J. Soc. Cosmetic Chemists, **15**, 564–577 (1964)

PROBLEMS IN COSMETIC RHEOLOGY

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Presented December 3, 1963, New York City

ABSTRACT

The role of empirical measurements in cosmetic rheology is examined and defined. The artifacts appearing in presumably absolute rheological data are explained on the basis of the non-Newtonian behavior of the system. The limitations of single point mesurements are reviewed. Emphasis is placed upon the role that slippage and plug flow have in cosmetic measurements, and it is suggested that ribbed bobs and cups and star bobs have not been sufficiently utilized until now. Viscoelasticity is a prevalent phenomenon in cosmetic rheology but has not been characterised in cosmetic measurements.

INTRODUCTION

"Give me a number, not a story" is a philosophy that may be said to have dominated most of cosmetic rheology. The fundamental rheological examination of a cosmetic can be best represented only by a full rheogram. Unfortunately, this rheogram can only be presented either graphically or tabularly by a series of numbers. Alternately, various empirical devices for the measure of slip, consistency, viscosity, ease of delivery, etc., abound. These, in general, give single numbers, on a relative scale, for the property or combination of properties involved by the test.

There have been many papers dealing with some aspect of cosmetic rheology published in this Journal and elsewhere. However, most have dealt with the fundamentals of rheology or have merely used cosmetics for routine rheologic measurements. What, then, can be so different or so special about cosmetics? In essence, it is the formulator's need for values which bear some relation to the consumer's subjective evaluation, often so critical to the acceptance of a product.

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It is the desire for the clean-cut correlation between a subjective and a measured property that has led to the rash of empirical measurement. There are indeed specialists in the field of cosmetic rheology who prefer arbitrary scale units to fundamental c.g.s. units. This thinking is both to be applauded and deplored.

Where it is practical to make either a fundamental unit measure or an empirical number measure, the use of the latter is to be regretted because it prevents an intercomparison of values between workers, except by an exact replication of the measuring device. This leads inevitably to either a proliferation of empirical devices or the misuse of a device to measure a similar but different phenomenon.

However, there is an important place for an empirical measurement. This is where it is recognized that the property of interest is actually a composite of the interaction of two or more physical parameters. Two examples from our own experience will serve to illustrate this point.

Instruments for Empirical Measurements

The Deformable Container: The act of removal of a paste, ointment or lotion from either a plastic squeeze bottle or tube or from a collapsible metal tube combines two basic phenomena. One is the truly rheological behavior of the contents passing through the orifice. The other involves the force to deform the container and its elastic response as a function of the degree of deformation and of the conditions of fill.

Some time ago, it was necessary to determine the force required to extrude the product from a plastic bottle as a function of bottle design, wall thickness, type of orifice and rheological character of the contents. An apparatus, shown schematically in Fig. 1, was constructed. The pressing "thumb" was $^1/_2$ in. diameter. With this device it was possible to measure the rate of delivery for different applied forces and hence the time for delivery of a fixed quantity with each of these variables. Thus, in Fig. 2 are shown data for three different nozzles for the same product and bottle. In Table I data are presented for different pastes using nozzle No. 1 of the

Table I—Relation between Rheologic Parameters and Squeeze Pressure for a Lotion Paste in a Squeeze Bottle

Orifice Nozzle	Yield Value, dynes/cm.^{2}	Plastic Viscosity, Poises	Flow Force, wt. g. for 5 g. flow in 10 sec.
#1	1150	20	3000
#1	1600	22	3750
#1	800	20	2200
#2	800	20	6750
#3	800	20	11300

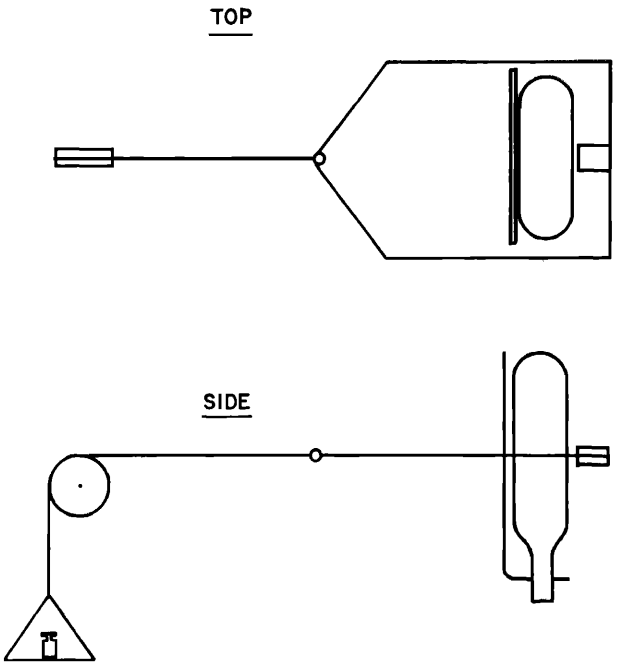

Figure 1.—An extrusion test device to measure force to expel product from a container.

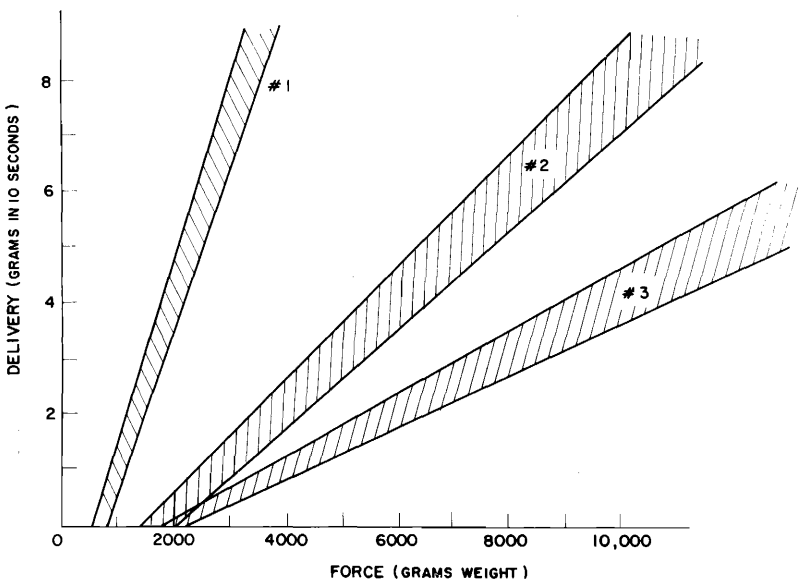

Figure 2.—Typical data obtained for force to expel product from containers containing the same paste but three different nozzles.

figure. More important, with the plastic bottle this also can be used to show the force necessary for a given delivery as a function of the amount remaining in the bottle. Because of elastic flow of contents during the squeezing of a plastic bottle this can be serious.

Exactly the same principles apply with the use of a collapsible metal tube. The force for extruding from a closed tube is greater than the force necessary to blow material out from a tube (1, 2), the difference being the force necessary to deform the tube. The latter force is a function of tube diameter, wall thickness and tube composition.

The Tackmeter: A while back we were studying the increase in tackiness that occurs with some lotions and ointments as they dry. Here the concern is with a combination of skin absorptive power and, possibly, evaporation for some preparations. An apparatus was adapted after that of Green (3) who had worked out the fundamental equations for a tackmeter. This apparatus, already described in the literature (4), was adequate for following drying and for distinguishing gross differences in rub-in capability of ointments and creams on the skin. However, in order to follow the rate of decrease of tackiness of skin after the rub-in of a deodorant cream and the slight differences in rub-in ability of different cream formulations it was necessary to refine this concept.

The new apparatus described here uses a copper disc of $^3/_4$ in. diameter attached to a 1.5 oz. Statham strain gauge. The force recorded by the strain gauge was followed as the skin (usually arm) was slowly lowered until break-away. Typical data for stickiness with time after 60 seconds rub-in are shown in Fig. 3. Since variations in skin texture, etc., may reflect somewhat on the values obtained with different diameters or shaped discs, this measurement falls into the category of an empirical test founded on fundamental principles; however, it is a direct measure of the cohesive-adhesive capability of a skin-surface during absorption after rub-in.

Instruments for Absolute Measurements

An absolute instrument is defined here as any rotational or extrusion rheometer where apparent shear stress and shear rate may be calculated as a function of the geometry of the system. It is customary in routine cosmetic use to use one of the many commercially available systems. Arbitrarily, let us first consider the rotational couette type instruments. Normally these utilize a series of cups and bobs with varying cup-to-bob radius ratios, depending upon the consistency of the sample.

As long as comparative measurements are always made with one cup and bob ratio, it is not critical that equations based upon Newtonian liquids are almost always used for the calculations for the rheogram. However, when

aging causes a viscosity increase such that the next cup and bob combination needs to be used, then the rheograms so obtained always differ significantly in magnitude, introducing discontinuities in aging profiles.

The explanation is simple but shocking: the usual Newtonian equations are not valid. The equations as normally applied assume a linear gradient in velocity between the rotating and the fixed member. This is true not only for moderately close-fitting bobs in Newtonian systems but does hold

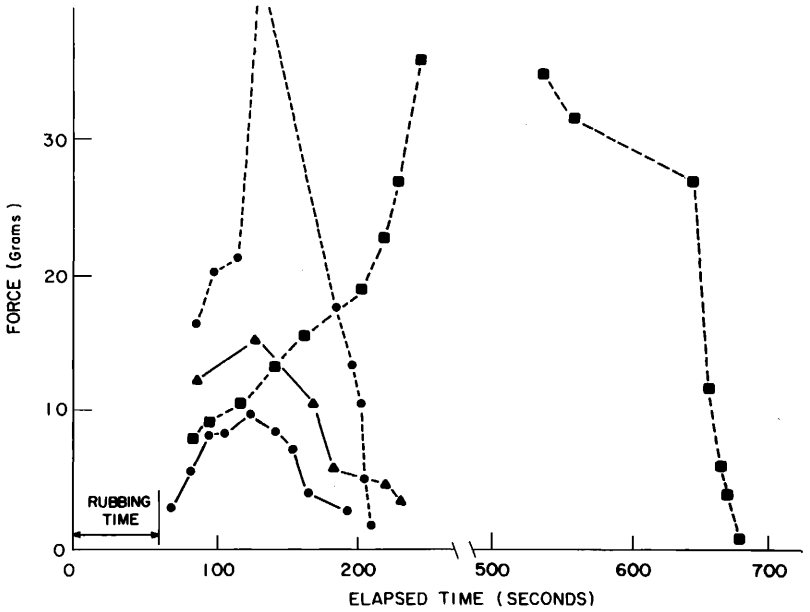

Figure 3.—Profiles for decay of stickiness after 60 sec. rub-in for four antiperspirant and deodorant creams.

remarkably well with Newtonian systems with even large gaps between cup and bob. The very definition of a non-Newtonian requires that this linear dependency cannot hold. The gradient across the gap must be dependent on the shear stress characteristics of the material. The problem has been described completely in the literature and is well summarized by Van Wazer (5).

A similar problem exists with capillary instruments and is dependent on the capillary diameter and on the ratio of length to diameter (6). Again, the Newtonian system assumes a linear gradient from zero velocity at the wall to maximum velocity at the center. In a non-Newtonian system the gradient is no longer linear.

This is typical of the problem that confronts a cosmetic rheologist. What he thought to be an absolute measurement can be so made only by extensive calculations. Even if he is a full-time rheologist, it is doubtful that he can call upon a computing center to help him. Certainly the casual part-time rheologist is completely scared off by such a concept. Thus it seems probable that, for some time to come, rheological studies with couette instruments will be reported in terms of apparent shear rates based on Newtonian concepts. The same consideration holds for the extrusion type rheometer. Since absolute measurements have now become instrument-dependent, it is incumbent always to specify the measuring bob system used or the capillary diameter of an extrusion device.

A second problem in the use of any instrument is the time-dependent nature of the sample's rheology. Normally, this is structural breakdown or thixotropy. In such systems, unless an automatic programing for continuous speed increase is inherent in the rheometer, the time profile used to determine a rheogram can affect the results obtained. If a different rate of increase is used, different shear stresses will result. In this respect, an extrusion rheometer has an advantage; it is continuously studying a new sample. The problem for the residence time under shears in capillaries of different diameters or of the shear gradient with extrusion rheometers is discussed elsewhere (2, 6). The rate of thixotropic breakdown has been defined by Weltmann by two indices of thixotropic breakdown (7). Both coefficients imply that changes in the rate of obtaining the measurement will give different results. It is of interest to realize that the work of the Eyring School (8) in applying the absolute reaction rate theory was capable of predicting, through three shearing cycles, the rheograms for a highly thixotropic cosmetic. Unfortunately, the calculations involved are prohibitive for any routine use.

There is a parallel phenomenon to thixotropy which often appears to be similar. This is the development of slippage planes, either within the material or at the wall of the rotating member. The development of slippage planes within the material, plug flow, is a true form of yield value. Plug flow occurs when the sample under study is unable to withstand the shear gradient imposed upon it and is easy to recognize on any rheogram. In two studies of montmorillonite gums systems (9, 10) a spur yield value was shown for very low shear. This would appear to be a plug flow.

However, wall slippage is another behavior which appears in rheological results to be equivalent but which can be avoided. The use of roughened bobs has been advocated by several workers (11, 12). One commercial instrument, the Rotovisko,®* has two such bobs available. Bruss (13) has observed that many of the spur value type rheograms can be explained

* Brinkman Instruments, New York, N. Y. 11590.

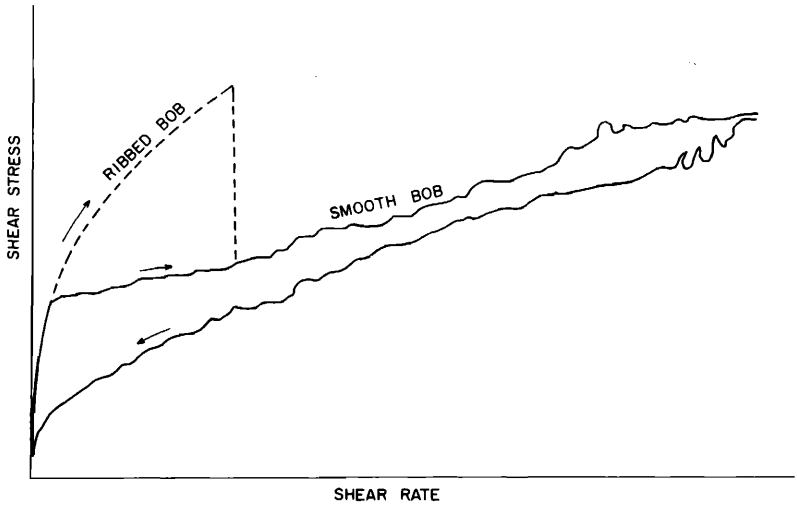

Figure 4.—Rheograms for a dentrifice with smooth and ribbed bobs as obtained on Hercules Hi-Shear Rheometer.

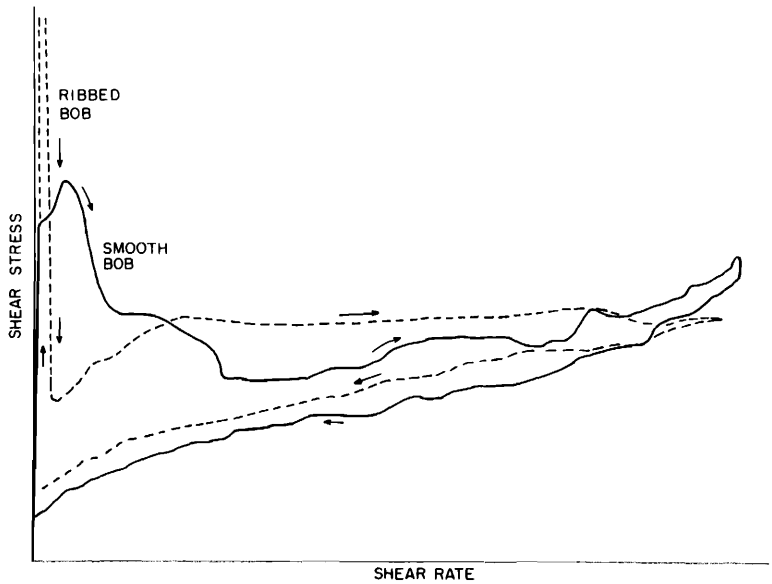

Figure 5.—Rheograms for an antiperspirant cream with smooth and ribbed bobs as obtained on Hercules Hi-Shear Rheometer.

by wall slippage and can be obviated by the ribbed bob. In Figs. 4 and 5 are shown examples of materials examined with the Hercules Hi-Shear Rheometer®** using smooth and ribbed bobs and cups. What often happens in cosmetic systems is a sort of syneresis in which a thin film of liquid is obtained at a shear face. This provides lubrication and slip. The viscosity of this film is then measured at high shears after breakdown. The apparent spur value then becomes but a reproducible artifact. The same anomalous results are possible with the cone and plate design for the same reason. The use of artificially roughened surfaces in the rheology of cosmetic lotions should be seriously considered by all workers in the field.

For the study of yield value behavior, Bruss (14) used a rotor which does not disturb the sample appreciably on insertion. This is of the star shape so that true structural behavior in the body is measured rather than interface dependent phenomena. This concept for a rotor deserves more attention. Indeed, it would seem desirable that all cosmetic rheologists consider the use of a design of this type of rotor for all samples loosely designated as semisolids. With such a rotor the rheogram will clearly show when a slippage plane develops and plug flow begins. Indeed, the rotor might well be applied in all studies of the yield value type. It should be mentioned that one such bob is available with the Rotovisko.

The use of ribs on both the cone and plate of such a rheometer and the design of suitable cones of a star-type design in conjunction with the ribbed plate are to be recommended for cosmetic studies with that instrument.

Multipoint vs. Single Point Measurements

Only a full rheogram can characterize a non-Newtonian liquid; it takes a minimum of two points to prove the existence of a Newtonian system, valid only within the range examined (curve A of Fig. 6).

Every basic study of rheology emphasizes that one cannot compare simply the properties of fluids of different rheological dependencies. Thus, in Fig. 6 at the shear equivalent to the point of intersection all three are identical; at lower shear values, major differences are exhibited, particularly between C and the other two curves. At shears above the crossing, a complete inversion of order occurs.

If the one point measurement corresponds to the shear region of the property of interest, it is accepted without question. If it does not, then another test, usually empirical, which does relate is employed. Thus an empirical test to relate to a property observed below the point of intersection must itself be in that shear range. If the test is below the intersection (and in general that itself is a wide range) while the property desired is at a

** Martinson Machine Co., Kalamazoo, Mich.

higher shear rate, then no test correlation will exist. Thus Kostenbauder (15) discusses an example of an empirical spreadability test in which it was not recognized that it did not give shear rates in the range of spreadability interest because insufficiently differing samples were examined. There are several different practical shear rates that need be considered in routine cosmetic rheology as those of importance to the product. Thus if yield value is necessary, then a series of extremely low shear rate measurements are critical (16). If ease of flow is the criterion, then intermediate shear rates of 10 to 100 sec.$^{-1}$ become important. If shear thinning or rubbing

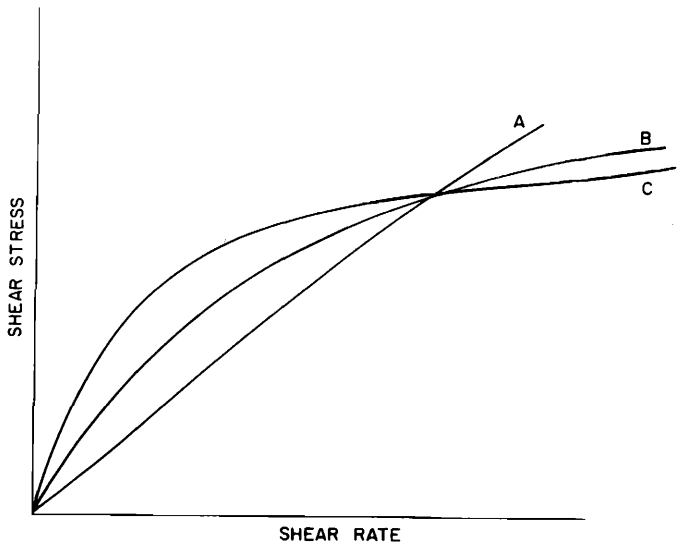

Figure 6.—Typical possible rheograms.

is of importance, then shear rates in thousands of reciprocal seconds are to be considered. Empirical testing based on other shear ranges are of value only in defined systems, where the rheograms do not cross, so measurements in one shear range parallel those in another.

In a given product, variations between batches may be known to lead to a continuous smooth family of rheograms. Where this *is known* to be the case, one-point measurements may be directly correlated to either high or low shear properties, but in *no* other case.

Sample History

The normal determination of a rheogram does not clearly demonstrate the possible artifacts that can result from the sample history problem. As mentioned earlier, most cosmetic formulations show thixotropy with

continued shear. The recovery from shear is often very slow and still apparent long after its occurrence (17).

Thus, earlier work with the calibration of shear imparted by commercial fillers (2) showed that the difference could still be observed weeks later. Indeed it was this prolonged dependency on the imparted shearing treatment that made this evaluation possible. This same prolonged dependency has been shown for the degree of homogenization of a cosmetic lotion (18). In general, shear recovery processes are logarithmic in time dependency (18), and so protracted recovery times are the general rule.

It has been alleged that pouring from a bottle can influence the rheologic properties of a lotion (19). If appreciable thixotropic breakdown occurs in the shear process, i.e., approximately 50 sec.$^{-1}$(13), then this must be so. This emphasizes the need to do the rheology study on the actual sample. Thus aged bulk samples can differ from material poured from a machine filled bottle or manually squeezed from a plastic bottle. In Table II are shown data on bulk samples poured from filled plastic squeeze bottles and samples squeezed out through the orifice of the bottle.

TABLE II—DIFFERENCES IN MEASURED APPARENT VISCOSITY WITH SHEAR RATE EXTRUDED FROM A SQUEEZE BOTTLE AT TWO DIFFERENT AGING PERIODS

Apparent Shear Rate, sec.$^{-1}$	8 days		75 days	
	Bulk, poises	Extruded, poises	Bulk, poises	Extruded, poises
0.066	324	245	920	900
0.13	249	199	626	572
0.33	150	113	389	345
0.66	105	79	265	245
1.33	76	56	190	168
2.65	57	43	130	118

By the same token, no shear in preparing a sample for examination should be a significant portion of the shear at which the measurement is to be made. Thus a "set" in a bottle may be destroyed by rapid pouring, so that no yield value is observed. The shear of rheometer loading can be a severe problem where pastes and other thick systems are loaded in narrow gap rheometers. This can be avoided by studying rheology from collapsible tubes with an extrusion rheometer (2).

VISCOELASTIC MATERIALS

Somewhere in the continuum of time-dependent pseudo-plastic systems we pass to those normally recognized as visco-elastic. This category is much more prevalent than has been normally recognized. Thus Kostenbauder (20) turned a coarse thread on his rotating bob in the direction opposite to rotation to prevent the up-pumping of his suspension. This

problem of the sample rising up out of a couette instrument is a problem in most cosmetic and pharmaceutical pastes. It is called the Weissenburg effect, and it is a necessary consequence to the balance of the parallelogram of forces in a visco-elastic material. Many workers have sought to avoid the problem by the use of caps over their instruments. Whether it be caps or threaded bobs, the measurements become somewhat dubious because of the interplay of stress components, and the measurements omit a portion of the observation.

The time dependent nature of many materials has been emphasized by Scott-Blair (21) and by Reiner (22) in their many publications in Britain. The presence of visco-elasticity in cosmetic and pharmaceutical rheological phenomena in the U. S. has received little published attention until Mc-

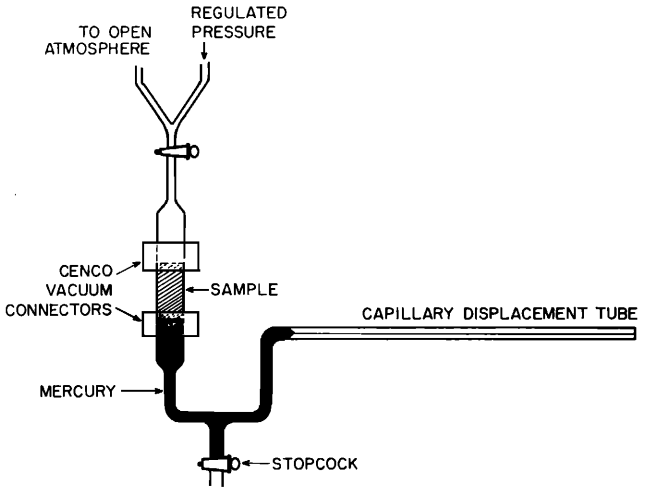

Figure 7.—Elastometer for viscoelastic systems.

Vean's work (23, 24) on the visco-elasticity of gum systems, although many of our systems do display this phenomenon.

A recent new product in the men's hair dressing field* has a distinct bounce due to its high degree of visco-elasticity. Conventional rheological measurements were of limited value in characterizing this material, since both wall slippage and plug flow seemed always to be involved. An elastometer was constructed (Fig. 7) that would permit a measure of the elastic deformation and the viscous flow. It is an improved version of one described by Saunders and Ward (25) for the study of the elasticity of gelatin. They sought to measure the instantaneous elastic components only. As a result they found their expected constant was stress dependent. In the apparatus shown the pressure gradient across the sample is always the

* Score, registered trade name of Bristol-Myers Co.

difference between the applied pressure and the atmosphere. Deformation of the plug was observed by capillary motion of the mercury. Upon application of pressure, an instantaneous and slow elastic deformation occurred. At higher pressures flow also was observed by capillary motion of the mercury. Upon release of the pressure, the instantaneous and delayed elastic rebounds were observed. Data treatment for evaluation of elastic and viscous flow is straightforward. However, for this product the variability due to material slippage against the cylinder wall was of the order of the variation between samples, preventing measurements of the needed accuracy.

Accordingly, an elastic damping measurement was employed. The damping of the vibration of a long needle resting on a flat foot in the material was followed electronically on an oscilloscope recorder. The logarithmic decay of the vibration from a displacement is determined directly; this viscous damping gives a measure of the viscosity. The frequency is dependent upon the elastic modulus of the sample. With this device aging measurements, temperature dependency, etc., can be determined for the variation in the elastic component. This work is now in progress.

The elastometer shown in Fig. 7 has proven to be of great value, both with this product and with many other cosmetic semisolids, in understanding the relative elasticity and degree of recovery possible during solid deformation. As the visco-elastic component of many cosmetic and pharmaceutical preparations is recognized, direct measurements and techniques will be devised which are suitable for the systems involved. With a better understanding of the time-dependent properties of cosmetic products, both in the influence of shear and the changes occurring with time, safer predictions can be made for the changes that will occur with prolonged time.

Summary

Empirical measurements have a role in cosmetic rheology only where there is an interplay of two or more variables. Where possible these empirical measurements should be grounded on fundamental concepts. The test must correspond to the rate of shear on the desired property to have any versatility.

The use of apparently absolute instruments for study of non-Newtonian systems can lead to artifacts which are characteristics of the measurement rather than of the sample. This problem may be handled completely with the aid of known mathematical procedures.

Visco-elasticity is a phenomenon present in many systems, and it must be evaluated for its role in the acceptance of a product. This characteristic has been inadequately considered in cosmetic studies.

(Received December 26, 1963)

References

(1) R. H. Marriott, *J. Soc. Cosmetic Chemists*, **12,** 89 (1961).
(2) J. H. Wood, G. Catacalos, and S. V. Lieberman, *J. Pharm. Sci.*, **52,** 375 (1963).
(3) H. Green, *Ind. Eng. Chem. Anal. Ed.*, **13,** 632 (1944).
(4) J. H. Wood and E. Lapham, *J. Pharm. Sci.*, accepted for publication.
(5) J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, *Viscosity and Flow Measurement*, Interscience Publishers, Inc., New York, N. Y., 1963, p. 55 ff.
(6) *Ibid.*, p. 189 ff.
(7) R. N. Weltmann, *J. Soc. Cosmetic Chemists*, **7,** 599 (1956).
(8) S. J. Hahn, T. Ree, and H. Eyring, *NLGI Spokesman*, **23,** 129 (1936).
(9) G. Levy, *J. Pharm. Sci.*, **52,** 947 (1962).
(10) J. H. Wood, G. Catacalos, and S. V. Lieberman, *Ibid.*, **52,** 354 (1963).
(11) E. Bantoft, *Rheology of Disperse Systems* in C. C. Mill, Pergamon Press, Ltd., London, 1957, p. 105.
(12) A. Fincke and W. Heinz, *Rheol. Acta*, **1,** 530 (1961).
(13) H. Bruss, personal communication.
(14) H. Bruss, *Parfumerie u. Kosmetik*, **41,** 141 (1960).
(15) N. L. Henderson, P. M. Meer, and H. B. Kostenbauder, *J. Pharm. Sci.*, **50,** 788 (1961).
(16) G. Catacalos and J. H. Wood, *Ibid.*, accepted for publication.
(17) J. H. Wood and G. Catacalos, *J. Soc. Cosmetic Chemists*, **14,** 147 (1963).
(18) J. H. Wood, *Am. Perfumer*, **76,** No. 10, 37 (1961).
(19) H. Heinrich and J. E. Clements, *Proc. Soc. Sect. Toilet Goods Assoc., No.* **33,** 16 (1960).
(20) H. B. Kostenbauder and A. N. Martin, *J. Am. Pharm. Assoc., Sci. Ed.*, **43,** 401 (1954).
(21) G. W. Scott-Blair, *A Survey of General and Applied Rheology*, Isaac Pitman & Sons, London, 1949, p. 163 ff.
(22) M. Reiner, *Deformation, Strain, and Flow*, H. K. Lewis & Co., Ltd., London, 1960, p. 126 ff.
(23) D. E. McVean and A. M. Mattocks, *J. Pharm. Sci.*, **50,** 785 (1961).
(24) D. E. McVean, Ph.D. Dissertation, Univ. of Michigan, Ann Arbor, 1962.
(25) P. R. Saunders and A. G. Ward, *Proc. Sect. Intern. Cong. Rheol.* in V. G. W. Harrison Academic Press, Ltd., London, 1954, p. 284.