function or series of functions. Shampoos, conditioning rinses, synthetic bar soaps, face creams, hand lotions, etc., are all possible with the use of one or more of the fatty amino acid derivatives.

SUMMARY

A new family of amphoteric surface active agents based on the condensation of a fatty primary amine and methyl acrylate have been made available commercially in both monoadduct and diadduct forms and in a variety of fatty chain lengths. Their flexibility as to chemical structure and their amphoteric polyfunctionality combine to provide an extremely versatile family of products offering promise in a wide variety of applications. These fatty amino acid derivatives are particularly adapted to cosmetic formulations, offering controlled surface active properties, compatibility with a wide range of products, mildness and polyfunctionality.

ROTATIONAL METHODS OF FLOW MEASUREMENTS*

WALTER K. ASBECK

Union Carbide Chemicals Company, South Charleston, W. Va.

A LARGE NUMBER of various types of rotational viscometers are obtainable commercially, and many more are described in the current literature. Some special advantage over available apparatus is usually claimed for each new instrument which is described. Often a very specialized knowledge of the field of rheology and the specific application of a given instrument is consequently required before an adequate choice of apparatus and the results which it may be expected to yield can be made. To aid in this choice, it is pertinent to consider the various aspects of rotational viscometers, and those related to them, and to determine their advantages and limitations. With this background a more adequate choice of commercial apparatus can be made, or the design of special equipment to meet specific needs can be more rapidly accomplished.

Although today rheology is playing an important and ever increasing role in industrial control and research, it was not until the latter part of the 18th century that Coulomb (1) laid the foundation for rotational type viscometers. In order to substantiate the derivations earlier carried out by Newton (2) for viscous flow, he suspended a circular plate from a

---

* Presented at the October 4, 1956, Seminar, New York City.

torsion wire and determined the logarithmic decrement of oscillation as the swing of the plate was damped by the surrounding liquid. Not until a hundred years later, in 1890, however, did Couette (3) construct and use a true concentric cylinder rotational viscometer, the mathematical theory of which had been earlier described by Stokes (4). This was to become the prototype of many of the presently employed rotational instruments. It consisted of a rotating cup, which imparted a given moment, M, to a bob, suspended concentrically within the cup on a torsion wire. It was found that the coefficient of viscosity, η, of the liquids measured by this device was a simple function of the moment imparted to the bob. The value of the coefficient of viscosity measured by this instrument was found to correspond very closely with that measured on the same liquid by capillary methods. A critical rotational velocity, where laminar flow changed to turbulent flow, as earlier predicted by Reynolds (5), was also found with this early Couette apparatus.

The experiences of the last several decades have shown, however, that the laws derived from the differential equations for "Newtonian" liquids:

$$\mathcal{Q} = \frac{1}{\eta}\frac{\pi}{8}\frac{pR^4}{L} \qquad \text{(Capillary System)} \qquad (1)$$

where $\mathcal{Q}$ is the volume extruded in unit time, and p is the differential pressure on the ends of the capillary of length L, and radius R; and

$$M = 4\pi L\eta W\left[\frac{R_o^2R_i^2}{R_o^2 - R_i^2}\right] \qquad \text{(Rotational System)} \qquad (2)$$

where M is the moment imparted to the cup or the bob, L is the bob length, W the angular velocity of the driven member, and R_o is the radius of the cup, and R_i the radius of the bob, respectively, do not hold for a large number of industrially important colloidal solutions as well as for suspensions of microscopic particles such as pigment dispersions and emulsions. Under otherwise similar circumstances the rate of flow through a capillary is no longer proportional to the pressure, and the moment produced in a rotational instrument is no longer proportional to the rotational velocity of the rotating cylinder for these materials.

This deviation from linearity signifies that the coefficient of viscosity is not a constant for these materials such as it is for Newtonian liquids, but that it either decreases or increases with increased shear velocity. Thus, a number of generalized typical flow patterns may result if stress is plotted against strain as shown in Fig. 1, where Curve I is classified as Newtonian flow, Curve II as pseudoplastic flow, Curve III thixotropic flow and Curve IV dilatant flow. The variable common to both capillary and rotational instruments is the shear velocity (also called the shear gradient). It increases with increased flow through a capillary and with increased angular velocity in rotational viscometers. Thus, it is the common denominator of the two types of instruments, and the flow anomaly encountered when non-Newtonian materials are measured with either type of equipment can be regarded as a function of shear velocity. The Newtonian equation:

$$F = A \cdot \frac{dv}{dz} \cdot \eta \qquad (3)$$

where F is the force required to attain a shear velocity dv/dz for a given area of shear surface A, must consequently be altered to:

$$F = A \cdot \frac{dv}{dz} \cdot \eta^* \qquad (4)$$

where $\eta^* = \Psi(dv/dz)$ and η^* is the "coefficient of apparent viscosity," more commonly referred to as the "apparent viscosity." Since the apparent viscosity of non-Newtonian fluids is a function of shear velocity, it is necessary to confine dv/dz to close, unambiguous limits if a meaningful value of η^* is to be extracted from the measured data.

This is most clearly brought out on the basis of theoretical achievements of the recent past. Although many attempts had been made to correlate the mechanisms of flow with the physical structure of non-Newtonian liquids, most of the proposed theories only attempt to explain special cases on the basis of special assumptions. Only recently, however, Eyring and Ree (6, 7) have proposed a generalized theory which apparently well

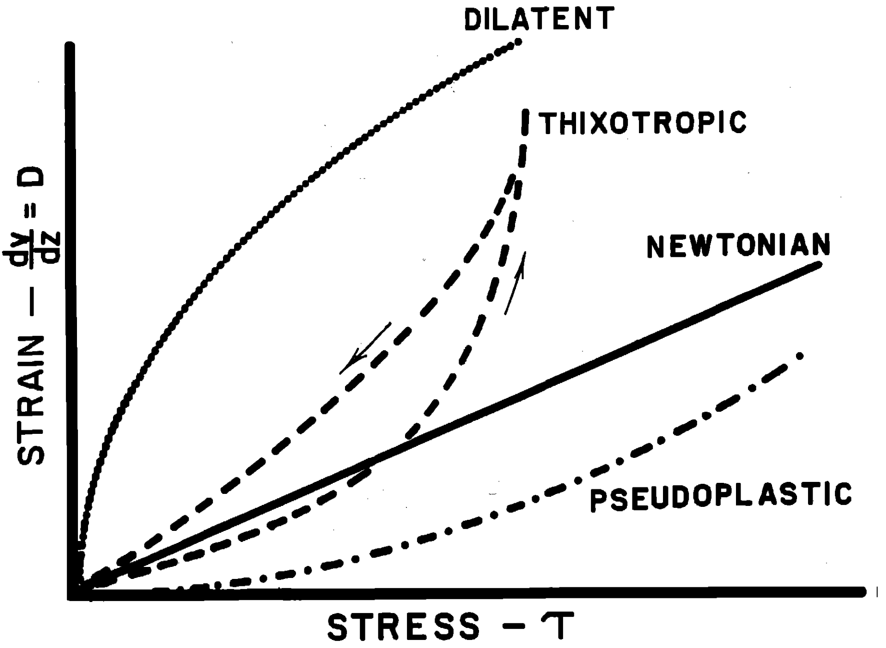

Figure 1.

describes the flow of plastics and fluids on the basis of well defined parameters of the systems. The theory makes a number of simple assumptions. It is hypothesized that the flow rate of a system is a function of the relaxation times of the flow units which contribute to the flow process, as well as the distribution of such relaxation times, and the deformation of the system with stress.

The generalized equation is of the form:

$$\eta^* = \sum_{n=1}^{n} \frac{x_n\beta_n}{\alpha_n} \frac{\sinh^{-1} \beta_n D}{\beta_n D} \tag{5}$$

where x_n is the fractional area occupied by the nth flow unit on the shear surface; $d_n = (\lambda\lambda_2\lambda_3/2kT)n$, where k is the Boltzmann constant; β_n, the average relaxation time $= \{1/[(\lambda/\lambda_1)2k']\}$ for each related group of flow elements, respectively; and $F = dv/dz$ is the shear velocity. In the above: λ is the distance a flow unit moves between equilibrium positions; λ_1 is the distance between planes of flow units of a given kind; λ_2 λ_3 is the cross-sectional area of a given flow unit; k' is the rate constant for the passage of a given flow unit over the potential energy barrier; and T is the absolute temperature.

Since an interpretation of x, α and β can, at the present time, be made only in terms of η^* and D, it becomes immediately apparent that only in

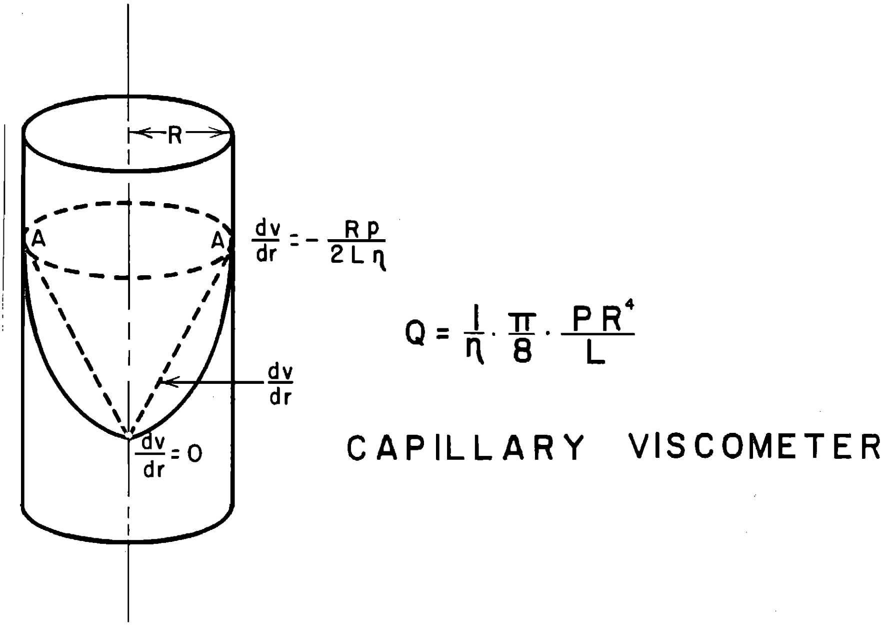

Figure 2.

an instrument where a constant shear velocity is obtained, can these parameters be accurately described. With an instrument yielding a distribution of shear velocities, the sum of a distribution of η^* values will be obtained leading to misinterpretations of the parameters of the equation.

SHEAR GRADIENT IN CAPILLARY VISCOMETERS

From simple derivations the shear velocity relationships in capillary instruments can be shown to be:

$$\frac{dv}{dr} = -\frac{rp}{2L} \tag{6}$$

This equation describes how the shear velocity is a function of the distance, r, from the center of the capillary to the concentrically moving, cylindrical flow elements as shown in Fig. 2, and how complicated the flow relationships must become where, in non-Newtonian liquids, η^*, becomes an unknown function of dv/dr. A decided deficiency of capillary instruments in measuring liquids with anomalous flow properties consequently becomes apparent: dv/dr varies over the whole of the flowing liquid stream, from the axis of the capillary where $dv/dr = 0$ to the inside of the capillary walls, where dv/dr attains its greatest value $Rp/2L\eta$. As a consequence, a whole distribution of shear velocities, which again is a function of the degree of deviation from Newtonian flow, is obtained in each measurement of extruded volume, $\mathcal{Q}$, at a given pressure, p. From this a backward interpolation of the apparent viscosity/shear velocity relationships must be made.

Although a number of attempts have been made to carry out this correlation between $\mathcal{Q}$ and p and dv/dr and η^*, respectively, these methods are very complicated and cumbersome and are not always reliable for fluids deviating considerably from Newtonian flow (*8–11*).

SHEAR GRADIENT IN CONCENTRIC CYLINDER VISCOMETERS

For properly constructed rotational viscometers, this limitation is not valid and definable. Relatively constant shear velocities can be readily produced over a considerable absolute shear range. This is the fact which has encouraged the use of rotational type instruments despite their comparative complexities, rather than capillaries for the measurement and study of non-Newtonian liquids.

In the concentric cylinder viscometer, Fig. 3, the shear relationships, dv/dr, in the cylindrical flow laminae can readily be shown to be:

$$r\frac{dw}{dr} = \frac{dv}{dr} = 2W\left[\frac{R_o^2R_i^2}{r^2\,(R_o^2 - R_i^2)}\right] \tag{7}$$

where W is the angular velocity, R_0 is the radius of the cup, R_i is the radius of the bob and $R_0 > r > Ri$.

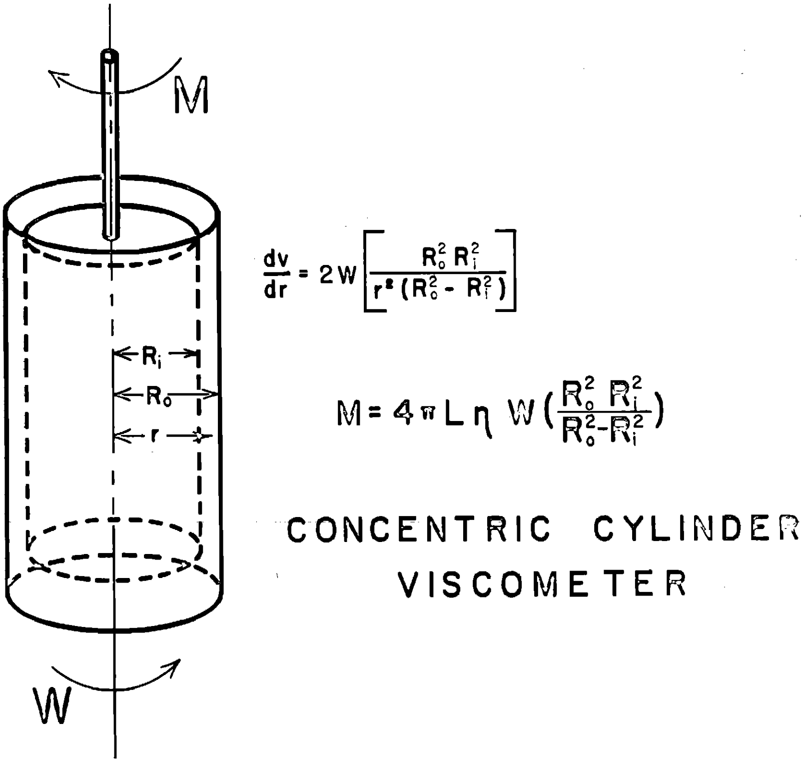

Figure 3.

This equation, too, appears to yield a complicated relationship between shear velocity and the radius of cup and bob. However, this is not the case when the difference between R_0 and Ri is small in relation to R_i. When the annular space between cup and bob is small for a given radius of bob, the shear velocity relationship reduces to:

$$r\frac{dw}{dr} = \frac{dv}{dr} = W\frac{R_i}{R_o - R_i} = W\frac{R}{\Delta R} \tag{8}$$

It can be seen that under these circumstances dv/dr becomes a linear function of rotational velocity, W, and is constant within the limits $R_o - R_i = \Delta R$.

A prerequisite for unambiguous measurement of non-Newtonian viscosities in concentric cylinder apparatus, consequently, is relatively small clearance between cup and bob. Only in this way is a constant shear velocity attained and η^* accurately defined in terms of dv/dr.

What the relationship between cup radius and bob radius must be in order to remain within the limits of a given percentage deviation between the shear velocity at the cup surface and at the bob surface can be readily obtained from a rearrangement of the shear velocity equation. Thus, if δ is the permissible percentage difference in shear velocities, the equation becomes:

$$\frac{100\,(R_o^2 - R_i^2)}{R_i^2} = \delta \qquad (9)$$

For a bob of 4 cm. diameter, for instance, the clearance between cup and bob consequently may not exceed 0.1 cm., if deviations of 10 per cent are not to be exceeded in the instrument. A clearance of 1 cm. in this apparatus could introduce a deviation in shear velocities of over 55 per cent. Similarly, for a smaller bob of, say, 1 cm. diameter, the clearance may not exceed 0.025 cm. for a maximum of 10 per cent deviation.

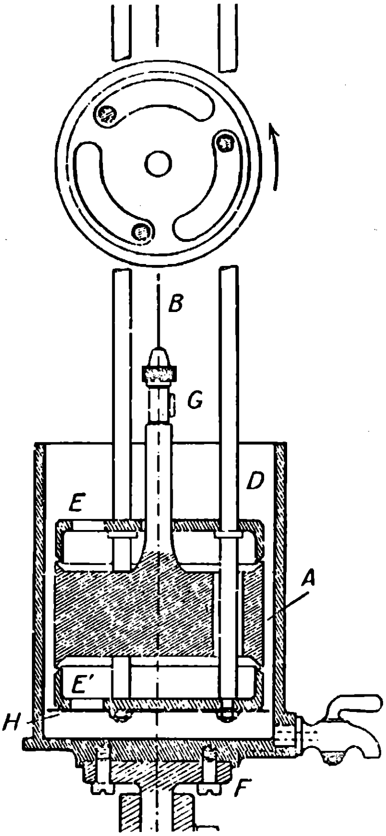

Figure 4.

Unfortunately, this fact has been neglected in the design and use of many of the currently employed, commercially available, concentric cylinder type viscometers. Thus, rotational instruments employing paddles of one sort or another are completely incapable of producing a theoretically valid flow curve for non-Newtonian liquids. In this case the shear velocity gradient is so complicated and undefinable that any description of apparent viscosities in relation to shear rate is illusory.

Instruments employing small bobs suspended in large cups also yield results which are highly empirical. The shear velocity distribution during the course of a single measurement is so great that the apparent viscosity at some intermediate "average" shear rate may deviate very considerably from the true value.

End Effects

Another basic source of error in concentric cylinder types of viscometers are the ends of the cylinders. Especially when the length of the bob is small compared to the diameter, a considerable portion of the torque meas-

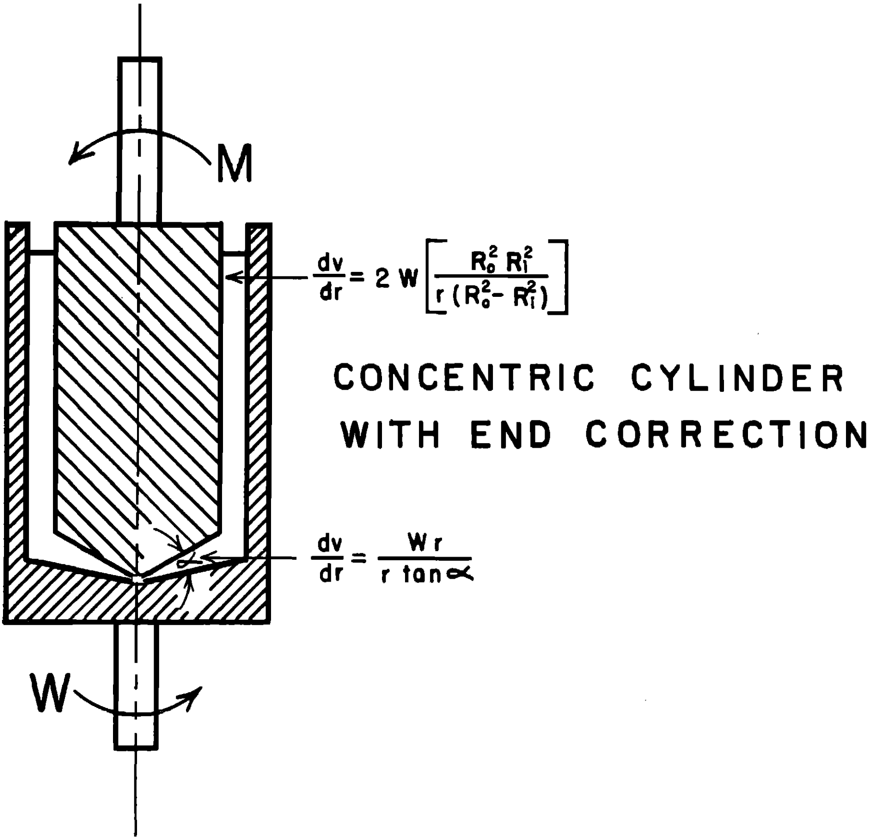

Figure 5

ured may be derived from the ends, where the shear velocities vary from low values (zero at the center of the bottom) to maximum at the outside diameter of the bob. Again, a distribution of shear velocities is obtained, and the associated distribution of viscosities makes the measured value unreliable.

A number of methods have been devised to eliminate this problem, which was recognized even by Couette in his original instrument. So-called "guard rings" were installed at the top and bottom of the bob as shown in Fig. 4. They absorb the torque imparted to these areas by the rotating cup and restrict the measurement to the annular space between cup and bob. Although effective in their purpose, the guard rings are complicated to construct and adjust and are consequently generally avoided.

A simple and elegant method for compensating for these end anomalies was introduced by Mooney and Ewart (12). Instead of employing cup and bobs which are parallel at their ends, conical bottoms are employed, having different angles from each other as shown in Fig. 5. These angles are calculated in such a way that the rate of shear between them is the same as that between the cylindrical surfaces of the viscometer. The error arising from the top end of the bob can readily be avoided by filling the viscometer only part way, and thus eliminating material from this point.

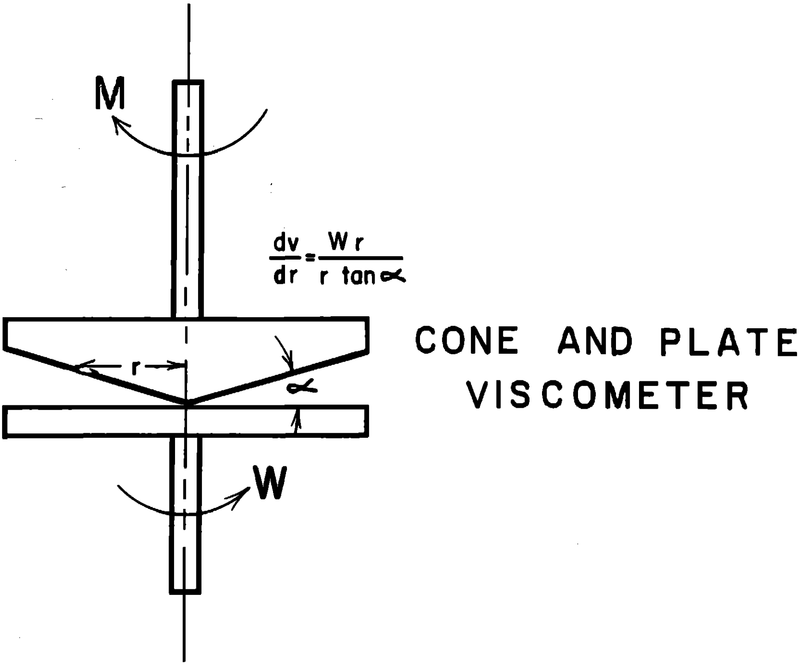

Figure 6.

CONE AND PLATE VISCOMETER

It is perhaps somewhat surprising that this simple expedient of conical bottoms was not employed earlier. Perhaps even more surprising is the fact that this principle was not used until recently in commercial viscometers to eliminate shear velocity distributions in a simple rotational instrument. Thus, by employing a plain bottom plate and a bob of low angle, while simultaneously eliminating the cylindrical portion of the instrument, the cone and plate viscometer illustrated in Fig. 6 is evolved. Properly constructed, this instrument has the feature of providing a constant shear gradient throughout its measuring surfaces, since:

$$\frac{dv}{dr} = \frac{rW}{r \tan \alpha} = K \tag{10}$$

where W is the rotational velocity of cone or plate, α is the angle between the two surfaces and K is a constant. It will be noted that a requirement of the geometry of this system for successful operation is that the apex of

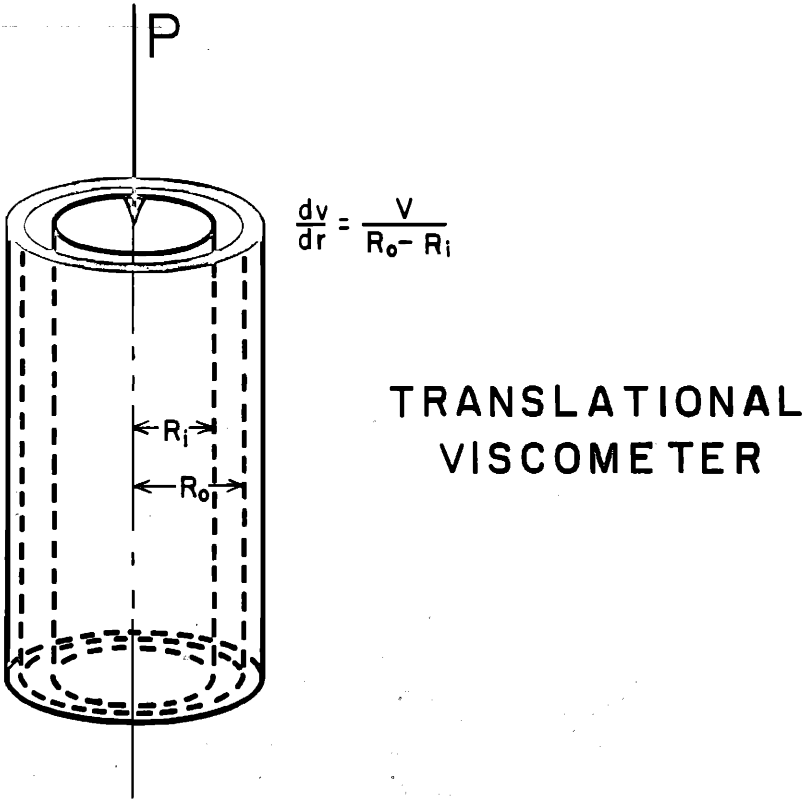

Figure 7.

the cone must lie in the plane of the plate. This limits α to some minimum value if extreme precision in machining and readjustment of the relative position of plate and cone in the assembled instrument, after cleaning and refilling with the measuring liquid, is to be avoided.

OTHER CONSTANT SHEAR GRADIENT VISCOMETERS

If, instead of rotating either the cup or bob of a concentric cylinder viscometer, the bob is translated axially, an instrument with relatively constant shear gradients can again be obtained which is related to some of the rotational instruments both in general appearance and in theoretical functioning, as shown in Fig. 7. These instruments of necessity are very low shear velocity devices since the bob cannot be translated over a considerable distance. They can be of relatively simple construction and consequently are of considerable utility in some instances. Provided, again, that the clearance between cup and bob is kept relatively small, the shear velocity gradient is a linear function from cup to bob surface. If V is the velocity of translation, the shear velocity has the simple function:

$$\frac{dv}{dr} = \frac{V}{R_o - R_i} = \frac{V}{\Delta R} \tag{11}$$

Two major variations of this type of instrument are feasible. In one, where materials of very high viscosity, such as pitch, are to be measured, the bottom of the cup may be omitted, and the stress applied directly to the bottom of the bob (13). For more fluid materials, this is no longer applicable, and the bob must be suspended in the cup. Since in this case the cup is closed at the bottom, the bob will displace a certain volume of the liquid as it moves up or down. The shear velocity gradient can consequently become complicated where a capillary type flow pattern in the annular space between cup and bob is superimposed upon the linear gradient. However, this difficulty has been substantially eliminated by the author by substituting a thin cylindrical shell for the solid bob. The liquid volume displacement becomes negligible under these circumstances and a substantially linear shear velocity gradient is established. Instruments of this general type are capable of measuring viscosity in the ultra-low shear velocity range down to as low as one millionth of a reciprocal second (14).

At the other extreme, another instrument, working on the translation principle, is capable of yielding measurements in the ultra high shear velocity range of up to 50,000 sec.$^{-1}$. This is the Band Viscometer (15), shown in Fig. 8, consisting of two closely spaced shear blocks between which a thin, flexible band carrying the test material is pulled. Hydrodynamic forces during a measurement maintain the band centered accurately between the two shear blocks, allowing the use of extremely small clearances

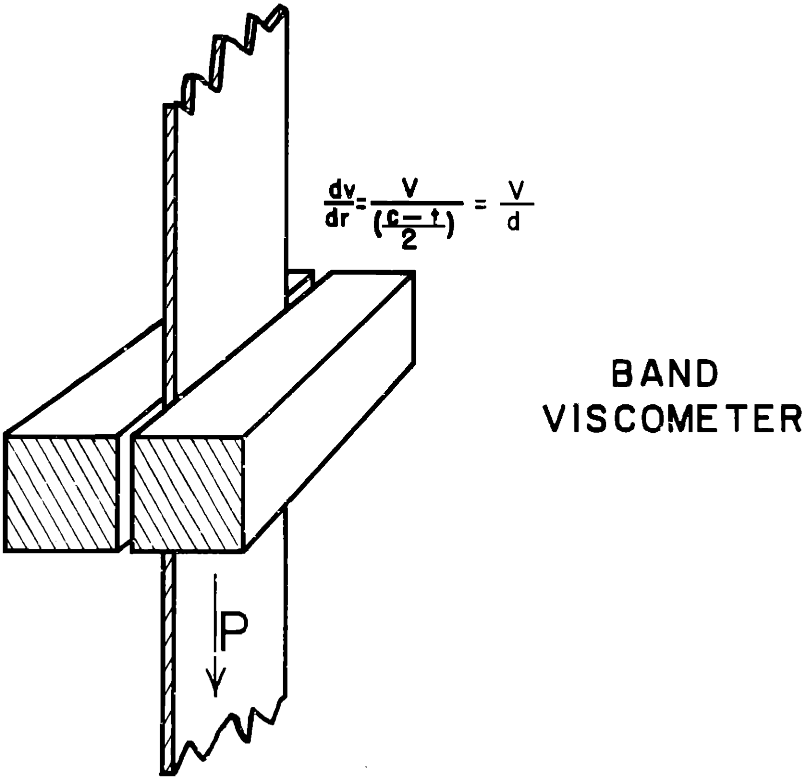

Figure 8.

down to 25μ between the shear surfaces for most materials before getting into difficulties caused by wall effects. If d is the distance between band surface and shear block surface, the shear velocity assumes the simple relationship:

$$\frac{dv}{dz} = \frac{V}{d} \tag{12}$$

Since d can be made very small, the shear velocity becomes very high even at moderate velocities, V, of the band.

Although simple to construct and operate these translational devices, despite their linear shear gradients, have one deficiency in common with capillary viscometers when compared to the true rotational type instruments. This is their incapability of imparting continued stress to the test material over an extended period of time. Thus, fluids having the characteristic of thixotropic breakdown cannot easily be identified with these instruments. Although some indication of thixotropy can be obtained by changing the length of the shear surface, this procedure is cumbersome, and more adequate, theoretically valid, results can be obtained with the true rotational instruments on thixotropic fluids.

Need for Various Shear Ranges

The Ree-Eyring equation (5) shows how the apparent viscosity of anomalous flow systems is a function of the average relaxation time, β_n, of the flow element involved. For many non-Newtonian fluids, the general equation takes the specific form:

$$\eta^* = \frac{x_1\beta_1}{\alpha_1} + \frac{x_2\beta_2 \sinh^{-1} \beta_2 D}{\alpha_2\beta_2 D} + \frac{x_3\beta_3 \sinh^{-1}\beta, D}{\alpha_3\beta_3 D} \qquad (13)$$

where the first term of the equation refers to the Newtonian contribution, often signified as η_∞, the viscosity at infinite shear velocity, whereas the second and third terms contain the elements contributing to the flow anomaly due to the different relaxation times. Ree and Eyring have found that three terms are usually sufficient to characterize the majority of non-Newtonian fluids, although often only the first two terms are required.

If the relaxation times β_2 and β_3 are fairly close together and are of an intermediate value, a viscosity measurement in the intermediate shear range will suffice to characterize the liquid. If, however, as is often the case, β_2 and β_3 are substantially different, and one is very small and the other very large, viscosity measurements in the range covered by a single instrument are often not enough to adequately characterize the system.

This is true because the shear velocity range of most, even very good, viscometers is limited to a range of about 200:1 or $^1/_2$ per cent of the maximum value. Thus, if the upper shear range limit of a device is, for example, 2000 sec.$^{-1}$, the lowest values identifiable will be about 10 sec.$^{-1}$. Similarly a viscometer with an upper range of 10 sec.$^{-1}$ will have a lowest range of 0.05 sec.$^{-1}$. If only the higher shear device is employed, the component with the long relaxation time may consequently be missed completely, whereas if the lower shear instrument were employed for measuring the same material, the short relaxation time material would not be found.

Although this point may appear to be only of academic interest, it has a very profound practical significance. As in many other commercial fields dealing with fluids and pastes, the cosmetic industry is concerned with a surprisingly large shear velocity range for the practical application of its products. Thus, the act of applying hand creams or face creams may subject the material to shear rates as high as 10,000 sec.$^{-1}$. This is due to the extremely thin layers being applied which cause these high shear velocities according to equation (12), even with moderate movement of the hand. Furthermore, for aesthetic appeal and other reasons, these materials may often be formulated with considerable rheological structure

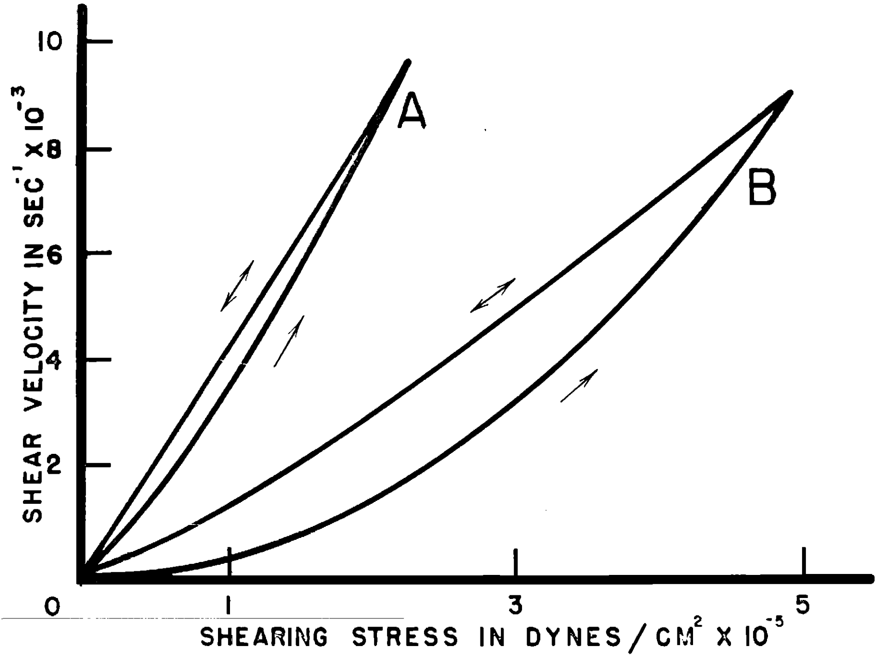

Figure 9.

of long relaxation time which appears most prominently in the low shear region.

The effects of these relationships are more clearly discernible from Figs. 9 and 10. These are high shear curves produced on the Asbeck High Shear Viscometer (16) and low shear curves, measured with the modified Bergen (14) Viscometer, respectively, of two commercial hand creams.

As can be seen from the high shear curves, which extends to about 10,000 sec.$^{-1}$ both materials show a thixotropic hysteresis loop. However, Sample B has a considerably higher viscosity at the practical commercial application shear velocities than sample A. Furthermore, B possesses considerably more structure with a relatively short relaxation time than A, which appears almost Newtonian. It is interesting to note that repeat runs on the same batch of material eliminate the hysteresis loops, and subsequent up and down curves lie on the down curve produced on the first run.

A number of pertinent points are well illustrated with these two high shear curves. One of the most important is the futility of attempting to obtain generally valid viscosity data from single point viscosity measurements if the material is not previously known. Thus, although curve *A* could be approximated with extrapolations from a single point measurement because of its reasonably close approach to Newtonian behavior at high shear

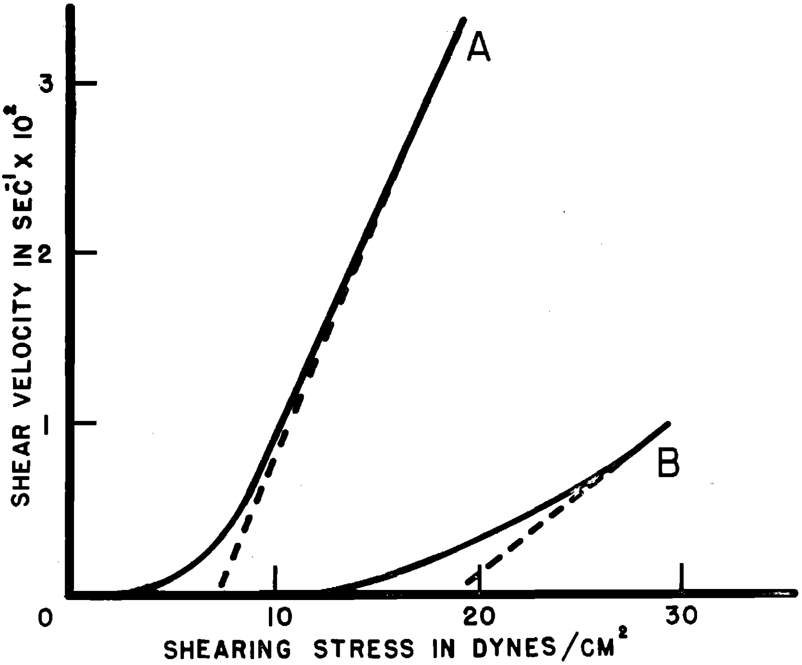

Figure 10.

rates, curve *B* would give meaningless results for any extrapolations from single point measurements over its entire length.

The other important factor previously stressed which is often disregarded in practical viscosity measurements is also well illustrated by these curves. This is the necessity of covering sufficiently large shear ranges to accommodate the materials. Curve B is a particularly good example of this point. Were measurement of the material stopped at 500 to 1000 sec.$^{-1}$ shear velocity, a completely erroneous picture of the viscosity at the application shear rates would result, with apparent values some four or five times higher than actually present. This misleading condition may also work in the direction of low shear rates. Thus, from the high shear curves, extrapolation into the zero axes would indicate that sample A is almost Newtonian and has a maximum low shear viscosity of about 1.8 poise and B of about 5.5 poise.

The low shear viscosity curves of these two samples, however, give a completely different picture. Far from being almost Newtonian, sample A shows a very considerable structure with viscosities in the very low shear range in excess of several thousand poise. Sample B shows even greater structure than A, and a substantial stress is required to overcome the initial resistance to flow.

YIELD VALUE

From these low shear curves, one is tempted to draw conclusions concerning the "Yield Values" of these materials. By laying a tangent to the steeply rising portion of the curves where it appears to become straight and extending this to intersect the stress axis, a threshold value of stress is indicated above which the material substantially will flow, and below which it will not. This concept of apparent "Yield Value" can often lead to misconceptions of the viscous behavior of the materials tested if it is not applied with the utmost caution, since very often it is a function determined solely by the shear range employed during the measurement. Thus, from the curves of Fig. 10 it is obvious that a decided curvature toward the origin exists at the very low shear ranges, and that the material obviously flows, although very slowly, below the apparent yield value. If measurements at still lower shear velocity ranges could have been made, spreading the shear velocity axis out over a considerably greater range, a similar analysis may have resulted in a substantially different apparent yield value.

This difficulty is particularly well illustrated by curve *B* of the high shear plot. An analysis similar to the low shear curve, by laying a tangent to the upcurve of this run and extrapolating down to the τ axis, indicates an apparent yield value in this shear range about 180 times greater than the apparent yield value obtained for the same material in the low shear region. Obviously, considerable ambiguity can consequently result if some regard to the shear ~~range covered~~ is not given in the interpretation of the commonly employed but often misapplied concept of apparent yield value.

It is thus apparent that considerable caution must be applied to the interpretation of rheological data obtained from measurements in a limited shear range. Fortunately, rotational type instruments, or related types when properly designed, are capable of covering an extreme range in shear velocities of more than 10,000,000,000 to 1 which is often required. Unfortunately, this cannot be done by a single instrument. Rather, a number of instruments, each capable of operating properly in its respective shear range must be employed.

With an increase in the theoretical knowledge governing non-Newtonian flow behavior, it is conceivable that in the future the flow determining parameters of the various systems may be measurable by some simple means, and that the whole flow curve or any part of it can be constructed without the necessity of obtaining rheological measurements. Thus, for instance, if x_n, α_n, and β_n, of the Ree-Eyring equation or others which will surely be derived could be determined independently, a large portion of the uncertainties of present viscosity measurements could be eliminated.

However, for the present this is not the case, and recourse to the traditional flow measurements must be taken.

INDUSTRIAL RHEOLOGY

This picture may appear excessively complicated to the industrial rheologist. Fortunately, for application and control purposes, the rheological information required or desired may be considerably abridged. Thus, in the cosmetic industry, as in most others, a few behavior parameters will often suffice to determine whether a given sample of product is up to specification or not. For instance, the ease with which a hand cream or face cream can be applied may determine its suitability or reject it for commercial sale. Very often this factor can readily be ascertained by a few viscosity measurements carried out in the shear range of the actual application or use. Thus, hand and face creams can be tested at high shear rates of, say, 10,000 sec.$^{-1}$. Low viscosity at this shear rate signifies easy application characteristics, high viscosity, poor ones. However, measurement of this characteristic at lower shear values, say 500 sec.$^{-1}$ could give meaningless results if extrapolated into the high shear application range for the reasons previously described and illustrated in Fig. 9.

Similarly, a single measurement, or a few measurements at low shear rates, suitable to the particular parameter controlling industrially desirable structure of the product may be sufficient to characterize it in this region. However, it should again be pointed out that these measurements must be made in the shear range of practical interest, and that extrapolations into this region from measurements made at other shear rates may lead to erroneous results. Thus, several determinations on two instruments, a high shear device and a low shear device, may be sufficient to characterize the material well industrially, whereas measurements made in the region intermediate to these shear ranges may often give insignificant and meaningless results.

AVAILABLE VISCOMETERS

No attempt is made in this paper to list or describe all the rotational viscometers or those working on similar principles which are available. However, in Table I is a listing of a few of the more common commercially available viscometers, or those having some special characteristics which may make them desirable for some phase of cosmetic research or control.

As can be seen, the shear ranges covered vary all the way from a low value of 10^{-6} sec.$^{-1}$ up to a maximum of more than 10^4 sec.$^{-1}$ for the various instruments. The shear gradient constancy leaves much to be desired in some of the more common commercial instruments. The Ferranti-Shirley cone and plate device seems to be the most versatile and covers the greatest shear range at the greatest shear rate constancy of any of the commercial viscometers available. However, it suffers from the possible disadvantage of high price which will make it unavailable to many rheologists.

Perhaps the simplest in construction of all the viscometers listed can be a modification of the Bergen low shear translation device. This consists essentially of an analytical balance (preferably chainomatic) from the left arm of which a bob is suspended into a cylindrical vial containing the test material. The right hand pan is loaded with various weights which just barely allow the bob to either sink or rise in the test medium. By determining the rate of fall or rise of the bob with a given loading, a stress-strain diagram can be constructed which will be a reversed image of itself going through the origin of the coordinates as the bob direction changes from falling to rising. In the original instrument, the bob velocity was determined by means of a differential transformer sensing element. In the author's modification, a cathetometer or other suitable magnifying device is used to visually monitor the velocity of the balance pointer. Also a hollow cylinder may be substituted for the original bob for the reasons previously described.

TABLE I

Name	Type	Approximate Shear Range in Sec.$^{-1}$	Shear Gradient Constancy	Thixotropy Measurabe
Brookfield	CCR* or cylindrical plate	10^{-1}—10^{2}	Poor	Yes
MacMichael	CCR	1–10^{2}	Poor	Yes
Stormer	Paddle	Undefined	Very poor	No
Interchemical	CCR	100—3×10^{2}	Fair	Yes
Hercules Hi-Shear	CCR	10—5×10^{3}	Fair	Yes
Ferranti-Shirley	Cone and plate	20—2×10^{4}	Very good	Yes
Merrill (17)	CCR	3×10^{2}–6×10^{3}	Very good	Yes
Asbeck (18)	CCR	10^{2}—2×10^{4}	Very good	Yes
Band (15)	Band, T†	10—5×10^{4}	Very good	No
Bergen (14)	CCT‡	10^{-6}–10^{-2}	Fair	No
Pochetino (13)	CCT	10^{-6}–10^{-2}	Fair	No

* CCR = Concentric Cylinder Rotational.
† T = Translational.
‡ CCT = Concentric Cylinder Translational.

The reader is referred to the literature cited, or to the pamphlets distributed by the manufacturers for details of the other instruments.

REFERENCES

(1) Coulomb, C. A., *Mem. inst. Natl.*, **3,** 261 (1798).
(2) Newton, I., *Principia Lib.* ii, Sect. IX.
(3) Couette, M., *Ann. chim. phys.*, **21,** 433 (1890).
(4) Stokes, G. G., *Math. and Phys. Papers*, **1,** 75 (1880).
(5) Reynolds, O., *Philo. Trans.*, **177,** 171 (1886).
(6) Eyring, H., *J. Chem. Phys.*, **4,** 283 (1936).
(7) Ree, T., and Eyring, H., *J. Applied Phys.*, **26,** 793 (1955).
(8) Rabinowitsch, B., *Z. physik. Chem.*, **A-145,** 1 (1929).
(9) Mooney, M., *J. Rheol.*, **2,** 210 (1931).

(10) Krieger, I. M., and Maron, S. H., *J. Applied Phys.*, **23**, 147 (1952).
(11) Cram, K. H., and Whitwell, J. C., *Ibid.*, **26**, 613 (1955).
(12) Mooney, M., and Ewart, R. H., *Physics*, **5**, 350 (1934).
(13) Pochetino, A., *Nuovo Cimento*, **8**, 77 (1914).
(14) Bergen, J. T., Patterson, W., Jr., *J. Applied Phys.*, **24**, 712 (1953).
(15) Wachholtz, F., Asbeck, W. K., *Kolloid-Z.*, **93**, 280 (1940); *ibid.*, **94**, 66 (1941).
(16) Asbeck, W. K., to be published.
(17) Merrill, E., *J. Colloid Sci.*, **9**, 7 (1954).
(18) Asbeck, W. K., Laiderman, D. D., and VanLoo, M., *ibid.*, **7**, 306 (1952).

FUNDAMENTAL AND COMPARATIVE ACTIONS OF CLEANSING CREAMS*

By ALBERT R. LATVEN

Pharmacology Research, Inc., Darby, Pa.

ALTHOUGH CLEANSING creams are purported to produce a number of beneficial effects upon the skin, their primary effect and fundamental use is as cleansing agents. The nature of this cleansing action has not been clear particularly in view of the fact that plain soaps are said to be equally effective in removing dirt and other foreign matter from the surface of the skin. However, since it is unlikely that cleansing cosmetic preparations would have received continued use for centuries in the absence of superior cleansing action, the cosmetic chemist has justly accepted the presence of superior cleansing properties and has formulated his products more or less on an empirical basis. It is the purpose of this paper to present hitherto unreported observations concerning the effects of cleansing creams and other products upon a specific type of natural skin soil, namely, upon sebum which has *solidified* in the form of "plaques" over the sebaceous or pilosebaceous orifices. The studies to be presented are preliminary in character and have been conducted as a matter of experimental orientation; it is hoped that the findings may serve as a guide to the refinement of less subjective techniques.

While pursuing studies along unrelated lines, we confirmed the published observation that the sebum lying in the exit of the sebaceous duct fluoresces white to yellow or orange when illuminated by filtered ultraviolet light. However, we also observed that the majority of the yellow and orange fluorescent points consisted of sebum which had solidified in the form of a "cap" loosely covering, but nevertheless adhered to, the surface opening of the sebaceous gland. These caps, or plaques, could be pried loose with a sharp instrument such as a scalpel or razor blade and

---

* Presented at the May 10, 1957, Meeting, New York City.