yellow will trap the red. This is so because at such speed the plastic viscosity of the yellow, as shown in Figure 41, is higher than that of the red ink. At approximately 200 rpm, both inks have broken down to the same plastic viscosity. At higher speeds than 200 rpm, the yellow breaks down more than the red, and so the red will now trap the yellow. This is desirable information to have; for, if the printer is unaware that the order of trapping of his inks reverses at high speed, he is more than likely to find himself in trouble when trying to apply such inks to high-speed printing.

The Laboratory Measurement of a Pseudoplastic Material

This class is represented by such a wide variety of materials that it might well be the dominating class in any rheological laboratory. Detailed knowledge of pseudoplastics is practically a prerequisite for the laboratory rheologist.

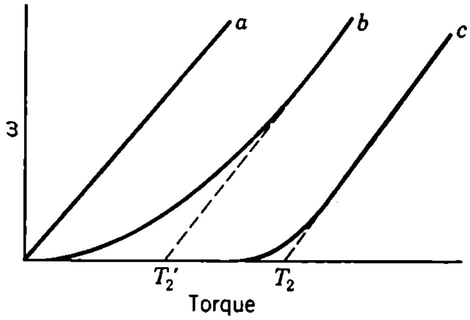


Fig. 42

Sometimes it is difficult to decide whether a material is a pseudoplastic or a Bingham body with a very small yield value. Then recourse to the microscope becomes necessary. Pseudoplastics are characterized by the type of consistency curve they give. In Figure 42 the curve *b* is that of a pseudoplastic. There is a modern tendency to look on the pseudoplastic as the general form of the consistency curve in which the Newtonian *a* and the Bingham body *c* are special limiting cases. See Reiner's work.[4] Then there is also a tendency to represent the consistency curve by the power equation,

$$\frac{dv}{dr} = A\sigma^{B} \tag{158}$$

When $B = 1$, the curve is obviously Newtonian. When $B > 1$, the curve appears to take a pseudoplastic form. When $B < 1$, the curve resembles the dilatant form, all of which is satisfying in a way; but whether it has anything to do with rheology or not is another matter. If Equation 158 had been derived from one of the original rheological concepts—either Newton's or Bingham's—then its use could be justified on the grounds that the variables are the rheological variables dv/dr and the shearing stress σ. Furthermore, it could be pointed out that the relationship between these variables is governed by two parameters (as shown in Equation 158) of known and stable constitution.

None of these conditions, however, is the case. Equation 158 is only a mathematical expression and quite unrelated to any rheological concept of flow. Furthermore, the dimensions of A, as previously pointed out, can be anything, depending on the magnitude of B. By suitable manipulation of A and B the curve can be made to fit, to a certain extent, experimental flow data. This coincidence is no proof that Equation 158 is a rheological equation and that it can be used as such with safety. The best that can be said for it is that, if the values of its parameters are known, then a curve can be plotted approximating in position and shape the consistency curve from which the parameters were originally obtained. Unfortunately the equation cannot indicate what its parameters represent or define. Therefore, the equation is of little value from a rheological viewpoint. As a laboratory check for plant-control work it might conceivably have some application especially if the investigator knows the true nature of the equation and accepts it only for what it is worth.

The types of materials that give pseudoplastic curves are those represented chiefly by the resins and the rubbers, both natural and synthetic. They are characterized by showing no evidence of yield value, are highly viscous and sticky, and are composed of long molecules. When they are subjected to a shearing stress and permitted to flow, there occurs an alignment of the long molecule parallel to the direction of flow. This produces a nonlinear flow curve convex to the stress axis, which from an experimental viewpoint results in a drop in the so-called "apparent viscosity."

Maxwell's Relaxation Time

When the long molecule has impressed on it a shearing stress, it will turn into a new position which is less random than it was previously. There will, therefore, in general be a tendency for this molecule to return to its more random state. This constitutes an increase in the potential energy of the system. When the imposed shearing stress is removed, the newly acquired energy will be converted to kinetic energy, returning the molecule to its original position. The actual time consumed in this operation should be infinitely great, because the magnitude of the returning force becomes smaller the nearer the molecule approaches its original position. However, the *rate of return* is a material constant and should receive a form of expression. Maxwell introduced the concept of "relaxation time." It is the time required to reduce the stress to F_0/e where F_0 is the original stress and e is the base of the natural logarithms. In this way an "infinite time" is avoided.

The concept of relaxation time is associated with elastic strain superimposed on viscous strain. The elastic strain s is proportional to the stress, the proportinality constant being $1/G$, the reciprocal of the modulus of elasticity G. The viscous strain is proportional to the stress, the proportionality constant being $1/\eta$, the reciprocal of the coefficient of viscosity. By adding these two strains and differentiating with respect to t, the Maxwell relaxation equation is obtained:

$$\frac{ds}{dt} = \frac{1}{G}\frac{dF}{dt} + \frac{F}{\eta} \qquad (159)$$

From Equation 159 it follows that

$$F = F_0 e^{-t/\tau} \qquad (160)$$

where τ is the relaxation time:

$$\tau = \frac{\eta}{G} \qquad (161)$$

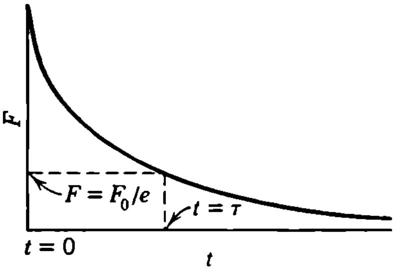


Fig. 43

From Equation 160, it can be readily seen that, when $F = F_0/e$, t becomes equal to τ. This is indicated in Figure 43. The relaxation time, then, is the time required to reduce the stress to the value F_0/e.

If the relaxation time is sufficiently short, the up- and down-curve of a material like a heavy-bodied pseudoplastic oil will coincide, and no loop will be formed. Weltmann[7] has shown, however, that, in most cases of this type, if the rates of shear are carried high enough, hysteresis loops are invariably formed. This formation could arise from structural breakdown of some unknown nature or from a relaxation time relatively large compared to the time required for making the downcurve.

A great deal of mathematical research has been done in attempts to develop rheological and instrumental equations of pseudoplastic flow. So far no general application of any such equation has been much in evidence. Evidently the best plan to follow is to plot the consistency curve of a pseudoplastic material and make no attempt to convert it to figures like yield value and viscosity. As already stated, the viscosity coefficient under low rates of shear can be recorded, for in that region of the curve (near the origin) the material has practically Newtonian flow. The consistency curves can be used for comparisons as follows (refer to Figure 44): Material b has a heavier consistency than a as far as it has been measured. Material c has a heavier consistency than b below ω_1. Above this shearing rate, the reverse condition holds true.

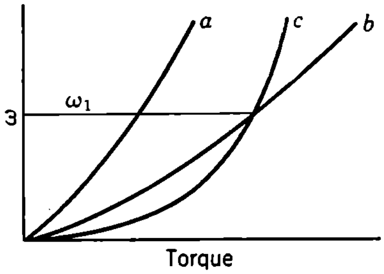


Fig. 44

Viscous-Elastic Flow and Creep

Maxwell recognized, about a hundred years ago, that there could be a *type of flow* composed of the sum of two strains. One arose from viscous deformation and the other from elastic strain. These can be represented mathematically as rates in the following manner:

$$\frac{ds}{dt} = \frac{F}{\eta} \quad \text{(viscous)} \tag{162}$$

and

$$\frac{ds}{dt} = \frac{1}{G}\frac{dF}{dt} \quad \text{(elastic)} \tag{163}$$

Adding 162 and 163 gives Equation 159. This is diagrammatically represented by the conventional spring and dashpot. However, as pointed out by Tobolsky and Andrews,[6] this model fails to explain the phenomenon of creeplike retraction after the load has been removed. Briefly, creep is the relatively slow flow (elongation) displayed by certain materials after a stress is applied and the elastic elongation has taken place. The Maxwell model can produce no slow retraction after the spring has returned elastically to its normal length. This reaction takes place practically instantly. On the other hand, creep can be explained by the Voigt model where the spring and dashpot are placed in parallel instead of in series (Figure 45a). However, Tobolsky and Andrews suggest the Wiechert model (Figure 45b) as more satisfactory. This is a series of Maxwell models in parallel, each unit possessing a different relaxation time. The objection to the Voigt model is that it does not account for relaxation under constant elongation.

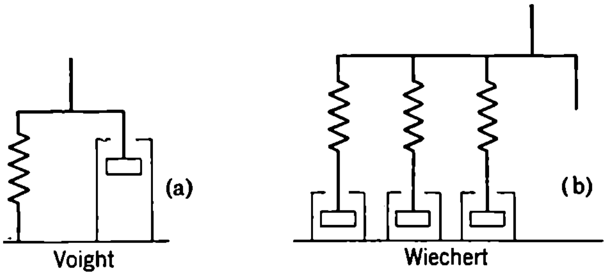


Fig. 45

No doubt, every material subject to viscometric measurement undergoes a certain initial elastic distortion. From a practical viewpoint, this usually takes place instantly, and then equilibrium is established. After this, a steady rate of viscous or plastic flow can be maintained (if the absence of thixotropic breakdown is assumed), and it is this steady rate of flow (no longer affected by elastic elongation) which the rheologist measures and uses when plotting flow curves as determined by the rotational viscometer. From these curves, in which elastic elongation is not manifest, the rheological constants of the material are calculated.

Laboratory Data for a Pseudoplastic Curve

In Figure 46 are shown the viscometric data plotted for a typical pseudoplastic material. It will be noticed that (1) the curve is nowhere linear, and (2) it evidently starts from the origin. Also that the up- and downcurves practically coincide. The actual measurements are recorded in Table 9.

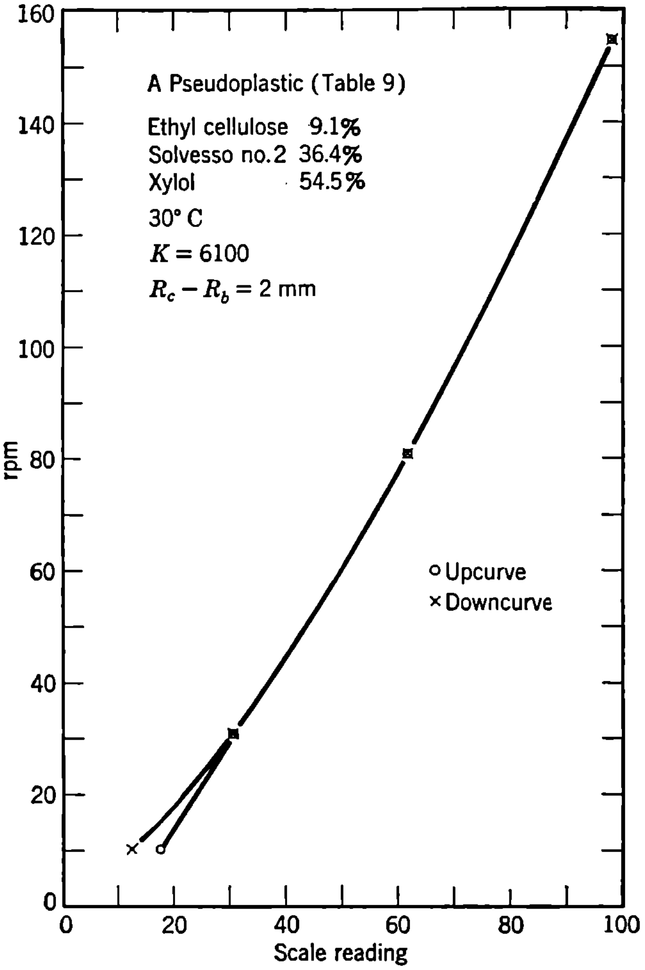


Fig. 46

Newtonians That Show Plastic Behavior at High Rates of Shear

It is generally assumed that oils (mineral and vegetable oils of the types encountered in the paint and printing-ink industries) are Newtonian. Weltmann[7] has shown that, when such oils are submitted to sufficiently high rates of shear, they not only cease to give linear curves but also form hysteresis loops somewhat similar to those of thixotropic Bingham bodies. In addition, their down-

TABLE 9

Data for Pseudoplastic Curve (Figure 46), Ethyl Cellulose Solution

	Spring No. 3			$K = 6100$	
rpm	Up-curve	Down-curve	rpm	Up-curve	Down-curve
10	17	11	86	63	64
16	22	18	93	68	68
23	25	25	100	70	73
31	30	30	112	79	80
38	35	35	126	85	85
44	39	39	140	92	92
52	44	45	153	98	98
58	49	49	172	107	108
66	53	53	192	114	113
72	55	55	200	119	
79	60	60			

curves when extrapolated to the torque axis give intercepts depending on the top rpm employed. This is exactly in accordance with plastic materials. (See Figure 47.)

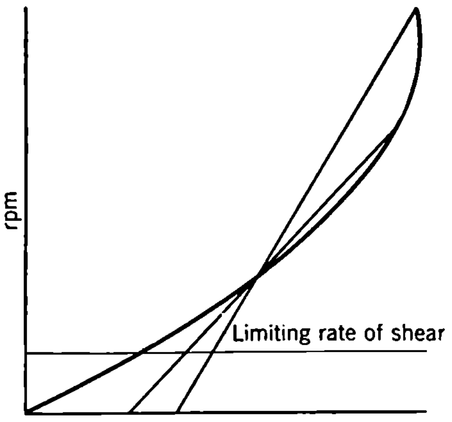


Fig. 47. The Type of Thixotropic Loop Made from Oils at High Rates of Shear

The point where the curve ceases to be linear, Weltmann calls the "limiting rate of shear." She has shown that the limiting rate of shear times the viscosity taken at the linear end of the upcurve (near the origin) always gives a value of approximately 7000 dynes per square centimeter, regardless of the nature of the oil.

The question has been raised at times as to the reality of the hysteresis loop of oils on the ground that, at high rates of shear, heat might be produced in sufficient quantity to cause the effect itself. However, Weltmann[7,8] has thoroughly explored this possibility and has found that the generation of heat is insufficient to explain the entire bending of the curve from its normal linear position. In this connection the work of Bondi[1] and also of Deutsch[2] is interesting.

Bondi points out that under high shearing stress "low" values of the coefficient of viscosity are often produced. He states that a large number of such cases can be attributed entirely to heat effects arising from a rapidly moving liquid but also notes that in a larger number of cases "it has not been possible to explain the observed viscosity decreases due to heat effects alone." Bondi develops a theory of flow orientation based on the change in entropy accompanying molecular orientation and on the Eyring theory of viscous flow. He is able to predict the temperature changes arising during adiabatic orientation. In conclusion he states: "At very high velocity gradients the temperature-gradient corrections have been found insufficient to explain the observed decreases in apparent viscosity."

Deutsch in an equally interesting paper has shown, from theoretical considerations, that flow orientation (alignment) should take place when the shearing stress reaches 8700 dynes per square centimeter. This is in good agreement with Weltmann's limiting shearing stress value, 7000.

It can be seen from what has preceded that there is well-established evidence indicating that Newtonian flow is perhaps entirely confined to relatively low rates of shear and that at high rates of shear all so-called Newtonians cease to follow a linear law. Though it is not necessary for the laboratory rheologist to master the mathematics of either of these papers, it is desirable that he becomes acquainted with their contents so that he understands the limiting conditions of Newtonian flow.

Dilatant Materials

The phenomenon of dilatancy, first recognized by Osborn Reynolds,[5] is encountered frequently by investigators who find it necessary to measure the consistencies of pigment suspensions. The best examples are found in enamels where the pigment is completely deflocculated and has had ample time to settle out. The pigment will be found at the bottom of the container forming a hard tough layer that is difficult to stir back into the supernatant vehicle. There are many other examples of this phenomenon, mainly clays and silica suspensions in water.

The consistency curve of a dilatant substance always bends toward the force axis. Contrary to common belief, it is possible to have suspensions that display both thixotropy and dilatancy. (See Table 10 and Figure 48.)

There is no satisfactory way of recording the rheological factors of a dilatant material. Curves can always be plotted, however, and the curves of different materials compared, demonstrating how the materials themselves differ in flow properties. That is the best that can be done at present.

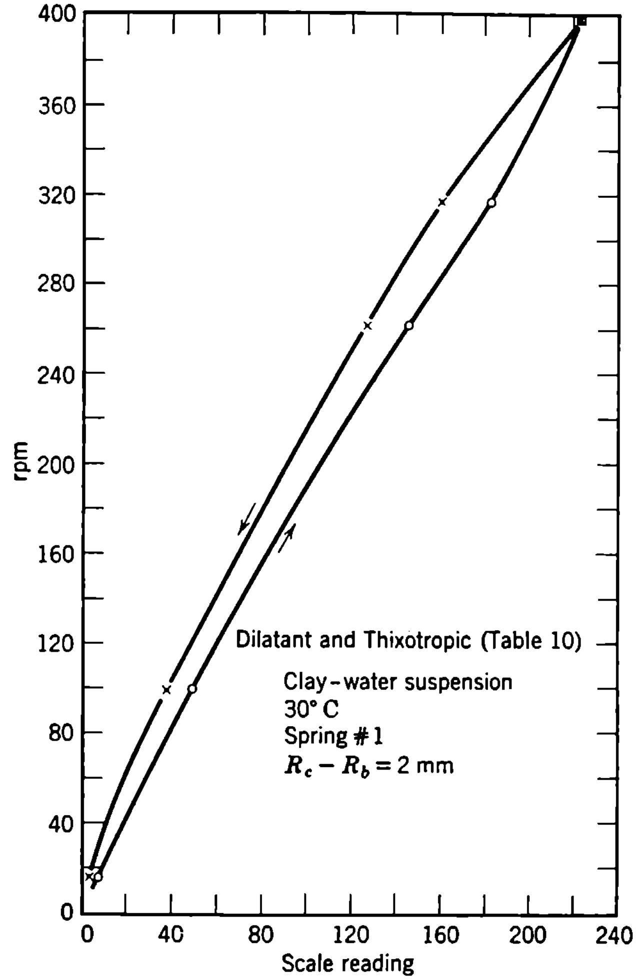


Fig. 48

A Thixotropic Emulsion

An emulsion has liquid droplets instead of solid particles in its dispersed phase. Liquid particles form spheres, often having a

TABLE 10

Data for Dilatant Material Shown in Figure 48

Spring No. 1 $K = 780$

rpm	Up-curve	Down-curve	rpm	Up-curve	Down-curve
16	7	4	172	90	74
31	13	9	203	109	91
44	20	14	233	129	114
58	28	20	262	145	136
72	35	27	290	161	145
86	41	32	317	181	160
100	49	38	342	194	179
112	55	43	369	209	194
126	64	52	387	215	205
140	70	56	400	218	

tendency to flocculate. They can accomplish such an operation without coalescing, thus retaining a definite particle size. The flocculating tendency produces yield value and, in the particular case (Figure 49), thixotropy and plasticity also. It should be

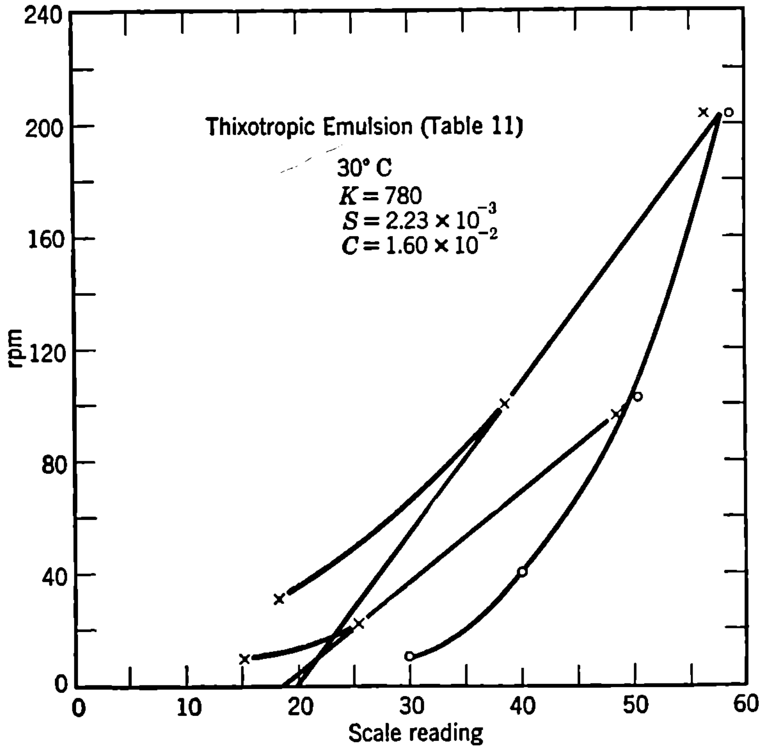


Fig. 49

noted that two downcurves have been run, one with a top rpm of 100 and the other with a top rpm of 200. The two downcurves cross each in a manner typical of thixotropic Bingham bodies. The laboratory data for the curves are given in Table 11.

TABLE 11

DATA FOR EMULSION SHOWN IN FIGURE 49

Spring No. 1 $K = 780$ $R_c - R_b = 2$ mm Temperature, 30.1°C

rpm	Deflection Upcurve	Deflection Downcurve, rpm = 100	rpm	Deflection Upcurve	Deflection Downcurve, rpm = 203
10	30	16	31		17
16	36	21	44		23
24	39	25	58		28
31	39	27	72		32
38	40	30	86		35
44	41	33	100		39
52	42	35	112	50	41
58	44	39	126	50	44
66	45	39	140	53	46
72	45	41	153	53	49
79	47	42	172	56	50
86	48	45	192	58	54
93	48	47	203	59	57
100	49				

Other Industrial Products

There are many products other than pigment suspensions that are well suited for measurement and plant control with the type of rotational viscometer described in this book. A small but representative list is included in this section. It is not intended to be comprehensive but simply to indicate to the laboratory investigator the nature of the materials that can be rheologically analyzed. Curves for these materials are given in Figures 50, 51, and 52. It will be noticed that the substances, chosen at random, all happen to be thixotropic. The laboratory data are not included, although the yield values and plastic viscosities are calculated.

Some Common Products. GELATINE. This material can be measured in a rotational viscometer, provided the material is not so stiff that it crumbles when stirred. As long as it remains of a consistency that allows it to be poured, measurements can be made. It should be noted that this material, like the others shown here, is thixotropic.

Wyoming Bentonite. This is a well-known thixotropic substance. Its curve illustrates this fact clearly. Unfortunately no information was available in regard to the wire constant and so the U and f could not be calculated.

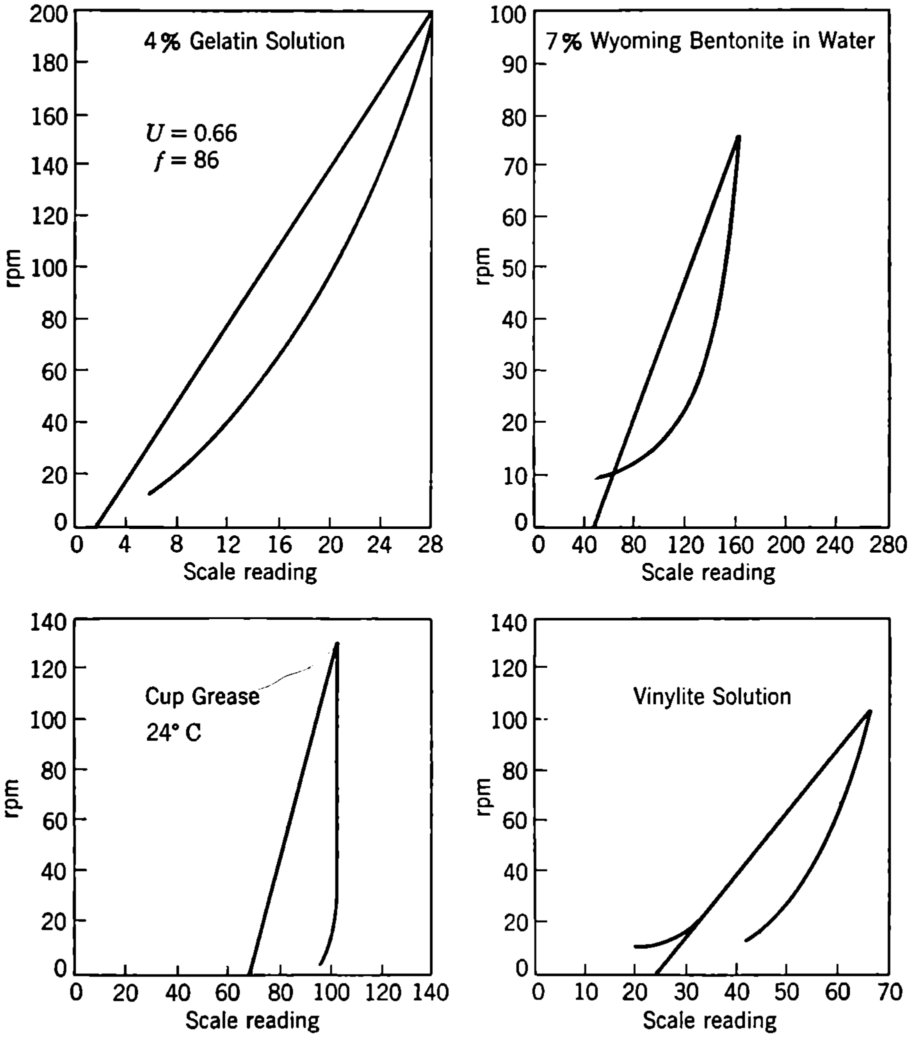


Fig. 50

Cup Grease. These materials are difficult to measure, regardless of the type of viscometer used. They have little or no tendency to cling or adhere to the walls of the viscometer; consequently, their tendency is to move as a solid plug instead of undergoing laminar flow. When this happens, their measurements mean nothing in terms of plastic viscosity and yield value.

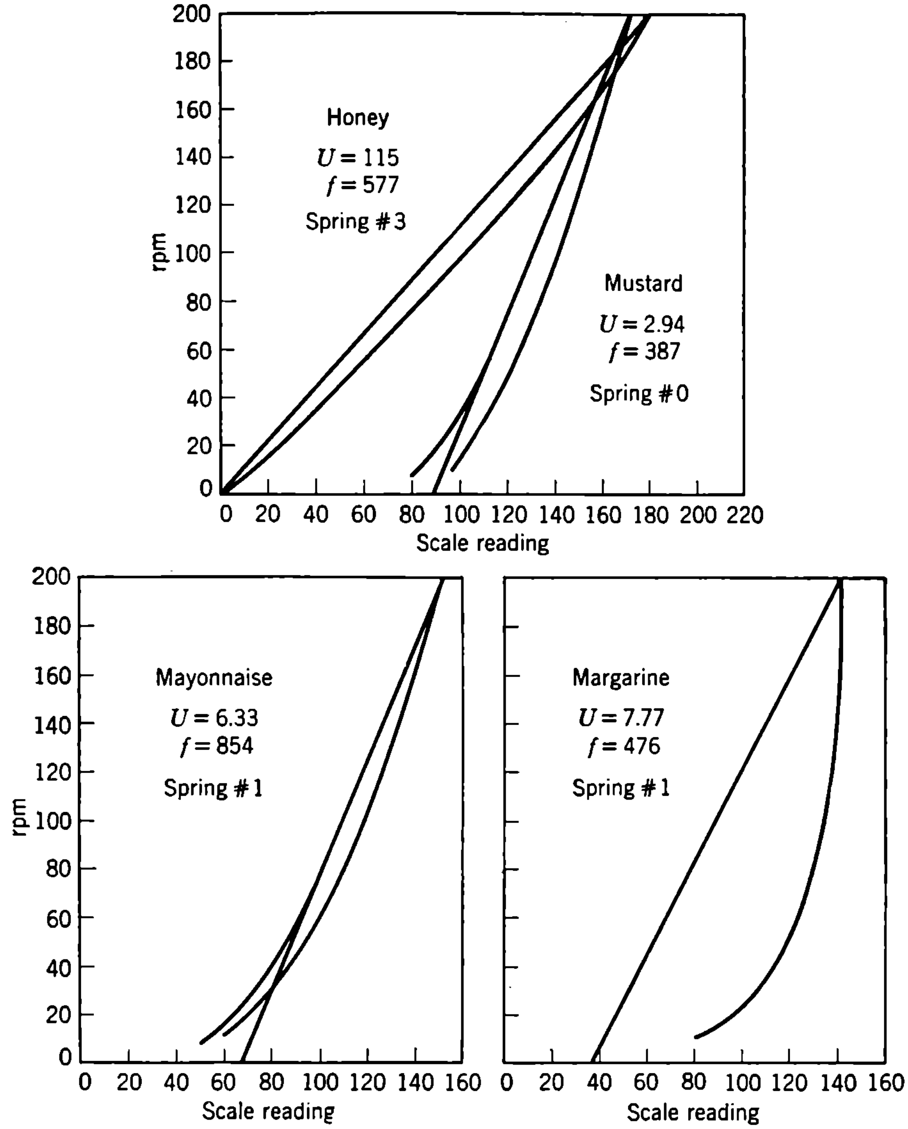


Fig. 51

Vinylite Solution. This is an unusual case. The curve is decidedly that of a thixotropic plastic rather than of a pseudoplastic, as would normally be expected.

In Figures 51 and 52 are shown the consistency curves for more familiar materials: honey, mustard, mayonnaise, margarine, shaving cream, ketchup, and Burma-Shave. This collection of products has been included in order to give the investigator some idea of the

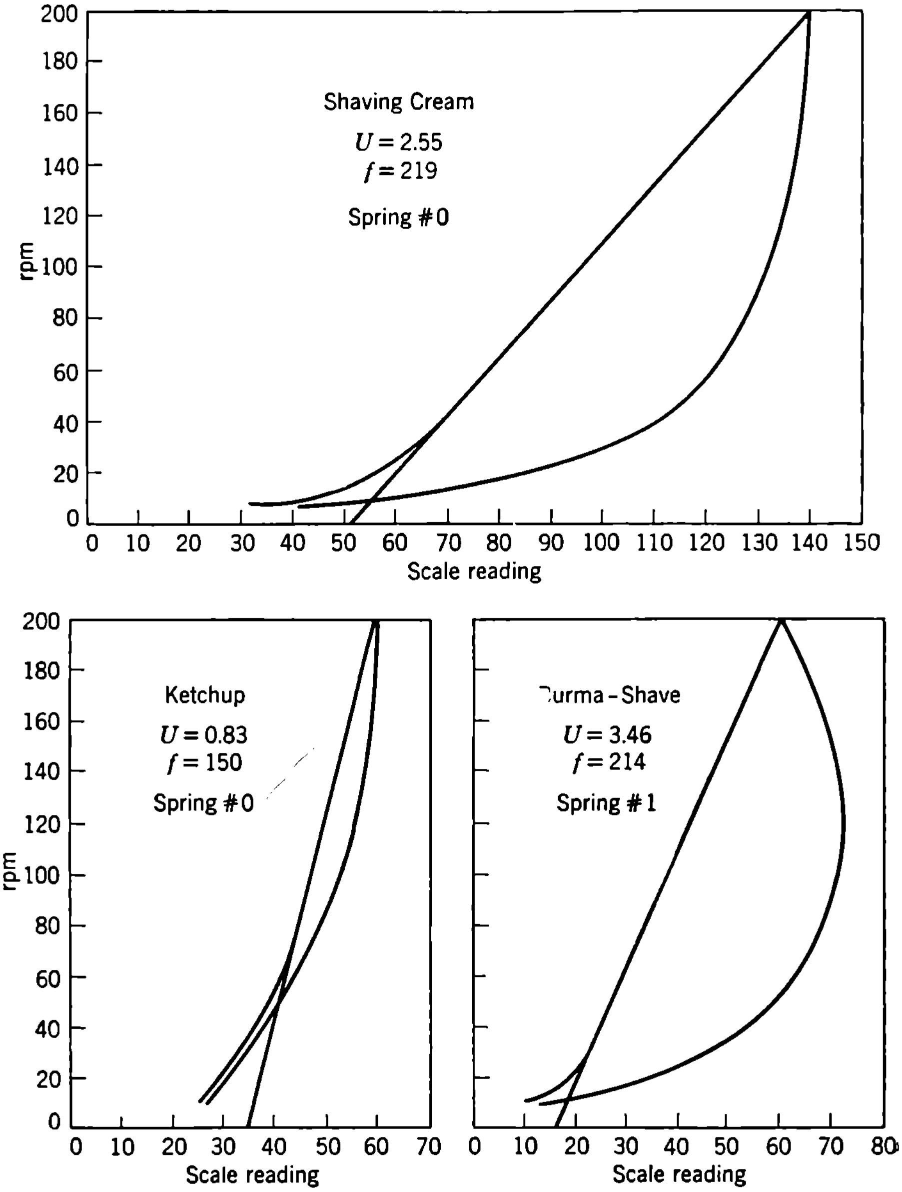


Fig. 52

types of materials that are subject to rheological analysis. The author is indebted to Dr. E. K. Fischer and Agnes D. Dyer for the curves of the last seven examples.

CHAPTER

11

Rheological Control of Plant Production

When a chemical industry adds a chemist to its technical staff, it usually selects someone with at least a college training in basic chemistry. At first the chemist finds that in making a chemical analysis he cannot compete in either time or accuracy with his comparatively untrained laboratory "assistant." The assistant has made his limited number of analyses so often that the operation practically has become automatic, and, as a consequence, he has developed rapidity and a high degree of accuracy, or at least of precision. However, on account of his broader training and knowledge acquired in college the new chemist should in time surpass his assistant. Practically all colleges prepare their students of chemistry for just such an eventuality.

Unfortunately, there is at present nothing similar to this in rheological training. The number of colleges that teach rheology is negligible. The industry that desires the services of a rheologist is compelled to hire a chemist. The chances are probably 100 to 1 that this chemist has never heard of the term "rheology." He is taken into the laboratory and shown the type of products to be measured. It is then explained to him that at present the company is practically dependent on the "say-so" of a single man, their foreman, in all matters pertaining to the plant control of consistency or "body" of their products. It is true that one of their men is experimenting with an inclined plane where the time taken by a material to flow down the plane is measured; but every once in a while something goes wrong, and results are obtained that "don't make sense." The company cannot trust the method until it is better understood.

Now our foreman's method is quite simple. He either feels the material between his forefinger and thumb or stirs the product with a spatula. Since he has been doing this probably for the last 40 years his judgment has become practically perfect. He rarely makes a mistake. But here is the rub. His method is subjective rather than objective. No way is known for recording in the laboratory files a subjective measurement. If he is asked to explain his method—to tell what he looks for—he is likely to resent the question as an intrusion into his personal affairs. Like all of us, he is aware of the fact that his job is most secure if he is unable to transfer his special knowledge and technique to anyone else. Or, perhaps, he simply lacks the ability to express himself in words. Hence, when he eventually leaves his company, he will take with him a vast amount of knowledge of no further use to himself but of inestimable value to his company. But his company alone is not the only sufferer. Industry as a whole has been a loser, too. Obviously, such a condition should not exist. Its remedy now is to be placed (by our hypothetical company) in the hands of the chemist—an untrained rheologist.

The Chemist as a Rheologist

As a rule, chemists get no training in rheology prior to their connection with industry. This fact more than any other is probably responsible for industry's hesitancy in adopting rheological controls in their laboratories and plants. Each chemist who becomes a laboratory rheologist, is, in a way, a pioneer. Being untrained, he is naturally unaware of the vast amount of rheological work that has preceded him. It will take him a number of years to discover most of that work. In the meantime he must "keep things going" in his own laboratory. A hasty survey of the more readily available literature will give him some idea how to start. In the course of time he will have devised an apparatus based, perhaps, on a multiple-point system that will have some scientific merit. His next step will be to "sell" his apparatus and method to his company. The usual expression is to "get it from the laboratory into the plant." If he is young, he will be surprised at the reaction. Instead of being welcomed with open arms, he will be met with opposition on all sides. In a way, this is natural. The men in the plant have been making their company's products in a satisfactory manner for years. Why change now in favor of a viscometer, especially when the viscometer requires a lot of troublesome brain work to operate it? The men themselves have spent years acquiring their special knowledge of product control.

Why throw that knowledge away and hand their job over to someone else? Their argument makes sense. They will do anything that they consider fair to slow down the transition of rheology from laboratory to plant.

The fairest argument they can employ is *that it takes too long to obtain a measurement with a viscometer.* Reports are then written by the plant superintendent, and management is informed of the facts. When the chemist finally turns to management for help or at least for a word of encouragement, he finds management ready for him. The verdict is that no doubt the chemist's method is highly "accurate," but it takes too long to be used for plant-control work. The plant foreman can make a finger test in 30 seconds; the chemist's method takes about 30 minutes for the material to come to temperature and, then, perhaps another 30 minutes to carry out the measurement. Management's parting advice is *make the method shorter.*

No doubt the last sentence will be ringing in the last rheologist's ears when the last atomic bomb makes short work of everything. The chemist now can follow either one or two procedures. (1) He can omit accurate temperature control by operating in a temperature-controlled room, and, against his better judgment, he can revert to some one-point method. In this case the defense will be the time-honored one: though the method is not "highly accurate," it is "accurate enough for all practical purposes." Or (2) he can induce management to employ the viscometer in measuring only its best and most expensive products. These materials are usually limited in number, and so one viscometer and one operator can handle the work. Lately there has been a noticeable tendency to follow such a procedure. In the opinion of the author the final solution of the problem will be the same as that taken by management in applying chemistry for plant-control work—that is, hire enough chemists and buy enough apparatus to take care of the job in a satisfactory manner.

Scientific Methods versus Short-Cut Plant Tests

When management requests that the method be made shorter and holds up as a shining example the foreman's finger test, management has already forgotten what it has asked its chemist to do, that is, replace the finger test by an objective measurement that can be recorded in a laboratory notebook. The entire matter involves a principle that every business and professional man recognizes—that you cannot get something for nothing and get it honestly. The foreman's test requires very little time and work and, consequently, gives very little in return—simply his personal opinion of the consistency of the material. By comparison, the viscometry method requires more time to carry out; but the returns are proportionately greater. Here one gets the rheological type of material, the plastic viscosity, the yield value, the three coefficients of thixotropic breakdown, the temperature, and a permanent notebook record of all of them.

Obviously, one has to pay for such information; and the price is the additional time consumed in making the measurement. By standardizing the procedure, getting the materials up to temperature beforehand, the entire process for obtaining all the required factors takes (with the rotational viscometer) about 30 minutes or even less. The actual instrumental work can be carried out in 10 minutes, the remaining time is that needed for plotting the curve and calculating the results. This time is short when compared with the time required for making certain chemical analyses for control purposes.

Turning now from the general to the specific, the industries that manufacture suspensions such as rubber, paint, and printing inks are probably amongst those that are most interested in the rheological control of their products. There probably has been no time in the history of these industries when plant control of consistency in some form or other has not been applied. Consistency measurements usually place a product in one of two categories. The material is either "long" or "short." Each category can be subdivided into viscous and comparatively "nonviscous" materials. The analytical approach progressed thus far at an early date and then made little or no progress for many years. There is no record that anyone examined long and short materials with a microscope to ascertain if any structural reasons existed that might explain the different properties of the materials.

Bingham's Concept of Yield Value

Before the microscope was employed, however, Bingham had obtained consistency curves for clay suspensions in water and as a result had introduced into the Newtonian law of flow the concept of yield value. Bingham, collaborating with the writer,[1] carried out similar work with pigment in oil suspensions and obtained the same type of consistency curves as those produced with clay. Extensive use of the microscope was then made, and it was found that yield value in materials like paints is dependent on pigment flocculation. This concept became one of the recognized factors in consistency control. Its operation is carried out by the use of flocculating or deflocculating agents.

All of the foregoing ideas were prevalent prior to 1920. However, satisfactory methods of measurement of plastic materials, like pigment suspensions, had not been developed that were generally acceptable. This does not imply that methods for estimating consistency of paints, printing inks, and such were not employed. The capillary viscometer must have been used for simple liquids, oils, and varnishes at least as far back as the days of Poiseuille. Paint and printing ink industries, however, existed long before then, and some form of consistency control was very likely practiced. It is perhaps possible to make a fair guess as to what was done without consulting the literature. It would take a man of considerable will power—that is, if he were a "dyed in the wool" paint or inkman—to resist sticking his finger into a paint (or ink) or to resist stirring it with a spatula, if he were asked for an opinion about its consistency. Those are the methods most frequently used today; and there is little doubt that such methods have always been employed.

It is impossible to say just when industry became interested in the possibility of applying more scientific methods for the measurement of consistency. Many industries are reticent about publishing the results of their own research because of the possibility that their competitors might benefit by it. Consequently, the literature does not always give the most accurate information as to when a certain method was first employed. From a purely American angle, the turning point probably occurred shortly after the pioneer work of Bingham became understood and recognized by industry. This was about 1918. The paint companies were the first to experiment with the possibility of controlling consistency by measurements with capillary-tube viscometers. The rubber companies were just as active, if not more so, in applying scientific methods of measurements; but they could not conveniently use capillary tubes and so devised other means, such as measuring the rate of compressibility of a sample at a known temperature.

At first it seemed that the task of measuring plastics was going to be a relatively simple one. The apparatus employed was to be a Bingham "plastometer," and the equation for calculating results, the Bingham formula (where the capillary constant could be obtained from a liquid of known viscosity or, as Bingham preferred, by direct measurement of the radius and length of the capillary). Disillusionment soon followed. The consistency curve for pigment suspensions was never linear (except with very low pigment concentrations) while Bingham's equation expressed only a straight-line relationship. Bingham attributed this lack of agreement to the possibility that seepage and slippage occurred at low (but not at high) rates of flow. This explanation was never accepted. Later it was shown by microscopical examination that slippage occurred throughout the *entire* consistency curve.[3] Buckingham (and, later independently, Reiner) assuming this to be a fact, and, in addition, assuming that the yield value remains constant, derived his well-known equation for the capillary flow of plastics. Unfortunately, this equation did not fit the facts any more closely than Bingham's; and, besides, the equation was practically impossible to solve. This left the industrial rheologist not much better off than he was prior to 1918.

Plant Control without the Use of Yield Value

In the meantime some form of plant control was imperative. In the ink industry the tap-out or finger test was about all the laboratory man had to depend on. As stated before, this test could not be recorded. Consequently, searching for other methods continued. Such means as observing the time of "strike through" or penetration of inks on news stock, and the bubble-tube method—timing the rise of a bubble in a tube of the material—were freely employed. About 1925 the rotational viscometer was used by L. Englehart[2] in the printing ink industry. The commercial rotational viscometers at that time were built for one-point methods, and, consequently, the results were not satisfactory when the instrument was employed for plastics, such as printing inks and paints. However, the commercial instruments were found useful when applied to Newtonians like oils, lacquers, and varnishes.

The work of Bingham was still practically unknown in most industries in the early 1920's, and, naturally, no attempt was made to alter the rotational viscometer so that consistency curves could be produced. Besides, prior to 1927 the Reiner and Riwlin equation of plastic flow in rotational viscometers had not been developed; hence, no way existed of using the consistency curve from such a viscometer even if the instrument had been correctly altered.

The Gardner-Holt Mobilometer

In 1932 the Gardner-Holt Mobilometer was recommended to the American Newspaper Publishers Association (ANPA) for consistency measurements. The instrument is made of a wide metal tube for holding the material. It is closed at the bottom. A weighted plunger is allowed to sink through the material. The time required for the plunger to travel a given distance is taken as a measure of the consistency. This is a one-point method, but it can easily be converted into a multipoint method by using a series of weights on the plunger and by plotting these weights against the *reciprocal* of the time. The instrumental constant can be obtained by calibration with a Newtonian of known viscosity. Whether any members of the ANPA ever used the mobilometer in that way is not generally known.

The Brookfield Synchrolectric Viscosimeter

Since the early 1940's an instrument known as the Brookfield Synchrolectric Viscosimeter has been used by some of the larger ink companies in America. Being essentially employed as a one-point method, this instrument is applicable to Newtonians like thin news inks and varnishes. It does, however, have four speeds and can produce 28 "ranges," which are probably shearing rates. In the manufacturer's report the principle of the viscometer is explained as follows:

> The principle upon which this instrument operates is the measurement of the drag produced upon a cylinder or disk rotating at a definite constant speed while immersed in the material under test. A synchronous motor assures unvarying speed, and the torque measuring unit (a beryllium–copper spiral spring) and affiliated parts are amply protected against strain, thus insuring permanent accuracy.

Again,

> Speed in testing is an important and outstanding feature. Only a few seconds are required for each reading, and several may be taken during a fraction of a degree change in temperature, thus generally eliminating the need of constant temperature control.

Further on,

> Operating technique is very simple and can be acquired by anyone in a few minutes. Extreme care or special skill is not required, and the element of human error is practically eliminated.

The Reed Inkometer

The Reed Inkometer, described previously in this book, has been accepted by a number of the larger manufacturers and users of printing inks. It is employed for control work. It operates at three different speeds and need not be used for a one-point method, though it always is, if the instructions recommended by the manufacturers are followed.

The Multipoint Rotational Viscometer

In 1936 the author started development on the multipoint rotational viscometer described in Chapter 8. This seemed the logical thing to do, in view of the deduction of the Reiner and Riwlin equation. Several of the largest printing-ink manufacturers in the United States are now using such instruments both for research and for plant-control work. It should not be implied, however, that these companies employ no other methods for consistency measurements. The finger test will always be with us, and instruments of the one-point type, claiming rapidity and an accuracy high enough for all practical purposes, will invariably have their adherents. The conscientious rheologist will be inclined to regret this condition, but eventually he will realize that learning how to compromise with the believers in "short"-cut methods is an essential part of his job.

Two Types of Plant Control of Consistency

Plant control of consistency is of two kinds. The one constitutes the measurements of yield value, plastic viscosity, and one or more of the coefficients of thixotropic breakdown. At first, this will be employed on the more expensive or more important products. If this proves of value to the company, more viscometers and a larger staff will be acquired until all desired control is attained.

The second kind is automatic control over batches of materials undergoing rheological changes from such conditions as evaporation and temperature variations. So far little has been accomplished in this direction, but the situation is by no means static. Various industries have shown their interest in the possibility of developing this field. An example exists, for instance, in the printing industry where rotogravure process inks are used. Evaporation takes place easily, and, if too great a change in the consistency is allowed, correct trapping becomes impossible. At present, no control exists except by visual observation and by thinning down to suitable consistency, a procedure based on the personal judgment of the foreman in charge.

The previous brief description is limited to the author's own contacts with certain industries. Its intention is to be indicative rather than comprehensive. It states the present trend; and, although this trend is not of an overwhelming nature, it is certainly not a discouraging one. At the least, rheology has its foot in the industrial doorway with full expectancy of entering in the none-too-distant future. In order to do this it must have available suitable commercial viscometers and operators who know the difference between Newtonian and plastic flow—above all, operators who do not confuse plasticity with thixotropy and "correct methods" with so-called "accuracy."

PART III

The Particle: the Basis of Rheological Structure

CHAPTER

12

Classification and Definitions

Rheological subjects belong fundamentally to one of two classes: (*a*) those that are composed of simple molecular species, including molecular solutions; and (*b*) those that are mixtures of insoluble particles suspended in a continuous phase or matrix. The latter type of particle can be solid, liquid, or gaseous. It may be a polymer, the monomer of which constitutes the continuous phase, or it can be totally unrelated to that phase. The size of the particle is likely to be greater than that of the molecule of the continuous phase though not necessarily so. The continuous phase is referred to as the "vehicle." In metals, the vehicle is the so-called "amorphous layer" surrounding the crystals of which the metal is comprised. In resins, rubbers, and fibers, the vehicle can conceivably be nonexistent, or it can be the smallest of the molecular species present provided there is enough of it to form a continuous phase. In paints, printing inks, and similar products the particles constitute the pigment. When dyes are used, instead of pigments, the particle is of colloidal dimensions and is usually referred to as a "micelle." When a particle is too small to be detected with "white-light" microscopy, it is said to be submicroscopic to white light. When it cannot be detected with the electron microscope, it is said to be submicroscopic to the electron microscope.

The preceding paragraph is perhaps an oversimplification of the subject and somewhat arbitrary. However, it is necessary to have an understanding in regard to the terminology employed so that the reader is not confused in what follows in Parts III and IV.

The Action of the Particle

When the particles are relatively few so that particle collision is negligible, their effect is simply to raise the viscosity of the suspension. This subject was first investigated by Einstein in 1906 and later by many others. However, when the particles are sufficiently numerous so that collision is unavoidable, their effect can be very complicated. This effect manifests itself in various ways. it can and usually does destroy the Newtonian behavior of the material. It produces such conditions as plasticity, pseudoplasticity, thixotropy, and dilatancy.

It is very likely that, if particles undergo simple flocculation without orientation or without any other type of particle readjustment, plasticity results. Also, if a definite particle orientation takes place, the material becomes thixotropic; and, if particle alignment without structural linkage is produced, when relatively high rates of shear are applied, then pseudoplasticity occurs. Dilatancy is the result of particle deflocculation and concentration, the interparticle space being just sufficient in volume to absorb all the vehicle present. This has been discussed in a previous chapter.

The Transition Stage

This expression has been used by Mark [8] in reference to the class of materials that bridges the gap between true solutions and obvious particle suspensions. The transition stage includes materials only of a colloidal nature whose particles are mainly submicroscopic. Resins, rubbers, asphalts, and similar materials are examples. The transition stage covers the larger share of rheological materials. Why then has it not been given the place of first importance instead of that position being granted to relatively large particle suspensions? The answer is quite important. In regard to the measurement of materials belonging in the transition stage, there is no equation of flow capable of easy solution and possessing constants of known rheological significance. It is impossible, therefore, to recommend the *industrial use* of any of the numerous empirical equations of flow that have been published so far. The situation is quite the opposite for suspensions of the Bingham-body type. The deduction of the Reiner and Riwlin equation and the development of the multipoint rotational viscometer have placed this latter branch of rheology on a substantial basis—one that is both practical and theoretically sound. Such a situation makes a good starting point for the development of a rheological system suited for industry. After the system is developed, there is nothing that makes it impossible to apply its technique and concepts to materials of the transition stage. The only difficulty is that the consistency curves, in the latter case, cannot be reduced to material constants like yield value and plastic viscosity.

Pure liquids and their mixtures, where miscibility is complete, contain no "particles," from the present viewpoint and, therefore, should not be included here. However, the subject matter is preparatory to what follows, and a brief discussion of it will not be altogether out of place.

The Staudinger Equation

One of the most noteworthy equations in this particular field of rheology is the one proposed by Staudinger.[10] It has received great attention and caused unlimited comment as to its validity. It is entirely empirical, relating specific viscosity to molecular weight and concentration. Specific viscosity η_{sp} is defined as follows,

$$\eta_{sp} = \frac{\eta_c}{\eta_0} - 1 \qquad (164)$$

where η_c is the viscosity of the solution at concentration c; and η_0 is the viscosity of the solvent (vehicle).

The Staudinger equation is:

$$\eta_{sp} = K_m Mc \qquad (165)$$

K_m is a constant for any given homologous series. Equation 165 is used for determining approximate molecular weights.

As a result of some very carefully carried out work, K. H. Meyer and V. D. Wyk believe that a more accurate statement of facts is given by the equation:

$$\eta_{sp} = 1.45.5Mc - 15.981c \qquad (166)$$

On the other hand Fordyce and Hibbert[2] conclude from experiments of their own that the Staudinger equation is valid only for comparatively high molecular weights.

The Einstein Equation

In 1906 Einstein[1] developed his equation relating the viscosity of a solution or suspension to the solute concentration and to the viscosity of the vehicle. Innumerable modifications, for various conditions, were subsequently derived by many rheologists who practically have become specialists in that field. The Einstein equation is

$$\eta_c = \eta_0(1 + 2.5c) \tag{167}$$

It is based on certain necessary assumptions, the principal ones being that the dissolved or suspended particles are rigid spheres, and that their concentration is so low that the particles exert no action on one another. The striking thing about the equation is the fact that the viscosity is independent of the size of the particles, depending only on the percentage volume of the suspension that they occupy. Einstein developed his equation for Couette streamline flow, that is, the type occurring in a rotational viscometer. Simha showed that the equation is also valid for capillary-tube flow.

There are 13 well-known modifications of the Einstein equation, covering conditions not included in Einstein's work. Einstein's particles are rigid spheres either without Brownian motion or with complete Brownian motion and at extreme dilution. An equation has been developed by Gold[3] and by Guth and Simha[7] for rigid spheres without Brownian motion, but at moderate concentrations:

$$\eta_c = \eta_0(1 + 2.5c + 14.1c^2) \tag{168}$$

Equations for rigid rodlike particles, either without Brownian motion or with complete Brownian motion, have been obtained by Jeffery, Guth, Huggins, Simha, and Eisenschitz; and also for rigid disks under similar conditions of Brownian motion by Jeffery and Guth.

The Arrhenius Equation

In 1887 Arrhenius published his equation showing how the viscosity of suspensions varied logarithmically with the concentration:

$$\eta = \eta_0 e^{kc} \tag{169}$$

where k depends on the solute, solvent, and temperature. This equation has been applied to a great many solutions and suspensions; but there apparently is nothing in the literature to state how valid Arrhenius' law is when the system is a crowded one, as occurs in base paints and printing inks.

Weltmann and Green [11] made a study of Equation 169 for high pigment vehicle ratios. They found that, although Arrhenius' law did not hold for such systems, a modification of it proved satisfactory. In the case of Bingham bodies two equations were derived. The first relates plastic viscosity U to the volume percentage P of the particles:

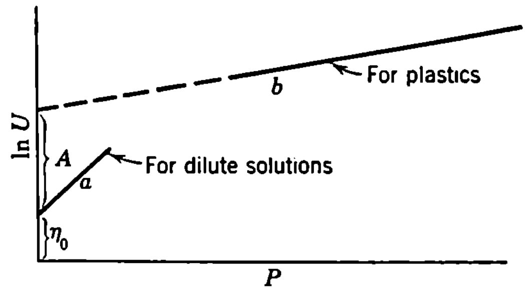


Fig. 53. Plastic Viscosity as a Function of Pigment Concentration P

$$U = (\eta_0 + A)e^{BP} \tag{170}$$

where A and B are material constants. Their second equation involves yield value and is

$$f = Me^{NP} \tag{171}$$

where M and N are the material constants. Figure 53 contains a plot of the Arrhenius equation, curve a. When $P = 0$, that is, when no particles are present, the viscosity will be that of the vehicle. Hence, the intercept will be η_0. When the solid content is high, the curve no longer follows Arrhenius' law but that given by Equation 170 and curve b. For $P = 0$, curve b gives the intercept $(\eta_0 + A)$. Actually b probably joins a, making a smooth continuous curve. In Figure 54, curve c is given the plot of Equation 171. It produces on extrapolation an intercept M on the ln f axis. Since f must be zero when $P = 0$, the actual curve probably follows the dotted line d.

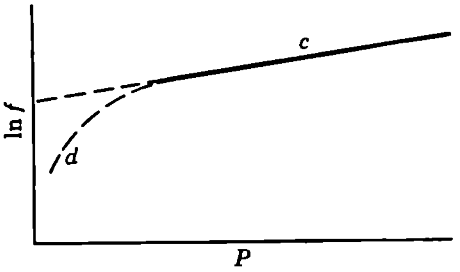


Fig. 54. Yield Value as a Function of Pigment Concentration P

In determining the effect of particle size on the constants A, B, M, and N, Weltmann and Green followed the procedure first used by Green and Haslam.[5] These investigators produced a series of material of different particle sizes, all possessing the same wettability. They made use of the fact that zinc oxide will grow in particle size, if reheated in a closed crucible above a temperature of 600°C. They produced a small-grained and a large-grained zinc oxide and then mixed them in various proportions so as to give samples of suitable average particle sizes. The particles were measured by the photomicrographic method.[4]

Weltmann and Green found when they plotted ln U versus P for their suspensions made with zinc oxides of different particle sizes that they got a family of linear curves intersecting the ln U axis at $(A + \eta_0)$. The cotangent of the angle made by the curve and the P axis increased as the average particle size increased. The average particle sizes varied from 0.55 micron to 2.50 microns. The "average diameter" is the d_3 diameter. It is equal to $\Sigma nd^3/\Sigma nd^2$ and is related to the specific surface of the pigment as follows: Specific surface $= 6/\rho d_3$ where ρ is the density. This is explained fully in a later chapter.

The afore-mentioned investigators also found that particle size had no effect on the constants A and M, but had a very substantial influence on the magnitudes of B and N. Both B and N varied linearly with ln d_3, both decreasing as d_3 increased in size.

Although Equations 170 and 171 are only empirical, they are often found useful, especially from an industrial viewpoint. For instance, if it is desired to make an ink of a certain plastic viscosity, for a set of materials whose constants η_0, A, and B are known, Equation 170 can be used to determine the percentage weight of pigment required. Similarly for Equation 171 when a given yield value is desired.

Gussman [6] and Mikusch [9] found that mixtures of linseed and dehydrated castor oils followed a law similar to Arrhenius'. Their work did not indicate, however, whether the exponential law held in the regions above the limiting rate of shear where oils behave like thixotropic plastics. This region was, therefore, investigated by others who also, unlike Gussman and Mikusch, studied mixtures of oils of different types. The conclusion arrived at can be summarized briefly: The exponential law is valid for mixtures of either like or unlike types of oils as long as neither constituent has a limiting rate of shear falling below the applied rates of shear used for the mixture. When the applied rate of shear exceeds the limiting rate of shear for either constituent, then the law ceases to be valid. For the Newtonian region the law is

$$\eta = \eta_1 \exp\left(P \ln \frac{\eta_2}{\eta_1}\right) 100 \tag{172}$$

CHAPTER

13

Crowded Particle Systems

In concentrated particle suspensions such as occur in printing inks and in paints, the plastic viscosity depends not only on the pigment–vehicle ratio and on the viscosity of the vehicle, but also on the force of flocculation (intensity factor) and on the specific surface (capacity factor) of the pigment. In this respect the rheology of crowded pigment systems differs from the highly diluted suspensions where the Einstein law is applicable. It should be recalled that the Einstein equation contains no factor related to particle size.

Specific surface, as used here, is the sum of all the surfaces of the individual particles whose combined weight is 1 g. It is customary to give it in square meters per gram. For instance, the specific surface of a certain titanium dioxide is 11 sq m per gram; a zinc oxide, 5 sq m per gram; and a carbon black, 200 sq m per gram.

The specific surface is inversely proportional to the first power of the average diameter. The average diameter is a particular average diameter written d_3. This diameter is described later. The "first power" is emphasized here because the early literature contains many misstatements to the effect that the inverse relationship refers to the second power.

Other factors remaining constant, yield value increases with the specific surface (symbolized S). This is one reason, and an important one, why the microscopical examination of particles, in regard to particle size, can be useful to the rheologist. For instance, suppose a material has a yield value that seems to be too high for the known pigment–vehicle ratio. The cause can arise from poor wetting (high interfacial tension), or from an average particle size that is too small, or from both possibilities. A microscopic inspection and study of the particle will often indicate the correct answer.

Particle Inspection

There are many instances where a simple microscopical inspection of a particulate substance gives sufficient information in regard to the particle size of a material and thereby obviates the necessity for a more time-consuming and laborious particle-size measurement. It is well for the laboratory man to become acquainted with the methods and technique of quick inspection, for in the course of time it will save him considerable unnecessary work.

It is assumed that the investigator is fairly well experienced in the use of the microscope in both visual and photographic work. The various parts of the microscope will not be described; and, also, familiar terms like "reflected light," "transmitted light," and "dark field" are not explained. If the investigator lacks sufficient familiarity with the subject, it would be well for him to have available a reliable textbook on microscopy for necessary reference.

Generally, pigments can be placed in well-defined categories in regard to size. The smallest size class has an upper limit of approximately 0.1 micron. The particles of this class require either a dark field or an electron microscope for detection. It is a truly colloidal class and includes pigments such as gas blacks, phthalocyanines, and dyes. The next size class extends from 0.1 to 0.2 micron. Particles in this category, although below the resolving power of the white-light microscope, can be *detected* with a white-light instrument, particularly if the observer's retina has been used much for observing fine detail. This class is composed of near colloids and contains a great many pigments such as the fine-grained zinc oxides and titanium dioxides. Such materials can be photographed with the Köhler ultraviolet microscope, using quartz lenses and the cadmium line 0.275 micron for the light source.

The next category in the scale is the one that contains by far the great majority of pigments. Its limits are approximately between 0.2 and 0.6 micron. Such materials as lithopone, white lead, lead chromate, most zinc oxides, iron oxides, and many organic colors lie within this region. The final category, that is, as far as pigment-like materials are concerned, covers the territory from 0.6 to 3.0 microns.

Besides pigment-like materials there is another type of particulate substances found in paints and printing inks. This is the so-called "filler or inert type" of material. These substances are usually ground products like barytes, silica, and aluminum hydroxide. Their particle size is of a different order of magnitude from that of pigments. The range is usually between 5 and 100 microns. They serve a number of purposes. They can act as diluents, reducing the cost of the product; they may be used as bases on which to precipitate colors, thus forming the "lake" pigments; they can act as flatting agents; or they can give "tooth" to substances like paint, causing increased adherence to the surface on which the paint has been applied.

The inerts have a low refractive index, almost matching that of the vehicle. They are, therefore, sometimes difficult to find, especially if they are covered or surrounded with highly flocculated pigment. Their size is usually of relatively minor importance as they are present in comparatively small percentages. If their particles are unusually large they can cause an objectionable amount of grittiness. A particle 100 microns in diameter can be detected under the finger tip, if pressed down on a smooth glass surface.

In large enough quantities the inerts can naturally affect the rheology of the suspension. It is, therefore, necessary that the rheologist be able to recognize them by microscopical inspection and learn to judge the percentage of the suspension volume they occupy. A technique of that kind is hard to teach but can be acquired with practice. As stated, their low refractive index makes inerts difficult to see in the microscope. This clue is the most trustworthy one to rely on when looking for them.

The Employment of Refractive Index

The investigator should refer to his textbooks on microscopy for a full and complete description of the subject of refractive index and how it is utilized by the microscopist. Certain important facts in regard to it, however, are noted here. (1) If a particle has but a single refractive index and is colorless, it will disappear completely when immersed in a liquid of the same refractive index. If the particle is still visible after immersion, it will appear as a patch of color instead of a sharply outlined particle. (2) If, on focusing upward, a bright surrounding band of light moves inward toward the center of the particle, the particle has a higher refractive index than the vehicle; if the band moves outward the reverse is true. (3) When the particles are too small to show any surrounding band, then, on focusing upward, all the particles that turn bright have a refractive index higher than the mounting medium; if they become darker than the field, then they have a lower refractive index. All these phenomena are easiest to observe when the substage diaphragm is reduced to a point where diffraction rings begin to show around the circumference of the particle.

The Limit of Resolution

There is a considerable difference in meaning between "limit of resolution" and "limit of detectability." The first expression refers to the smallest distance two parallel lines can approach each other and still be recognized as two lines and not one. It should be noted that the diffraction rings surrounding each line will partially overlap; but, just as long as the observer recognizes that this condition exists, it can be said that the lines are resolved. The same conditions hold for two approaching particles.

The Limit of Detectability

The limit of detectability depends not only on the lenses and lighting system employed, but also on the condition of the observer's retina. For someone who has had little or no experience in using the microscope, the field (which has been adjusted to a comfortable light intensity for the experienced microscopist) will seem dazzling bright. Under the circumstances all fine detail and small particles are blurred out. This condition can be remedied by reducing the amount of light employed, but in so doing the resolving power is lowered. It is only after the beginner has had his retina dulled to intensity but made acute to fine detail that he can obtain the optimum in detectability. With the best white-light apochromatic objective and compensating eyepiece the limit of detectability should be about 0.1 micron. With the electron microscope the limit of detectability is not yet established. However, the limit of resolution is usually placed somewhere between 20 to 40 angstroms. This is 0.002 to 0.004 micron.

The Technique of Judging Class Size

For all particles smaller than 0.4 micron, a 2 mm (90×) apochromatic objective, preferably with a numerical aperture of 1.4 is indispensable. A 6× or 10× compensating eyepiece should be used with it. An aplanatic condenser is also desirable. Any source of light that is sufficiently concentrated will be satisfactory. Concentrated filaments, platinum ribbons, and arcs of the tungsten type are the best. Some microscopists find carbon arcs satisfactory; but such arcs emit a lot of heat; and the carbons have to be renewed at critical moments.

At least 75% of the success of a microscopical examination of a particulate material depends on making a correct and suitable mount. This, of course, is done on a microscope slide and constitutes quite an art in itself. An entire chapter will be devoted to it. For the present it is assumed that the mount has been made. The pigment has been spread out so that the individual particles are visible and anchored fast to the slide, preventing motion of any kind.

If the set of lenses previously recommended is used, then the smallest particle capable of showing its opposite sides separated will be approximately 0.3 micron. However, the corners of the particle will not be resolved into sharp angles. The net result will be a minute circle clear in the center, evidenced by a small bright spot, and sharply delineated edges. It is taken for granted that a suitable mounting medium, in which the particles are immersed, has been used and that the particle is in exact focus.

If the particle is smaller than 0.3 micron but larger than 0.2 micron, it will appear as a minute dark disk. If it is smaller than 0.2 micron, but larger than 0.1 micron, the disk will be gray and will become lighter in shade until it fades from view at about 0.1 micron. The diameter of the disk is not the magnified particle size but simply a diffraction image. This image does not change noticeably in diameter as the true particle size decreases from 0.2 micron toward the limit of detectability.

When the individual particle is below 0.1 micron, it cannot be seen with the white-light microscope; but, if the pigment is flocculated, particle groups can be detected easily. If these groups are examined with the electron microscope, the individual particles often can be observed and even measured. Such is the case with the iron-blue pigments. Their shape is cubical, and their diameter varies from 0.05 to 0.08 micron.

If the investigator has had sufficient experience, he can estimate fairly accurately the size of particles in the 0.3- to 0.5-micron range. Unless opaque, these particles all will be clear centered, but any crystal angles still will appear rounded, on account of diffraction. From 0.5 micron upward it is best to use a calibrated eyepiece. The scale in the eyepiece must be calibrated for each magnification employed.

For the inexperienced, the pitfalls in estimating particle size are many. Two should receive particular attention. The first is the error involved in estimating from an incorrectly made mount. Mounts where the pigment is piled together in concentrated masses or mounts where the pigment is densely flocculated always give the impression that the particles are larger than they actually are. Mounts of medium density give the best average. Thin mounts are the reverse of dense mounts; that is, the average particle size appears to be too small.

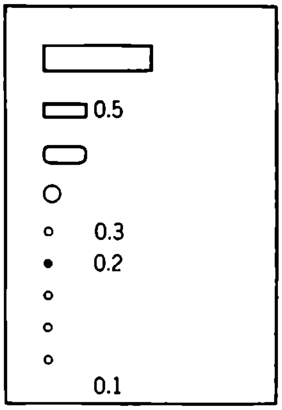


Fig. 55. Types of Images for Various Particle Sizes

The second difficulty is in deciding which particle represents the average particle size. Before this point can be discussed, the meaning of average particle size must be explained. This explanation is given in Chapter 15. Unless the investigator has a clear understanding of the meaning of average particle size, he will be unable to give a satisfactory particle-size estimate.

To summarize the important points mentioned in this chapter: If the investigator knows that he has a suspension but is unable to see any particles, then either the refractive index of the medium matches that of the particle (which is highly improbable) or else the particles are less than 0.1 micron in diameter. If the particles all appear as pale grayish diffraction disks, their size is between 0.1 and 0.2 micron. If all the particles appear as distinct black dots, their average size will be between 0.2 and 0.3 micron. The smallest clear-centered particles are about 0.3 micron. That is one of the most useful pieces of information the pigment microscopist can have. A simple inspection, using the foregoing classification in regard to size, is often sufficient, giving the rheologist all the information he needs in the matter. Figure 55 shows diagrammatically the change in appearance of the particle image as the particle varies in diameter. It should be noticed as stated, that the image gets progressively smaller down to about 0.2 micron after which the diffraction image gets fainter but remains constant in size.

CHAPTER

14

Mounting the Particle

The earliest attempts at mounting particles consisted of little more than spreading the dry powder out on a microscope slide and looking at it with the lowest powers available. All that could be seen was an aggregation of pigment pellets. It was known that these pellets were not single particles but soft aggregates composed of countless numbers of individual particles. It was believed to be impossible, however, to disperse the pellets and examine them for the ultimate particle. Hence, pigments were called "impalpable powders." It was stated that it is as "impossible to obtain an average particle size as it is to average the stars in the sky where every increasing telescopic power reveals a new infinity of stars"; it was thought, that the same condition was obtained with the microscope. It is true that increased resolving power together with increased magnification brings into view smaller particles in any given sample; but the weight or volume percentage of these smaller particles can be so small that they have a negligible effect on the average size of the sample as a whole.

Pigment Microscopy

In order to examine a powder for particle size it is necessary to have the proper technique and a proficiency in using it. That important point was hardly given any consideration prior to the 1920's. A microscopical examination of pigments was apparently something that any chemist should be able to do on the spur of the moment. It was not fully realized that pigment microscopy is a science perhaps as complex and difficult to master as rheology itself.

In the preparation of a correct pigment mount, questions like the following must first be answered.

(*a*) Is the task at hand a question of particle-size measurement?
(*b*) Does it involve the problem of dispersion?
(*c*) Does it involve the problem of flocculation?
(*d*) Does it pertain to the state of aggregation?
(*e*) Is it one of particle identification?
(*f*) Is it one of particle structure?
(*g*) Is it one of particle uniformity?

Each of these constitutes a different type of problem; and each involves some special method of mounting. The student should rid his mind of the idea that the answers are all in the book. As a matter of fact very little is in the book. The problem can very well resolve itself into a game of wits where the investigator's past experience is his only guide.

Once the nature of the task has been decided, the next question is: What kind of mount is needed? Suppose that the problem is to find the average particle size. If the substance is very uniform like lithopone or titanium dioxide, only one or two mounts are required. However, if it is nonuniform, that is, has a wide particle-size distribution curve like ground barytes, many mounts might be necessary before a sufficient number of particles can be measured to give a fair average diameter. What the situation is will be discovered on the initial inspection.

Particle Dispersion

It is possible to measure particles with the microscope only when they are separated from one another and do not overlap. Means for accomplishing this have been described in the literature.[1] One of the simplest methods is to rub out about a milligram of the dry powder into a thin layer on a microscope slide, using redistilled turpentine for the dispersing agent. This procedure is carried out with a small glass rod, using a forward and backward motion. During the process the vehicle dries. Just before the dry stage is reached, the rod is lifted, allowing the pigment to adhere to the microscope slide. The slide is then placed on a hot plate, and the last trace of the dispersing material is evaporated. With a little practice, "wedges" can be produced. At the thick edge of the wedge the particle distribution is dense; at the thin edge the reverse condition exists. Somewhere between the two edges the particle distribution is most suitable for examination (particularly for photography). If the investigator holds the mounting rod firmly so that it does not twist, then by a rotary motion in the plane of the slide a series of small wedges can be produced. This gives a mount that is more likely to have areas of good dispersion than one containing a single wedge.

After the last trace of turpentine is evaporated, a drop of mounting medium is added and then covered with a cover glass. Because the refractive index of most pigments is high, a medium of low index should be used. A 50% solution of glycerine in water is usually satisfactory. A 2-mm objective is inserted in the microscope, immersed in cedarwood oil (or a good substitute), and the mount is examined. If the dispersion is found satisfactory, the material is photographed, and measurements are made from it as will be explained.

When the pigment covers a wide range of particle sizes, say, 0.2 micron to 20.0 microns, the best procedure is not to measure it. If a measurement cannot be avoided, then there are several compromises that can be made. (1) Measurements can be reported on the size of the largest particles present, the size of the smallest particles present, and an estimated average size, using a calibrated eyepiece. (2) The material can be elutriated, separated into fractions, and each fraction photographed and measured. From these measurements an average size can be calculated. (3) An electron micrograph can be made at relatively low power. The depth of focus of this instrument is so great that the largest and smallest particles can be focused at the same time. This condition is not true for white light when using a 2-mm objective. That is a real source of trouble in photographing highly nonuniform materials.

In following the mounting procedure just described, a number of essential things have been done: The pigment particles have been made to lie in one plane; they do not overlap; they are not flocculated; they are free from all motion except convection currents and Brownian motion; a representative sample can be selected for measurement; and a mounting medium of suitable refractive index can be used so as to give the necessary image contrast with the field or background.

It should be evident that a mount made for particle-size measurement (*a*) is quite unsatisfactory for problems (*b*), (*c*), and (*d*); but it could be a desirable mount for particle identification (*e*). For (*e*), the mount must be such that the particle shape, color, and size are discernible. It might also be necessary to determine the refractive index of the particle, in which case different mounting media can be used.

Case (*b*) involves a condition referred to as "dispersion," sometimes as "degree of dispersion." Both are unfortunate expressions, for they convey no definite information as to what is meant. When a pigment is received by the user who is going to incorporate it into a vehicle or matrix of some kind, it is often in the form of a dry powder which consists of a collection of soft pellets. When this powder immersed in a vehicle goes through the mill, a number of things can happen to it. It can become completely wet, or partially wet by the vehicle. In the first case, deflocculation accompanied by Brownian motion normally happens. Also at the same time there can be a residue of hard unbroken aggregates. In the second case the particles can be flocculated; they might show Brownian motion; and there can exist at the same time some deflocculated particles and some hard aggregates. The question now arises: What constitutes dispersion? Does it mean deflocculation? Would a material that had all its aggregates broken down to the ultimate particles and then had them immediately flocculate be considered dispersed? Each investigator has his own opinion on the subject, and the result is confusion and misunderstanding. It would be much better not to use the word "dispersion" if exact information could be given in its place. For instance, one might say: The material is deflocculated; the material contains hard aggregates; the material is highly flocculated, and so on.

Examining Particle Suspensions

In examining a suspension for "dispersion" or for pigment structure, the investigator must be careful not to destroy the condition for which he is looking. Most paints and printing inks are too dense for microscopical examination without dilution. The only safe diluent is the vehicle employed in making the material. Any other liquid could very easily change the state of flocculation by altering the interfacial tension of the system.

The safest method for making an examination is to place a very small drop of the material on the center of a microscope slide and then carefully cover it with a drop of its own vehicle. A cover glass is placed on top of this and pressed down slightly. Examination is made at the edge of the drop where the suspension is in contact with the vehicle. At this point the state of flocculation is easily observed. If the cover glass is pressed down until light can get through the center of the drop, then at that spot the material can be examined for hard aggregates, which usually show up clearly against a continuous pigment background. In order to be sure that aggregates are hard unbroken lumps and not simply pieces of the soft undispersed suspension, the cover glass should be moved around slightly. This operation will not break down the aggregate, but it will "smear out" the soft piece of undispersed suspension in a way that clearly indicates its lack of hardness.

Hard Aggregates. Hard aggregates and soft pieces of ink or paint pastes that have not been rubbed out in the covering vehicle are both likely to be opaque. Large *single* particles of the same size as the aggregates are *clear and transparent.* This fact often enables the investigator to understand the nature of the particle he is examining.

In the hands of the experienced, a microscope slide with its cover glass constitutes a small laboratory in itself. Pressing down on the cover glass with a dull pointed implement can concentrate a tremendous pressure on a small point. Keeping the cover glass pressed down and sliding it forward and backward can produce a grinding action large enough to reduce small particles of coal to a particle size comparable with gas black. In fact the manipulation of the cover glass is an art that will repay any investigator willing to take the time to learn its possibilities. In Figure 56 are illustrated some of the main points discussed in this chapter.

Wedge Mounts

In Figure 56 (a) is shown a simple wedge made by a straight forward and backward motion of the dispersing rod. At (b) is a multiple wedge mount made by tracing with the rod the pattern shown by the arrow. At (c) is a circular wedge.[2] This is used when perfect separation of the particles is desired. The particles are dispersed in a melted resin; the cover glass is pressed down in its center with a blunt point, which is moved (under high pressure) forward and backward on the surface until dispersion is complete.

The pressure is maintained until the resin has cooled off and solidified. The thin edge of the wedge is in the center where the pressure was the greatest. Out towards the edge of the cover glass the particles will be flocculated and too densely mounted for examination.

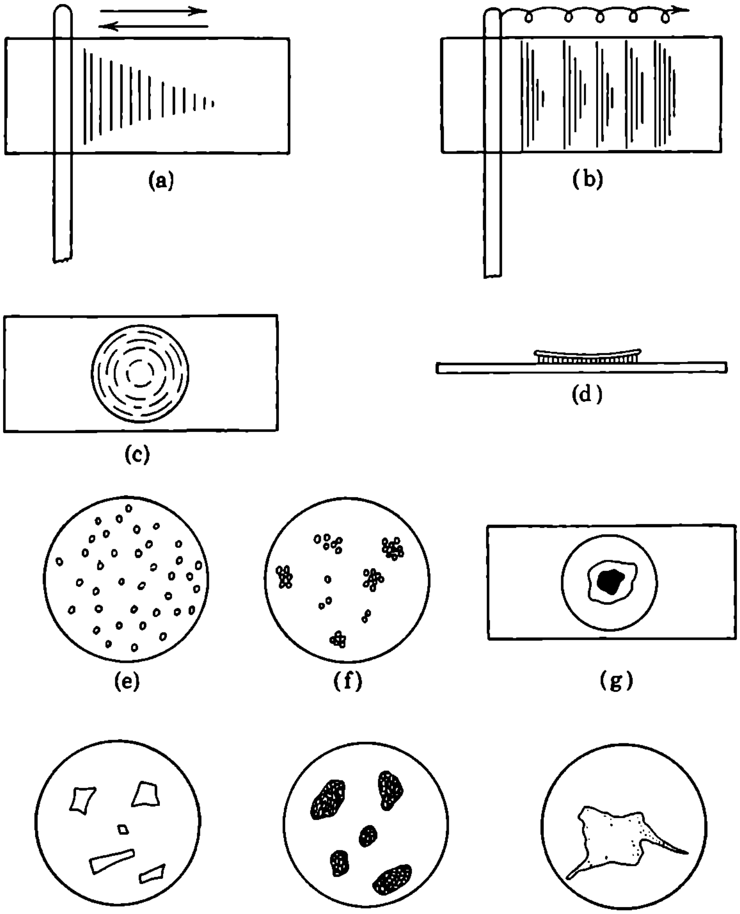


Fig. 56

At (d) is shown the cross-sectional view of a pressed-down cover glass. This gives a view of the wedge. Sketches (e) and (f) are self-explanatory. At (g) is illustrated the method of mounting a drop of suspension for the study of its structure, that is, whether the pigment is flocculated or deflocculated; also, whether it contains hard aggregates or not. A single large particle is usually clear centered unless it is so densely colored that no light can penetrate.

Metallic particles are usually opaque. The hard aggregate is likely to be opaque because of the internal reflecting particle surfaces it contains. These facts are illustrated in (h) and (i). When a soft undispersed lump is disturbed by sliding the cover glass, there is usually a string of particles found flowing from one side as shown at (j).

Mounting Emulsions

The procedure for mounting emulsions is practically the same as that used for suspensions of solid particles. Care must be taken not to add anything to the emulsion that will change the interfacial tension. If dilution is required in order to get enough light through for microscopical examination, the diluent must be a drop of the clear vehicle. Another precaution also must be taken. When the cover glass is pressed down too far, the globules of the emulsion will be squeezed between the cover glass and the slide, thus making the particles appear bigger than they actually are. The investigator must be sure that he has not compressed the material that far.

CHAPTER

15

The Size of the Individual Particle

The "size" of a particle must not be confused with "average particle size." Both are arbitrarily selected quantities, depending on what the investigator chooses to measure and decides to call by those names. In the entire subject of particle-size measurement there are only two quantities that are completely objective and cannot be changed by definition. One is the amount of surface per unit weight, known as specific surface; the other is the number of particles per unit weight.

It is comparatively easy to decide what to call the "size" of a spherical particle. It can be its diameter, its volume or its surface. Usually size is given as "diameter." The unit of measurement is the *micron*, a thousandth of a millimeter. When the particle is nonspherical, the choice of size is reduced to a single thing—volume. Unfortunately, it is customary to refer to size as *diameter*. This complicates matters by making the size of a particle an arbitrary choice of one of its dimensions and calling that its diameter. The subject becomes even more complex when the average size of a mass of nonuniform particles is considered. In addition, when it is realized that the measurement of the particle is made under a microscope and that the particle is too small to be picked up and turned over into some convenient position, then the subject ceases to be a science and becomes a system of arbitrary decisions.

Suppose the particle is a cube. Its edge or a diagonal (either through the center of a face or the center of the particle) can arbitrarily be called its diameter. Then, with suitable *shape factors* its surface and its volume can be calculated. From these factors and the density can be determined the specific surface S and the number of particles per gram N. This is true, as shown later, whether the material is uniform (all particles the same size) or nonuniform.

Unfortunately, under the microscope the measurement of the edge or the diagonal of a pigment particle is almost impossible, because neither of these dimensions is likely to lie perpendicular to the optic axis of the microscope. Hence, if the edge is arbitrarily taken as the diameter, the measured diameter will be, on the average, too large, for it will include more than the edge. Thin needles and thin plates standing at a steep angle form an exception. If the diagonal is taken, then the measured diameter will similarly be too small. (See Figure 57.) These discrepancies arise from the fact that in small pigment-like particles only the outer edges can be recognized as edges. The measurement is made across the entire particle image between the outer edges, all inner-appearing edges not being detectable. In Figure 57 the outer and inner edges are marked respectively *o* and *i*. By "correct projection" is meant one that gives the true length (multiplied by the magnification) of the edge or diagonal. In Fig. 57 is shown what happens on random orientation.

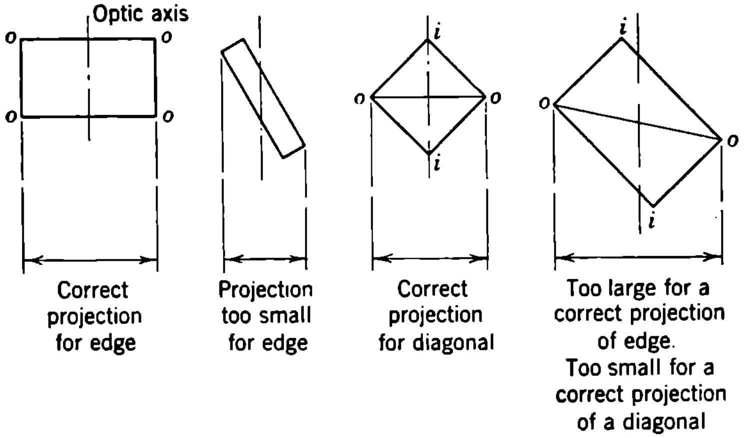


Fig. 57

Assume that the particle is a rectangular parallelepiped. What can be taken for its diameter? Either any of its edges or any of its diagonals could be used; however, as is shown subsequently, it is more desirable to use the harmonic mean of its three edges. Since the particle cannot be moved around in order to get a convenient orientation, the two shorter edges are assumed to be equal. This is a very arbitrary compromise introducing error. However, the error involved is part of the error of measurement; and, since this error is just as likely to be negative as positive, it can be assumed with reasonable assurance that, for materials that are not too nonuniform, the positive and negative errors cancel out.

The Shape Factor

There are an infinite number of particle shapes. This becomes apparent when the fact is considered that particles can be fractured pieces, or imperfectly crystallized ones, taking any conceivable form. It is convenient, therefore, to invent a classification that will reduce this infinite number to as few general forms as possible. This can be accomplished as follows:

A. Isotropic: This group includes the spherical particles of emulsion; also particles of certain metals that can be made in spherical form such as zinc, aluminum, and nickel.
This group also includes all cubical particles such as certain titanium, dioxides, and iron blues.
B. Plates: This contains such materials as certain clays, aluminum flake, mica, and basic carbonate of white lead.
C. Needles: All particles having a single long axis. The crystal system is immaterial. Examples: zinc oxide, lead chromate, and some clays.

There is no sharp line of division between groups *B* and *C*. A plate becomes a needle when two of its dimensions are small compared to the third. And, likewise, needles merge into plate form. The classification given is simply a convenience for easy reference.

The *shape factor* does not identify shape. That ideal factor has not yet been developed. The term "shape factor" as used here has the following meaning: There are two shape factors. The *surface* shape factor σ is a number which when multiplied by the *square* of the particle diameter gives the surface of the particle. The *volume* shape factor ν is a number which when multiplied by the cube of the particle diameter gives the volume of the particle.

If d is the diameter of a sphere or the edge of a cube, then, the surface of a sphere is σd^2, and σ, in this case, is π. Likewise, the volume of a sphere is νd^3, and ν is $\pi/6$. The specific surface of a mass of spheres of density ρ is the total surface divided by the total weight:

$$S = \frac{6\pi d^2 N}{\rho \pi d^3 N} = \frac{6}{\rho d} \tag{173}$$

The number of particles per gram of density ρ is

$$N = \frac{1}{\rho \nu d^3} = \frac{6}{\pi \rho d^3} \tag{174}$$

Likewise, for cubes: The surface $= \sigma d^2$, where $\sigma = 6$. The volume $= \nu d^3$, where $\nu = 1$. Then for cubes,

$$S = \frac{6d^2}{\rho d^3} = \frac{6}{\rho d} \tag{175}$$

and

$$N = \frac{1}{\rho d^3} \tag{176}$$

It is easily shown that for parallelepipeds

$$S = \frac{6}{\rho d} \tag{177}$$

where $d = 3abc/(ab + ac + bc)$, the harmonic mean of the three dimensions, a, b, and c. It should be noted that the ratio σ/ν for the three shapes is 6 in each case.

The Horizontal Diameter

It has been stated that the particle under measurement cannot be moved around so that some desirable edge or diagonal can be placed perpendicularly to the optic axis of the microscope. This being so, no exact measurement can be made of a known part of the particle. A compromise is necessary. In some work published in 1921, the author[1] used what he called the *horizontal diameter* of the particle image. A photomicrograph of the pigment is made, the negative put into a lantern, and its image projected on a screen. Each particle image is then measured across its center from the middle of its left edge to the middle of its right edge. (See Figure 58.) The edge of the particles appear thick because of diffraction. The true image edge is in the center of the diffraction image.

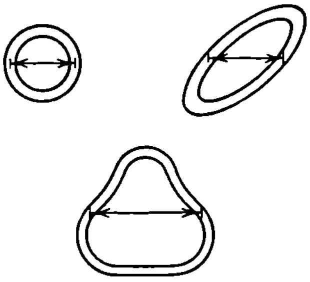

Horizontal diameters

Fig. 58

By using only the horizontal diameter, preference is given to no particular diameter; and, since the particles are randomly oriented on the microscope slide, the horizontal diameter constitutes about as fair a choice for particle diameter as can be made.

The employment of the horizontal diameter instead of a known edge or diagonal makes it impossible to calculate the exact values of σ and ν. However, their ratio is apparently not seriously affected, for measurements of specific surface made with the microscope, letting $\sigma/\nu = 6$, check in many cases remarkably well with specific surface determinations made by adsorption methods.[5]

It has been the custom of colloid chemists to assume a definite particle shape in experiments involving particle size. The shape assumed is usually that of a sphere. This is only another way of saying that $\sigma/\nu = 6$. However, this assumption, as pointed out, applies to cubes, if the edge is the diameter, and to any rectangular parallelepiped, if the harmonic mean of its three dimensions is taken as its diameter.

When the diagonal through the center of the cube is taken as the diameter, the values of σ and ν are changed. Their ratio now becomes $6\sqrt{3}$. Also the diameter is changed by the same factor; that is, the diagonal equals the edge multiplied by $\sqrt{3}$. The specific surface is not changed because it is something that belongs to the pigment and is independent of the definition of diameter.

When the diagonal of the cube is used for "diameter," $\sigma/\nu = 6\sqrt{3}$. This is the largest value σ/ν can take for cubes, because the diagonal is the largest diameter of the cube. In practice it is hardly likely that all the particles are oriented in such a way that the diagonals will always be measured for particle diameter. Therefore, in practice σ/ν will fall somewhere between 6 and $6\sqrt{3}$. The chance is that is will be more nearly equal to 6 than to $6\sqrt{3}$. The reason is that the probability of the particle lying flat is greater than its being balanced on one corner. Hence, it is fairly safe to take the shape-factor ratio as equal to 6.

To summarize the statements made in regard to the shape factor: (*a*) There are two shape factors. (*b*) One for surface and one for volume. (*c*) Neither identifies shape. (*d*) Both depend on the shape of the particle and on the particular dimension taken for the diameter of the particle. For spheres, cubes, and rectangular parallelepipeds $\sigma/\nu = 6$, where the edge of the cube and the harmonic mean of the three edges of the parallelepiped are taken as their diameters. In actual practice the desired edges and diagonals cannot be measured. As a compromise the "horizontal diameter" is used. This introduces an error, but it is of such nature that the positive errors are just as likely to be as great as the negative errors, and, when a great many particles are measured, it is safe to assume that the positive and negative errors cancel each other.

The Meaning of Average Particle Size

If all the particles in a mass of material were of the same size (perfect uniformity), then there would be no significance to the term "average particle size." It is in normal cases where nonuniformity exists that it becomes necessary to express "size" in terms of an "average." Just what average to use depends on what use is to be made of it. Most particle-size problems are in regard to specific surface. The particular average diameter, then, that is related to specific surface is the important one. It is determined for nonuniform but geometrically similar materials as follows:

$$\text{The total surface is } \sigma\Sigma nd^2 \tag{178}$$

$$\text{The total weight is } \nu\rho\Sigma nd^3 \tag{179}$$

Then,

$$S = \frac{\sigma\Sigma nd^2}{\nu\rho\Sigma nd^3} \tag{180}$$

where n is the particle frequency.

In the series of various possible average diameters $\Sigma nd^3/\Sigma nd^2$ is written d_3. Assuming the particles to be spheres or rectangular parallelepipeds gives

$$S = \frac{6}{\rho d_3} \tag{181}$$

where d_3 is the "average diameter" (related to specific surface). It is the most useful of all the average diameters. There is no other that can take its place. For instance, the arithmetical mean diameter is often determined, but it bears no relationship to specific surface, and any attempt to substitute it for d_3 in Equation 181 is a serious mistake. The arithmetical mean is

$$d_1 = \frac{\Sigma nd}{\Sigma n} \tag{182}$$

If the number of particles per gram is desired from the average diameter, then an entirely different "average" is employed:

$$N = \frac{1}{\rho\nu D^3} \tag{183}$$

and

$$D = \sqrt[3]{\frac{\Sigma nd^3}{\Sigma n}} \tag{184}$$

The shape factor ν will take different values when geometrical similarity is absent.[2]

The average diameter D is the average particle diameter determined with the slit ultramicroscope. This determination is made by counting the number of particles Σn in a known weight of material. Then, for cubes, $\nu = 1$, and for spheres, $\nu = \pi/6$, in Equation 183.

There are other average diameters besides d_1, d_3, and D, but it would be outside the scope of this book to include a detailed description of them. The reader is referred to the original literature.[2,4] Average particle size is defined as "the size of a hypothetical particle that in some particular way represents the total mass of particles." [3]

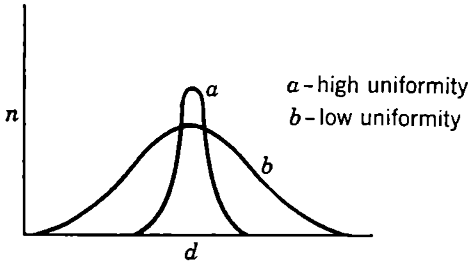


FIG. 59. Particle-size Frequency Curves at Different Uniformities

The Uniformity Coefficient. When particle size d is plotted against particle frequency n a size distribution curve is obtained. If the particles are quite uniform, there will result a steep and narrow curve; otherwise, it will be broad and flat. (See Figure 59.) The type of curve produced, that is, broad or narrow, is expressed by the *uniformity coefficient U.*

$$U = d_1 \sqrt{\frac{\Sigma n}{2\Sigma n(d_1 - d)^2}} \tag{185}$$

In practice the size distribution curves are always skewed to the right. The uniformity coefficient is based on a symmetrical curve; consequently, the definition of uniformity of a material is *the uniformity of a hypothetical material that has a symmetrical prob-*

ability curve and the same values for d_1 and $\Sigma n/\Sigma n[(d_1 - d)^2]$ as the material itself.

When all the particles are of equal size, $U = \infty$. When no two particles have the same size, then $U = 0$. The d_1 diameter enters the uniformity coefficient for a very definite reason. If it was omitted, then a powder in which the largest and smallest particles differed, say, by 0.1 micron would have the same uniformity coefficient as a group of large objects, like ball bearings, that differed by only 0.1 micron. Obviously, the powder with an average particle size of 0.2 micron would be quite nonuniform, if its particles varied by 0.1 micron, whereas such a variation in 10-mm ball bearings would be negligible.

Measuring Average Particle Size

There are numerous ways employed for obtaining average particle size. All of them have at least some bad features. None is free from adverse criticism. The worst fault that any method can have is one that gives a measurement of an unknown average diameter. Such a measurement cannot be used with safety any more than an arithmetic mean diameter can be employed in calculating specific surface. Adsorption methods definitely give specific surface; and, if a particle shape is assumed, the specific surface can be converted into d_3. Adsorption methods cannot give U, d_1, D, and N. Adsorption methods are carried out by allowing molecules of known cross-section area to be adsorbed on the particle surface. From the amount of material adsorbed, the specific surface can then be calculated.

There are various types of settling methods based on Stokes's law,[6] and other methods where the rate of gaseous or liquid flow, through a compacted mass of the material, is related to particle size, but, unless the investigator understands what the term "particle size" means in such cases, he will find it difficult to convert it into objective quantities like S and N.

The method that attempts to cover the subject most extensively is the photomicrographic method. It is also the one that has received the most adverse criticism, but, paradoxically, the one most frequently called on as a check on other methods. It is probably a question of "seeing is believing." An investigator might develop a new method for obtaining an average particle size, but, until he can examine his material with a microscope, he never can feel quite sure whether his measurements even approximate the truth or not. The most serious criticisms of the photomicrographic method are the assumptions made regarding the use of the horizontal diameter, those in regard to particle shape, and the minute quantity of the material that actually gets measured. These are undoubtedly serious faults that must be considered. Since many particles are small enough to appear like round dots (lithopone, titanium dioxide), the use of the horizontal diameter cannot be severely criticized. If, however, the shape of the particle is that encountered in diatomaceous earth, the commonsense thing to do is to refuse to measure it. As far as minuteness of the size of the sample is concerned, this is not serious with materials of high uniformity. If the uniformity is very low, the material should be separated into sections by elutriation and each section measured by itself. Average diameters can be calculated by such procedure.

The success of the photomicrographic method depends on the quality of the mount. Is it representative? Are the particles deflocculated? The only way to ascertain whether the mount is representative of the entire mass of material is to make and examine a sufficient number of them. By this procedure, and by using the fact that the midway point between the edge and back of the "wedge" is the spot most likely to be representative, it is possible to obtain satisfactory results. This conclusion cannot be proved correct; but it is the conclusion that most pigment microscopists reach after they have had a sufficient number of years experience in the field.

After a satisfactory mount is made (which includes a satisfactory mounting medium), it is put on the microscope and examined. If the material is a fine-particle-size pigment, the highest available magnification is used (not over 1000 times the numerical aperture). If the material is one that contains a fine-particle-size background, the magnification might have to be reduced so as to be able to focus on all particles at once. For very coarse particles, like grains of sand, the lowest powers must be used. The experienced investigator will never find any special difficulty in selecting the correct lenses for any particle work.

The next step is to make the photomicrograph. This is best made with a contrast plate and developed with a contrast developer. After the negative is developed and dried, it is put into a projection lantern, and an image of the particles is thrown on a screen. The magnification should be sufficient to measure the smallest particle with ease. Obviously the total magnification is the product of the magnification of the microscope and of the projector. For pigments like zinc oxide this product should be about 25,000×.

In order to avoid skipping particles, the screen is marked off into small sections with a piece of crayon. There should be enough light in the room so that the operator can read his ruler at the same time he is measuring the particle image.

Horizontal diameters are measured and called off to an assistant who marks them down as shown in Figure 60. The Σnd, Σnd^2, and Σnd^3 are determined. From these, $d_1 = \Sigma nd/\Sigma n$, $d_3 = \Sigma nd^3/\Sigma nd^2$, $D = \sqrt[3]{\Sigma nd^3/\Sigma n}$, S, N, and U can be calculated, if it is assumed that $\sigma/\nu = 6$.

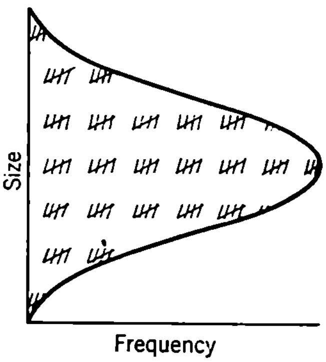


Fig. 60. Quick Method for Plotting a Frequency Curve

Particle Size with Dark Field. Some investigators prefer to use dark-field illumination for making particle-size determinations. Undoubtedly, this type of illumination shows more fine particles, but this has very little effect on d_3.

The main use for dark field is in the slit ultramicroscope where it is necessary to *count* (not measure) the number of particles present in a known volume of the dispersed phase. When dark field is used for *measuring* the diameter of the particle image, the measurement will be a little too large on account of the loss of numerical aperture arising from the stop placed in back of the objective. If this stop is not used, the field does not get black, and the finest particles will not be seen.

Particle Size with Ultraviolet Light. This is one of the most efficient forms of microscopy to be developed, yet one that has not received the attention it deserves. The microscopical equipment for this work consists of a source of monochromatic ultraviolet light, a quartz condenser, quartz slide and cover glass, a quartz objective, and a quartz eyepiece. For rough adjustment the intense series of magnesium spark lines at 0.280 micron is employed.

The final photograph is taken with the weaker but monochromatic cadmium line 0.275 micron. This illumination seems to bring out just as many particles as dark field does, but each particle image is small and sharply defined.

The apparatus for using ultraviolet light necessitates a monochromator consisting of two quartz prisms, one cut from a right-hand and one from a left-hand crystal. It also demands that strip photographs be taken through the focus. The fine adjustment is then turned back to the exact position used where the strip photograph showed the best focus to exist. This makes the process complicated, but the results pay for all the trouble taken in acquiring them.

The ultraviolet microscope was developed by Köhler in 1907. These instruments are difficult to get. Other instruments have been built where glass is used instead of quartz; but the wave length, although in the ultraviolet, is considerably greater than 0.275 micron. The light source is a mercury lamp, and the line selected is one to which glass is transparent.

CHAPTER

16

Measuring Particle Size with the Electron Microscope

This constitutes practically a new branch of the art of particle measurement. It is a tremendous step forward in the study of colloidal particles in the range from 0.1 to 0.004 micron.

Fundamentally the electron-microscope method does not differ in principle from any other microscopical method for particle measurement. Since electrons will not pass through glass, substances other than glass must be employed for supporting the particles. These materials are resin films of such exceeding thinness that they are readily transparent to the electron beam. The ability to select the right resin and the technique for dispersing the particles in it constitute the most important part of the subject now to be discussed.

Mounting the Particles for the Electron Microscope

The methods described here are those developed by Schuster and Fullam.[1] Particles are mounted either (*a*) *on* the film or (*b*) *in* the film. Which method the investigator employs depends on the nature of the problem and the type of particle to be examined. If method (*a*) is used, the particles are dusted on or rubbed on, depending on how the film is made. If method (*b*) is employed, the particles are incorporated in the resin before the film is formed. Before explaining how this is done we must describe the nature and composition of the film and how it is formed.

The Mounting Film. The film should be 100 to 300 angstroms thick, if it is to be sufficiently transparent to the electron beam and at the same time have necessary supporting strength. The films are supported on ⅛-inch disks of metal, nickel-plated copper screen, or on calendered screening of stainless steel, phosphor bronze, or copper. The size of the hole varies from 20 microns for the electrolytic screens to over 100 microns for the woven screens.

According to Schuster and Fullam:

1. The film must be as thin as possible without its weakening too much.
2. The film must show no structure of its own.
3. An ideal film is one that breaks under the full intensity of the electron beam but holds together under intensities sufficient to give a clearly visible image on the fluorescent screen of the microscope.
4. The larger the particle, the thicker the film must be for proper support.
5. Paralodion is the most generally used resin; but greater toughness and heat resistance is given by Polyvinyl formal polymer (Formvar 15/95, grade E).

Two methods are employed for making films: spread films and cast films.

SPREAD FILMS. The resin is dissolved in a suitable solvent. A small amount of this solution is dropped onto a clean water surface and allowed to spread. The solvent evaporates, and the resin solidifies. The film is then picked up on a screen by means of a special annular tool or a glass microscope slide. The tool or slide is inserted *under* the film and then carefully raised. The thickness of the film is regulated by the concentration of the resin solution, by the volatility of the solvent, and by the spreading coefficient of the solution on water.

Paralodion dissolved in methyl, ethyl, amyl, or cellosolve acetate spreads well. Formvar (5%) dissolved in dichlorethylene or in propylene dichloride also spreads well. However, Formvar dissolved in ethylene dichloride or dibromide does not spread, but forms lenses on water. Formvar dissolved in ethylene dichloride can be made to spread on water with a wetting agent such as aerosol OT or oleic acid.

The water bath on which the films are spread is contained in a rectangular Pyrex dish coated inside with a layer of paraffin. The water meniscus protrudes above the edge of the dish and, consequently, can be swept clean with a paraffin-coated glass rod.

CAST FILMS. The spread-film method is substantially the method recommended by the manufacturers of the electron microscope. The cast-film method has been developed practically entirely by

Schuster and Fullam and their coworkers. This method has many uses and should be mastered by any investigator who contemplates making a serious study of electron-microscope technique.

The cast film is made directly on a microscope slide or on any other suitable piece of glass. Resin solutions, 0.2 to 0.4% by weight, are made in very volatile solvents. A solution is taken in a long narrow pipette (made by drawing out a piece of glass tubing) and gently expelled onto the slide. It is then spread out quickly, the long narrow shank of the pipette being used as a spreader. This is done with a sideways motion of the pipette. Streaking is eliminated by holding the slide vertically in an atmosphere of the solvent, in a jar or beaker where it drains until dry. Ethylene dichloride solutions must not be allowed to turn acid, or they will form weak films that are difficult to strip.

Care must be taken in the selection and cleansing of the slides. They must be free from scratches, cleaned with soap and water, rinsed, and stored in distilled water. They must be handled only with forceps. Before using, the slide is drained, polished with fine magnesium powder, and then wiped with a clean soft cloth.

After the film has been cast and dried, it is loosened around the edges of the slide and cut into quarter-inch squares by scratching with a needle. When lowered into the water bath, glass side down, the film peels and floats off. Breathing on the sample before and during peeling facilitates the process. If interference colors appear, the film is too thick. A grey of the first order is the heaviest film permitted. The best films are nearly invisible on water.

Dry Mounting. The pigment can be dusted either on the film-covered screen or on the film-covered slide. If the last method is employed, the slide can be examined with an ordinary microscope and some desirable spot selected. This area is then covered with a screen which is kept from slipping with a small drop of rubber cement. The screen and attached film are peeled off the slide together.

Wet Mounting. Quoting from Schuster and Fullam.

> Any powder that can be dispersed in a volatile liquid which does not dissolve the film on the screen can be mounted by placing a drop of the suspension on a film and allowing it to dry. To keep the particles from clumping together, some form of vibration must be applied. Or the investigator can use quick drying in liquid air, or a dry ice–alcohol mixture and then sublime the ice under high vacuum.

The Dispersion of Powders

Turpentine Dispersion. A standard turpentine dispersion is made on a microscope slide. This has been described elsewhere. The slide is then flooded with a dilute resin solution, drained, dried, and stripped onto water. The particles are imbedded in the film and come off with it. This method is well suited for particles of 0.5 micron and upwards. This method can also be reversed; that is, the film can be laid down first and the particles dispersed on it with a dispersing rod. The film is easily torn, however, but pieces as small as $\frac{1}{16}$ inch square are all that is necessary for the electron microscope.

Mill Dispersion. Pigments can be mechanically dispersed in such apparatus as ball, colloidal, rubber, and roller mills. The size of the sample must be large, which is often an inconvenience. Furthermore, contamination can easily take place under such circumstances. Mill dispersions are not, as a rule, recommended.

Spatula Dispersion. These are made with the edge of a stiff spatula drawn over a flat white glass table with a fine-grain "suede" finish. The table is first cleaned and then resurfaced. A no. 600 carborundum is recommended for this purpose. This step is followed by cleansing with a cleaning powder and then rinsing liberally with water.

The graininess of the surface is likely to be such that coarse aggregates will be broken down. The dispersing force arises from a shearing action and is accentuated by using a highly viscous dispersion medium. This high viscosity is obtained by the volatility of the solvent employed in dissolving the resin. The powder is mixed into this solution and then rubbed out with the edge of the spatula. Just before going to dryness the mixture has a tarlike consistency. The spatula is tilted in the direction of the rubbing. An area of a few square inches is used for this purpose. The material is worked until it becomes too stiff to manipulate. If the mixture becomes too dry before satisfactory dispersion is attained, then more vehicle must be added and the rubbing continued. Normally the rubbing time for a good dispersion is approximately 30 minutes for $\frac{1}{2}$ cc of mixture. The pigment–vehicle ratio to be employed depends on particle size. The smaller the particle, the smaller the ratio. Thus, a gas black will require 1 to 2 mg for $\frac{1}{2}$ cc of 10% resin solution. A basic carbonate of white lead requires a bulk as large as the resin solution.

Mounting the Dispersion

After the dispersion is obtained, a film suitable for the electron microscope must be made. The method to be selected depends on the nature of the substance to be studied.

Cast Mounts. A small amount of the resin dispersion is dissolved in a suitable solvent and cast on a microscope slide. If the film is found to be too thick, the solution is diluted until it gives a film that is just right. Any further dilution causes it to break when peeled onto water. This method is the one that should be used for gas blacks and organic pigments. Formvar in ethylene dichloride is usually employed because of its superior toughness. Pigments that flocculate readily should not be mounted in this way unless the material can be deflocculated by changing the solvent or resin. Very large particles might settle out before casting can be accomplished, in which case another method must be used.

Spread Mounts. This is a method derived from the one originally described in the RCA electron microscope instruction book. It is useful for particles ranging from 0.2 to 2.0 microns. The material is dispersed as described in the previous section. This is mixed with a solvent of positive spreading coefficient and allowed to evaporate until it reaches the consistency of thin cream. This material is then spread on water by drawing a drop of it rapidly across the surface with a spatula. Screens are placed on selected areas, lifted, and dried as usual. Such a film often contains holes.

Drawn-Down Mounts. This method has the widest application of any of those used for mounting dispersed powders. The former dispersed (in resin) pigment mixture is dissolved in a vehicle of volatility equal to or greater than that employed in spreading films on water. This material is stirred and allowed to evaporate to the consistency of heavy cream. It is then drawn on a slide with a spatula, using a series of short strokes. It is now dried, cut into squares with a needle point, and floated off onto water. A somewhat higher pigment–resin ratio is used than with other methods. The sample shows fewer holes and less flocculation. The particles are mechanically deflocculated (by the series of short strokes) and fixed in position by drying before they have time to reflocculate.

DRAWDOWNS IN LIQUIDS. Materials of large particle size (1 to 10 microns) are mounted by a variation of the drawdown procedure. The particles are wetted with a very small amount of a high-boiling hydrocarbon, such as dibutylphthalate, and rubbed out on the dispersion table. They are then drawn down on a film-covered slide by using short strokes. Next the film is floated onto water and mounted on a screen with large holes (because the particles are very large). The hydrocarbon and dibutylphthalate are practically nonvolatile at atmospheric pressure and room temperature but disappear completely in the high vacuum of the electron microscope.

This type of dispersion is not so complete as in the resin draw-down method because of the low viscosity of the mixture. It is well suited, however, for the stereoscopic study of large particles in distinguishing between flat plates and thick ones.

Suspensions. Suspensions of pigments in semivolatile and nonvolatile media, such as paints and printing inks, can be examined with the electron microscope when mounted by smearing on film-coated slides. The smear must be made very thin for, otherwise, the vehicle would be completely opaque to the electron beam. Some fuzziness must, naturally, be expected.

PART IV

Particle Groups
Rheological Structures

CHAPTER 17

The Nature of Structure

In Part III, the particle was studied as a complete unit in itself, performing certain functions of its own and having certain measurable attributes. In Part IV, particle groups or aggregates will be investigated. If the particle aggregation is continuous and homogeneous throughout the material, it is referred to as "structure." Briefly, *a structure is an aggregate of particles.* The individual particles of the structure can be molecules, micelle, microscopic particles, or macroscopic particles.

Obviously, liquids and gases possess structure from this viewpoint, but theirs is not the kind usually visualized when one is thinking about structure. The difference is that normally the term "structure" implies a kind of network, held together by linkage forces, imparting an amount of rigidity to the material. In liquids and gases the linkage forces are negligible, and, consequently, such materials appear structureless. For completeness, however, liquids and gases are included in the list of materials possessing rheological structures. So that no misunderstanding arises, the gas and liquid type of structure is classified here as "loose," and the rigid type as "connected." A table of structures follows:

RHEOLOGICAL STRUCTURES

A. Loose Structures.
- 1. Newtonian.
    - (*a*) Liquids.
    - (*b*) Gases.
    - (*c*) Suspensions (solid particles, highly diluted)—Einstein model.
      (liquid particles, highly diluted)—opposite of the "crowded system."
    - (*d*) Suspensions, deflocculated (in Brownian motion).

2. Pseudoplastic.
    - (*a*) Solutions of resins, rubbers, bitumens.
    - (*b*) Heavy oils.
    - (*c*) Resins, bitumens.
    - (*d*) Glasses.
3. Dilatant materials.
    - (*a*) Particle–vehicle suspensions.

B. Connected Structures.

4. Plastic
    - (*a*) Bingham bodies (crowded flocculated systems—solid microscopic particles).
      (crowded flocculated systems—liquid microscopic particles).
    - (*b*) Jellies (crowded systems—solid submicroscopic particles).
    - (*c*) Soaps (from chemical reaction in a suspension).
    - (*d*) Plastics, fibers, and rubbers (as described by Mark).
    - (*e*) Metals.
5. Brittle materials.
    - (*a*) Soft aggregates.
    - (*b*) Hard aggregates.
    - (*c*) Complexes (lithopone, lakes).
6. Thixotropic materials.
    - (*a*) Suspensions (Bingham bodies).
    - (*b*) Heavy oils, etc. (Newtonian-like and pseudoplastic-like).
7. Two-dimensional flocculates.
    - (*a*) Bingham bodies.
8. Artifacts.
    - (*a*) Rolled aggregates.
    - (*b*) Residues from evaporation.
    - (*c*) Magnetic structures.

Loose Structures

Newtonians. LIQUIDS AND GASES. In liquids and gases the structural units are molecules. In liquids, van der Waals forces create cohesiveness without producing a connected structure; hence, the material lacks observable rigidity. The resulting looseness of structure allows any layer of the liquid to move relatively to its adjacent layers without causing internal rupture in the system. This means that there is no structural breakdown during flow. That is one of the prerequisites for Newtonian flow. There is still another requirement. The particles must not be elongated, so that flow orientation or alignment takes place. When both these conditions are fulfilled, it is reasonable to suppose that the rate of shear is then proportional to the stress and that the consistency curve is linear, starting from the origin. Photomicrographs of such structures are not possible.

The structure of liquids produces viscous resistance by the interaction of molecular forces between adjacent planes. This is a different procedure from that employed by gases where the transfer of momentum is caused by (*a*) diffusion of the molecules in a direction perpendicular to the direction of flow, and (*b*) *elastic* collision between the molecules. By raising the temperature of a gas (keeping the volume constant), elastic collisions and diffusion are increased. This causes an increase in the viscosity of the material. When the temperature of a liquid is raised, the viscosity invariably *decreases.*

There have been numerous empirical equations set forth showing the relation between viscosity and temperature, none of which has been universally accepted. The only safe conclusion is the one given in the preceding paragraph. Bingham's conception is that in highly rarefied gases viscous resistance is entirely diffusional, whereas in very viscous liquids it is (what he calls) "collisional." Evidently, this phenomenon is not the elastic collision encountered in gases, but simply contact of a molecule in one layer with a molecule in an adjacent layer while the layers are moving relatively to each other. In materials that are not extremes, he visualizes viscous resistance as composed of the sum of diffusional and collisional viscosities:

$$\eta = \eta_{\text{dif}} + \eta_{\text{col}} \qquad (186)$$

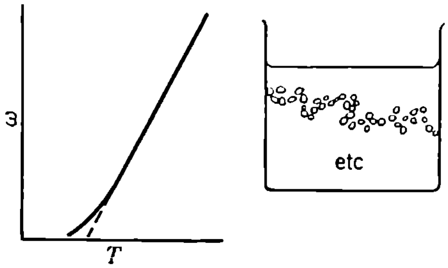


Fig. 61. Bingham-Body. Structure Continuous

NEWTONIAN SUSPENSIONS. Suspensions are of two kinds—one where the suspended particles are solid, the other where they are liquid. If the suspension is a "crowded" system so that it forms a continuous structure from one side of the container to the other (Figure 61), then the resulting material is most likely a Bingham body. However, if the pigment–vehicle ratio is sufficiently small, then the structure will be discontinuous, and shear will take place in the clear Newtonian liquid spaces. The suspension as a whole will be Newtonian (Figure 62). This conclusion follows whether the particles are solid or liquid. Such suspensions are easily examined in capillary tubes with a microscope. In the case shown in Figure 62, the small flocculates simply rotate without shear or plastic flow, when submitted to a shearing stress.

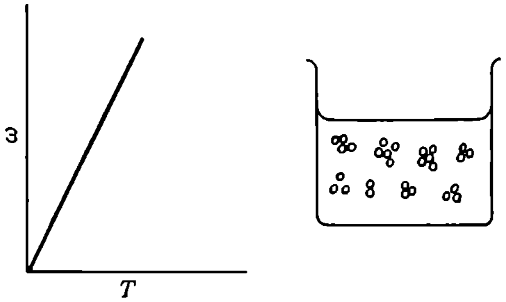


Fig. 62. Newtonian Suspension. Structure Discontinuous

Suspensions of liquid particles are called *emulsions.* The particles are spherical, and as a rule large enough so that medium microscopic power is sufficient for inspection. When two liquid particles come in contact with each other, they do not necessarily coalesce, forming a single large particle. During contact they can remain intact and form large flocculated groups. They act as though they possess a protective coating that prevents coalescence. Milk is a well-known example of this type. Certain kinds of inks used for printing on fabrics have, at times, water globules coated with resins. In this case the globule never appears to be quite spherical. Often it will contain a flat side, particularly if it has been in contact with another globule.

In the case of contacting globules, an optical illusion is often produced (with the microscope) that should be pointed out. If two irregular edges are held close together (but not in contact) and placed close to the eye, they will appear to join at all protruding spots. (See Figure 63a.) This is due to the phenomenon called "diffraction." Diffraction bands are formed at the edge which merge when the two edges are sufficiently close together. The same thing happens when two globules touch (Figure 63b). When a globule becomes surrounded by other globules, the necking illusion will appear like small globules placed between the big ones (Figure 63c). When it is badly out of focus, the design in Figure 63c changes so that the particles, instead of appearing spherical, seem hexagonal (Figure 63d). By careful focusing and adjustment of the illumination, so that diffraction is reduced to a minimum the necking illusion will vanish (Figure 63e).

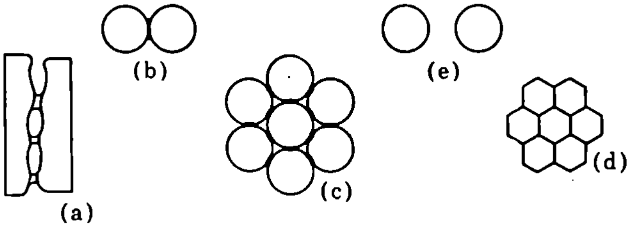


Fig. 63. Illusions Sometimes Arising When Particles Get Close Together

Deflocculated Suspensions. If the vehicle sufficiently wets the pigment, the suspension becomes deflocculated. By "wetting" is meant a decrease in the free energy of the system when the particle is immersed in the vehicle. If the interfacial tension drops to zero, the contact angle also becomes zero. The attraction between the particle and the liquid can go farther than this, in which case it will cause spreading. If the material is completely deflocculated, it can have a comparatively high pigment–vehicle ratio and still have Newtonian flow. Under the microscope the particles will be in Brownian motion. It is important that rheologists know something about this phenomenon and are able to recognize it when it exists.

Suspensions in Brownian Motion. Brownian motion was discovered by the botanist Brown during the early part of the last century. It is a particular type of movement exhibited by small vehicle-suspended particles and is readily seen on microscopic examination. A number of theories have been advanced as an explanation. The classical or kinetic theory is the one most generally accepted. This theory visualizes a suspended particle as being bombarded on all sides by the molecules of the suspending vehicle. When the particle is large, the number of bombarding molecules is likewise large and uniformly distributed over the particle surface so that the net result when the particle is pushed in any one direction is zero. When the particle is very small, an exact balance no longer exists, for the number of bombarding particles is also small, and their distribution over the surface of the particle is uneven. The result is that in any particular instant one side of the particle receives a greater bombarding force than any of the others; the net result is a particle motion in the direction of maximum bombardment.

Theoretically, all suspended particles are in Brownian motion, except at absolute zero. It is the kinetic energy of the molecule (due to heat) that is transferred to the particle, causing it to move. However, it is only when the particle is sufficiently small that this motion can be observed with a microscope. The best size for observation is about 0.2 micron. When the particles are much smaller than this, they are difficult to see unless dark-field illumination is employed. If the particles are much larger, the amplitude of the motion becomes small and correspondingly difficult to observe. It should be mentioned in regard to this point that particles as large as 20 microns and over can be made to exhibit a visible Brownian motion, if they are not too dense and are suspended in a liquid of high molecular weight. Methylene iodide is such a liquid.

Brownian motion is a particular type of motion that must not be confused with a lateral or streamline flow which often occurs when a cover glass is placed on a suspension dropped on a microscope slide. Brownian motion is a vibratory motion in which the particle seems to cling to a given central spot for an appreciable time. Eventually, it will leave that spot; but its lateral progress is a comparatively slow one.

From what has been stated, it follows as a result of the classical theory that visible Brownian motion is simply a matter of having small enough freely suspended particles (that is, not flocculated). A law of Brownian motion has been calculated by Einstein [2] and Smoluchowski [13] and experimentally verified by Perrin and Lottermoser [10] and Svedberg: [14] *The mean square distances traveled by the particles in Brownian motion are proportional to the duration of their motion.* Naturally, the viscosity of the vehicle has a retarding action on this motion, and this fact must always be taken into consideration when suspensions for Brownian motion are examined.

The kinetic theory of Brownian motion cannot explain the cessation of movement except by an increase in particle size or an increase in the viscosity of the vehicle; consequently, when it was discovered that the addition of certain electrolytes stopped Brownian motion under conditions where flocculation did not seem to occur and where the change in viscosity was negligible, it was thought that the classical theory was inadequate. A new theory, the ionization theory, was suggested. This was proposed in 1930 by Taggart, Taylor, and Knoll.[15] As considerable work has been done on it, it is suggested to the reader that he form no opinion without a thorough study of the original papers. Kellogg,[6] who has made an exhaustive examination of the theory, summarizes it as follows:

> This theory accepts the picture of suspended particle surfaces as having an anchored ion and a free swimming or counter ion. It is postulated that Brownian movement is caused by the impacts occurring during the equilibrium exchange of ions (between the ionized and unionized states) at the particle surface. Furthermore, any condition that either prevents surface ionization (an extremely insoluble surface compound) or prevents anchorage of an ion on the surface (very soluble surface compound) will stop the Brownian motion.

Kellogg after extensive study and investigation has found that, in all cases where Brownian motion has ceased (for the addition of electrolytes), adhesion of the particle either against the cover glass or against the microscope slide has occurred. All particles that remained freely suspended still had Brownian motion.

It should be apparent that the question of the existence or non-existence of Brownian motion can be an important one to the rheologist, especially if he is interested in the study of structure. The presence of Brownian motion means complete deflocculation, and such a loose structure should give a Newtonian rather than a Bingham-body consistency curve. In the case of a very high pigment–vehicle ratio, even though the entire material seems to be in Brownian motion, there is always likely to be at least a slight yield-value intercept. (See Figure 64.) Curve *a* is a flocculated Bingham body with no evidence of Brownian motion. Curve *b* is a deflocculated material with a high pigment–vehicle ratio. Curve *c* shows complete deflocculation and full Brownian motion. Materials of the pigment–vehicle type can be photo-

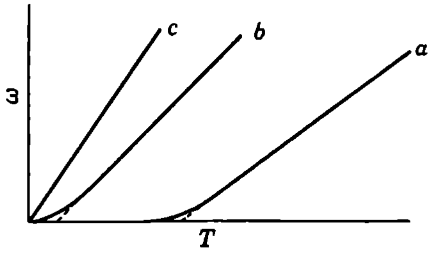


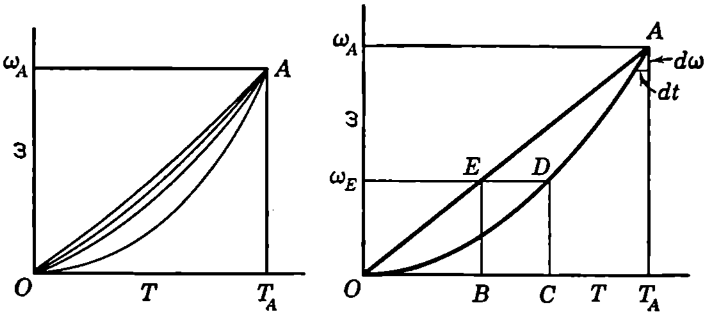
Fig. 64

graphed easily enough even if the pigment is in Brownian motion. Time exposures can be made. The blurring resulting from the motion is usually too slight to be noticed. Probably, the reason is that the pigment particle, during the few seconds required to make the exposure, remains approximately in the same spot. Its numerous excursions to the side are of such short duration that no evidence of them is recorded on the photographic plate.

Pseudoplastics. HEAVY SOLUTIONS OF RESINS, RUBBERS, ASPHALTS, TARS, AND PITCHES. Pseudoplastics, in general, constitute probably the largest of the rheological groups. Unfortunately, most of these materials possess a structure that is submicroscopic to both white light and electron microscopy. The structure that is revealed is mostly of the nature of carbonaceous particles. There are some electron microscopists, however, who believe that they have electron-micrographed resinous molecules. The most promising possibility in that direction is in the structure found in replicas taken from resin surfaces.

If electron microscopy has revealed little of the structural nature of pseudoplastics, rheology has compensated for this deficit to a considerable extent. This is seen by a survey of the literature. The great majority of the rheological papers published in recent years seems to be in regard to pseudoplastic materials. In fact, pseudoplastic rheology has been developed so extensively that it practically constitutes a science within a science. The men who have enriched this field by their work have become internationally known and correctly rank today among the world's top rheologists. Yet in spite of all that has been accomplished, there is still a "fly in the ointment" that makes pseudoplastics the most difficult of the rheological groups to handle. This "fly" is the absence of an equation, *derived from rheological concepts*, that will permit the pseudoplastic consistency curve to be interpreted in terms of parameters similar to "viscosity" and "yield value." Without such a consummation it is difficult to understand the exact meaning of pseudoplastic measurements. There are two logical ways, however, to avoid the issue: one, by dilution until the pseudoplastic gives a Newtonian curve; the other, by presenting the entire curve instead of a meaningless number in its place.

Though the afore-mentioned methods might be logical, they are hardly satisfactory. To dilute a rheological material is to change its consistency, and that, usually, is not permitted, especially in plant-control work. The presentation or recording of the entire consistency curve not only is awkward but also gives an experimental result difficult to talk about, especially when comparisons are being made. There is a third way to avoid the issue, which is not logical, but, nevertheless, is used extensively, the method of recording the so-called "apparent viscosity." The apparent viscosity at a given point on the consistency curve is the stress divided by the rate of shear. In Figure 65a this would be OT_A/T_AA. This figure shows that an infinity of pseudoplastic curves can be drawn between the points O and A, all of which will have the same apparent viscosity at the same shearing rate ω_A. Apparent viscosity does not distinguish between these curves and, consequently, is valueless as a control measurement.



(a) (b)

Fig. 65

Every rheologist should try to clarify in his own mind the meaning of "apparent viscosity." By definition (from Newton's concept) the coefficient of viscosity is numerically equal to the stress in dynes that will produce a unit velocity gradient. (Refer to Figure 65b.) Let ω_E be the rate of shear that corresponds to a unit velocity gradient. Then, for the Newtonian curve OEA, the line OB will be equal to the coefficient of viscosity. Now the apparent viscosity of the pseudoplastic ODA at the shearing rate ω_A is OT_A/T_AA, which is equal to OB/BE. Since BE is unity, the apparent viscosity of the pseudoplastic is OB, which is the same as the viscosity of the Newtonian. Hence, the apparent viscosity of a pseudoplastic is *the viscosity that it would have if it were a Newtonian material with a consistency curve passing through the point of measurement.*

Now, if the pseudoplastic were a Newtonian (which it is not), there would be no argument; so the entire conception of apparent viscosity is based on a contradiction. Since *CD* is equal to unity, the line *OC* corresponds to the Newtonian viscosity, which is considerably greater than the apparent viscosity *OB*. If the tangent $dt/d\omega$ at the point *A* were used for apparent viscosity, then, the definition would be changed to: *The apparent viscosity is the viscosity the material would have if it were a Bingham body, etc.*; which is also an obvious contradiction. The basic trouble is that a nonlinear curve cannot be defined by two points—the origin and the point of measurement.

The pseudoplastic curve is always convex toward the stress axis. This departure from linearity could arise from accumulated heat, or from thixotropic breakdown, or from a decrease in the coefficient of viscosity brought about by structural changes induced by increasing shearing rates. Carefully controlled experiments have eliminated heat increase as a possibility. The fact that the pseudoplastic curve forms no loop (except possibly at very high rates of shear) indicates the absence of thixotropic breakdown. This leaves only the viscosity decrease arising from structural change. This explanation seems to be universally accepted.

The types of substances that constitute the bulk of pseudoplastic materials are those composed of long molecules. When pseudoplastics are not forced to flow, the molecules are randomly oriented so that molecular entanglement is at an optimum. The coefficient of viscosity is, then, also at its maximum. Laminar flow causes an alignment of the molecules, thus producing a decrease in the amount of entanglement. This change in the structure gives less viscous resistance to flow, and, consequently, the consistency curve bends upward (away from the stress axis).

A great many investigators have attempted to fit empirical equations to the experimental pseudoplastic curve. These equations sometimes give a good reproduction of the experimental data; but, unfortunately, they have no rheological interpretation.

In the system given in this book, two concepts of flow have been presented. These are the Newtonian, where the rate of shear is directly proportional to the shear stress; and Bingham's, where the rate of shear is proportional to that part of the shear stress in excess of the yield value. The Newtonian concept, when applied to capillary flow gives an instrumental equation relating volume of flow per second to pressure. When applied to Couette flow, it gives a similar equation, showing the relationship between angular velocity and torque. These equations, however, are valid only for that class of materials possessing a "loose" structure and molecules that do not align when flowing. This class has been called "Newtonian." When the structure of the material is "connected," and yield value (or elastic limit) exists as a consequence, Newton's concept must be replaced by Bingham's. This procedure gives an instrumental equation that has been found valid for Couette flow in the region where laminar flow is complete. This is sufficient for calculating plastic viscosity and yield value.

When no yield value exists, and the molecules align on flow, then neither the Newtonian nor the Bingham concepts can be developed into satisfactory instrumental equations. No fundamental concept exists that will define such a material rheologically and lead to a valid instrumental equation of flow. Rabinowitsch [11] and Weissenberg [16] have employed an indeterminate function, $dv/dr = f(F)$, in the calculation of an instrumental equation of capillary flow and determined its value from experimental results. By this means they obtained the empirical equation,

$$\frac{dv}{dr} = 8aF + 10bF^2 \tag{187}$$

where F is the stress at the wall of the capillary, and a and b are constants of unknown significance. Their curve obviously starts from the origin. If 8 is dimensionless, a is probably the coefficient of fluidity. That is about all that can be said for Equation 187.

Reiner, from the study of benzene solutions of rubber (by Herschel and Bulkly) has proposed the following modification of Equation 187:

$$\frac{dv}{dr} = aF + bF^2 - CF^3 \tag{188}$$

According to Mark: [7]

to express the hydrodynamics of a solution of high polymers it appears necessary to employ, instead of the Newtonian expression, one of the forms

$$\frac{dv}{dr} = aF + bF^2 + cF^3 + \cdots \tag{189}$$

There are many other empirical equations that have been proposed for pseudoplastics; but the present author feels that the safest course to follow is to record the entire consistency curve and, if desired, calculate the Newtonian viscosity as near to the origin as possible (if this can be done without sacrificing too much accuracy). Nutting,[8] de Waele,[1] and W. Oswald [2] have proposed well-known empirical equations, which the reader would do well to investigate.

HEAVY OILS. Light mineral and vegetable oils give linear consistency curves and are generally correctly classified as Newtonians. With increasing molecular weight and chain length the situation changes, and, consequently, heavy oils are invariably pseudoplastic. At high shearing rates, Weltmann [17] has produced evidence showing that such materials give a hysteresis loop, indicating a condition like thixotropy to be present. Because of this departure from Newtonian behavior, it is inadvisable to employ heavy oils for calibration purposes. It does not matter if the rate of shear for the stated viscosity is known or not, for rate of shear varies from bob to cup and from the axis of the capillary to the capillary wall.

RESINS AND BITUMENS. Microscopically, the resins show nothing in the nature of a structure. The natural resins contain visible impurities, but not in sufficient volume to constitute structure. The real structure of resins is molecular and, therefore, submicroscopic. The consistency curve of a firm resin cannot, usually, be obtained with a rotational viscometer. The material is too viscous for the easy operation of such instruments. Recourse must be had to a parallel-plate type of viscometer such as the Tackmeter. The method employed is as follows:

Warm the sample slightly so that it can be rolled into a pellet approximately the size of a shoebutton. The pellet is then placed between the plates of the viscometer (Tackmeter) and sufficient weight applied to squeeze the pellet out flat. The ultimate thickness of the sample must be noted. A weight is placed at the end of the lever arm and the squeezing weight removed. Necking down commences immediately. The time required for the stop to be reached is taken. This process is repeated 5 to 10 times. A curve is plotted—weight versus the reciprocal of the time taken to reach the stop (the setscrew, Figure 35). The consistency curve thus obtained will be of the pseudoplastic type. Materials with an initial viscosity as high as 200,000,000 poises can be run easily by this procedure. Viscosities much higher than this, no doubt, can be handled, the only requirement being the ability of the material to adhere firmly to the metals of which the plates are made. The rest is a matter of time. The more viscous the material, the greater the length of time required for the measurement, other factors remaining the same.

The bitumens include the asphalts, tars and pitches. These are dark-colored materials and owe their color to small dispersed particles of carbon or carbonaceous substances. The carbon particles can be seen with the microscope, but it is necessary to squeeze the material into a thin enough sheet between the microscope slide and cover glass before the particles become visible. The squeezing is done between the thumb and forefinger. Slight heating of the slide on a hot plate facilitates this operation considerably.

Bitumens are usually pseudoplastic. Either a rotational viscometer or a parallel-plate viscometer can be used for obtaining their consistency curves, the one selected depending on the magnitude of the viscosity. Penetrometers, falling ball, and efflux viscometers are also employed. Some investigators claim that evidence of thixotropy exists in bitumens; but it should be remembered that the term "thixotropy" is often applied to any material that is non-Newtonian.

GLASSES. Glasses show no microscopic structure rheologically. They belong, in all probability, to the pseudoplastic group. The term "glass" is synonomous with such expressions as "vitreous substance," "vitreous solid," "supercooled liquid." The vitreous state has been defined by Huggins[4] in the following way.

> If a substance possesses a degree of rigidity comparable to that possessed by typical crystalline substances, yet lacks the dependence on direction (characteristic of the crystalline state) of such properties as hardness, rate of growth, and solution, and (sometimes) refractive index, it is said to be in the vitreous state.

Again

> the vitreous state is that state in which the arrangement of the atoms, ions, or molecules possess a *permanence* similar to that of the crystalline state; and a *randomness* similar to that characteristic of liquids.

In any condensed system—crystalline, vitreous, or liquid—there is a tendency toward regularity in atomic arrangement in the neighborhood of each atom. For instance, a silicon atom can be surrounded by four oxygen atoms at a distance of about 1.6 angstroms; and each oxygen atom can have adjacent to it either two silicon atoms or one silicon and one other atom of another element. This structure constitutes a local regularity. If, in addition, there is a long-distance regularity, then the substance is classified as crystalline; otherwise, it is vitreous or liquid.

Rotating-cylinder viscometers have been used by English[3] for measuring the viscosities of glasses in the range of 10^3 to 10^7 poises. Lillie[5] rotated the outer cylinder, measured the torque on the inner cylinder, and measured viscosities to 10^4 poises. By turning the outer cylinder through a small angle and timing the aperiodic return of the inner cylinder, he measured viscosities from 10^3 to 10^8 poises. Viscosities greater than 10^8 poises have been measured by observing the rate of deformation of a glass rod under a given force; other investigators have measured the rate of twisting under a known torsion, and still others by measuring the rate of extension under a known load.

All evidence indicates that the consistency curve for glass passes through the origin, and that there is no region of true plasticity. Lillie[5] has measured viscosities as high as 10^{16} poises.

Dilatant Materials. PARTICLE–VEHICLE SUSPENSIONS. One of the most remarkable types of loose structure is found in the so-called *dilatant* materials. These substances, which are particle suspensions, were first observed and described by Reynolds[12] in 1885. The characteristic feature of dilatancy is that the material possessing it will harden when submitted to shearing action. On examination it will be found that such materials have a high degree of Brownian motion (if the particles are small enough) and that the particles have settled into a position of "minimum voids." Consequently, any particle disturbance, such as occurs under shear, will tend to expand or dilate the volume of voids, and the result will be an insufficiency of vehicle to fill them; hence, the suspension will take on a dry appearance and harden. As soon as the shearing action stops, the material will revert to its original condition of minimum voids, it will appear wet again, and its consistency will soften. The hardening action is never permanent. Permanency would indicate a chemical reaction, which never plays a part in either thixotropic or dilatant changes.

It is apparent that the dilatant structure is a loose one, for, otherwise, it would be impossible for the particles to settle into a position of minimum voids. Any kind of linkage bond would effectively prevent such a settling. Furthermore, the presence of Brownian motion, which is strikingly apparent in cases of dilatancy, is sufficient evidence that particle linkage does not occur. This means that there is no structural breakdown during flow; consequently, the consistency curve cannot turn upward. In fact, it turns toward the stress axis as the shearing stress increases. This turning is the result of the drying or stiffening action occurring from the expansion of the voids. In Figure 66 is shown a photomicrograph of a dilatant suspension together with its consistency curve.

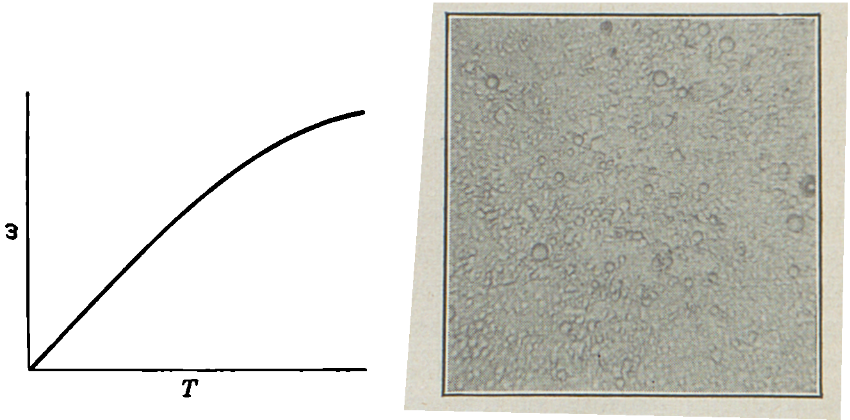


Fig. 66. A Dilatant Suspension and Its Consistency Curve

Dilatancy is frequently found in suspensions like enamels that have aged for some time. During the aging process progressive wetting occurs, causing complete deflocculation. This permits the particles to settle down into the container much farther than they would if flocculated. In addition, Brownian motion facilitates the settling of the larger particles so that eventually they eliminate as much of the voids as possible. The very small particles (in Brownian motion) will probably stay suspended indefinitely. Only the material that has settled into a firm tough layer at the bottom of the container is dilatant. In order to examine it, it is necessary to pour off carefully all the supernatant liquid. If a spatula is now suddenly thrust down into the bottom layer, there will be considerable resistance to penetration. If the spatula is allowed to sink into the layer gradually, there seems to be only slight resistance. The same thing happens when one attempts to stir the layer. Slow stirring meets with comparatively little resistance; fast stirring practically solidifies the material.

Very striking examples of dilatancy have been made with potassium silicate solutions. This material can be made up to a very heavy sticky consistency. If the hand is thrust into it and pulled out slowly, the material adheres tenaciously to the skin; but, if the hand is withdrawn suddenly, it comes out clean and free from all traces of the silicate. Dilatant materials have been made from lead chromates in oil vehicles which under the slightest pressure would crumble like a dry powder, and yet on standing undisturbed were as fluid as mercury. The belief is common that dilatancy is the opposite of thixotropy. That is quite contrary to the rheological ideas embodied in the system outlined in this book. Both thixotropy and dilatancy can exist in the same material at the same time. The author had an example of a clay suspension in water which was quite thixotropic; however, after stirring, the broken-down material had all the characteristic features of dilatancy. The consistency curve of such a material is given in Figure 67. Printing inks are frequently found to be slightly dilatant; but the majority of them, however, are thixotropic.

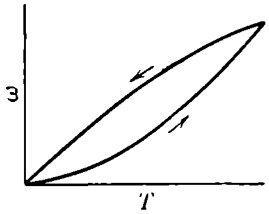


Fig. 67. A Combination of Thixotropy and Dilatancy

CHAPTER

18

Connected Structures

Plastic Materials. BINGHAM BODIES. This is one of the important rheological groups. It includes those materials that are composed of microscopically visible particles suspended in a liquid medium, the particle–vehicle ratio being such that the particle structure (which is flocculated) is continuous throughout, thereby imparting a yield value to the material. Well-known examples of such substances are paints and printing inks. There are many others besides these; but the ones mentioned dominate the field at present. It hardly need be pointed out that our system is more applicable here than to any other part of industrial rheology.

When Bingham first confirmed the existence of an intercept on the pressure axis while working with clay–water suspensions, he called it the "friction." His belief was, at the time, that the intercept gave a measurement of the force necessary to overcome the frictional resistance of the particles before flow started. Later, while he was working on paints in collaboration with the author,[1] it became apparent that flocculation played an important part in the production of the intercept. It was then decided that the term "friction" might not be broad enough to include all the causes for the creation of the intercept, and so the term "friction" was dropped and "yield value" used in its place. However, in the final analysis it might very well be that friction is the sole cause of the intercept, the part played by flocculation being one of an internal pressure holding the particles together, enabling friction to manifest itself. The more strongly the particles are held together (flocculated), the greater would be their frictional resistance (yield value). It seems reasonable to assume that, although it takes work to push one particle away from another, to which it has been adhering, the next particle in its path will exert an attraction on the moving particle of such magnitude as to nullify the work done on it by the externally applied shearing force. The net result in energy input should be zero, and the intercept likewise should be zero. This conclusion follows from the fact that particles are being pushed apart (because of laminar shear) no faster than they are being brought into contact with new particles. Under the circumstances it is difficult to see how yield value can exist unless there is a reason more basic than the force of flocculation. That "reason" could be the friction that the particles exert on themselves during laminar flow.

When the pigment is deflocculated so that the entire suspension is in Brownian motion, yield value is reduced. It might even disappear completely; but there are plenty of such cases where there is also evidence of yield value. The yield-value intercept comes into existence *only when some of the externally applied energy is not consumed in producing flow.* If a completely deflocculated system has a yield-value intercept, then, that part of the energy input (given by the intercept) is either employed in rotating the particles or in overcoming or in tending to overcome their frictional resistance on contact.

The structure of most Bingham bodies is easily observed under the microscope. The examination should be carried out by the technique previously described where a drop of the material is covered with a drop of the vehicle and covered with a cover glass. This glass is pushed down firmly until a good pigment–vehicle edge is produced. Examination of this edge shows the state of flocculation existing in the material. Figure 68 gives a photomicrograph of a Bingham body together with its consistency curve.

There has been much discussion concerning the distance between flocculated particles. The most general conception seems to be that the space is about 0.5 micron. Some investigators, however, have suggested distances as great as 20 microns. It is the author's opinion, after many years' experience in the pigment field, that the distance separating flocculated particles is not only below the limit of resolution of white-light microscopy but even below the limit of resolution of the electron microscope. In other words, the distance is of a molecular order of magnitude.

The electron microscope, however, is the only instrument capable of making a direct attack on the subject of interparticle distance where flocculation has occurred. It should be recalled that the term "flocculate" is applied only to particles suspended in a continuous medium or vehicle. Just previous to the formation of the flocculate, the particles were separate, but suspended in the medium. The particles are brought together (from currents in the medium, arising from milling, stirring, and the like). If the particles touch each other, and there is a decrease in the free energy of the system, a flocculate is formed. The particles will cling together until an outside force can do sufficient work on them to pull them apart.

Van der Waals forces are probably the ultimate cause of flocculation. If so, the small distance through which they operate would indicate that the interparticle space in a flocculate is not large enough to be seen by means of ordinary microscopy. The electron microscope, on the other hand, offers no easy solution to the problem either, for the particles must be suspended in the medium in which flocculation occurs. This medium, whatever it is, is opaque to the electron beam, except in exceedingly thin layers. Furthermore, the vehicle is probably volatile, particularly in the vacuum in the electron microscope. If the particles are greater than 0.1 micron in size, the suspending medium must be at least that deep; but a layer that thick, as stated, is practically opaque. Therefore, only the distances between particles which are considerably less than 0.1 micron have any chance of being examined.

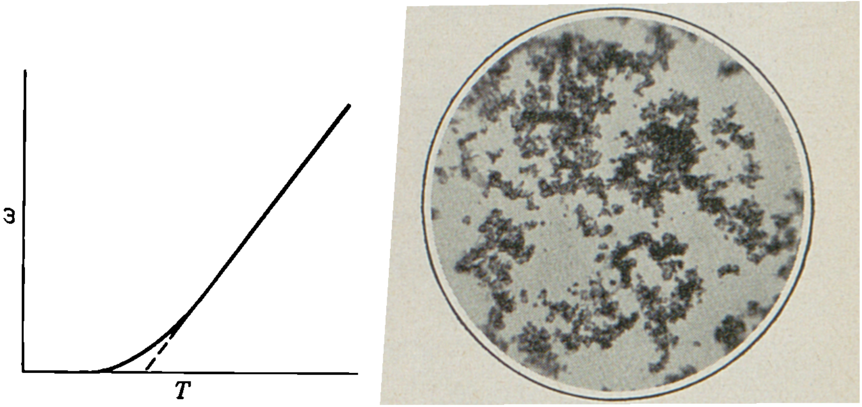


Fig. 68. A Bingham Body Photomicrograph and Consistency Curve

In order to meet the afore-mentioned requirements, the investigator is limited to particles of about 0.05 micron or less and to liquid media that do not volatilize in the vacuum of the microscope. These liquids must cause pigment flocculation, and also wet the supporting resin film so that they can be spread out into sufficiently thin layers. When this is accomplished, the resulting electron micrograph will not be very clearly defined because of the diffusing effect that the supporting film has on the beam. In addition, the electron micrograph should be a stereo pair so that the particles stand out in three dimensions. This is a real necessity, for, otherwise, the observer cannot tell whether two particles are in the same horizontal plane or not. If they are in the same plane, then, the distance between them is the observed length of a line connecting their edge divided by the magnification. (See Figure 69a.) If the particles are in different planes, the observed distance

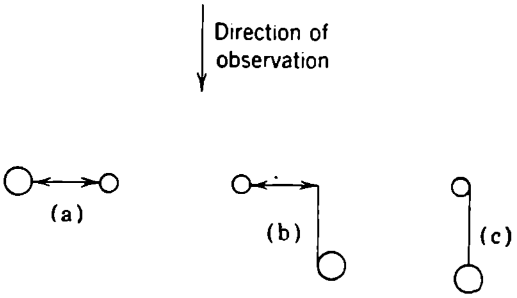


Fig. 69. Arrangement of Particles

will be too small (Figure 69b and c). In Figure 70 is shown a stereo electron micrograph of an iron blue pigment flocculate in a layer of linseed oil film. In examining such a micrograph, the eyes must be relaxed as they are when focused on the horizon. Three pictures will then be seen. The one in the middle will appear in three dimensions.

Bingham-Body Emulsions. The suspended particles of a Bingham body need not be solid materials. They can be liquid droplets, in which case the suspensions formed are called "emulsions." When two droplets adhere, but do not coalesce to form a single larger drop, a liquid flocculate is the result, the same as occurs with pigment particles. Such suspensions produce typical Bingham-body curves giving a yield-value intercept. It is presupposed that the flocculated structure is crowded and continuous. Milk is a good example of an emulsion. Normally the droplets are detached and in Brownian movement. A trace of acetic acid, however, causes flocculation. In this case the system is not crowded, and the suspension would give a Newtonian curve. Butter and many cheeses are systems with a continuous flocculated structure and give Bingham-body consistency curves. Certain printing inks used in the textile industry are also Bingham-body emulsions. The droplets are used to produce a structure that will give the necessary stiffness or body to the material so that the ink will stay on the surface of the cloth, when printed, and not soak into it. Pigment particles are incorporated into these emulsions.

When the continuous phase is water, the suspension is usually referred to as an "oil-in-water" emulsion whether the droplets are oil-like materials or not. When the reverse is true, then, they are called "water-in-oil" emulsions. Because the refractive index of water is only 1.33, it becomes easy to tell which phase—continuous or discontinuous—is water and which is the oil. Stop down the substage condenser until the field is fairly dark, and then focus upward. If the droplets become bright-centered, they have a higher refractive index than the continuous phase; therefore, the continuous phase is water (having the lowest refractive index of practically all liquids). If the droplets become dark-centered, then, they constitute the water phase.

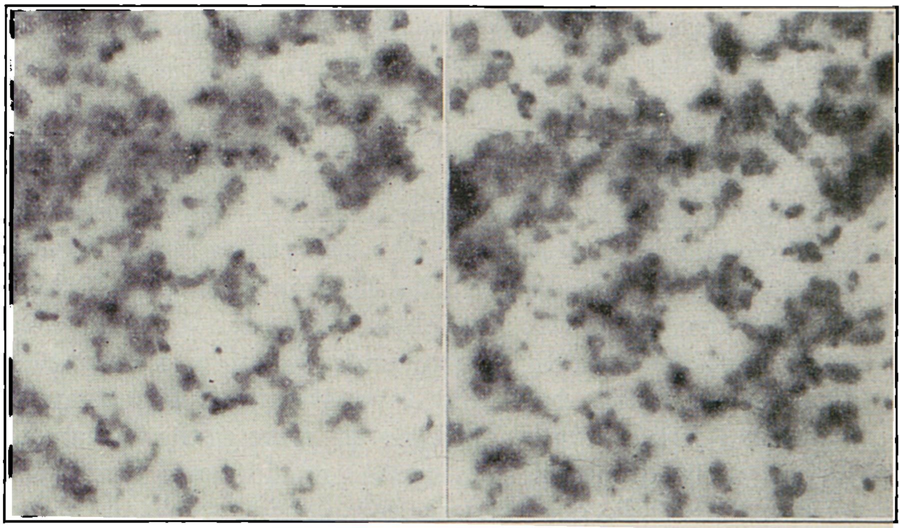


Fig. 70. Stereoscopic Electronmicrograph of an Iron-Blue Pigment Flocculated in a Thin Layer of Vehicle

The shape of the droplet is spherical when observed under the microscope. However, if the cover glass presses on it, it will flatten out, but still retain a circular appearance in the plane perpendicular to the optic axis of the microscope. If it could be viewed in any other direction, it would no longer have circular cross section. It is important to remember this fact in case the particle size of the droplet should be measured. The flatter the droplet, the larger its diameter will be, but its volume has not changed any.

When the droplet is not completely spherical, it is probably not a Newtonian liquid; or, if it is, it has a plastic coating of some kind on its surface. Both cases frequently happen. When water is emulsified into an organic solution of a water-insoluble resin, the droplet will have precipitated on its surface just such a coating as mentioned. This coating might remain invisible, or it might wrinkle, in which case it is easily observed.

A useful technique to acquire is one for examining an emulsion microscopically in order to learn something of the mechanism of its structure. This is carried out as follows: A small drop of the emulsion is placed on the center of a microscope slide. This is then covered and pressed on so that the drop spreads about halfway out to the edge of the cover glass. This edge is then focused on, and a vehicle is allowed to flow under the cover glass until it reaches the edge of the drop. Capillary attraction will accomplish this readily. If the entering vehicle is the same as the continuous phase, then the drop will disintegrate and flow into it. If the vehicle is that of the dispersed phase, no change will take place, the drop remaining intact.

JELLIES. The structures of most jellies have never been seen. The structure of certain soap jellies constitutes one of the few exceptions. These are discussed in the next section. In colloid chemistry a "gel" is a flocculated mass of particles. In this book, the term gel is not used. "Jellies" are suspensions of continuous structure where the particles are usually entirely submicroscopic. The forces holding them together are relatively high compared to the analogous forces existing in a flocculated pigment suspension. This condition of high flocculating force is probably the natural outcome of the very high specific surface of the solid phase.

Although it is convenient to visualize jellies as products similar to pigment suspensions, except with very much smaller particles, the ultimate differences are of degree rather than of kind. Many jellies can be liquefied by heating, a phenomenon that is not nearly so marked in pigment suspensions of high yield values. Jellies of comparatively low solid–liquid ratio often crumble rather than flow when stirred. This is a condition indicating a much higher order of brittleness than found in normal Bingham bodies, unless the pigment–vehicle ratio in this latter case is quite high. Firm jellies show little or no tendency to be thixotropic as compared with Bingham bodies of the pigment–vehicle type.

It is impossible to draw a sharp line of demarkation between the jellies of submicroscopic particles (micelles) and of those where the particles are just visible microscopically, as in the case of certain oxides of iron. One of the first of the thixotropic materials studied was a colloidal suspension of this latter type, but such particles are often close to the borderline of pigments as far as particle size is concerned, and a pronounced thixotropic behavior (rather than crumbling) might be expected on stirring. There are various pigments both organic and inorganic with particles so small that they form transparent jellies. When the pigment–vehicle ratio is sufficiently high, these jellies crumble rather than break down thixotropically and, consequently, do not flow on agitation.

SOAPS. The rheologist is likely to encounter these materials from two different sources: (1) soap as a subject material, and (2) soap as an undesired by-product. In the first case, if the soap is solid and hard, it cannot be measured in a rotational viscometer unless an instrument can be made that will induce laminar flow throughout the entire mass of material. That is, the flow must be genuine and not simply slippage along the side walls of the cup and bob. This might be carried out by cutting longitudinal grooves in the walls,[2] but as a rule the rheologist finds it much more convenient to employ some form of penetrometer for measurement and product control. In this case the investigator must be equally sure that he obtains true flow if his results are to be reduced to plastic viscosity and yield value. The writer has always felt that penetrometer methods, in the case of greases and soaps, are dangerous because of the great possibility of slippage taking place, rather than flow. No specific recommendations, therefore, will be made in regard to methods and instruments to be employed in this field. The same conclusion applies equally to the measurement of most jellies whether they are soaps or not.

A soap structure easy to see with dark-field microscopy is made from 1% solution of Ivory Soap. This concentration is sufficient to form a continuous structure. It should be placed on the microscope slide when warm so the micelles are all in solution. As the material cools, long micellar threads of the soap can be seen to form until finally the field is completely filled with them. By opening up the substage diaphragm more heat from the microscope lamp can be admitted, and the micelles will go back into solution again and become invisible. This procedure can be repeated indefinitely. Figure 71 is a dark-field photomicrograph of such a material.

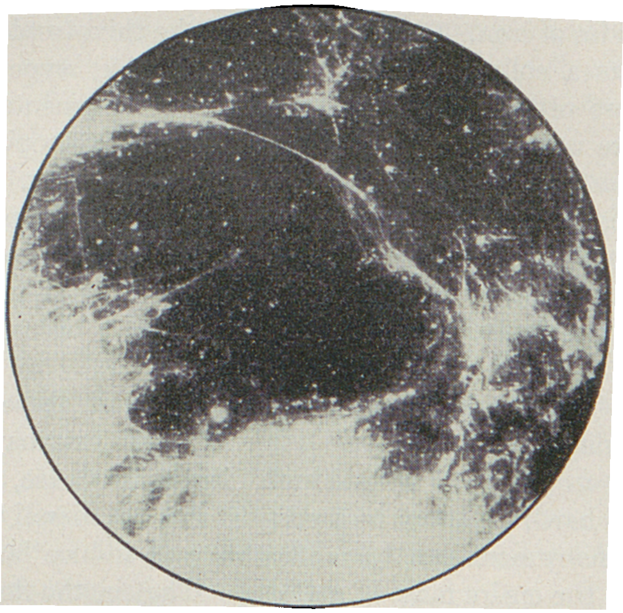


Fig. 71. Dark-Field Photomicrograph of a 1% Ivory Soap Jelly

Soaps are often formed in certain pigment suspensions. This happens when the pigment is basic and the vehicle contains a soap-forming acid, such as oleic acid, for instance. The zinc and lead containing pigments are, under such circumstances, soap-productive. It is difficult, however, for the microscopist to discover these soaps when examining a suspension that contains them. The reason is that the refractive index of the soap and of the vehicle differ by only a small amount. It is necessary to reduce the aperture by nearly closing the substage diaphragm. When present, the soaps, if sufficient time has been allowed for their crystallization, will appear as single crystals of curvilinear outline or as tufts of crystals radiating from the center of a sphere.

Sometimes soap formation, in pigment–vehicle suspensions can be so great as to cause complete solidification of the material. An interesting experiment illustrating this phenomenon can be carried out as follows: The pigment to be used is zinc oxide. The vehicle is made of rosin dissolved in kerosene or any similar material. In mixing these together care must be used to keep them free from any trace of water. After mixing, the suspension should be about as fluid as an outside paint. Now stir in a few drops of water. Almost instantly the "paint" will become a solid mass of zinc resinate. The water, in this case, did not function as a flocculator but permitted sufficient ionization to allow the zinc oxide and the acid of the rosin to react chemically on each other. If this solid mass is stirred, it will crumble and break into small pieces. On resting, these pieces will *not* unite and form the large solid mass which existed before stirring. Such a structure is, therefore, not thixotropic.

Structure arising from soap formation is of common occurrence. It is of strictly chemical origin and usually referred to as "livering," in the paint and printing-ink industries. The beginner is likely at times to confuse this phenomenon with thixotropy.

PLASTICS, FIBERS, AND RUBBERS. There are many materials that are not suitable for measurement in rotational viscometers of the kind that has been described for pigment–vehicle suspensions. However, much is known sometimes about their molecular structure, and from such data deductions can be made as to their visible behavior. Mark and his school have developed some of the most interesting features of this work.

According to Mark,[6] there is no fundamental difference in kind but one only of degree in the structures of certain high polymers. He gives as typical examples those materials that are classified as plastics, fibers, and rubbers. The nature of its molecular structure determines to which of these classes a polymer belongs. There are several basic concepts from which deductions can be made. They are: (1) If the molecular chains "fit" into a lattice readily, their tendency will be to form crystallite groups. (2) If the chains are bulky, they will be unable to form lattice structures. (3) Forces of attraction between chains can vary from strong to weak, and these forces, together with the lattice-forming ability, determine the class to which the polymer belongs.

If a high polymer forms crystallites easily, and the forces of molecular attraction are high, the material will lack the high elastic extension of rubbers and their ability to flow in nature. If the material has medium forces of attraction and medium lattice-forming ability, its ability to flow plastically will not be restricted, and it will have the nature of a plastic material. The remaining possibility, the formation of rubbers, depends on weak forces of attraction and on little or no tendency to produce crystallites. In such cases the material under elastic elongation will tend to return to its original form when all tension is removed.

In terms of molar cohesion the following relationships are found. These values are, according to Mark:[6]

	Fibers	Plastics	Rubbers
Molar cohesion	Above 5000	2000–5000	1000–2000
Examples	Cellulose Nylon	Polyvinyl alcohol	Neoprene Polybutadiene Polyisobutylene

The molecular cohesion is calculated for a 5.0 angstroms length.

Fibers have a relatively high tensile strength and a high modulus of elasticity (10^{11} to 10^{12} dynes per square centimeter). When a fiber is put under tension in a direction parallel to its length, it will stretch a certain amount before breaking. The percentage elongation is small, however, compared to the elastic elongation of rubbers. When the fiber reaches its elastic limit, or even before it does, a small amount of flow takes place. This flow is the result of the molecular chains sliding past one another, though still in mutual contact. This is the model of flow used in this book to illustrate plastic flow. At rupture, the molecular chains have separated, but the molecule itself has not broken.

METALS. The malleable metals like lead and gold are obviously plastic and capable of plastic flow at room temperatures. They cannot be run in rotational viscometers of the conventional type, however. If they could, they would undoubtedly show a yield value and consistency curves similar to the Bingham-body type. That kind of curve is characteristic of materials composed of particles suspended in a liquid. Cross section of metals when examined with a microscope shows a conglomeration of crystals packed closely together. In order that such materials can flow plastically, it is necessary to have a continuous phase surrounding the crystal particles. Metalographers have postulated the existence of an "amorphous layer" of metal that can fulfill this purpose.

If the crystal particles remained intact during flow of the metal, the consistency curve should be exactly of the Bingham-body type. However, it is more than likely that the dense crowding of the system will induce some of the crystals to shear along their cleavage planes. This means a reduction in particle size with no change in the particle–vehicle ratio. The result should be an increase in the plastic viscosity. This will cause the consistency curve to bend toward the shearing stress axis.

Elastic materials like steel will probably flow without rupture (that is, plastically), if confined on all sides except on the sides perpendicular to the direction of flow. The yield value would be a simple function of the elastic limit.

Sometimes there exists a lack of understanding in regard to the tensile-strength measurements of metals. The tests are made by clamping a rod or test piece of the metal at each end in a device that exerts a pulling force on it. This force can be applied at various rates. As the pulling continues, the force increases and ultimately attains a value that produces rupture. The value at rupture is the tensile strength of the material.

As the metal is elongated, it "necks down" at its center, where break occurs. The area of the cross section has, therefore, decreased. This new area should be (and often is) divided into the tensile reading in order to give the more comparable value, tensile strength per unit area. The afore-mentioned trouble arises when the rate at which the load (the pulling force) is applied is increased; the tensile also increases. The reason for this can be twofold, but usually only the first one is recognized. The rheologist must give consideration to both. The first is that a change of structure has taken place, causing an increase in plastic viscosity and yield value; the second is that, since volume of flow is the rate times the time, less flow has taken place to attain a given pulling force when its rate of application has been increased. This means that there has been less necking down for the amount of pull; consequently, the cross-sectional area is greater than it was before, and so a greater pulling force is required to produce rupture. This is the obvious rheological way of explaining the results and does not depend on hypothecating any structural change.

Brittle Materials. DRY PELLETS. There are certain structural units that are not single particles and yet do not flow in the normal rheological sense. The most elementary form of these entities is the soft *dry aggregate* or *pellet.* All dry pigments packed in a container exist there in pellet form, because pigment particles cannot exist in a package without touching one another. As soon as they touch, they form pellets. Each pellet is composed of many single particles. Between the particles are spaces called "voids." In the dry soft pellet the voids contain air and a layer of moisture covering the surfaces of the particles. It is probably this layer of moisture that holds the pellets together. The binding force, however, is slight, because the pellet can readily be smeared out between the thumb and finger.

The reason that it is necessary to devote time to the discussion of anything so obvious as pellets is that there has been in the past, and no doubt will continue to be in the future, confusion on the part of the beginner as to whether the soft pellet is a single particle or not. It is quite essential that the rheologist clearly sees the difference in the nature of these units. The dry pellet with its voids filled with air is a brittle material, for any attempt to make it flow by applying a shearing force will cause it to crumble. When the voids of the pellet are filled with liquid vehicle, the pellet, then, becomes plastic and can be made to flow without rupture.

HARD AGGREGATES. It very often happens that, during the manufacture of pigments and pigment-like substances, groups of particles get so firmly cemented together that they form hard permanent aggregates. Such groups function rheologically as single particles. The cementing takes place during drying or muffling. The cementing agents are probably soluble substances that were not completely removed during the working and filtering of the pigment. Hard aggregates, being composed of more than one particle, possess, according to our definition, a structure. This structure, however, cannot be sheared without permanent rupture.

The characteristics of a hard aggregate, as observed microscopically, are: noncrystalline outline; opaque rather than clear-centered; will break on compression and not flow out plastically. When the hard aggregate is composed of colloidal particles, it shows a conchoidal fracture. Aggregates, if not too large, can flocculate in a vehicle, in which case they can resemble single particles.

COMPLEXES. These are particles composed of more than one material. There are, in general, several kinds: (1) one material precipitated on another, (2) one material adsorbed on another, and (3) solid solutions. Group 1 is best known by such materials as the double precipitate, lithopone; group 2 by the *lakes*; and group 3 by leaded zinc oxides.

The structure of the lithopone particle is revealed by the ultraviolet-light microscope. The particle has a nucleus of barium sulfate which is transparent to wave length 0.275 micron. Surrounding the nucleus and forming a crust on it is a layer of zinc sulfid. This second material is opaque to ultraviolet light. The difference between the transparent barium sulfate and the opaque zinc sulfid is well brought out in the ultraviolet-light photographs.

Some of the lithopone particles will appear completely opaque. These are either sulfate particles completely covered with the sulfid, or else they are parts of the sulfid crust that have become detached from the nucleus. Other particles are entirely transparent, indicating that they are free from their sulfid layer. The remaining particles are composed of both ingredients. This is seen to be so in the free edges and corners of the sulfate nucleus which failed to become completely covered with the sulfid.

The afore-mentioned situation is maintained when the lithopone particle is not subjected to too much shearing tension. If the investigator mounts the pigment in a melted resin and uses the circular-wedge type of mount, then *all* the zinc sulfid can be removed from the barium sulfate, and only completely transparent and completely opaque particles appear on the photomicrograph. Reference should be made to the work of Haslem and Hall.[5] In the actual usage of lithopone paints it is safe to conclude that what shearing action takes place is insufficient to cause the severance of the sulfate from the sulfid. Regardless of its structure, the lithopone particle acts rheologically as a single particle.

Lakes. Lakes are composed of colorless particles that have been dyed to some desired hue. Their object is to dilute a dye which would otherwise be too concentrated. The dilution, of course, is carried out by an "inert" or base, which receives the adsorbed dye. A surprising number of white pigments will adsorb dyes of one kind or another, but one of the objects of laking is to produce a relatively inexpensive product, so the base selected is never a pigment. The bases used most frequently are aluminum hydrates and silica in various forms. The lakes are easily recognized by microscopical inspection. The base particle is often large (10 microns) and readily examined. Its surface contains the adsorbed dye, which is there in layers probably of molecular dimensions only. Because of the thinness of the layer it will be transparent, and its color strength will seem very low. The color is not removable, however, as in the case of the zinc sulfid crust of the lithopone particle. Though the lake particle is a group (a base covered with innumerable colloid dye particles), it functions rheologically as a single particle.

Leaded Zinc Oxide. Leaded zinc oxides are normally solid solutions of basic lead sulfate (probably) in zinc oxide. The object in manufacturing them is to utilize both the lead and the zinc contents of the ore without going to the expense of separating them. Microscopically, zinc oxide and basic lead sulfate are quite different in appearance. The former material is an acicular particle with a pyramid at one end and a basil pinacoid at the other. The sulfate forms cubelike particles. An examination, however, of a leaded zinc oxide reveals only one kind of particle, though it varies somewhat from particle to particle in its various dimensions. The most typical form is a short broad needle with a well-formed pyramid at one end.

If only one kind of particle exists in a leaded zinc oxide, then there should be both zinc and lead in each particle. That this conclusion is a fact is easily proved by chemical tests.[3] The procedure is as follows: A turpentine multiple-wedge dispersion is made on a microscope slide and the turpentine removed by evaporation on a hot plate. The slide is then immersed in hydrogen sulfide water, taken out, dried, and the mount finished with glycerine as the mounting medium. Microscopical examination will show the blackening of each particle present, proving that each contains lead. The test for zinc oxide depends on the little-known fact that chlorinated rubber blackens, if heated in the presence of zinc oxide. This test is quite sensitive and will detect the minute quantities of zinc oxide sometimes occurring on the surface of particles. To conduct the test, make another turpentine dispersion. When it is dry, spread a thin coating of Paravar (chlorinated rubber) over the slide. Place the slide on a hot plate at a temperature of about 150°C. Watch carefully for darkening. As soon as this occurs, remove the slide, cool it, and finish the mount as before. Microscopical examination will show each particle surrounded by a dark-brown area of Paravar. Wherever this occurs, zinc oxide is present.

Assume that it has now been proved that the leaded zinc oxide particle contains both zinc and lead. The question to be answered next is, Are these materials present in chemical combination or as a physical mixture, that is, as a solid solution? This cannot be ascertained readily, unless the investigator has a series of leaded oxides varying in their ratio of zinc to lead. Such series have been made by the manufacturers of that pigment. If such a series is examined microscopically, it will be found that the crystalline form of the particle changes gradually from a needle to a cube as the zinc oxide content varies from 100% to 0%. This change could not take place if the leaded zinc oxide particle is a chemical combination; therefore, the only possible conclusion is that this pigment is a solid solution. Rheologically, the particles behave as single units; that is, there is no change in their size or shape under flow indicating deaggregation.

Thixotropic Materials. SUSPENSIONS. Of all the known rheological structures, thixotropic structure is perhaps by far the most interesting one to study. Unfortunately, the exact meaning of the term differs with each investigator, so that at times it becomes extremely difficult to discuss the matter without confusion. The present author has endeavored to describe the term so that it would be applicable to the thixotropic materials first studied by the pioneers in this field. These early investigators saw their thixotropic materials break down on stirring and observed them rebuild on resting. Materials which showed no visible evidence of breakdown and buildup were not classified as thixotropic. The mere ability of flow, either viscously or plastically, was not considered evidence of thixotropic breakdown; neither were non-Newtonian consistency curves viewed as proof of the existence of a thixotropic structure. The concepts of a practically instantaneous breakdown and an instantaneous buildup taking place so fast that neither the eye nor the viscometer could obtain any record of them was still unthought of. Today, however, there are many adherents to that philosophy. Such ideas have not been adopted here because they are not actually necessary; they complicate the subject unduly, and, furthermore, they are conjectural, not subject to proof. Anything that cannot be detected physically, or proved to exist from either facts or theory, is usually considered to be nonexistent.

The possible structures of thixotropic materials have been discussed in detail, and nothing further will be added here. It is well, however, to re-emphasize the cardinal principles lest they be forgotten. They are: Flocculation is necessary for the existence of thixotropy, but all flocculated systems are not necessarily thixotropic. All thixotropic materials rebuild their structure when undisturbed. The energy to do this resides within the system itself. The thixotropic change from solid to liquid to solid is an isothermal reaction. Thixotropic materials give hysteresis loops when their up- and downcurves (as determined with a rotational viscometer) are plotted together. A large area loop means a large thixotropic breakdown. No loop means the absence of thixotropy.

HEAVY OILS. It will probably be shown, eventually, that liquids composed of elongated molecules produce hysteresis loops, if the shearing stresses are taken high enough. For the present, however, no assumptions will be made in that direction. It is known that liquids of relatively low viscosity (under 20 poises) give normal Newtonian consistency curves and that liquids of higher viscosities show a marked hysteresis effect in the upper portion of the curve.[7]

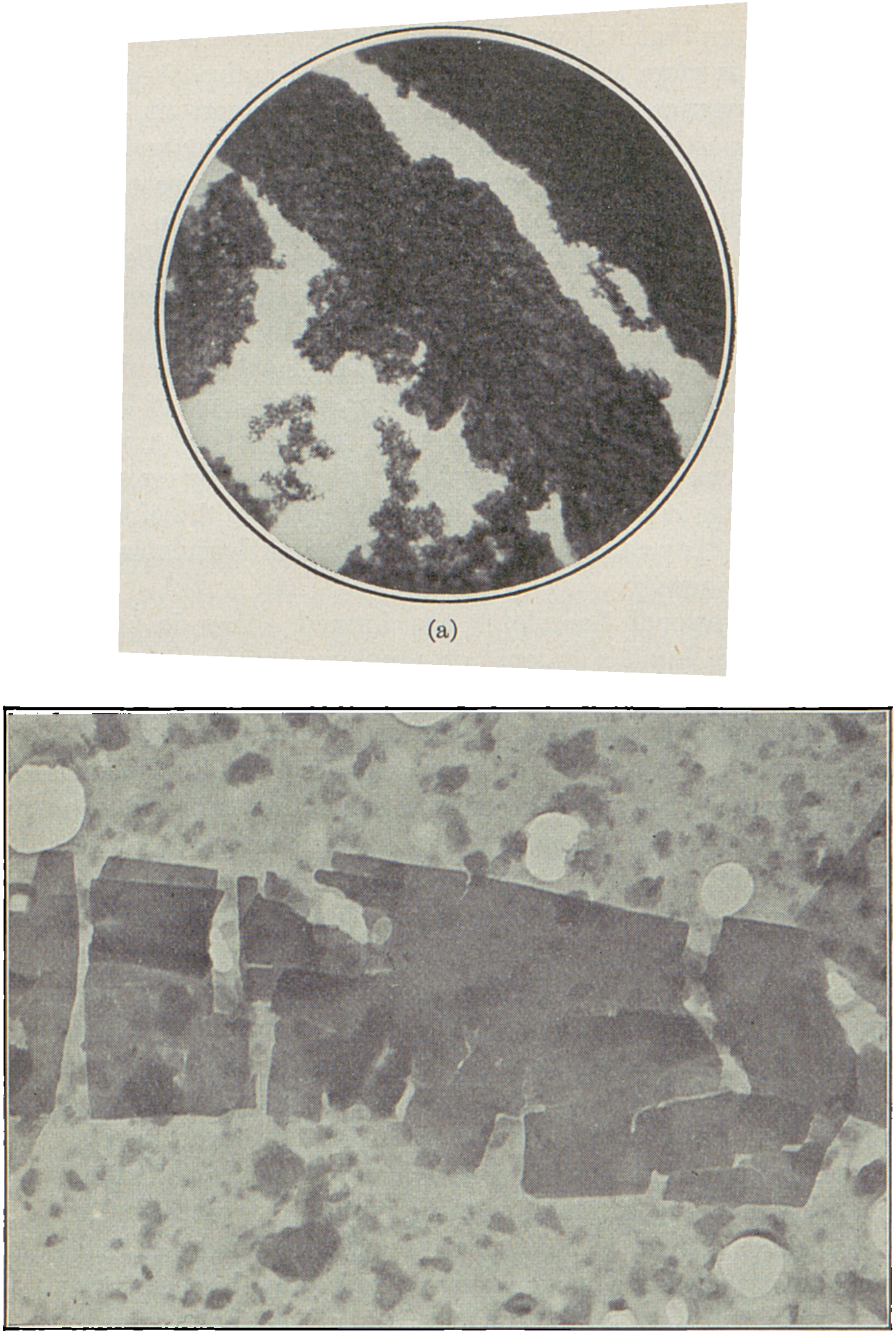
A hysteresis loop is the result of a broken-down structure. This statement implies that before breakdown the structure was a connected one. However, if the liquid had connected structure originally, it would show a yield-value intercept under low rates of shear, that is, at the lower end of its consistency curve. Normally, oils do not do that but exhibit in this region a Newtonian curve passing through the origin. How, then, can a disconnected structure behave like a connected one? The answer must lie in the possibility that, if it requires high shearing stresses to align large entangled (and curled) molecules, it must take an appreciable time for them to return to their random positions as the shearing stress is gradually reduced. Thus, a hysteresis loop of detectable and measurable area can form. In brief, there are two distinct types of hysteresis loop: The kind produced from a connected structure extends the entire length of the curve. The other type takes place in loose structure materials like heavy oils, where the molecules are long and are entangled in the rest state. After an aligning force has been applied and removed, an appreciable time lag occurs before random orientation is again taken.

Two-dimensional Flocculates. In the study of pigment–vehicle structures the investigator will frequently meet with a type of flocculation which will appear as a thin sheet of highly compacted pigment particles. The appearance of this pigment group is of such a nature that it is not likely to be recognized as a flocculate. In fact, it is more than likely to be ignored and pushed aside as of no importance. This structural group is important, however, and its importance lies in the fact that an understanding of it makes possible the "interpretation" of other microscopical phenomena that otherwise would lack suitable explanation.

Two-dimensional flocculates are sometimes made by the pigment manufacturer, and sometimes by the investigator when making his pigment–vehicle mounts. When made by the manufacturer and received in a dry state, they are no longer flocculates but either hard or soft aggregates. However, at the time of formation they were flocculates, for they were then part of a pigment–vehicle system. However, the vehicle was ultimately removed and the flocculates compacted into hard dry masses; therefore, being vehicle free, they can no longer be classified as flocculates, as that term is used here.

Two-dimensional flocculates are formed either in interfaces between two liquid solutions, or else by compressing a suitable pigment–vehicle mass out into a thin layer.

If solution *A* is poured into solution *B*, then, where every drop of *A* comes in contact with *B*, an interface is formed. If the materials dissolved in *A* and *B* precipitate each other, a precipitate will form where *A* and *B* meet, that is, at their interface. Again, if the precipitate is highly insoluble and the concentration is sufficient, the particles of the precipitated pigment will be exceedingly small. If a force of flocculation exists, the particles will form a thin compact sheet (referred to here as two-dimensional) of pigment spreading over the interface. The force of flocculation may be weak, but the capacity factor (specific surface) is large, and, consequently, the sheet often has considerable tenacity. Subsequently, when the precipitating solutions are stirred, these sheets will break up into small pieces. Often these pieces are rectangular in shape, resembling crystals, and the novice can easily be misled into believing them to be ultimate particles. When the real ultimate particle is large enough to see, which often happens, then no confusion will arise at this point. Figure 72a shows two-dimensional flocculates that do not look like crystals, because the ultimate particles are readily visible. Figure 72b shows the type where the ultimate particle is below the limit of microscopical detectability and the sheets as a whole appear to be crystals. A careful examina-



(a)

(b)

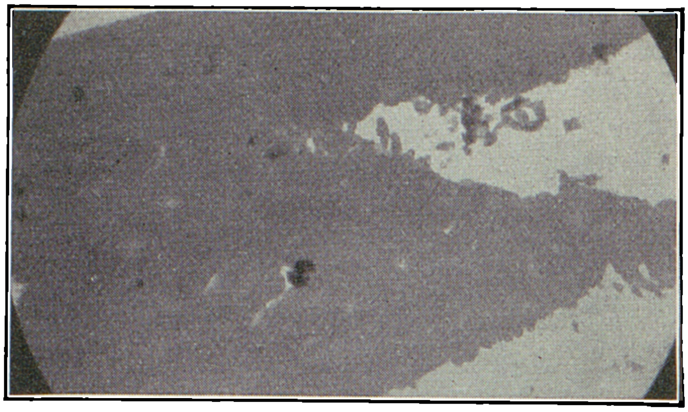
Fig. 72. Two-Dimensional Flocculation. (a) Pigment Particles Relatively Large. (b) Pigment Particles Submicroscopic

tion of their edges and angles will reveal irregularities that indicate that the particles are not crystals.

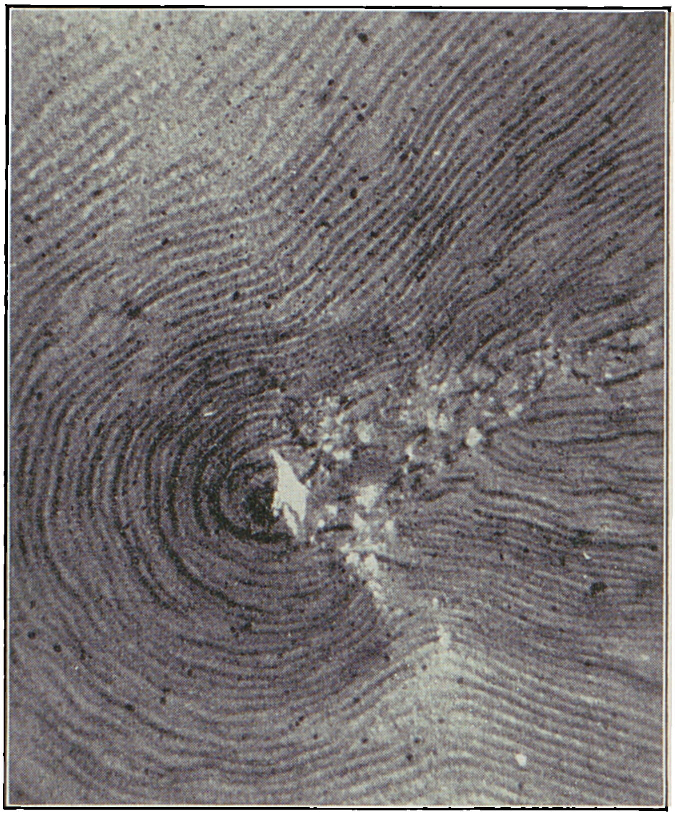
Two-dimensional flocculation is often produced on the microscope slide without the investigator being conscious that he has done so. It is often necessary, when examining a crowded pigment suspension, to squeeze the cover glass tightly against the microscope slide. This is done in order to make a section thin enough to allow light to pass through so that the microscopist can see what he is looking at. If the particles are sufficiently small and flocculated, this squeezing process will invariably form a pigment sheet, that is, a "two-dimensional flocculate." In cases where the particles are near or below the colloidal border (0.1 micron) in size, the squeezed-out sheet can become transparent like a piece of colored glass, all evidence that the individual particles have disappeared. However, at the edge of the sheet the texture will be different, and the dotted or speckled appearance of a crowded system composed of near colloidal particles will appear.

There are a number of characteristic tests that can be employed for the detection of two-dimensional flocculation. The tear test is one of them. By proper manipulation of the cover glass through pressing and sliding, the sheet can be torn just like a piece of paper. The edges of the tear will be ragged or smooth, according to whether the particles are large or small (Figure 73a). Ordinarily three-dimensional flocculation shows no such formation. Another test, is to show the ability of the sheet to wrinkle. This test is performed by sliding the cover glass along until the sheet catches in an irregularity in the slide and then piles up against this barrier. Wrinkles are formed (Figure 73b).

There are other characteristics which serve as evidence of the existence of two-dimensional flocculation. The sheet, as a rule, possesses sufficient tensile strength so that it can be lifted without breaking. Another feature is the conchoidal nature of its fracture. It breaks along cleavage planes, but the line of cleavage is always slightly curved, proving that it is not a crystal cleavage plane. Finally, sheet flocculates can be squeezed out or molded without rupture. This proves beyond any doubt that the material is a plastic mass and not a crystal or single particle. It is true that zinc oxide and leaded zinc oxide crystals, if small enough, can be squeezed out under a cover glass without rupture, but the extension is always laterally and not along the axis of the crystal. Besides,



(a)



(b)

Fig. 73. (a) The Tear Test on Sheet Flocculation. (b) The Wrinkle Test on Sheet Flocculation

the crystalline nature of these particles is apparent beyond any doubt.

The most remarkable feature of the sheet flocculate is its great tenacity. It cannot be temporarily deflocculated by stirring, like ordinary flocculates. As pointed out, however, this condition is not necessarily due to a high flocculating force, although that is the way it appears, but can arise from a large specific surface of the pigment. This means fine particle size and many points of particle contact, which naturally will result in good adherence.

It is a strong temptation to associate sheet flocculation with thixotropy, but there is probably no connection. If such a flocculate were thixotropic, any shear imposed on it through manipulation of the cover glass would cause a structural breakdown that should appear as deflocculation under the microscope. It is conceivable that such a condition might exist, but so far no one has reported having seen such a phenomenon take place.

The recognition of two-dimensional flocculation is of recent origin,[4] and very little work has been done on it, but its study will well repay any investigator who is interested in rheological structures.

Structural Artifacts. Rolled Flocculate. The sheet flocculate is a natural structure when it appears during the course of manufacture. When it is produced on a microscope slide (under a cover glass manipulated by the investigator), then, it becomes an artifact. The rolled flocculate is closely related to the sheet flocculate. It is entirely an artifact, but one so genuine looking that it can lead the beginner far astray in his microscopical analysis of a mount.

The rolled flocculate is obtained from the same kinds of materials that produce two-dimensional flocculation, that is, from very fine particle pigments that flocculate in the vehicle in which they are suspended. The flocculate is produced by placing a drop of the suspension on the microscope slide, covering it, and then under pressure moving the cover glass backward and forward in a straight line. Sheets are evidently formed first and then rolled into masses that resemble rectangular particles. (See Figure 74.)

The rolled flocculate is exceedingly difficult to make. It usually occurs accidentally, and, when the investigator tries to duplicate the phenomenon, he may or may not succeed in doing so. The best conditions for producing the flocculate are not known, anc if they were, they would probably be uncontrollable.

Rolled flocculates have been made from benzedine yellow. I this case the ultimate particle is so small that it is totally invisible Even the electron microscope can hardly show it. As a result, th

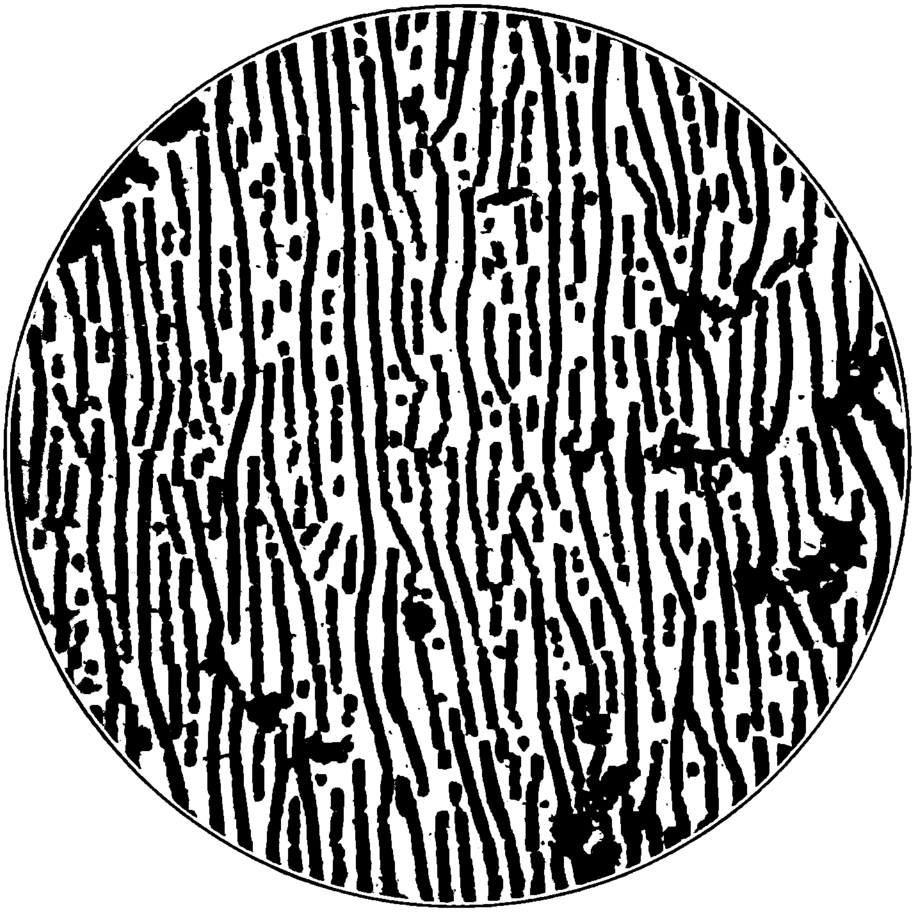


Fig. 74. Flocculates Formed by Rolling

rolled flocculate is clear and transparent and appears like a gigantic acicular crystal particle. This material would deceive even a pigment microscopist of long experience, unless he actually witnessed the formation of the flocculate himself.

The flocculates shown in Figure 74 are made from iron blue. The particle size of the ultimate particle is about 0.08 micron. This is large enough to scatter and reflect light. Consequently, the flocculates are opaque. This opacity is sufficient evidence to warn the investigator not to interpret each rectangular piece as a single crystal. The reason the flocculates are lined up as they are is that originally each row was a single long flocculate. During the rolling operation these long flocculates broke into many parts, producing the effect seen in the photomicrograph.

Rolled flocculates often appear in mounts prepared from gas-black suspensions. The particles of this material have averaged as low as 0.02 micron in certain grades of the pigment. Even the coarser grades do not normally attain an average size as large as 0.10 micron. Furthermore, unless specially prepared, they are strong flocculators in almost any vehicle. This means that they are ideally suited for forming rolled flocculates. An accidental movement of the cover glass can produce them. The investigator should be aware of this fact so that an unexpected appearance of what looks like large black or greyish crystals in his gas-black mount does not mislead him.

Particles as coarse as 0.10 micron and somewhat over have been successfully used for making rolled flocculates. Such materials can be found among the white pigments. Fine-grained zinc oxides are manufactured in this size. The rolled flocculates in this case are quite noticeably an aggregation of many particles. This is shown by the highly speckled appearance of the flocculate.

Rolled flocculates have no direct connection with rheology, for they do not exist as products of manufacture. They have been described and discussed here because the plant rheologist, if he uses a microscope, is likely to find them on his microscope slide. It is best that he knows what they are, so that he does not condemn the pigment and jump to false conclusions in regard to the matter.

RESIDUES FROM EVAPORATION. There is a type of artificial structure that every microscopist has seen innumerable times. The rheologist, who is not usually a microscopist, is not so familiar with this particular artifact. He should receive, therefore, some instruction as to what it is, so that he will form no misleading opinions about it. This particular artifact results from the evaporation of a suspension. The pattern it leaves on the slide can resemble almost anything for it can take all kinds of forms. Figure 75 shows a typical example of this artifact. The residue is dry, the vehicle having been evaporated, and, therefore, is best observed with powers not over 200 diameters.

Mounts made with volatile vehicles and not sealed usually show such structure the next morning after the vehicle has evaporated during the night. The residual structure forms most easily when the particles are small and well wetted by the vehicle. As the vehicle evaporates, it retracts and draws along with it any particles in suspension that it contains. These particles are swept forward and in so doing collect in the receding edge of the vehicle. Therefore, when evaporation is complete, the residual particles remain distributed in a thin line which often resembles the outlines of cellular structure. This artifact occurs only on the microscopist's slide and has no rheological value.

Fig. 75. A Structure-like Artifact from an Evaporated Drop of a Suspension

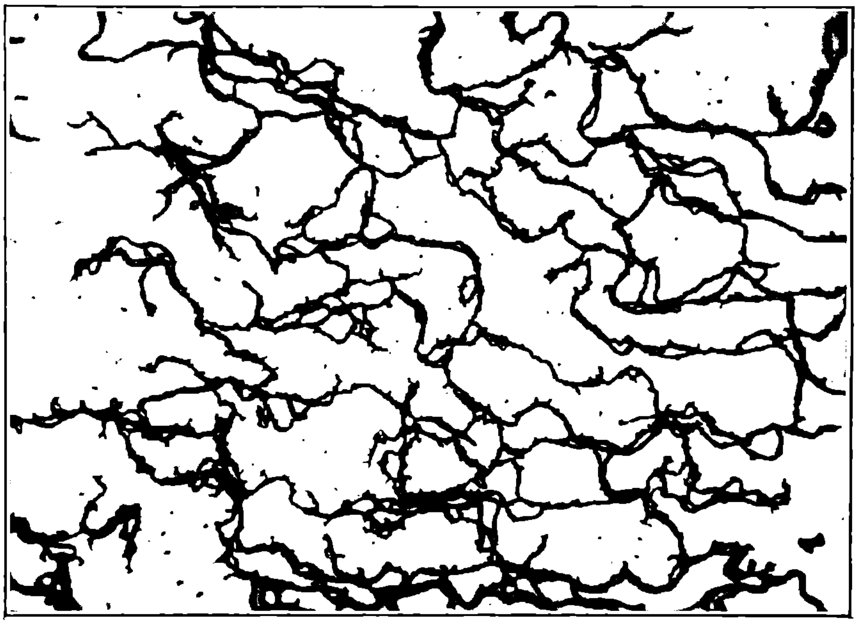
Magnetic Structures. When iron filings are brought into a magnetic field, they line up and produce chainlike groups. Every microscopist has witnessed this at one time or another under a microscope. From a rheological viewpoint that is an interesting experiment. Rheologists have speculated as to the effect of electric charges on the particles of a suspension. There are two possibilities. Particles are either all charged alike (that is, either all positive, or all negative), or else they each contain a positive and negative charge separated by a definite distance.

In the first case the particles will repel one another and deflocculation will be the result. What happens in the second case, no doubt, depends on how far apart the two charges are on each particle. The experiment with the iron filings answers the question.

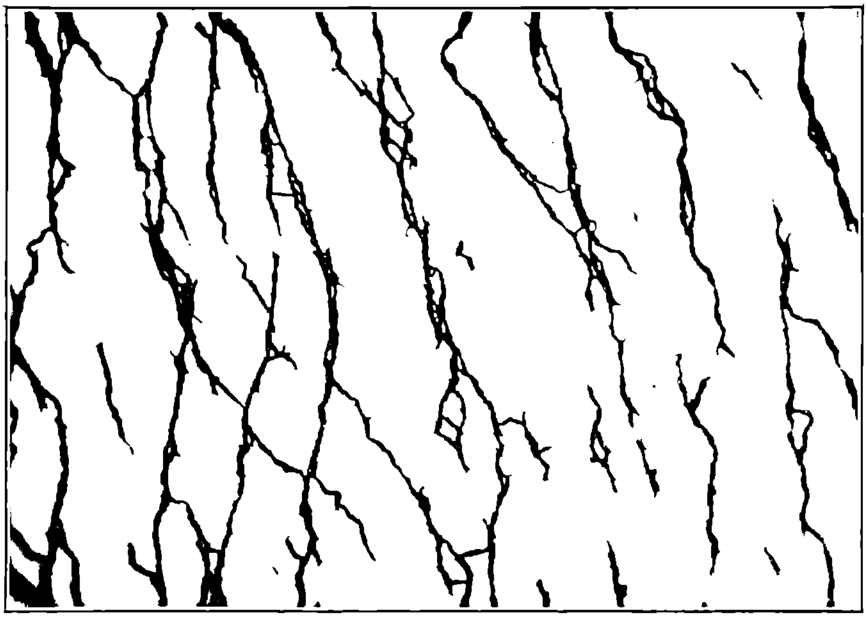
Iron filings are far from being pigment-like particles. It is interesting to repeat the experiment with particles of pigment size. Fortunately, such materials of pigment size that become polar in a magnetic field are now obtainable.

In Figure 76 is shown a magnetic iron oxide which has been mounted in glycerine and covered with a cover glass. A magnet has been placed close to the edge of the mount. Figure 76a shows the alignment of the particles in long chainlike groups all pointing, approximately, in the same direction. The individual particles are not discernible at the magnification of 125 diameters. Photomicrograph (b) shows what happens when the magnet is withdrawn. The particles do not disperse but continue to retain their magnetism and mutually adhere. The straight alignment brought about by the magnetic field, however, is absent, and the groups have become curled and randomly distributed. High polymers might conceivably take on such an appearance before stretching or flowing. Figure 76a would be the formation taken during stretching and flowing. In Figure 76c the concentration of the chains has been increased to give a better visualization of the structural appearance of practical materials. Another analogy to high polymers can be pointed out here, the phenomenon of cross linkage. It will be noticed that there are several bands running perpendicularly to the direction of the chains. These bands occur where the chains come close to one another, forming a somewhat indistinct banded pattern across the picture. The distance between the bands is approximately the same for each set.

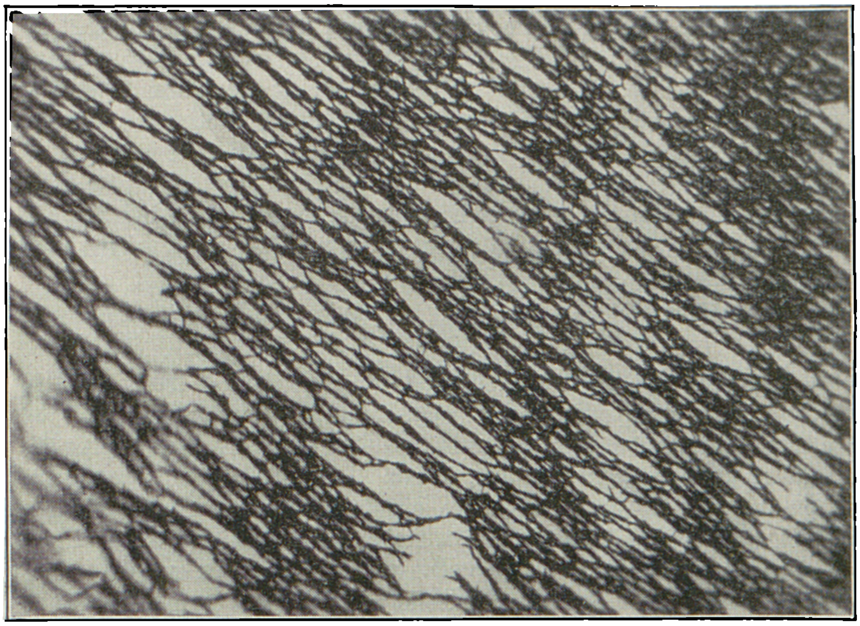
With a few possible exceptions, there has been no microscopical evidence of flocculated pigment particles taking on an alignment of the kind illustrated in Figure 76. It is true that a two-dimensional flocculate can be pulled apart in such a manner that long thick chainlike rolls of pigment can be produced; but the examination of pigment suspensions *en masse* shows no evidence of such formation. Again, there is no evidence that flocculated particles select preferred spots on which to adhere. That is, there is no evidence of polarity. This lack of visual evidence is not necessarily a proof that polarity does not exist, for in the great majority of cases the particles are too small for even the best microscopes to resolve the particle area into distinct patterns. The kind of structure shown in Figure 76 will produce yield value just as though it were a normal flocculated structure.



(b)



(a)



(c)

Fig. 76. (a) Magnetic Iron-Oxide Particles in a Magnetic Field. (b) The Field Has Been Removed. (c) A Denser Mount of (a)

ANSWERS TO PROBLEMS AND QUESTIONS

Chapter 2

1. (*a*) The shearing stress that will induce a unit rate of shear. (*b*) The shearing stress in excess of the yield value that will induce a unit rate of shear. (*c*) The viscosity a material would have if it were a Newtonian material. 2. (*a*) The unit of viscosity. (*b*) From Poiseuille. (*c*) No. For the present "poise" is used. 3. (*a*) The wire constant of the rotational viscometer. (*b*) Torque per degree deflection. (*c*) M/LT. (*d*) No. 4. 2.489×10^{-4}. 5. Approximately 1 centipoise. 6. (*a*) 490 dynes per square centimeter. (*b*) 254 dynes per square centimeter. (*c*) 49 dynes per square centimeter. (*d*) 0. (*e*) 0, 735, 968, 980. 7. 3694. Yield value. 8. It revealed the existence of slippage and of plug flow. 9. 184. 10. Using some material (like glass powder) of suitable refractive index so as to match the refractive index of the vehicle. This makes the suspension transparent, and the inside of the plug can be observed.

Chapter 3

1. $S = 9.39 \times 10^{-4}$; $C = 8.97 \times 10^{-3}$. 2. $T = 24{,}000$; $f = 1002$. 3. $U = 161$. 4. It gives a linear curve for a Bingham body. It makes possible the study of thixotropic materials by means of the hysteresis loop. In studying the flow of materials under the microscope. 5. No. The parallel-plate viscometer. 6. Newtonians and Bingham bodies in either rotational or parallel-plate viscometers. 7. If they do not coincide, the experimental and theoretically derived yield values, which are points on the lower end of these curves, cannot be equal. In the rotational viscometer, the yield value is a function of the intercept and can be calculated from the equation of the linear portion of the curve. Since this portion of the curve coincides with the experimental curve, the calculated and experimental yield values must be equal. 8. Yes. None at present.

Chapter 4

1. A base printing ink. A suspension of quartz powder in carbon tetrachloride. The first gives a hysteresis loop. The second one does not. 2. By a breaking of the linkages during flow and a re-forming of the linkages during rest. 3. Progressive flocculation, deflocculation, soap formation. 4. No. 5. *Breakdown by time.* Prolonging the time of application of the shearing force causes a decrease in plastic viscosity until equilibrium is attained. *Breakdown by rate of shear.* Increasing the rate of shear increases breakdown. 6. Power $= ab$. 7. By increasing ω. Yes, when T begins to fall off sufficiently from thixotropic breakdown. Then T can decrease with increasing ω. 8. 238 rpm. 9. 316. 10. $B = 16.3$. 11. $M = 68.1$.

Chapter 6

1. (*a*) Yes. (*b*) No. 2. (*a*) Increases it. (*b*) Increases it. (*c*) Lessens the interfacial tension. 3. (*a*) It is always formed in a vehicle. A loss of free energy must result when the particles touch one another. (*b*) A cemented aggregate can exist outside a vehicle. (*c*) No. (*d*) No.

Chapter 7

1. It can make rapid changes in the rpm without stopping the cup. It is temperature-controlled. 2. In the study of thixotropic breakdown. 3. Saves time and records the very rapid changes in torque that occur in the initial stages of an upcurve determination.

Chapter 9

1. (*a*) Weight. Initial film thickness. Area of the finger tip. (*b*) By adding different weights on the end of the lever arm. By changing the micrometer screw setting. By using finger tips of different areas. 2. Yes. 3. No. 4. Lack of perfect flatness in the finger-tip area. Because it is first rectified by introducing *d*, which makes it pass through the origin. If *d* is omitted, the curve would revert to its original form and position. 5. (*a*) 17.5 (*b*) 55.4.

SYMBOLS

Symbol		Dimensions
A	Area of hysteresis loop.	L^2
A_{t_0}	Area of hysteresis loop formed in zero time (hypothetical).	L^2
A_t	Area of hysteresis loop formed in t time.	L^2
A_E	Area of hysteresis loop formed in equilibrium time.	L^2
B	Coefficient of thixotropic breakdown with time.	M/LT
C	Instrumental constant. Converts T_2 into f.	$1/L^3$
D	Diameter of particle of average volume.	L
d_1	$\Sigma nd/\Sigma n$. Arithmetical mean diameter.	L
d_2	$\Sigma nd^2/\Sigma nd$.	L
d_3	$\Sigma nd^3/\Sigma nd^2$. Average diameter for specific surface.	L
d_4	$\Sigma nd^4/\Sigma nd^3$.	L
dv/dr	Rate of shear. Velocity gradient.	$1/T$
d	Particle diameter of frequency n.	L
d	Tackmeter correction. To be added to initial film thickness.	L
D	Initial film thickness for Tackmeter.	L
dT'	Loss in torque from a rise in ω to $(\omega + d\omega)$.	ML^2/T^2
e	Base of natural logarithms.	
e	Shearing strain (Reiner).	Dimensionless
$\dot{e}$	Time derivative of shearing strain.	$1/T$
f	Yield value.	M/T^2L
f	Houwink's "lower" yield value.	M/T^2L
f_B	Houwink's Bingham yield value.	M/T^2L
f_h	Houwink's "high" yield value.	M/T^2L
F_0	Initial stress in Maxwell's relaxation time equation.	M/T^2L

SYMBOL		DIMENSIONS
$f_1, f_2, f_3,$ *etc.*	Different yield values for a series of curves with a common crossing point.	M/T^2L
F	Shearing stress. $F = Pgr/2l$ in capillaries.	M/T^2L
G	Modulus of elasticity.	M/T^2L
g	Acceleration due to gravity.	L/T^2
h	Depth of immersion of the bob in a rotational viscometer.	L
J	Slope of yield-value curve, f versus $\ln(\omega - \omega_0)^2$.	
K	Torsion wire constant for the rotational viscometer equals torque per degree of rotation.	ML^2/T^2
K, K', K'', and K'''	Constants used in the development of the tack equation. Their dimensions are	$1/L^2$, LT/M, $1/L^4$, L^2
K	Constant of integration, independent of Δt.	Dimensionless
K	Instrumental constant. The amount of torque per degree of deflection.	ML^2/T^2
k	Constant of integration in the U versus RPM^2 thixotropy curve. Dependent on Δt. Also equals the square of the top rpm when $U = 0$.	$1/T^2$
k	Intercept on the weight axis (tack curve).	ML/T^2
k_0	Equals k when M_o takes the place of M.	$1/T^2$
k'	Constant of integration when $(\omega - \omega_o)$ replaces ω.	$1/T^2$
k''	Proportionality constant in yield-value curve, f versus $\ln(\omega - \omega_o)^2$. Dependent on Δt.	$1/T^2$
l	Length of capillary tube.	L
ln	Sign of natural logarithm.	
log	Logarithm to base 10.	

Symbol		Dimensions
m	Slope of the U versus ln $(1/\text{RPM}^2)$ curve.	LT/M
M	Coefficient of thixotropic breakdown. Independent of Δt.	M/LT
M_0	That part of M depending only on ω.	M/LT
n	Frequency of particles of size d.	
N	Number of particles per gram.	
N	Number of points in upcurve.	
P	Stress. Used by Reiner.	M/LT^2
$\dot{P}$	Time derivative of P (Reiner).	M/LT^3
P	Pressure (drop in pressure) applied to capillary-tube viscometers. Pressure is in mass per unit area.	M/L^2
p	The pressure that causes the yield-value intercept on the pressure axis. Applied only to capillary-tube viscometers.	M/L^2
Pg	Stress, when P is mass per unit area.	M/LT^2
pg	Minimum stress which will cause flow in a Bingham body.	M/LT^2
Q	Proportionality constant. It is the area of the hysteresis loop divided by the top $(\text{rpm})^2$.	L^2T^2
R	Proportionality constant. $R = t/\omega$.	T^2
R	Radius, of capillary, cup, or bob.	L
R_b	Radius of bob.	L
R_c	Radius of cup.	L
r	Any radius between R_b and R_c; or any radius between the center and the wall of a capillary.	L
R	Radius of finger tip on Tackmeter.	L
rpm	Revolutions per minute. rpm $= 9.55\omega$.	$1/T$
RPM	Top rpm of hysteresis loop.	$1/T$
rps	Revolutions per second.	$1/T$
S	Constant used with Reiner equation for obtaining plastic viscosity. Converts, cotangent of angle into poises.	$1/L^3$

SYMBOL		DIMENSIONS
S	Specific surface. Total particle surface per gram of material. Usually meters per gram.	L^3/M
s	Surface of particle.	L^3
s	Elastic strain (Maxwell). As used here, it is	Dimensionless
T	Torque. Dyne-centimeters.	ML^2/T^2
T_0	Torque where slippage flow starts.	ML^2/T^2
T_1	Torque where all flow is laminar.	ML^2/T^2
T_2	Torque where initial shear takes place. Intercept from which yield value is calculated.	ML^2/T^2
T_E	Equilibrium torque (hysteresis loop).	ML^2/T^2
t_E	Equilibrium time for thixotropic breakdown at a given ω.	T
t	Time. Especially here, time for up-curve.	T
t	Time of plate separation (tack).	T
(T)	Tack (pull resistance—Weight).	ML/T^2
$(T)_{1/t}$	Tack at rate of plate separation $1/t$.	ML/T^2
(T^o)	Tack of standard substance.	ML/T^2
$(T^o)_{1/t}$	Tack of standard substance at rate of plate separation, $1/t$.	ML/T^2
$(T)_{1/tp}$	Tack at rate of printing press.	ML/T^2
$(T^o)_{1/tp}$	Tack of standard substance at rate of printing press.	ML/T^2
T'	Loss of torque in passing from T_2 to T.	ML^2/T^2
U	Uniformity coefficient.	Dimensionless
U	Plastic viscosity.	M/LT
dU	Change in plastic viscosity from change in rate of shear.	M/LT
dU_t	Change in plastic viscosity from change in duration of shear.	M/LT
V	Coefficient of thixotropic breakdown. Independent of Δt.	$1/T$
V	Volume.	L^3
v	Velocity.	L/T

SYMBOL		DIMENSIONS
v_R	Velocity at capillary wall due to slippage.	L/T
v_r	Velocity at radius r.	L/T
v_{r_0}	Velocity of plug (Buckingham equation).	L/T
V/t	Volume of flow per second.	L^3/T
w	Weight. Force. Pull resistance (tack).	ML/T^2
Z	Loss in torque per unit rise in rate of shear.	ML/T^2

GREEK LETTERS

α	Angle in Mooney's equation for end effect.	
α	Angle of tack curve (Newtonian) with weight axis.	
β	Angle of Mooney's equation for end effect.	
β	Angle of tack curve (Bingham body) with weight axis.	
γ	Modulus of elasticity as used by Reiner.	M/LT^2
Δ	Average diameter related to average particle surface.	L
Δt	Time interval. $\Delta t = t/\omega$.	T
ϵ	Thickness of lubricating layer (Buckingham).	L
η	Viscosity coefficient (Newtonian).	M/LT
η_o	Viscosity coefficient of standard liquid (for tack).	M/LT
θ	Bragg angle.	
θ	Degrees deflection on rotational viscometer.	
ϑ	Yield value (Reiner).	M/LT^2
μ	Mobility.	LT/M
ν	Volume shape factor.	Dimensionless
π	3.1416.	Dimensionless
σ	Shape factor for surface.	Dimensionless
τ	Maxwell's relaxation time.	T
φ	Fluidity.	LT/M
Ω	Angular velocity when all flow is laminar (Reiner).	$1/T$
ω	Angular velocity.	$1/T$
ω_o	Angular velocity at crossing point of down-curves in hysteresis loops.	$1/T$

The Appendixes

The following appendixes were written for the laboratory investigator whose mathematical ability extends as far as elementary calculus. It is assumed that the investigator's knowledge of mathematics is in the condition it normally attains when this subject has been neglected for some time. The author has endeavored to remedy the situation by inserting additional equations where the mathematician would intentionally omit them. Consequently, the various subjects are not quite so condensed as they would usually be; but it is hoped that they will be easier to understand and, therefore, more useful to the laboratory man for whom they are intended.

Appendixes A, B, C, D, E, F, and G contain information that will be found useful to the student of rheology. They can be omitted, however, without impairing an understanding of the rheological system developed here. The work presented in these sections was not included in the text because it was believed that by omitting them discontinuity in the development of the system could be avoided.

Sections H and I are something of an innovation for books on rheology. The belief that they have a part to play in the system has arisen from the many years of association the author has had with industrial rheologists and research laboratories in general. It is suggested that these final sections be read; and it is hoped that they will be received with the spirit in which they were written.

APPENDIX A

Deduction of the Poiseuille Equation

When a steady rate of flow is maintained, the total activating force applied at the end of any cylinder within the capillary is equal to the total shearing force on the wall of the cylinder. Newton's concept states that the shearing force per unit area F is

$$F = \eta \frac{dv}{dr} \tag{190}$$

Then the total shearing force over the wall of the cylinder of length l and radius r is $2\pi rl(dv/dr)$. Now the activating force per unit area is pg, where p is the pressure per unit area in grams (mass) and g is the acceleration. Then, the total activating force is $-\pi r^2 pg$. This is written with a negative sign because it is opposite in direction to the force resisting flow. If this were not so, the two forces would not balance each other, and steady flow would not ensue. Therefore,

$$2\pi rl\eta \frac{dv}{dr} = -\pi r^2 pg \tag{191}$$

Canceling and rearranging gives

$$dv = -\frac{pg}{2l\eta} r\,dr \tag{192}$$

Then

$$v = -\frac{pg}{2l\eta} \int r\,dr \tag{193}$$

or

$$v = -\left(\frac{pg}{4l\eta}\right) r^2 + \text{constant of integration} \tag{194}$$

When $r = R$, $v = 0$. Then, the

$$\text{Constant} = \frac{pgR^2}{4l\eta} \tag{195}$$

Substituting (195) in (194), we have

$$v = \frac{pg}{4l\eta}(R^2 - r^2) \tag{196}$$

Now

$$\frac{V}{t} = -\pi\int_r^R r^2\,dv \tag{197}$$

The negative sign is introduced in Equation 197 because as r increases v decreases, meaning that dv is negative. Substituting Equation 192 in Equation 197 gives

$$\frac{V}{t} = \frac{\pi pg}{8l\eta}\int_r^R 4r^3\,dr = \frac{\pi pg}{8l\eta}\Big[r^4\Big]_0^R \tag{198}$$

or

$$\frac{V}{t} = \frac{\pi R^4 pg}{8l\eta} \tag{199}$$

which is the equation of flow for Newtonians through a capillary tube.

APPENDIX B

Modification of the Poiseuille Equation

After Poiseuille's equation was developed, it was found necessary to modify it. Such a step is not uncommon in connection with deduced equations. The modifications in this case deal with the distribution of energy resulting from several factors in connection with tube viscometers. All the energy employed in creating flow is not used in overcoming viscous resistance. Bingham[1] lists the following ways in which the energy is used.

1. Overcoming viscous resistance.
2. Creating kinetic energy.
3. Producing slipping at the walls of the capillary.
4. Producing eddies (turbulence).
5. Creating distortion of the streamline motion.
6. Energy irregularities arising from uncontrollable temperature changes in the tube.

Only 1, 2, and 5 are important. The others can be neglected. Number 2 is of sufficient magnitude to necessitate a kinetic-energy correction for the Poiseuille equation.

The Kinetic-Energy Correction

Hagenbach[2] was one of the first mathematicians to attempt the deduction of a kinetic-energy term. Later Wilberforce[3] showed that Hagenbach's term was not correct and gave a more satisfactory solution of the problem. The kinetic-energy correction is deduced as follows:

First, it is necessary to obtain an expression that gives the total energy employed to produce flow. Next, the energy is dissipated as heat is derived. This last term is mainly the energy used in overcoming viscous resistance. Finally the second term is subtracted from the first, the difference being the energy consumed in producing kinetic energy. The particles of the material, naturally, are at rest before flow starts. They must be accelerated until they acquire the speed of the flow that is employed in making the viscosity measurement. This consumes energy and is the cause of the kinetic-energy correction.

The method does not deal with energy but with energy input *per unit of time*, that is, with power. Kinetic energy is one-half the mass of the moving material multiplied by the square of its velocity.

$$\text{Kinetic energy} = \frac{m}{2} v^2 \tag{200}$$

where m is the mass and v is the velocity.

The cross section of liquid flow in a tube is a parabola as shown in Figure 6. The contents of the tube, from the mathematical viewpoint, are a collection of telescopic hollow cylinders with walls of thickness dr. Each section of the "telescope" moves, during steady flow, at a different velocity. The velocity depends on the radius r. The larger r is, the smaller is v. Since v is the distance per second any cross section of the cylinder moves, with respect to the capillary wall, the volume of the wall of the hollow cylinder must be $(2\pi r\, dr)v$. Then, its mass and its kinetic energy are, respectively,

$$m = (2\pi r\, dr)v\rho \tag{201}$$

and

$$\text{Kinetic energy per second} = (2\pi r\, dr)v\rho \frac{v^2}{2} \tag{202}$$

To obtain these values for the entire content of the tube, it is necessary to integrate between $r = 0$ and $r = R$. Let the kinetic energy produced per second be E_k. Then,

$$E_k = \int_0^R (2\pi r\, dr)v\rho \frac{v^2}{2} \tag{203}$$

It was shown in Appendix A, Equation 196, that the velocity v of any cylinder of radius r is

$$v = \frac{pg}{4\eta l}(R^2 - r^2) \tag{204}$$

where p is pressure in grams (mass) per unit area. Substituting

(204) in (205) and noting that $d(R^2 - r^2)$ is $(-2r\,dr)$, we find

$$E_k = -\frac{\pi \rho p^3 g^3}{2 \times 4 \times 4^3 \eta^3 l^3} \int_0^R 4(R^2 - r^2)(2r)\,dr \qquad (205)$$

or

$$E_k = -\frac{\pi \rho p^3 g^3}{4 \times 2(4^3 \eta^3 l^3)} \left[(R^2 - r^2)^4\right]_0^R \qquad (206)$$

and

$$E_k = \left[\frac{\pi \rho p^3 g^3 R^6}{8^3 \eta^3 l^3}\right] R^2 \qquad (207)$$

If I is the mean velocity of all the cylinders, then,

$$I = \frac{V}{\pi R^2 t} = \frac{pgR^2}{8\eta l} \qquad (208)$$

and

$$E_k = \pi \rho I^3 R^2 \qquad (209)$$

The pressure causing flow is in grams (mass) per square centimeter and is given the symbol p. Force is mass times acceleration. Then, pg is the force per unit area, and $\pi R^2 pg$ is the force over the entire cross section. Since I is the mean velocity of all the telescopic layers in the tube, it is also the average distance traveled per second, along the length of the tube, by all the particles that moved from a fixed cross section at the same instant of time. Then since energy is force times distance, the energy input per second of time is $\pi R^2 pgI$.

The total energy per second E causing flow is

$$E = \pi R^2 pgI \qquad (210)$$

Subtracting Equation 209 from Equation 210 gives the energy converted into heat:

$$E - E_k = \pi R^2 I(pg - \rho I^2) \qquad (211)$$

Rewriting Equation 209 gives

$$E_k = (\pi R^2 I)(\rho I^2) \qquad (212)$$

which shows that E_k is composed of two factors, the first $\pi R^2 I$ being the volume of flow per second. According to Equation 212, when this factor is multiplied by the second factor ρI^2, the product is the energy consumed per second. Therefore, ρI^2 must be equal to force per square centimeter; otherwise, the product of the two factors could not give energy per second.

When $p = p_k$ (the pressure per square centimeter used in creating the kinetic energy), then,

$$\rho I^2 = p_k g \tag{213}$$

but

$$\rho I^2 = \frac{\rho V^2}{\pi^2 R^4 t^2} \tag{214}$$

Then

$$p_k g = \frac{\rho V^2}{\pi^2 R^4 t^2} \tag{215}$$

Correcting the Poiseuille equation for kinetic energy gives

$$\eta = \frac{\pi R^4 t g(p - p_k)}{8Vl} \tag{216}$$

Substituting 215 in 216 gives

$$\eta = \frac{\pi R^4 p g t}{8Vl} - \frac{\rho V}{8\pi l t} \tag{217}$$

The End Correction (Constant *m*)

A dimensionless factor *m* is added, so that the final equation corrected for kinetic energy is

$$\eta = \frac{\pi R^4 p g t}{8Vl} - \frac{m\rho V}{8\pi l t} \tag{218}$$

The value of *m* probably varies with each capillary tube; but, unless a very great accuracy is desired, the value of *m* is usually taken as 1.12. This number was deduced by Boussinesq on the basis of the kinetic theory. Knibbs, using the experimental data of Poiseuille, derived an average value of 1.14 for *m*. Many values at various times have been assigned to it, ranging from 0.75 to 1.87. Knibbs came to the conclusion that the variation in *m* could not be accounted for entirely as experimental error.

The Rotational Viscometers. Kinetic-energy corrections are not necessary for either one of the rotational viscometers. In the case of the Couette type, the energy is obtained from the motor that drives the cup. This is not the amount of energy that is measured, however. The amount of energy recorded as torque is only that part of the total energy input that is consumed in overcoming the flow resistance of the material after a steady state of flow is attained. This energy is used neither in rotating the cup nor in continuously raising the material from zero to the prevailing velocity (as happens in the capillary-tube viscometer).

The Stormer type of viscometer is somewhat different. The energy is supplied from a falling weight. At the beginning of the fall some of the energy is used in bringing the rotating bob up to its final speed, and some of the energy is consumed in overcoming resistance to flow. When a steady state of rotation is attained, all the energy being expended is then used in overcoming resistance to flow. It is at this point that the rpm is recorded and not during the initial state of fall. Hence, the torque, weight times the radius of the pulley wheel, needs no kinetic energy correction.

APPENDIX C

The Effect of the Immersed End of the Bob on the Torque

The Reiner and Riwlin equation, $U = TS/\omega$, is derived on the assumption that all the torque arises from the lateral face of the bob. The viscous drag on the bottom of the bob is not taken into consideration. This introduces an error in the calculation of S. Correction, however, can be made. The following experimental procedure is recommended.

The bob is immersed to its full length h. The torque T is recorded. The bob is then pulled out in successive steps, and both the depth of immersion and the corresponding torque are recorded at each step. T is plotted against h. This gives a straight-line relation. The curve crosses the T axis where $h = 0$. (See Figure 77.) The intercept, $T_1{}^0$ is the amount of torque arising from the bottom of the bob. It is assumed that the distance between the bottom of the bob and the bottom of the cup is infinite.

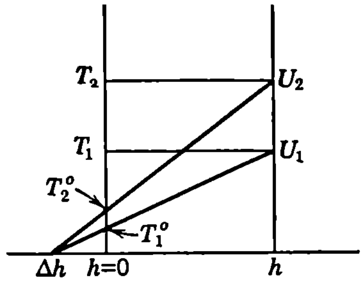


Fig. 77. Method for Determining End Effect in a Rotational Viscometer

It would seem that it should be easier to measure the torque produced by simple contact of the bottom of the bob with the surface of the material; but such a procedure is not sensitive enough to give practical results.

The torque varies with the viscosity. It would not be convenient, then, to attempt a correction by subtracting the end torque from the total torque. It is better to apply a correction that is independent of the consistency of the material and depends only on the dimensions of the instrument. This can be done.

It follows from the preceding equation that, for a given value of h, T varies directly as U. Therefore, for a series of viscosities a series of curves, U_1, U_2, etc., will intersect the h axis at a common point Δh. It is evident that Δh is independent of U. The corrected value of h is $h + \Delta h$, and the percentage error involved in neglect-ing the end effect is $\Delta h/(h + \Delta h)$. When $h + \Delta h$ is used in place of h for calculating S and C, then, the values of these instrumental constants are corrected for the end effect.

Corrections for the End Effect Used by Other Investigators. Two well-known methods, other than the afore-mentioned, have been employed for eliminating the end effect. Mercier[4] used an air pocket in a concavity in the lower end of the bob. The viscous drag of the air on the surface of the material in contact with it is negligible, and so no end correction is necessary. The only objection to this method is that one cannot be sure that air has been entrapped and has remained in the concavity during operation.

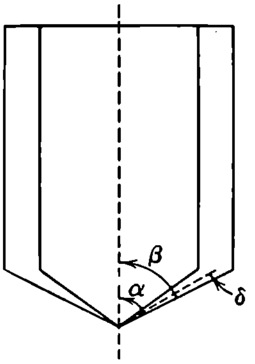


Fig. 78. The Mooney Method for Correcting for End Effect

The most ingenious method for making an end correction is the one developed by Mooney and Ewart.[5] These investigators used cups and bobs with conical bottoms. The angle of the bob bottom is smaller than that of the cup; consequently, it is possible to allow the bob to rest on the cup. (See Figure 78.) Mooney and Ewart's plan is to calculate the angles α and β (Figure 78) in such a way that the "shearing stress and the rate of shear between the conical surfaces shall be the same or approximately the same as between the cylindrical surfaces of the viscometer."

The angle θ_0 is any convenient angle and is chosen arbitrarily. Then the correct angle for fulfilling the requirements for stress and shearing rate is calculated from the following equation:

$$\delta = \epsilon \sin \theta_0 + \epsilon^2(\tfrac{3}{8} \sin^3 \theta_0 - \tfrac{1}{2} \sin \theta_0) \tag{219}$$

where

$$\epsilon = \frac{R_c^2 - R_b^2}{R_c^2 + R_b^2} \tag{220}$$

The only unknown is δ, which can be determined. When its value is found, then α and β are calculated from the following,

$$\frac{\delta}{2} = \beta - \theta_0 = \theta_0 - \alpha \tag{221}$$

If the correct α and β are determined for the arbitrarily chosen θ_0, then the corrected depth of immersion h_o is

$$h_0 = h + \frac{R_c - R_b}{2} \cdot \frac{1 - \cos \theta_0}{\sin \theta_0} \tag{222}$$

where h is the actual depth of immersion. Obviously, the correction is made by adding a small length, $(R_c - R_b)/2 \times (1 - \cos \theta_0)/\sin \theta_0$, to the actual bob length.

APPENDIX D

The Torque on a Disk

Let

$$\omega = \text{radians per second}$$

$$r = \text{length of the radian}$$

Then,

$r\omega$ = distance traveled per second = velocity.
$r\omega/a$ = rate of shear, where a is distance between bob bottom and cup bottom.

$$\text{Force} = U\frac{r\omega}{a} \quad (\text{since } U = \text{force/rate of shear}) \tag{223}$$

$$\text{The torque on the disk} = \text{force} \times r \times \text{area of disk} \tag{224}$$

Then,

$$T = \int_0^{R_b} U\frac{r\omega}{a} \times r \times 2\pi r\,dr \tag{225}$$

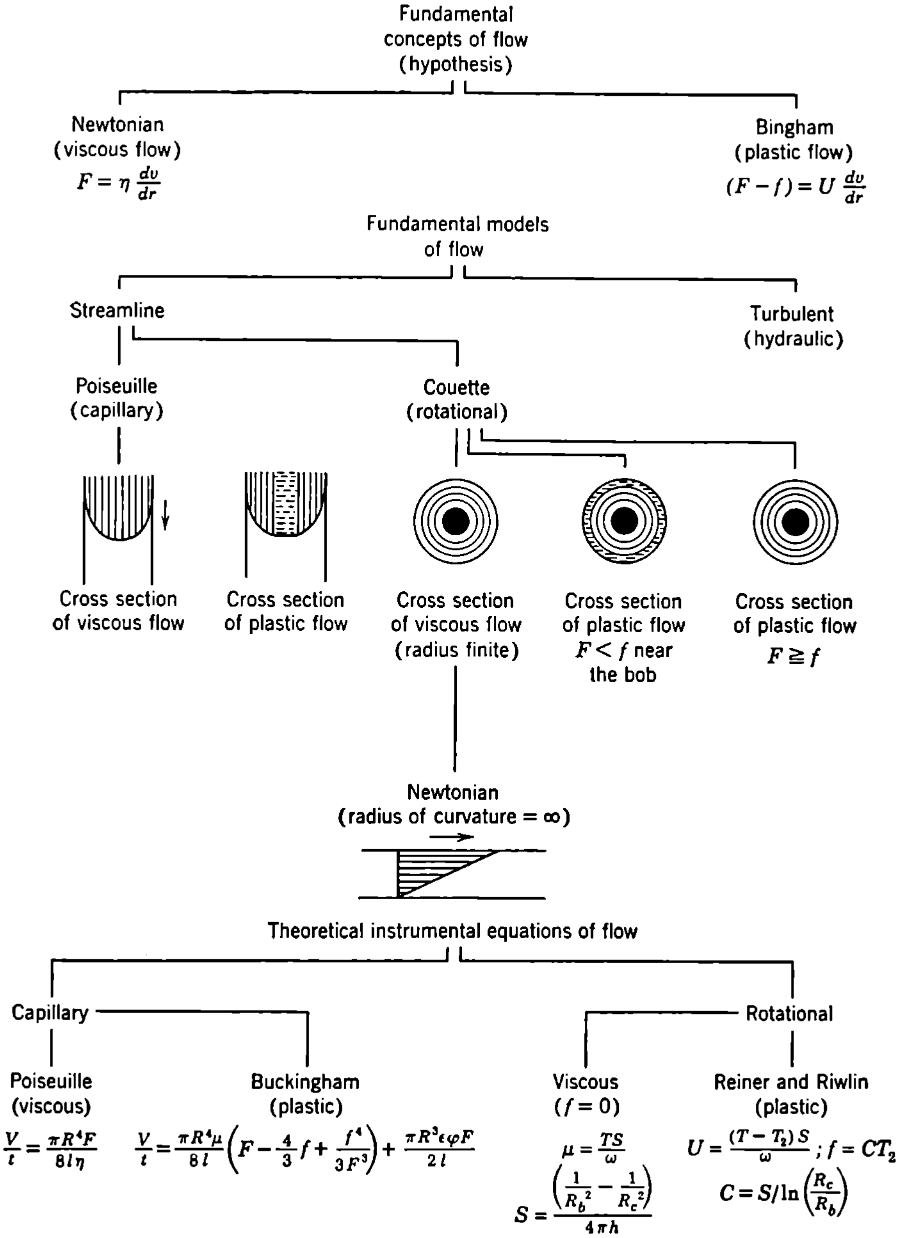
where $2\pi r\,dr$ is the width of a circular strip dr wide, and r is the distance of the strip from the axis of the bob. Then,

$$T = \frac{2\pi U\omega}{a}\int_0^{R_b} r^3\,dr \tag{226}$$

or

$$T = \frac{\pi U\omega R_b{}^4}{2a} \tag{227}$$

APPENDIX E


Fundamental concepts of flow (hypothesis)
Newtonian (viscous flow)
$F = \eta \frac{dv}{dr}$
Bingham (plastic flow)
$(F - f) = U \frac{dv}{dr}$
Fundamental models of flow
Streamline
Turbulent (hydraulic)
Poiseuille (capillary)
Couette (rotational)
Cross section of viscous flow
Cross section of plastic flow
Cross section of viscous flow (radius finite)
Cross section of plastic flow $F < f$ near the bob
Cross section of plastic flow $F \geqq f$
Newtonian (radius of curvature = ∞)
Theoretical instrumental equations of flow
Capillary
Rotational
Poiseuille (viscous)
$\frac{V}{t} = \frac{\pi R^4 F}{8 l \eta}$
Buckingham (plastic)
$\frac{V}{t} = \frac{\pi R^4 \mu}{8 l}\left(F - \frac{4}{3} f + \frac{f^4}{3F^3}\right) + \frac{\pi R^3 \epsilon \varphi F}{2 l}$
Viscous ($f = 0$)
$\mu = \frac{TS}{\omega}$
$S = \frac{\left(\frac{1}{R_b{}^2} - \frac{1}{R_c{}^2}\right)}{4\pi h}$
Reiner and Riwlin (plastic)
$U = \frac{(T - T_2) S}{\omega}; f = CT_2$
$C = S/\ln\left(\frac{R_c}{R_b}\right)$

APPENDIX F

Determining the Magnification of the Electron Microscope

Two methods have been published for obtaining the magnification of the electron microscope. Both have received considerable attention. The first one, by Burton, Barnes and Rochow,[7] is accomplished by using a replica of a diffraction grating. The spacing of the grating being known, the magnification at a given "stop" on the microscope is determined. This process is called the "external calibration." Next, the relative magnifications for all the stops are obtained. This is the internal calibration. By combining the external with the internal calibrations, the magnification for the entire range of the instrument is calculated.

The replica is made from 0.5% solution of Formvar 15/95 dissolved in ethylene dichloride. This solution is poured onto the grating, dried, and floated off on water. It is picked up on a 200-mesh nickel screen support. The distance between the lines of the grating is determined on a spectrometer, using the sodium doublet. A shrinkage of 1.5% was found when the replica was dried. With these facts known it is easy to determine the magnification at a convenient stop.

The internal calibration is carried out as follows: An object large enough to be measured at the lowest magnification and yet small enough so that its entire image appears on the screen with the highest magnification is mounted on a film. The relative image sizes of the object for all the stops are then determined. Since the actual magnification has been obtained from the replica for one of the stops, the magnification for any of the stops is easily calculated.

The replica method has also been used in another manner. An object to be measured can be placed directly on the replica. The replica lines and the object are electron-micrographed together. The distance between the lines being known, the size of the object is determined by dividing the width of the image as it appears on the electron micrograph by the width of the space image of the replica lines.

Unfortunately, there can be no guarantee that the magnification determined for any particular stop by methods like the one just described will remain constant. Mechanical and electrical variations can take place in the electron microscope unexpectedly while the operator is unaware that any change has taken place. Obviously, this is a dangerous condition that must be avoided, if confidence in measurement is to be maintained. Fullam[8] has attempted to correct this situation by a method of calibration, using small glass spheres of known size placed near the material that is to be measured.

The glass spheres are made by the method described by Bloomquist.[6] Pulverized glass is blown through a blast lamp where the particles are melted and form spheres. They are collected at the end of the furnace-like apparatus by means of a vacuum cleaner. The particles are then suspended in water and elutriated. The fraction containing spheres 3.0 microns in diameter is the one most convenient for use.

These spheres are measured directly on a grating replica under low magnification and low electron-beam intensity. In this way distortion of the Formvar replica does not occur. A size-frequency distribution curve is plotted and the diameter of the sphere of greatest frequency noted. When a pigment particle-size measurement is to be made, a drop of a water suspension of the elutriated spheres is placed on the film where the pigment is mounted. This drop is allowed to dry and deposit its spheres in the neighborhood of the pigment.

The electron microscope is now set for the desired magnification. The image of the spheres on the fluorescent screen is measured and a sphere selected that belongs to the group of greatest frequency. The diameters of the spheres of this group has already been determined. It is best to select a sphere that is near the pigment sample. This lessens the possibility of introducing magnification error owing to moving the specimen. The mount is now electron-micrographed. The plate will have on it the sample image as well as the image of the sphere of known diameter. Simple calculation from the latter gives the magnification from which the size of the pigment particles can be determined. A size-frequency distribution curve is plotted and the average diameters determined in exactly the same manner as described for white-light photography.

As stated, the advantages of the Fullam method reside in the fact that any change in the instrument that will affect magnification will produce a corresponding change in the image of the calibrated sphere. However, the diameter of the sphere is known, and so any change in the magnification is immaterial.

The mechanical variations that occur are caused by inability to insert the specimen screen in exactly the same plane of the microscope each time a new specimen is examined. This changes the distance between the specimen and the lens, thus changing the magnification, as it would in a white-light microscope. Irregularities in the specimen screens also cause the same difficulty in maintaining constant magnification. Other sources of trouble in this direction are fluctuations in line voltage, lens current, and accelerating-voltage changes, foreign particles in the lens pole pieces, and various other causes.

Image Distortion with the Electron Microscope

In making particle-size measurements with the electron microscope, one should bear in mind that the electron image is not a true geometrical representation of the particle unless the particle is small and in the center of the field. Hillier[9] has pointed out that this condition is the result of image distortion. Like the white-light microscope there are three lenses in the electron microscope. They are the condenser, the objective, and the projection lens. The resolving power depends on the objective. Distortion arises from the projection lens.

There are two distortions, circumferential and radial. It has been shown that, for a zinc oxide with a d_3 diameter of 0.105 micron, the circumferential distortion increases the measurement to 0.109 micron, and the radial distortion to 0.120 micron.

Hillier states that a mathematical study has been carried out to show that it is possible to obtain any desired degree of correction with a properly adjusted two-lens system, and, in practice, it is possible to design a distortion-free pole-piece system actuated by a single lens coil.

APPENDIX G

Measuring Particle Size with X Rays

The limit of resolution of the electron microscope is usually put at 40 angstroms. For practical purposes it is safer, perhaps, to put it at 100 angstroms, or 0.01 micron. Even this value is not easy to attain. Particles exist, however, that are smaller in diameter than 0.01 micron, and a means of measuring them is highly desirable. Fortunately, there exists a possibility of doing this. The procedure depends on the fact that particles in this region and downward give broadened lines in their X-ray diffraction pattern. From the amount of this broadening, particle size can be calculated. The theory connecting line broadening with particle size was developed by Scherrer,[16] von Laue,[17] and Bragg.[11] It was studied in more detail by Warren,[18, 19] Patterson,[15] Jones,[13] Murdock,[14] and others.

A crystal, on account of its regularity in molecular structure, acts towards a narrow beam of X rays like a diffraction grating. The angle made by the diffracted ray with the crystal face is the Bragg angle θ. The angle made by the diffracted ray and the incident ray is equal to 2θ. Pigment particles are small crystals or fragments thereof. When these crystal particles are as large as 0.10 micron, the diffracted beam gives a sharp line at the Bragg angle. Such a line has a width of only a few seconds of arc on either side of the theoretical angle. When the particles become smaller than 0.10 micron, a broadening of the lines occur. Bunn [12] explains this effect as being similar to an optical diffraction grating with few lines. Such a grating gives diffuse diffracted beams.

The matter is more complex than would appear from the previous statement. Broadening can be the result of numerous causes. Bunn lists them as follows:

(*a*) The fact that some crystals have slightly different unit-cell dimensions from others.

(*b*) The fact that the unit-cell dimensions vary in different regions of the same crystal, owing to variations of composition or to strain.

(*c*) The thermal movement of the atoms.

(*d*) Extremely small particles.

Bunn emphasized the fact that the real problem is to distinguish between the different possible causes of line broadening; and, then, "if a definite verdict on this point can be given, to attempt quantitative interpretation."

The "breadth" of a line is defined as the angular width between the points at which the line intensity falls to half its maximum value. If the breadth at the half height is β and the size of the crystal is the thickness t, then,

$$\beta \text{ (in radians)} = \frac{c\lambda}{t} \sec \theta$$

where c is a constant (equal approximately to 0.98) and λ the wave length of the X ray. This equation is strictly true only for spherical particles in the cubic system and of perfect uniformity in regard to particle size. The equation is used, however, with comparative safety for nonuniform materials in any crystalline system.

Pure diffraction broadening occurs only when the particles are less than 0.10 micron in diameter. In order to find the amount of broadening, therefore, it is necessary to know the breadth b of lines produced by particles greater than 0.10 micron. This factor must be determined with the same camera conditions as used in finding B, the total breadth at half height. $\beta = B - b$.

Jones[13] accomplishes this by mixing with the sample a material whose particles are greater than 0.10 micron. This insures the condition that the diffraction arcs of both specimens are treated exactly alike. Scherrer assumes that $\beta = B - b$. In his formula, β is proportional to $\sec \theta$; therefore, if the broadening is found proportional to $\sec \theta$, the conclusion is that the broadening is caused by very small particles.

The investigators Birks and Friedman[10] heated magnesium carbonate flakes at temperatures ranging from 200° to 1000°C over 6-hour periods. The flakes were composed of particles submicroscopic in regard to the electron microscope. That is, each flake appeared clear without any evidence of an internal particle structure. Above 400°C the individual particles (which composed the flakes) had grown large enough (by isothermic distillation) to appear as minute dots. The flakes, however, retained their original size and shape. The temperature was raised in steps of 200°C and the material electron micrographed each time. Each increase of temperature produced an increase in the size of the internal particles. They were measured by the usual photomicrographic method. They were also measured by the X-ray method previously described. The agreement at 40 angstroms was 20 parts in 60, whereas at 600 angstroms it was 50 parts in 600. The low agreement at 40 angstroms was due to the inaccuracy of measurement with the electron microscope of such small particles at the limit of resolutions of the instrument. For particles between 0.10 and 0.01 micron, the agreement was ±10%.

The specimens were prepared by mixing one-half gram of material in a 2% solution of paralodion in amyl acetate. The mixture was smeared on a microscope slide to give a flat surface of approximately one square inch. A Geiger counter spectrometer was used to read the X-ray pattern for width of lines. This work was done with essentially uniform material. When nonuniformity was produced by making mixtures of different particle sizes, the results became uncertain.

APPENDIX H

For the Laboratory Investigator

This is perhaps the most important section in the book and should be of particular interest to the inexperienced investigator who is entering the field of rheology for the first time. Its object is to help him with certain problems which he will eventually encounter and for which he will find no solutions in the literature of rheology. The contents of this section are not so much concerned with rheology the science, as they are with the rheologist the man—the man who intends to hold down a difficult job and to make it a successful one.

It would be a dereliction of duty on the part of the author to allow the investigator to believe that all he needs for a successful career is a suitable viscometer and the ability to use it as outlined in the preceding chapters. That would constitute but half the problem. The other half is equally important; and, fortunately, it can be stated briefly within the confines of a few paragraphs.

To be specific, the immediate task is to help the investigator make his work secure and profitable. By "secure" is meant the continuance of his job over a period of time as long as desired. By "profitable" is implied a monetary return to the investigator's company considerably greater than the amount the company has invested in rheology. It is true that rheology can produce intangible as well as tangible assets; but companies that are small cannot survive on intangibles. They must have something more substantial to maintain their existence. It is wise, therefore, to discount by 100% the intangibles of rheology and strive to bring in returns in the form of dollars and cents. This is not so easy.

Large companies are more willing to invest their money in long-range possibilities. Immediate returns are not usually expected, and even the intangible assets are not completely discounted. These assets, in the case of rheology, include the rationalization of the subject in regard to fundamental concepts, methods of measurement, and terminology. This gives a common language in which flow properties of products can be discussed understandingly by anyone from the investigator to the top official in the organization.

In addition, there are intangible assets arising from the fact that in the mind of the purchaser a product "controlled by scientific measurements" is more likely to be dependable than one that is not so controlled. Even though such a conclusion may be false, as would be the case where the measurements are made incorrectly, the psychological effect of the expression "controlled products" can still bring in cash returns to the company. However, if the investigator can sell the idea to his customers that he has developed a method of measurement which not only is better than "single-point" tests, but also furnishes a complete rheological analysis of the product, he will have developed his work in a manner that will be satisfactory both from a scientific and a business point of view.

This brings up the subject of "selling" oneself to the company. In no field is this task more difficult than in rheology. Often it is necessary to build up an outside reputation before the rheologist can make his work known within his own organization. It is an accepted fact that technical directors have no time to read the reports of the men under them. If the few "higher-ups" who do read laboratory reports cannot understand them, then such reports are filed away and forgotten. This procedure is so general that the investigator should learn to accept it and not let it discourage him or lessen his efforts to turn out anything but grade-A work.

Obviously, the investigator cannot transfer his work to the plant until his work receives the recognition and approval of his director. If laboratory reports do not provide the means for securing recognition and approval, then how can this necessary task be accomplished? Fortunately, many industries permit their laboratory men to publish fundamental discoveries and research where no involvement of trade secrets occurs. Advantage must be taken of this situation, if it constitutes the only approach to the solution of suitable recognition.

Of the two fields in which recognition can be attained, the one outside the company is the easier. This is unfortunate and perhaps confusing to the beginner, but the fact is this would be considered axiomatic, if it were not subject to actual proof. If a little splash is all the investigator can make within his own organization, he can be sure that no ripple of it will ever lap at the door of the director's room. A large outside splash is easier to attain. Coming from a customer or competitor, news of the investigator's accomplishments is more impressive and arrives sooner than by the seemingly short route the laboratory report takes of climbing a few stairs and being placed directly on the director's desk.

Such being the case, the investigator should be instructed as to his proper course of action. Papers can be submitted for publication without presentation before an audience. There is a disadvantage, however, in always following that procedure. Valuable personal contacts cannot be made. It is better to appear in public every so often and present papers in person. It is not necessary to master the technique of public speaking; but there are certain rules in presenting a paper that must never be broken. The most obvious of these are:

1. Never speak facing the screen or the blackboard, for in that position the speaker's back is turned toward the audience and the audience cannot hear what is being said.
2. If a microphone is to be employed, get to the hall before the meeting, and find the correct distance to stand from the instrument so that the best results are obtained.
3. Do not show tables with innumerable typewritten figures in them. No one can read them.
4. See that the meaning of the co-ordinates of all curves is clearly marked, and then *read* them to the audience *before* explaining anything else.
5. Tell the audience what the paper is about. Do not expect anyone to guess it.
6. Always listen to the audience. If the proverbial pin can be heard when dropped, everything is progressing smoothly. If audience noises are in evidence, change the method of attack or bring the paper to a speedy close. There is no sense in boring anyone.
7. Remember that fully 98% of the audience have not devoted their life to the subject being presented. Therefore, papers being given should be prefaced by introductory paragraphs dealing with fundamentals leading up to the subject itself.
8. All important points in the paper should have their significance emphasized by being repeated, in one form or another, not less than three times.
9. Use less time than allowed on the program for presentation. It never fails to make a favorable impression.

If any of these rules is persistently broken, the investigator can do himself more damage than good. It is, therefore, wise to spend ample time and thought on how the paper is to be presented. It is best to write out the introductory and concluding paragraphs and commit them to memory. The titles of all intermediate paragraphs should be written down in their proper order, and these also should be committed to memory. Never refer to notes during the presentation, as that interrupts the continuity of thought. Never read the paper except on those occasions which demand that type of presentation. Try to present at least one or two papers a year. In about five years' time the investigator should be well established as a recognized contributor in the field of rheology. In case his own company fails to give him recognition, he need not feel that he has lost five years of his time. The reputation that he has gained for himself outside his company should be a marked aid in helping him to secure a rheological position in a more suitable company.

In many cases, especially where the company is comparatively small, the inevitable day arrives when the investigator is asked why his organization should continue to invest any more money in rheology. This question is asked because of several reasons. Somewhere within the confines of the establishment there is an individual who, for want of a better term, will be called a "bookkeeper," and who has in his files a complete record, down to the last penny, of the various expenditures paid by his company for the maintenance of rheology. Unfortunately, there is no record of any returns that would compensate for the expense. There is, then, no visible way to strike a balance, and, as far as the bookkeeper is concerned, the investment is a total loss. This fact is reported.

The investigator, then, will have to defend his job, perhaps unassisted, unless there are other rheologists in his department who can be of help. His own technical director cannot be of much assistance, for he is not a rheologist. The innumerable laboratory reports submitted during the previous years are not of value, for no one has ever read them. The hundreds of consultations on flow problems granted to various members of the plant and laboratory staffs have mostly been forgotten, for the investigator has had no biographer at his elbow to record such discussions for future possible use. Just what can he do. Unfortunately, very little, unless his outside reputation is sufficient to secure him a job as rheologist for another company.

The questions which the investigator most likely will be called on to answer are those given in the preface of this book. The author has striven to answer them in the preceding chapters and hopes that the investigator will experience no difficulty in finding the answers there.

APPENDIX I

For the Laboratory Director

This section is written for the laboratory director, in order to ease the task of understanding what his rheological department is trying to accomplish.

Rheology, as practiced today, is a comparatively new science; hence, the chances are none too great that a formal college training contains any course that touches even lightly on rheology. Equally slight are the chances that it will be possible to acquire a satisfactory understanding of the science through casual conversations on the subject with the laboratory rheologist. If these are the conditions that prevail, then, this section should be helpful.

Naturally, no attempt is going to be made to reduce rheology to terms of one syllable, and to cover the field in a single chapter. Rather the intention is to state what the subject is about and how it can be used to advantage in the control and production of manufactured products.

From the rheologist's point of view all things can be made to flow. The quantity and manner of flow differs in various materials. Since many physical properties depend on the flow nature of the material, the measurement of quantity and manner of flow becomes important. If this is not true, then, any investment in rheology is a waste of money, at least from the management's way of looking at it. This point should be given consideration by technical directors who contemplate the establishment of a rheological department in their laboratories. If the director were a rheologist, he would be a specialist and not an executive. This is one fact that the rheologist never completely understands. When he talks to the director, it will be as one rheologist to another. It will take him some time to find out that most of his conversation never "gets across." It will take, perhaps, several years to discover that none of his reports has ever been really studied. The reason given will be "lack of time." That is only partly true. The principal reason is that each report starts where the previous one left off. Such reports, therefore, are understandable only to rheologists. Only the initial report is likely to include necessary fundamental information. Consequently, after the director has finished the first report, subsequent reports will appear so obscure that attempts to read them can be nothing but a gesture.

That is the actual situation. There seems to be no way to change it. The best that can be done is to list the "high spots" of the science, learn to understand them, and then review them every so often. The "high spots" are given and explained in what follows:

The system of rheology given in this book is composed of a series of connected ideas that are highlighted by five important subjects. A mastery of these subjects should enable any official, whose time is limited, to understand general rheological laboratory reports and to discuss them with the laboratory rheologist. These subjects are:

1. The difference between Newtonian and plastic flow.
2. "Consistency" expressed as a curve.
3. The danger of the single-point method of measurement.
4. The advantages of the multiple-point method.
5. Thixotropic breakdown and the hysteresis loop.

1. If a dime is placed on the surface of water, it will sink to the bottom. If a dime is placed on the surface of butter (room temperature) it will remain on the surface. The reason is that butter has a structure that supports the dime. The strength of this structure, however, is not infinite. If a sufficient pile of dimes be placed on the butter, they too will sink like the single dime on the surface of the water. This experiment illustrates two kinds of flow. The first kind is known as "Newtonian Flow" and is characteristic of all true liquids (like alcohol, ether, gasoline, thin oils). The second kind is called "plastic flow." It is characteristic of those materials that can be molded (like putty, clay, cheese, pastes).

In the case of Newtonians, it would be found that, even if the dime were cut into small pieces, these pieces would likewise sink. This fact leads to an important rheological conclusion: Newtonians flow under any pressure, no matter how small. Plastics flow only when the pressure exceeds a certain minimum value. That is, one dime was not enough to sink through the butter. A vertical pile of two or three dimes might still have been insufficient. Four dimes placed on top each other might have sunk. If that is so, the four dimes cause the structure in the butter to yield. The weight of the four dimes, then, is the *yield value* of the butter. Newtonians have zero yield value. *That difference in yield value between Newtonians and Plastics constitutes one of the most important facts in industrial rheology.*

Besides yield value, there exists another flow factor. This factor is called the "coefficient of viscosity," or, in short, just "viscosity." Viscosity deals with the rate of flow (strictly speaking, the *rate of shear*). When the dimes are piled onto the water or onto the butter so that the flow is at exactly a unit rate, then the weight of the dimes in each case constitutes the respective viscosities. Viscosities, unlike yield value, cover all things that flow. Thick sluggish liquids have a high viscosity; thin limpid ones, a low viscosity. Neither or both can have a yield value.

2. There is a general term used when referring to the flow nature of a material. That term is "consistency." It covers all the flow properties such as yield value and viscosity. Consistency is too complicated to be measured, but it is easy enough to express in the form of a curve. The business man is familiar with the use of curves. His curves are generally prices versus time. The stock-market curve is a familiar example. Such a curve tells the change in price with time. The rheologist's consistency curve shows the change in the rate of flow with pressure. In the case of Newtonians, if the pressure is doubled, the rate of flow is also doubled. That is the simple Newtonian law from which Newtonians take their name. Plastics follow a slightly more complicated law. If the pressure *in excess of the yield value* is doubled, the rate of flow doubles.

Consistency-curve examples can be found throughout this book. It should be noticed that they are composed of two factors, rate of flow (given as rpm) and force (given as torque). All rheological consistency curves are composed of these two variables in one form or another. These factors are obtained by direct measurement with a viscometer. From these consistency curves, yield value and viscosity are calculated. How this is accomplished is described in the text.

3. When the rheologist first takes up his duties, he will be informed that methods for determining consistency have been in use for many years in the plant and that there is no necessity to introduce any new ideas. He will be told that the methods em-

ployed are "accurate enough for all practical purposes." Now your rheologist is interested in correctness of method and not in accuracy, for there is no yardstick for determining accuracy of measurement of plastic materials. Yet such an idea is hard to sell, and constant pressure will be exerted to prevent the rheologist from introducing such revolutionary ideas and methods into the plant.

The plant laboratories have been using, probably for years, simple tests for "determining" consistency. These tests depend on a single measurement and are, therefore, called "single-point" methods. They include such procedures as stirring with a spatula, tapping out on paper, flow through an orifice, and flow down an inclined plane. Since none of these methods gives a consistency curve, yield value cannot be determined, and, consequently, the viscosity of a plastic cannot be calculated.

The procedure has been in the past (and will continue to be in the future) to assume that Newtonians and plastics can be measured in the same way, that is, by single-point methods. It takes two points to determine the position of a linear curve. Single-point methods, therefore, cannot do this; hence, they are a source of danger and should be barred from the laboratory. No method should be accepted that cannot produce a full consistency curve.

4. The more advanced rheologists of today have given up single-point methods for measuring non-Newtonians. They use, instead, viscometers built for the purpose of producing multiple-point measurements. This method is best carried out with what are called rotational viscometers. Such instruments have the advantage of giving consistency curves from which both yield value and viscosity can be determined. In addition they can give valuable information on thixotropic materials (see item 5).

5. There are a great many rheological substances (like paints and printing inks) that thin down on being stirred and thicken up again when allowed to rest. Such materials are called "thixotropic." The term means to "change by touch." The thing that is changed is the structure of the material. It breaks down and so affects the rheological properties of the material.

Thixotropic subjects present a particularly difficult problem in measurement. How can a measurement be made if the material changes while it is being measured? The solution is in the so-called hysteresis loop. This loop is formed by plotting together two consistency curves taken on the same material as close together in time as possible. The first curve is the upcurve. This is made by starting the viscometer at the lowest rpm and increasing the speed gradually until the highest rpm is attained. This curve will be bow-shaped, if the material is thixotropic.

The downcurve is started immediately the upcurve is finished. The downcurve will be straight. When the upcurve is plotted together with the downcurve, a loop is formed. The size of the area of the loop indicates the extent of the thixotropic breakdown. Like yield value and viscosity, thixotropic breakdown can be recorded as a single number.

The five topics just discussed give a bird's-eye view of practical industrial rheology. They do not indicate, however, whether rheology will be of value to a company or not. The answer to that question can be had from any experienced rheologist who knows the nature of the flow problems encountered in the manufacture of the company's products. It is conceivable that rheology can be useful in the following ways:

1. The control of consistency.
2. The advantage gained by advertising controlled consistency.
3. Improvement of old products.
4. The development of new products.
5. The investigation of the rheological differences between competitor's products and the company's.

Objections from the plant will be made against the "control of consistency" by consistency-curve methods. The arguments will be that it is "too expensive" and "too time-consuming." There may be no answers to those arguments. If any solution is found, it will depend on circumstances that will differ for each laboratory and plant. Generalities cannot very well be made. The four remaining points are usually not contested. Their value and possibilities are self-evident. They might in themselves be enough to warrant the installation and development of a rheological department in the company's laboratory. If that is the decision, plan on making such a department permanent. Do not try to make it a side issue to be of temporary value only. It costs money to build an efficient rheological department. It can bring back returns to the company *only as long as it is allowed to exist.*

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GLOSSARY

(The terms are defined as used in this book.)

Absorption. Penetration of a liquid into pore space.

Adhesion. Adherence of two (chemically) different materials.

Adsorption. Adherence of one material on the surface of another, usually in monomolecular layers. It is not a chemical reaction, and the binding force is a loose one.

Aggregation. A group of two or more particles. If the particles are "cemented" together, a hard aggregate is formed. Soft flocculates are also classified as aggregates, but such aggregates do not function rheologically as single particles (as do hard aggregates).

Angstrom. A unit of length. It is equal to 0.1 millimicron ($m\mu$), or to 0.0001 micron (1×10^{-8} cm). The angstrom is the unit used in optics, in spectroscopy and in electron microscopy.

Apparent viscosity. An imaginary quantity applied to non-Newtonians. It is the viscosity the non-Newtonian would have (at a given rate of shear) if it were a Newtonian. It is obtained experimentally by dividing the shearing stress by the rate of shear, and then multiplying by the instrumental constant.

Area of the hysteresis loop. Area of the loop formed from a thixotropic material when its up- and downcurves are plotted together. If the area of the loop is zero, the material is nonthixotropic. The extent of breakdown is given by the coefficient M.

Arithemetical mean. This is an average obtained by dividing the sum of all the measurements by the total number of measurements.

Average particle diameter. This expression is in reference to a mass of particles and must not be confused with the expression "average diameter of a particle." *The average particle diameter is the diameter of a hypothetical particle which in some particular way represents the total mass of particles.* The average particle diameters most frequently used are:

$$d_1 = \text{arithmetical mean} = \Sigma nd/\Sigma n$$

$$d_2 = \Sigma nd^2/\Sigma nd$$

$$d_3\text{, the specific diameter} = \Sigma nd^3/\Sigma nd^2$$

$$d_4 = \Sigma nd^3/\Sigma nd^2$$

$$\Delta = \sqrt{\Sigma nd^2/\Sigma n}$$

$$D^3 = \sqrt[3]{\Sigma nd^3/\Sigma n}$$

Average particle size. Usually synonomous with "average particle diameter" though it can refer to surface, volume, or weight.

BEKK'S VISCOMETER. An instrument for the measurement of printing inks. It consists of a ball plunger and a spherical container for the ink. The apparatus is operated by a series of levers somewhat similar to those used on the Tackmeter. Bekk defines "viscosity" as the resistance to compression, and "tack" as the resistance to pulling. Bekk states that a mathematical relationship exists between his terms "viscosity" and "tack" but does not give this relationship in the form of an equation.

BINGHAM BODY. A term employed by Reiner, and applied to those ideal materials that have a definite yield value. The nearest approach to this condition is found in materials like putty, printing inks, and paints, that is in pigment–vehicle suspensions where the pigment–vehicle ratio is sufficiently high.

BINGHAM CONCEPT. The concept that plastic materials will not flow until the shearing stress exceeds a certain definite value.

BINGHAM YIELD VALUE. The shearing stress in dynes per square centimeter below which value flow will not take place.

BODY. A technical term synonomous with the rheological term "consistency."

BREAKDOWN WITH SHEAR. One of the two types of thixotropic breakdown: dependent only on the rate of shear and not on *duration* of shear.

BREAKDOWN WITH TIME. That part of thixotropic breakdown that accumulates with time when a constant shearing stress is being applied.

BROWNIAN MOTION. B. MOVEMENT. A vibratory-like motion that small suspended particles undergo, produced by bombardment of the molecules of the suspending medium. The energy involved is that arising from the heat of the system.

BUBBLE-TUBE VISCOMETER. A viscometer composed of a short glass tube closed at both ends. The tube contains the material under test together with a substantial-size air bubble. The test is run by turning the tube upside down and recording the time required by the bubble to travel the length of the tube. This time is compared with a set of standard tubes containing materials of known viscosity.

CALIBRATION OF VISCOMETER. For rotational viscometers, this is the process of determining the wire constant K. K is the torque per degree of deflection. For capillary viscometers, this is determining the value of the instrumental constant $\pi R^4/8l$. It can be carried out by direct measurement of R and l, or by using a liquid of known viscosity.

CAPILLARY VISCOMETER. A viscometer where the flow takes place in a capillary tube. Either gravity or air pressure is used to produce the flow. Volume of flow per second and the activating pressure are the factors measured.

CENTIPOISE. One hundredth of a poise, the unit of viscosity.

CIRCULAR WEDGE MOUNT. A microscopical mount used for pigments in which the material is dispersed in a melted resin on a microscope slide and the cover glass is pressed down at the center so that a circular wedge is produced. The particle density is small at the center of the mount and increases radially toward the edge of the mount.

COEFFICIENT OF THIXOTROPY. A term used by Goodeve and Whitfield to express the thixotropic nature of a material.

Coefficient of thixotropic breakdown. An expression used by Green and Weltmann. There are three of these coefficients symbolized by the letters M, B, and V. These coefficients express the various changes that take place in the consistency of a thixotropic material when it is broken down by a shearing action.

Cohesion. The attraction of like molecules in a substance.

Colloid. A material composed of colloidal particles. A colloidal particle is one that is larger than molecular in structure and smaller than 0.1 micron. It is immaterial whether the particle is crystalline or amorphous.

Colloidal suspension. A suspension in which the dispersed phase consists of particles of colloidal size. These particles are in suspension and not in molecular solution.

Connected structure. A structure in which the suspended particles are present in the form of a continuous network, giving a form of rigidity to the material. A flocculated-pigment suspension where the pigment–vehicle ratio is sufficiently high is a common example.

Consistency. The flow nature a material possesses by virtue of its internal structure. Consistency is represented by a curve (shearing stress versus rate of shear) and not by a single value except in the case of Newtonians. The consistency of a Newtonian is defined by its coefficient of viscosity.

Contact angle. The internal angle made by a drop of liquid on a solid surface. This angle adjusts itself so that the cohesional force of the liquid and the adhesional force between liquid and solid balance each other.

Convection currents. As used in this book, the expression refers to currents in a liquid mount. These currents take place under a cover glass and can arise from evaporation at the edge of the cover glass, from heat from the microscope lamp, and from pressure of the cover glass just after it has been placed on the mount.

Couette flow. The concentric cylindrical flow that takes place in a rotational viscometer.

Couette viscometer. A rotational viscometer, especially the type in which the cup rotates.

Dark-field microscope. A microscope in which the central light around the optic axis is stopped out. This gives an illuminated image on a dark background. Colloidal particles can be detected in this manner that are too small to be found with a light field.

Deflocculation. The act of separating flocculated particles. Stirring can do this, if the system is not a crowded one. Reflocculation takes place when stirring stops. Deflocculation can be accomplished by lowering the interfacial tension with a suitable "wetting agent."

Deflocculation agent. A material that can be adsorbed on the surface of flocculated particles and thereby lower the intefacial tension. If the lowering is sufficient, deflocculation will take place.

Diameter (magnification). In photomicroscopy the magnification is given by the number of times any diameter of the object is enlarged. The enlargement of the area will be equal to the square of the enlargement of any diameter.

Diameter of particle. This is not an "average diameter" but the length of an imaginary line drawn through the particle in some particular manner. In the case of a sphere it is the diameter of the sphere. In the case of a cube it can be the edge, the diagonal of a face, or the internal diagonal of the cube. For a parallelepiped, the harmonic mean of its three edges is a "diameter" that is related to specific surface. Also, there is a "horizontal diameter" used in particle-size measurement. Refer to "horizontal diameter."

DILATANT. A type of consistency described originally by Osborne Reynolds. Dilatant materials are particle suspensions which are deflocculated and are in a settled state of minimum voids. An attempt to make such a system flow dilates the voids and thereby increases the resistance to flow. Also the material takes on a dry appearance when pressure is applied to it.

DISPERSING AGENT. An agent that deflocculates. Sometimes it is an agent that assists in breaking down hard aggregates.

DISPERSION. A mixture of particles in a vehicle. The particles may contain hard aggregates or may be flocculated, or both conditions might exist together. A dispersion is considered to be good when the hard aggregates are ground down to fine particles. A good dispersion may be either flocculated or deflocculated. For this reason the term is a poor one and should never be used unless defined.

DOOLITTLE VISCOMETER. A viscometer of the rotational type in which the bob is deflected to one side and then the deflecting force is released. The viscosity is calculated from the dampening effect the material produces on the oscillations on the bob.

DOWNCURVE. That part of the hysteresis loop of a thixotropic material that records the torque (on a rotational viscometer) when the rpm is being decreased.

DYE. A colloidal material that imparts its color to a surface by the process of adsorption. There are also dyes which react chemically with surfaces. Dyes usually form colloid suspensions of particles too small to be seen with white-light microscopy. Normally, pigment particles are considerably larger than dye particles. A dye can be exhausted from its bath. A true solution cannot.

EFFLUX VISCOMETER. A viscometer that discharges the test material through an orifice or through a capillary tube.

EINSTEIN MODEL OF FLOW. A model in which the suspended particles are spherical and at such a dilution that no particle collisions take place.

ELASTIC DEFORMATION. A type of deformation in which no true flow takes place. Each molecule, though displaced from its initial position, still remains within the range of attraction of its original neighboring molecules. When the stress is removed, the displaced molecules return to the position they occupied before the stress was applied. As a consequence, in elastic deformation, strain is proportional to stress.

ELECTRON MICROSCOPE. A microscope that produces an image by means of a beam of electrons instead of a beam of light. The "lenses" are magnetic and electric fields.

END CORRECTION FOR BOB. A correction factor that is added to the length of the bob immersed, in a rotational viscometer. The correction takes care of the torque on the bottom of the bob.

End correction for capillary viscometer. This correction arises from the disturbance to streamline flow at the ends of the capillary. The correction constant is given the symbol m. It is determined experimentally and is multiplied by the kinetic-energy factor.

Falling-ball viscometer. A viscometer composed of a large tube containing a metal ball. The material to be measured is placed in the tube together with the ball. No air bubbles are allowed to enter. The measurement of viscosity is made by obtaining the rate of fall of the ball through the material. Stokes' law is used for the calculation. It is necessary to know the radius of the ball, the density of the ball, and the density of the liquid.

False body. A technical expression with various meanings. To some investigators "false body" means yield value; to others it means thixotropy.

Flocculation. The clustering of suspended particles. Flocculation takes place if there is a decrease in free energy of the system when particles collide.

Fluidity. The reciprocal of the coefficient of viscosity. Fluidity is the rate of shear induced by a unit shearing stress.

Force of adhesion. The force of molecular attraction exerted by materials of unlike chemical composition.

Force of cohesion. The force of molecular attraction exerted by materials of like chemical composition.

Force of flocculation. The van der Waals forces that hold together the particles of a flocculate.

Force per unit area. This is an alternate expression for "shearing stress."

Friction. As used here, it refers to the Bingham concept of a minimum force that will just induce flow.

Fundamental particle. This is a particle composed of either a single crystal, a fragment of a crystal, a twin, a threeling, or a fourling.

Gel. A flocculated mass of microscopic particles.

Goodeve's viscometer. A rotational viscometer in which the bob and cup are cone-shaped. The rate of shear is changed by raising or lowering the cone-shaped bob.

Green's rotational viscometer. A viscometer of the Couette type so constructed that the rpm can be increased or decreased in small steps over a wide range. The cup is immersed in a temperature-controlled bath and is rotated by a shaft that enters the bottom or side of the bath through a watertight connection. Calibration of the wire is done with weights and not with standard liquids.

Hard aggregate. One in which the particles are cemented together; not a flocculate.

Hooke's law. The law of deformation for a perfectly elastic body. It states the stress–strain relationship for a Hook body.

Hooke solid. A name given by Reiner to an ideal body in which stress is directly proportional to strain.

Horizontal diameter. A particle diameter, proposed by Green (1921), to be used with the photomicrographic method of particle-size determination. The diameter is the horizontal distance through the projected center of the particle image and terminated at the image boundary.

HYDRAULIC FLOW. Turbulent flow; the type of flow existing in pipes rather than in capillary tubes.

HYDROPHOBIC. Literally, water fearing. It refers to materials that are not wet by water. Hydrophobic pigments flocculate in water.

HYSTERESIS LOOP. The consistency curve of a thixotropic material, obtained on a rotational viscometer and formed by plotting the up- and downcurves together. The extent of the area indicates the amount of thixotropic breakdown.

INCLINED-PLANE VISCOMETER. Any viscometer that employs an inclined plane and a rolling device. The test material is spread on the plane, and the time required for a cylinder or sphere to roll down the plane over the film is considered to be a measure of its viscosity.

INKOMETER. An instrument employed for measuring certain properties of printing inks. These properties are called "tack" and "length." The apparatus consists of a series of ink rollers. The ink exerts a viscous drag on one of these, pulling it away from its normal position. The restoring force is measured at several speeds from which the calculations are made.

INTRINSIC VISCOSITY. This is a name given by Kraemer to a ratio obtained by the specific viscosity and by the volume concentration c. Intrinsic viscosity is numerically equal to the constant in the Einstein equation for the viscosity of colloidal suspensions.

JELLY. This should not be confused with the term "gel." A jelly is almost always composed of *submicroscopic* particles. These particles form a firm network showing marked elasticity.

KELVIN SOLID. A real body. A Hooke solid in parallel with a Newtonian liquid. The full elastic effect is not instantaneous, and there is a time lag in the appearance and disappearance of the elastic strain.

KINEMATIC VISCOSITY. The viscosity of a material divided by its density.

KINETIC ENERGY. The energy associated with a body when in motion with respect to another. It is equal to one-half the mass times the square of the relative velocity.

KINETIC-ENERGY CORRECTION. A correction applied to the Poiseuille equation. It arises from the fact that all the energy input is not used in overcoming viscous resistance. Some of it is employed in raising the velocity of the material from zero to the velocity of flow.

LAMINAR FLOW. Orderly flow; flow in parallel layers—sometimes called telescopic flow—the opposite of turbulent flow.

LIVERING. Thickening of suspensions arising from chemical reaction. Usually soap formation is the result.

LOOSE STRUCTURE. A structure where the linkage forces are zero. A molecular or particle aggregation that possesses no rigidity. The particles are disconnected.

LOWER YIELD VALUE. A Houwink term used to designate the shearing stress that produces the initial shear at the wall of the capillary tube. It is the stress where the consistency curve appears to start on the force axis.

LYOPHOBIC. The opposite of hydrophobic. Lyophobic materials are those that are wet by water but not by oil.

MAC MICHAEL VISCOMETER. A rotational viscometer of the Couette type.

MAGNETIC STRUCTURE. A structure in which the particles are held together by magnetic forces.

MAXWELL LIQUID. A real body composed of a Hooke solid and a Newtonian liquid. Its characteristic is instantaneous elastic elongation together with a steady Newtonian flow.

MEGAPOISE. One million poises.

MICELLE. A colloidal particle.

MICRON. One thousandth of a millimeter. Approximately one twenty-five thousandth of an inch.

MILLIMICRON. One millionth of a millimeter, or one thousandth of a micron; written $m\mu$.

MIXED REGIME OF FLOW. The flow of a Bingham body in a capillary or rotational viscometer where the shearing stresses are not all greater than the yield value. The result is that the flow is composed partly of plug and partly of laminar flow. This condition produces (or helps to produce) the curvilinear end of the consistency curve.

MOBILITY. The reciprocal of plastic viscosity. It is analogous to the term fluidity for liquids. Mobility is the rate of shear induced by a shearing stress of one dyne in excess of the yield value.

MOBILOMETER. A viscometer composed of a metal tube and a plunger. The plunger is a perforated plate, and the liquid under test is squeezed through the perforations as the plunger descends in the tube. Different weights can be applied to the plunger and a consistency curve obtained by plotting these weights against the reciprocal of the time it takes the plunger to descend.

MOLECULAR ALIGNMENT. This is an alignment in the direction of flow taken by long molecules when subjected to a shearing force. This alignment accounts for the curvilinear nature of the pseudoplastic consistency curve.

MOLECULAR SOLUTION. This is a term used in distinction to colloidal suspension. It designates true solution in which the dissolved particles are molecules and not micelles. Unlike a dye, a molecularly dissolved material cannot be exhausted from solution.

MOUNT. A microscopical term. It refers to a preparation of a material made on a microscope slide so that it is in a condition suitable for examination.

MOUNTING MEDIUM. A liquid or plastic of suitable refractive index in which a microscopical object is mounted.

NEWTON CONCEPT. For liquids, the rate of flow is proportional to the shearing stress.

NEWTON MODEL OF FLOW. A model composed of plane-parallel laminas of indefinite extent. The tangential shearing stresses are equal on all the laminas.

NONUNIFORMITY. A term used in reference to the "width" of the particle-frequency-distribution curve. The wider this curve (other things being equal), the less uniform the particle size is. A completely uniform mass of particles gives a straight up-and-down distribution curve, If no two particles are the same in size, the distribution curve is flat and coincides with the particle-size axis.

PARALLEL-PLATE VISCOMETER. A plastometer in which the flow is radial and takes place between two parallel plates. These plates can be either pulled apart or squeezed together.

Particle counts. A term used in dark-field microscopy where the number of suspended particles in a given volume are counted. The average diameter D is determined from such counts.

Particle measurements. The diameter of a particle is measured, usually from its photographic image. The "horizontal diameter" is the one most commonly employed. From such measurements "average diameters" for a mass of material are calculated.

Pigment. Particulate materials used for imparting color (hue) usually to a surface. A pigment is nonsoluble in its vehicle. Its particle size is usually large enough to be seen with a microscope. The particles are larger than dye particles.

Plastic. As used by rheologists, this word has a double meaning. In one case it means Bingham bodies; in another, it refers to the synthetic plastics.

Plastic consistency. The consistency of a material that has a Bingham yield value.

Plastic viscosity. The shearing stress in excess of the yield value that will induce a unit rate of shear.

Plastometer. A viscometer in which Bingham bodies can be run for obtaining their consistency curves.

Plug flow. That part of the flow where the shearing stress is less than the yield value.

Poise. The unit of viscosity. A material has a viscosity of one poise when a shearing stress of one dyne per square centimeter will induce a unit rate of shear.

Poiseuille flow. The type of laminar flow that takes place in a capillary tube when streamline motion prevails. The term is applicable to Newtonians. In this book it is also applied to Bingham bodies.

Poisson's ratio. The ratio of the fractional transverse contraction to the fractional longitudinal extension of a body under a tensile stress.

Pressure. The air pressure used in viscometers or in plastometers to produce flow. It usually refers to the pressure in excess of atmospheric pressure, or to the drop in pressure from one part of the capillary tube to another.

Process inks. Printing inks, usually in sets of four colors. The most frequent combination is yellow, red, blue, and black. These are printed over one another in that order, the result being a colored print containing the desired hues, whites, blacks, and grays.

Pseudoplastic. A non-Newtonian that gives a consistency curve which starts at the origin and curves away from the force axis. It is nonlinear. Pseudoplastics have no Bingham yield value.

Pull resistance. Tack—the resistance offered by a viscous material, if a fingertip is pushed down firmly on it and then pulled away.

Rate of shear. The velocity of one plane with respect to another plane divided by the perpendicular distance between them. If the rate of shear between the planes is not constant then it is expressed by the ratio dv/dr. The Newton model is an example of the first case. Couette flow (rotational viscometer) is an example of the second case.

Redfield viscometer. Efflux type of viscometer used mainly in England.

Refractive index. The ratio of the velocity of light in a vacuum to the velocity of light in a substance.

Relative tack. The tack of the sample divided by the tack of a standard sample. At high velocities, relative tack approaches the value of plastic viscosity.

Relative viscosity. The ratio between the viscosity of a liquid and the viscosity of water at the same temperature. For suspensions: the viscosity of the suspension minus the viscosity of the vehicle divided by the viscosity of the vehicle. This latter expression has been proposed by Staudinger.

Relaxation time. An expression employed by Maxwell. It is the time required for a stress (applied to a viscous material) to drop to f_0/e when the strain is maintained constant. f_0 is the optimum or initial force. e is the base of the natural logarithms.

Resolution. A term used in microscopy. Resolution is the ability of the microscope to separate two objects lying close together. It is given approximately by the equation, $d = \lambda/2$ N.A., where d is the smallest distance between two particles or edges that can just be resolved by light of wave length λ and an objective of numerical aperture, N.A.

Rhe. The unit of fluidity. A material has a fluidity of one rhe when a shearing force of one dyne per square centimeter induces a unit rate of shear.

Rotational viscometer. A viscometer composed of a cylindrical cup and of a cylindrical bob. The bob is suspended in the cup and the test material is put into the space between the bob and cup. Either the bob or cup can be made to rotate. The speed of rotation and the torque imposed by the viscous drag resulting therefrom are the measurements from which the coefficient of viscosity and the yield value (U and f) can be calculated.

Saybolt viscometer. An efflux viscometer, used mainly for oils.

Seepage. A term applied to capillary viscometry. It refers to the flow of the vehicle through stationary suspended particles instead of complete flow of the suspension. It constitutes a filtering action. Bingham employed the term "seepage" in attempting to explain the cause of the curvature of the Bingham-body consistency curve.

Shape factors. Used in connection with particle-size measurement as determined by the photomicrographic method. There are two shape factors: ν with respect to particle volume, and σ with respect to particle surface.

Shearing force. The force applied by a viscometer to produce flow.

Shearing stress. Shearing force per unit area.

Size of particle. Not to be confused with "average particle size." The "size" of a particle can be an arbitrary measurement such as particle volume, particle surface, and horizontal diameter. In the case of regular materials such as cubes, the size of the particle can be designated by the edge, the diagonal of the face, or the diagonal through the center of the particle.

Slippage flow. A phenomenon that can take place only with suspensions. It occurs at the walls of a capillary-tube viscometer and, to a negligible extent, at the inner surface of the cup and the surface of the bob in rotational viscometers. The particles are held together (by the force of flocculation) as a solid plug. This plug is lubricated by a thin layer of the vehicle.

When flow starts, the plug moves as a single piece. Its flow is not laminar. It is called slippage flow.

SLIT ULTRAMICROSCOPE. A dark-field microscope employed in studying colloid suspensions. The field is illuminated with a narrow beam of light that has passed through an adjustable slit so that the volume of the suspension is known. The number of particles in this volume is counted, and from the known concentration the number of particle per gram N is determined.

SPECIFIC SURFACE. The total particle surface per gram of material.

SPECIFIC VISCOSITY. See relative viscosity. These terms are interchangeable.

STOKE. A unit of kinematic viscosity. A liquid with a viscosity of one poise has a kinematic viscosity of one stoke, if its density is one.

STOKES' LAW OF FALL. $\eta = 2(\rho_b - \rho)gR^2/9V$ where η is the viscosity of the test material; ρ is its density; ρ_b is the density of the ball, and V is its velocity.

STORMER VISCOMETER. A rotational viscometer in which the bob rotates. The force causing the rotation is a falling weight fastened by a string wound around a drum on the upper end of the bob shaft.

STRAIN. The alteration in shape due to an applied stress.

STREAMLINE FLOW. Nonturbulent flow. It takes place in parallel layers which can be flat or cylindrical. Streamline flow is the type employed in viscometers.

STRESS. The force that causes strain.

STRUCTURAL VISCOSITY. A term applied to non-Newtonians; a type of viscosity that depends at least in part, on the structure of the test material.

ST. VENANT BODY. An ideal body. One to which no force can be applied that is greater than its "yield value." Any attempt to increase the applied force simply results in an increased velocity of flow (or motion).

TACK. Pull resistance—a function of viscosity or of viscosity and yield value. At high speeds it is practically synonomous with plastic viscosity, in the case of printing inks. Rubber-like materials have a tack that is influenced by the elasticity of the material. In all cases it should be considered as pull resistance and not as adhesion, which is an entirely different phenomenon.

TACKMETER. An instrument made for the purpose of analyzing pull resistance. It is composed of a flat metallic finger tip, a flat plate on which the material is put, a micrometer screw for changing the initial film thickness, and a lever on which different pulling weights are hung. Each of these factors can be changed without changing the others. The effect of each is thus observed.

THIXOTROPIC LEVEL. This is the temporary stable state attained in the downcurve of the hysteresis loop of a thixotropic material.

THIXOTROPY. A phenomenon possessed by certain suspensions. Such suspensions possess a type of structure which is destroyed by agitation and which rebuilds itself upon rest. The reaction is nonchemical and isothermal.

TORQUE. Force times distance. The distance is measured from the point of application of the force, to the axis or fulcrum about which the system rotates.

TRAPPING OF INKS. A term used in the printing-ink industry. An ink is trapped by another ink (previously printed on the stock) if the first down ink pulls the second ink from the printing plate and retains it. In process printing the usual order is first down yellow; second down red; third down blue; and fourth down black.

TURBULENT FLOW. Disorganized flow; the opposite of streamline flow; nonlaminar flow—sometimes referred to as hydraulic flow.

TURPENTINE MOUNT. A term used in pigment microscopy. The pigment is dispersed by wetting it with a drop or two of freshly distilled turpentine and rubbing this mixture with a glass rod backward and forward on a microscope slide.

TWO-DIMENSIONAL FLOCCULATION. A phenomenon in which the particles flocculate in the form of thin sheets.

ULTIMATE WORKING UNIT. A term used in pigment microscopy. It is the smallest unit in a dispersion and functions as a single particle throughout the use and application of the material. It is never a flocculate, which is temporary with no permanent existence. The ultimate working unit can be a single particle or a group of tightly bound particles.

ULTRAVIOLET MICROSCOPY. Microscopy in which the source of light is in the ultraviolet region of the spectrum. In the Köhler system, the optical parts are made entirely of quartz.

UNIFORMITY COEFFICIENT. Used here only in reference to particle-size measurements, it is the factor which states how nearly alike all particles are in a given mass. Infinite uniformity means that all the particles are of the same size. Zero uniformity means that no two particles are the same.

UPCURVE. That part of the consistency curve produced on a rotational viscometer that starts with the lowest rpm and increases to the highest. In a thixotropic material the upcurve is bowed, indicating thixotropic breakdown.

VAN DER WAALS FORCES. The forces of cohesion; forces arising from secondary valences. They do not produce true chemical bonds. They are presumably responsible for pigment flocculation and also for adhesion.

VEHICLE. The liquid medium in which pigments and particulate substances are ground and suspended. In materials like paint, the vehicle is often linseed oil.

VELOCITY GRADIENT. The same as rate of shear.

VISCOMETER. An apparatus for measuring shearing stress and the ensuing rate of shear from which viscosity, plastic viscosity, and yield value can be determined. It is used for materials that can be made to flow.

VISCOSIMETER. Same as a viscometer.

VISCOSITY. The resistance of a rheological material, such as liquids and plastics, to flow.

WET. A term used in surface chemistry which has not been adequately defined. As used in this book, it is a comparable term; that is, there are different degrees of wetting. A material is wet by the liquid in which it is immersed when the free energy in the interface is less than the sum of the free energy of the surfaces, if they were not within range of molecular attraction of each other.

WETTING AGENT. A material that has the ability to reduce interfacial energy in a suspension or in an analogous system.

White-light microscopy. A term used to imply that the microscopy employed is not electron microscopy. Likewise, it does not refer to ultraviolet microscopy.

Yield value. The Bingham yield value is the tangential shearing force in dynes per square centimeter that will just cause flow between two adjacent layers of a material. Houwink recognizes three yield values. The "lower yield value," where flow commences in the outer layer of a material in a capillary tube; the "Bingham yield value," which to Houwink is the intercept of the "straight" part of the consistency curve extrapolated to the force axis, and the "upper yield value," which is the shearing stress where laminar flow is complete.

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