sensitivity, et cetera. Under intense filtered ultraviolet illumination, fluorescent areas could be clearly focused upon the ground glass of the camera but curiously did not appear in the processed panchromatic negatives. However, it was discovered that when a pale yellow filter was used on the lens during exposure, the fluorescent sites were recorded in excellent detail and were greatly dependent upon the density of the particular filter used. The accompanying figures are presented as general examples of sebum fluorescence and glandular excretion. All were photographed by Lewis J. Sunny, B.P.A., using filtered ultraviolet light as the sole source of illumination.

BIBLIOGRAPHY

(1) Rothman, Stephan, "Physiology and Biochemistry of the Skin," Chicago, The University of Chicago Press (1954), pp. 284–336.
(2) Montagna, W., "The Structure and Function of Skin," New York, Academic Press, Inc. (1956), pp. 255–293.
(3) Weitkamp, A. W., *J. Am. Chem. Soc.*, **67,** 447 (1945).
(4) MacKenna, R. M. B., Wheatley, V. R., and Wormall, A., *J. Invest. Dermatol.*, **15,** 33 (1950).
(5) Wheatley, V. R., *St. Bartholomew's Hosp. J.*, **57,** 5 (1953).
(6) Rothman, S., and Schaaf, F., in Jadassohn, "Handb. d. Haut- u. Geschlechtskr.," Vol. 1, Berlin, J. Springer (1929), p. 161.
(7) Peck, S. M., Rosenfeld, H., Leifer, W., and Bierman, W., *Acrh. Dermatol. and Syphilol.*, **39,** 126 (1939).
(8) Burtenshaw, J. M. L., *J. Hyg.*, **42,** 184 (1942).

RHEOLOGICAL REVIEW FOR COSMETIC CHEMISTS*

By A. L. Scarbrough

National Lead Company, New York, N. Y.

Rheology is the science of the deformation and flow of matter. That is a rather sweeping definition, since it allows ample room for studies from mayonnaise to volcanic lava, as well as from blood serum to wet sea sand. Our purpose here, since the scope of the subject is enormous, is to choose a few aspects which might have a direct and practical bearing in the field of cosmetic chemistry. We should like to suggest a few thoughts which may be helpful in your work of continual improvement of various pastes, creams, solutions and emulsions, the bulwark of your trade.

Perhaps it would also be well to enter a standard disclaimer clause at this point. We are all familiar with the necessary custom in the chemical industry. The printed brochure describes wonderful new products and rec-

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* Presented at the October 24, 1956, Meeting, New York Chapter, New York City,

ipes which will solve all of the problems that have been keeping you awake at night. Then, on the last page, is a formidable paragraph which says, in effect, that the foregoing data "ain't necessarily so." Well, our position may be similar in that we are speaking not as either a cosmetic or rheology expert, but as one who has enjoyed our combination of theoretical and practical interests in the flow properties of matter. What we have observed and read in the pigment, paint, ink and plastics fields seems to us to have a very definite bearing on your products and problems.

Let us begin with a review of our definitions, so that we have a base of mutual agreement for later discussion of practical mixtures. The following section on types of flow properties may be familiar ground, but we have a choice to make in some instances as to terms and schools of thought. There is such a network of conflicting beliefs in non-Newtonian flow that one must thread his own way, depending on experience and training.

Types of Flow

The term "Newtonian flow" is not a subject of dispute. It comes from Newton's basic law of viscosity, which produced a definition of coefficient of viscosity as the tangential force per unit area that will produce a unit rate of shear. More specifically, a substance has a viscosity of one poise when a shearing stress of one dyne per sq. cm. produces a velocity gradient of 1 cm. per sec. per cm. The classical model used by Newton consisted of two parallel planes confining the liquid being tested. It is not suitable as such for a practical instrument, because no one has devised a way of making the liquid retain its shape and position without using some type of side walls. The derivation of the cylindrical cup-and-bob type of viscometer was not only a logical expedient of simply curving the planes so that the liquid was continuous, but it was actually anticipated by Newton himself. In 1713, his *Principia* specifically outlined the action of a fluid between fixed and rotating concentric cylinders, pointing to translation of motion from one to the other by the fluid (1).

Though about a century and a half passed before further interest came to light, finally Poiseulle in 1846 reported that the volume per second of liquid flowing through a capillary tube is directly proportional to the activating stress. This was followed promptly by the work of other scientists leading directly to the first theoretical analysis of flow and definition of the coefficient of viscosity. Fig. 1 shows the performance of a Newtonian liquid when rate of shear is plotted against shearing stress, on a rotational viscometer. The curve is always a straight line intersecting the origin in Newtonian liquids, because the rate of flow is directly proportional to the force exerted on the liquid. At any chosen point on the curve, the viscosity coefficient is equal to the shearing stress divided by the flow.

The curve can be established by determining only one point and drawing a line through it and the origin.

Most pure substances show Newtonian flow properties, and so do solutions of low molecular weight compounds. This would include water, glycerin, alcohols, ethers, and common oils, esters, and aldehydes. For these, any reliable single point method of measurement is perfectly satisfactory.

Now comes the major reason for such extensive work in the field of rheology. As soon as you begin to add pigment particles, gelling agents, high molecular weight substances, and surface active agents, or to emulsify immiscible systems, the flow properties nearly always become non-Newtonian, and the single point measurement ought to be discarded if reasonable knowledge of flow properties is desired.

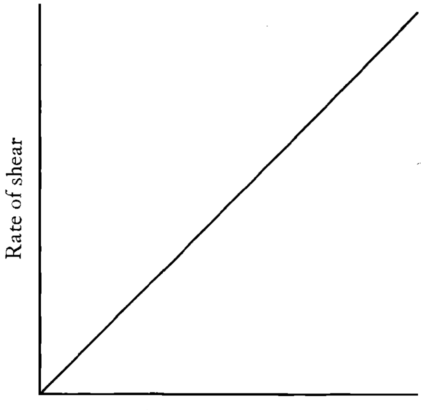

Figure 1.—Model of Newtonian flow.

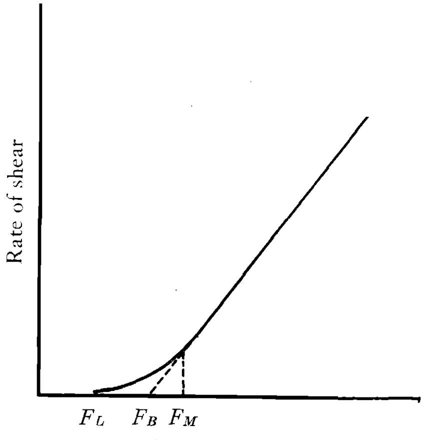

Figure 2.—Model of plastic flow.

Plastic flow is shown by the plot in Fig. 2. It is of considerable importance in many industrial applications, since it is so often typical of pigment dispersions. The essential feature is the presence of a limited shearing stress below which flow does not occur. The system behaves as if an energy barrier has to be overcome before flow then becomes proportional to additional increments of force exerted. The common designation for this minimum stress is "yield value," and there are three different points considered significant as yield value intercepts, which we should settle upon here to avoid confusion. The dotted line extension to intercept the abscissa is designated f_B, called the "Bingham yield value." It is the only one which has been justified mathematically and was developed by Bingham in his pioneer work on plastic flow. On a purely scientific basis, it seems to be preferred by rheologists. The other two were suggested by Houwink in addition to the Bingham concept (2). The value f_L, a lower yield value, is fixed at the beginning of shear, and f_M, a maximum yield value, is fixed at the beginning of laminar flow. While f_L is sometimes employed as a "practical yield value," f_M is not often encountered, and the usual practice today is to use the extrapolated intercept according to Bingham.

The nature of plastic flow is important and interesting because so many practical applications of pigmented industrial products have this characteristic. It has been the subject of considerable argument, but the general explanation which seems to be supported by microscopic evidence is as follows. The particles suspended in the system tend to aggregate through the action of van der Waals forces and form a network of floccules, which in turn are broken down through shearing. During shear both breaking down and reformation are taking place, and a steady state can be achieved if the shear rate is held constant. A type of equilibrium will be reached at each rate of shear. This view is supported by the fact that a plastic body will come down the curve in a straight line if shear is started at the maximum rate and decreased rapidly.

Many examples of pigment suspension exhibiting plastic flow have been studied. The yield value, which is obviously quite important in a tube of paste or cream, or in a paint, for example, can be varied in a given system by a number of factors. The addition of surface active agents will lower yield values, as a rule, by improving the wetting of the particles. Agents which deflocculate particles give lower yield values; flocculating agents raise yield values. Materials which increase interfacial tension will raise the yield value and vice versa. The yield value usually goes up with increasing ratio of pigment to vehicle and with the specific surface of the pigment. As we will see later, large changes in these factors will often alter the type of flow property completely.

The property known as *thixotropy* is often associated with plastic flow, and in some respects would appear to be a sort of subspecies with closely related character. Suspensions are termed thixotropic when they have the property of becoming fluid on agitation and of setting to a gel when undisturbed. We are all familiar with the classic case of bentonite gels in water as an example of thixotropic behavior. But we should consider the question of what the basic differences are from plastic flow which was shown in Fig. 2. When the yield point has been exceeded, a plastic body shows deformation which is roughly proportional to the applied force, and many suspensions of this type will liquefy when shaken or stirred vigorously. The similarity between plastic and thixotropic flow has been a source of confusion, and has led to a great deal of controversy, because the time factor and measurement conditions are vital in determining which rheological definition should be applied. In thixotropic flow, there is a finite and characteristic recovery time in the rebuilding of floccule networks, whereas rebuilding occurs immediately in plastic flow. This can be shown readily by examining the cup-and-bob viscometer curves as shown in Fig. 3. The upcurve is run, using increasing rates of shear, and immediately afterward, the down curve is run over the same distance. Since further breaking down of networks is not taking place, the downcurve of thixotropic bodies does not coincide with the upcurve. In plastic bodies the two curves will coincide, except at the lower end near the yield point. This is the "hysteresis loop" method, advocated by many eminent rheologists, and calculations of a coefficient of thixotropic breakdown have been made in which the area of the loop is measured. There is little question but that the approach is the most suitable one for any reasonable development of quantitative data. Those who object to it cite the arbitrary elements involved in the measurement, since the area of the loop is sharply influenced by the time taken in recording the upcurve, and the slope of the downcurve is determined by the top rate of shear chosen for the test condition. Even though this definition of thixotropic behavior may seem narrow because of the empirical nature of the method, there is large-scale agreement that the occurrence of a hysteresis loop should be the deciding factor. It is understood that certain suspensions would not show a loop under one set of time-stress conditions and would appear to be non-thixotropic; but in another measurement taken over an extremely short time period, a loop could be obtained. That illustrates the relative nature of thixotropy and why so much confusion has arisen where different criteria and methods of measurement have been used. In recent years it is unfortunate that the term thixotropy has been applied

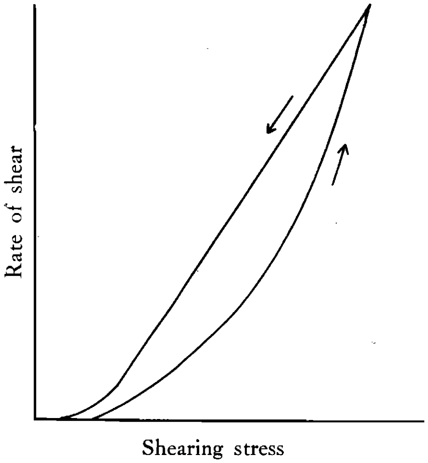

Figure 3.—Model of thixotropic flow.

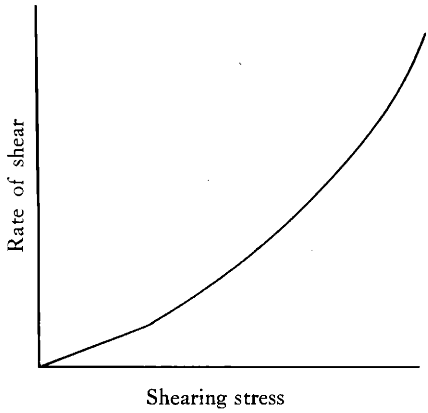

Figure 4.—Model of pseudoplastic flow.

to all types of bodies having plastic flow without regard to a specific definition. Where a need exists for knowledge of the time-recovery factor in a commercial product, an instrument which is capable of controlled variation of rates of shear must be employed and the double curve is required to define the rheological change during shearing.

Pseudoplastic flow starts out like Newtonian flow and then becomes more plastic in nature, as shown in Fig. 4. Notice that there is no "yield value" concept in this case, since flow begins at a very small shearing stress. The class of pseudoplastics includes mostly resinous materials and compounds having long chain molecules, either alone or in solutions of sufficiently high concentration. The following explanation of the pseudoplastic behavior in resinous products has been suggested (3). The long chain molecules are in a random state of orientation at rest. At low shear rates there is little or no tendency to align themselves in the direction of flow which corresponds to the lower portion of the curve. As the rate of shear increases, however, a regular alignment of molecules starts which reduces the frictional resistance between parallel chains. The curve begins to turn upward as the resistance to increasing rates of shear diminishes. This is, of course, a speculative type of explanation rather than strictly factual. Considerable evidence has been advanced to show that the lower part of the curve is actually non-linear and therefore non-Newtonian. Another note of interest is that at high rates of shear, some resinous materials have been shown to give hysteresis loops in the upper portion of the curve only, though the up- and down-curves coincide over the rest of the range.

There is one other generally recognized type of flow which is not Newtonian. Materials which tend to become more viscous when they are sheared and to revert to a flowing state at rest are called *dilatant*. A dilatant flow curve is shown in Fig. 5. The consistency curve at first glance appears to be the reverse of a pseudoplastic one. The original use of the term dilatancy was based on the dilation and increase in rigidity of closely packed masses of fine particles, such as sand, when disturbed. The familiar example is wet sea sand. When it is disturbed by stepping on it, the area appears to dry off. The explanation is postulated that the particles of a dilatant system settle to a state of minimum voids, and agitation causes them to rearrange to a larger void volume, causing any free suspending liquid to be drawn into the mass. Actually, the dilation of the mass on shearing is not considered a primary requirement today, since it is considered likely that materials exist with consistency curves of this type which do not show volume changes (4).

Dilatancy occurs most frequently at relatively high pigment volume concentrations and usually with small particle sizes. Aging of pigment dispersions has a strong effect, though the change in dilatancy with aging time is not predictable for different cases. Particle shape is important, and good correlation has been obtained in comparing critical volume concentrations with calculated void spaces (4). Particles which are nearer to spherical shapes reach maximum dilatancy at higher solids concentrations; cubes and more irregular shapes have lower concentrations for maximum effect, presumably because they are able to pack down closely at rest and create larger voids when disturbed.

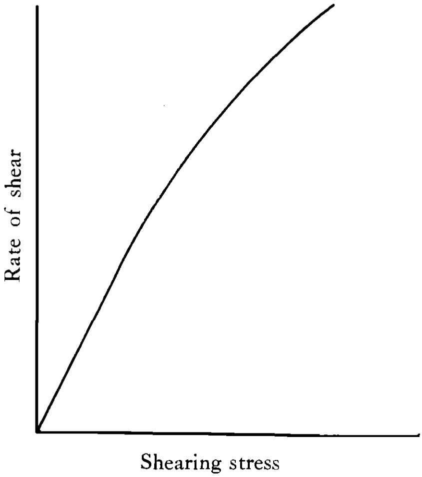

Figure 5.—Model of dilatant flow.

Dilatancy seems to require that the suspended particles be deflocculated; the mechanism, as indicated in the "packing" idea discussed above, is entirely different from that assumed for plastic or thixotropic flow. It is not surprising, therefore, that some pigment dispersions show both properties. Aqueous suspensions of carbon black, zinc oxide and iron oxide are known which give a dilatant curve with a loop.

The types of flow we have just discussed in some detail are important because we know that many problems of formulation and production involve the effect of small variables on the flow characteristics of industrial products. We should next consider some of the common raw materials which are important in establishing or modifying the rheological pattern of our products.

Gelling agents or thickening agents are an important group of modifiers. Concentration of the gelling agent may influence the nature of flow, as for example starch. Pastes containing 10 per cent dry starch form pseudoplastic bodies and yet when the amount is increased up to 35 per cent or 40 per cent, they become entirely dilatant. Such pastes can be poured readily, but they seem to solidify if an attempt is made to stir them vigorously. Starch gels also vary somewhat according to the history used in making them up as shown in Fig. 6. Curve *A* is a 10% starch paste which was cooked for thirty minutes, while curve *B* is the same starch with a one hour cooking period. Dependence on method of preparation is common among the hydrophilic colloid gelling agents, and it points up the need for accurate rheological knowledge as a control means for good quality production in industrial work.

Ordinary gelatin also tends to change type of flow with concentration. A 4 per cent water dispersion of gelatin gives an excellent thixotropic curve, but higher concentrations approach dilatancy rather rapidly. Again there is a noticeable sensitivity in the type of gelatin chosen and the method used in gel formation with respect to flow properties. Aging of both starch and gelatin pastes leads to very definite changes in their rheology.

Dispersions of both sodium alginate and methyl cellulose show pseudoplastic flow, somewhat similar to starch. Most water soluble gums are in the same rheological family, though frequently they are mistakenly called thixotropic.

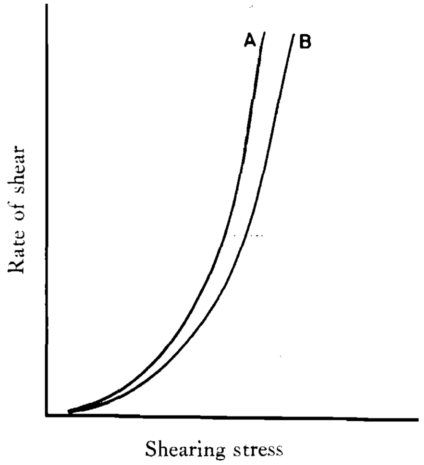

Figure 6.—Pseudoplastic flow of 10% starch pastes. Curve *A* = one hour cook. Curve *B* = half hour cook.

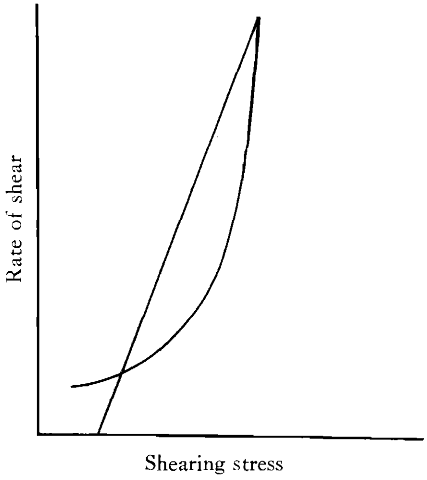

Figure 7.—2.5% Ben-A-Gel in water.

The mineral type of gelling agent usually behaves somewhat differently. Bentonite, or a refined magnesium montmorillonite, such as Ben-A-Gel, gives a definite thixotropic loop. Fig. 7 shows the flow curve of a suspension of 2.5 per cent Ben-A-Gel in water. There is no evidence of any other type of flow at higher concentrations up to a virtually solid gel. Assuming the proper minimum work is done initially to form the gel, no effect is noticed from variations in temperature or milling times on the rheological properties. Stability on standing is a remarkable feature since duplicate measurements can be obtained after extremely long periods of time.

Pigment dispersions were mentioned in passing during the flow curve discussion. At higher concentrations they often tend to be dilatant, with strong dependence on the shape, size and surface character of the particles. At lower levels of pigment to vehicle thixotropic flow is often noted. Strong effects are obtained with small amounts of surface active agents; a specific case is the change in an ultramarine blue dispersion in mineral oil which has been reported (4). The thixotropic curve lost its loop almost entirely, becoming plastic flow, with the addition of a small amount of Aerosol OT. The addition of lecithin to a suspension of quartz in water which is originally nonthixotropic changes it to a plastic and thixotropic material (5).

These examples are useful to illustrate the powerful nature of such additives. They are double-edged weapons, and we suspect that at times an undesirable consequence in flow properties, especially with aging, which was not foreseen has caused many headaches in industrial cosmetic products. Our own reason for advocating agents, such as Ben-A-Gel where modification of flow properties or the state of pigment flocculation is desired, is based on their inert behavior; they do not affect surface tension, and any influence on pigment flocculation seems to be a mechanical matter of holding larger vehicle layers around particles rather than changing the character of the vehicle-particle interface.

Thickening nonaqueous liquids satisfactorily has posed problems in uniformity and package stability for many years. The metallic soaps as a class are well known for gelling mineral and vegetable oils. Most of the anomalous results obtained with them from time to time can be traced to two sources. Variables in the soaps themselves, such as the amount of free acid, moisture, metal content and so on, cause serious differences in the rheological properties of the gels. In addition, the same soap with different heat and milling histories will produce correspondingly different flow curves.

Resinous or polymeric products are also frequently used as thickeners. As we have seen, the predominant effect tends toward a pseudoplastic system, though plastic flow is frequently associated with such polymers as bodied drying oils. Reproducibility and stability in the package must be studied carefully in each case.

The Bentones, which are organic compounds of montmorillonite, have been phenomenally successful in the protective coating field for thickening and gelling various vehicles since their introduction a few years ago. They will undoubtedly become a similarly useful adjunct to the cosmetic formulating industry. Bentone gels produce thixotropic curves of the same type as shown previously for Ben-A-Gel, and there is special value in their uniform behavior. The relationship between concentration of Bentone and the area of the loop in the thixotropic curve is essentially linear in nature, making it quite possible to predict the behavior of a Bentone with comfortable accuracy. The Bentone gel is also unaffected by temperature variations, which we would like you to keep in mind when you formulate a face cream for use in cold climates.

In your everyday formulating work, we should like to suggest, in closing, a few points which might be useful:

1. When such factors as yield point, extent of thixotropy and changes in body during package aging are in question, the use of a good multi-point method to determine what flow properties you actually have in hand is the most reliable means of collecting fundamental data. We hope it is clear that a measurement taken at a single point, such as at one rate of shear, has extremely limited value, even for control purposes.
2. Knowing something of the rheology of the individual components of your formulations should be very helpful. The combining of the flow types we have discussed is often exactly what you are doing to reach an esthetically pleasing product.
3. Keep a close check on the powerful modifiers in emulsions, pastes and dispersions. Surface active agents, dispersing agents and gelling agents should be checked to determine the relationship between the concentration of the agent and its effect on flow properties.
4. Where systems are pigmented, you can modify the rheology effectively by changes in the shape, size and specific surface of the particle. Sometimes a different grade of titanium dioxide, iron oxide, talc or whiting may produce exactly the effect you need.

References

(1) Cajori, F., "Sir Isaac Newton's Mathematical Principles of Natural Philosophy and His System of the World," Berkeley, The University of California Press (1947).
(2) Houwink, R., "Elasticity, Plasticity, and Structure of Matter," Cambridge, Cambridge University Press (1940).
(3) Green, H., "Industrial Rheology and Rheological Structures," New York, John Wiley & Sons, Inc. (1949).
(4) Fischer, E. K., "Colloidal Dispersions," New York, John Wiley and Sons, Inc. (1950).
(5) Freundlich, J., *J. Soc. Chem. Ind.*, **53**, 223T (1934).