were the emulsifying agent not affected. We conclude therefore that the changes in hydrogen-ion concentration influence the permanency of the gel, and thus affect the stability of the emulsion.

A close examination of Fig. 13 will show that only those tragacanth gels between p_H 0.4 and 2.1 remain free from the separation of water at the surface, however the liquids between p_H 1 and 2.1 prepare the most stable gels with tragacanth; it will be recalled that the stable range of p_H for emulsions made with tragacanth practically lies within this scale. This supports Fischer's (6) Hydrate theory of emulsification, which postulates that oil is most permanently emulsified in a hydrophile colloid when just a sufficient amount of water is present to form a hydrate. We believe that with tragacanth this amount of water is a function of its hydrogen-ion concentration, therefore at the range of the p_H scale where tragacanth shows itself to possess the highest degree of hydratability, this range is the stable point for emulsions prepared with this colloid.

CONCLUSIONS.

1. The range of greatest stability for either vegetable or mineral oils prepared with acacia lies between p_H 2 to 10 and with tragacanth the range is p_H 1.9–2.3.
2. The size of the particles, surface tension, interfacial tension and viscosity have been determined at various points on the p_H scale. Changes in particle size and viscosity is caused by changing the hydrogen-ion concentration of emulsions prepared with tragacanth. The viscosities of acacia emulsions are not altered by changing the p_H, the size of the particle, however, increases on the alkaline side of the p_H scale.
3. Fischer's Hydrate Theory is substantiated in emulsions prepared with tragacanth.

BIBLIOGRAPHY.

(1) Blakiston's Son & Co., Philadelphia.
(2) *Z. physik. Chem.*, 31, 42 (1899); *Brit. Med. J.* (Dec. 23, 1905).
(3) *J. Am. Chem. Soc.*, 42, 2049 (1920).
(4) *Ibid.*, 39, 1848 (1917).
(5) Koll, *Zeits.*, 4, 208 (1910).
(6) "Fats & Fatty Degeneration," (N. Y.), p. 5 (1917).

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PLASTICITY MEASUREMENTS IN PHARMACY.*

BY E. MONESS AND P. M. GIESY.

In the manufacture of various products, such as dental creams, cold creams, ointments, etc., it is important to maintain uniformity in what is generally referred to as "consistency." It is therefore highly desirable to have a method for measuring quantitatively this property of these substances.

The substances above mentioned belong to the class known as plastic materials, and should be sharply differentiated from viscous liquids. In general, a plastic substance is one which will undergo continuous deformation or flow under a shearing stress only after the latter exceeds a certain value which we call the "yield shearing stress" or "yield value." In a viscous liquid this yield shearing stress

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is equal to zero, that is to say, the liquid will flow under any stress, no matter how small, if sufficient time is allowed. As Maxwell expresses it in his "Theory of Heat," in the case of a plastic what is required to alter its form is sufficient force, while with a liquid it is time. Some substances that appear hard and solid are in reality viscous liquids, while others appearing to be rather soft must be classified as plastic solids. Thus a block of pitch which is so hard that it cannot be dented with your knuckles will in the course of time flatten itself out by its own weight. Similarly, if a tallow candle and a stick of sealing wax are placed horizontally between two supports, the sealing wax will in a few weeks bend under its own weight, while the softer candle will remain rigid. The pitch and the sealing wax in Maxwell's examples must therefore be considered as very viscous liquids, while the candle is a plastic solid.

In dealing then with liquids we may express by "fluidity" the speed with which the liquid will flow under a certain shearing stress. If we were to plot the speed of flow through a tube against the shearing stress, we would obtain a straight line which would pass through the origin. (Fig. 1.)

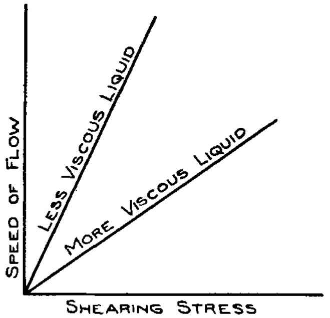

Fig. 1.

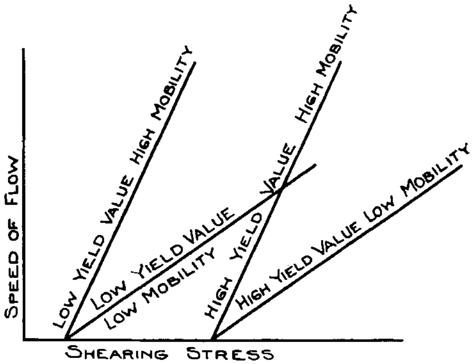

Fig. 2.

In a plastic, flow will only occur after the shearing stress exceeds the yield value, which is a characteristic of the material in question. When the yield value has been exceeded the flow will depend on the "mobility" of the plastic, a property analogous to the fluidity of a liquid. Plasticity is thus a complex property which is determined by two independent factors: "yield value" and "mobility." If we were to plot the speed of flow against shearing stress in the case of a plastic we would again, as in the case of a viscous liquid, obtain a straight line, but it would not pass through the origin. (Fig. 2.)

Of the methods existing for the measurement of the two characteristics of a plastic we shall mention only the tube method of Bingham.[1] It consists essentially in allowing the plastic to flow out of a capillary tube under different shearing stresses, and measuring the rate of flow under these stresses. The graphical method is the simplest one for obtaining "yield value" and "mobility." For this purpose we plot the rate of flow against shearing stress and obtain a straight line which when produced or extrapolated to the X-axis intersects the latter at some distance from the origin. This intercept is proportional to the yield value, while the slope of the curve, or what is the same thing, the ratio of the change

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[1] "Fluidity and Plasticity," p. 222 (1922).

of rate of flow to the change of shearing stress, is proportional to the mobility. It often happens, and more especially at low shearing stresses, that the curve departs from linearity and shows a decided tendency to curve in towards the origin. This is explained by Bingham on the assumption of "slippage," that is, a partial movement of the plastic irrespective of plastic flow and due to slipping along the walls of the capillary as a solid rod. However, experimentally this can be avoided by using sufficiently high shearing stresses.

In our procedure we have adopted a modification of the Bingham procedure described above, which was proposed by Bingham in April 1923, before the Division of Industrial and Engineering Chemistry at the New Haven Meeting of the American Chemical Society.[1] He suggested that plasticity measurements could be made by timing the flow over successive increments of length of a capillary, this being equivalent to determining the speed of flow through capillaries of the same diameter and varying lengths.

The use of gas pressure involves complicated and expensive apparatus for keeping the pressure constant and measuring it. We decided to try to use a mercury column to supply pressure, measuring the pressure by the height of the column. The plastic material is pushed by the pressure of the mercury through the graduated capillary, and the time at which the head of the column passes alternate centimeter divisions is noted.

Under these conditions $\Delta l/\Delta t$, where $\Delta l = 2$ cm. and Δt is the actual time taken by the dental cream to traverse this length of capillary, is a variable which is a linear function of P/l, where P is the total pressure applied and l the mean length of capillary filled by the material during this time. So, when a curve is plotted with $\Delta l/\Delta t$ as ordinate and P/l as abscissa, a straight line should result, the slope of which is proportional to the mobility of the plastic, and the intercept of which on the X-axis is proportional to the yield shearing stress of the material under test. To get absolute values for mobility and yield value let us take Buckingham's formula for plastic flow when the method of allowing the material to extrude from a capillary is used:

$$\frac{V}{t} = \frac{\pi\mu R^4}{8l}\left(P - \frac{4}{3}p\right) \qquad (1)$$

where V/t is the volume rate of flow, μ is the mobility, R and l respectively the radius and length of the capillary, P the total applied pressure, and p that part of the applied pressure that goes to overcome the yield shearing stress. Under our conditions, V/t becomes $\pi R^2 dl/dt$, π, μ, R, and P are constants, and l and p are variables. Substituting $2fl/R$ for p (f being constant) we have

$$\frac{dl}{dt} = \frac{\mu R^2}{8}\left(\frac{P}{l} - \frac{8f}{3R}\right) \qquad (2)$$

If, therefore, we plot dl/dt as a function of P/l, as we have done for the sake of convenience, we see that the slope is $\mu R^2/8$, and the x-intercept $8f/3R$. The slope, therefore is proportional to the mobility, and the x-intercept to the yield shearing stress; each value is also a function of the radius of the capillary. As long as the same capillary is used, slopes give comparative mobilities, and x-intercepts comparative yield shearing stresses.

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[1] Bingham and Murray ("Proc. Am. Soc. for Testing Materials," 23, II, 655 (1923)).

If we plot rate of flow dl/dt as a function of shearing stress, $F = RP/2l$, equation (2) reduces to the form

$$\frac{dl}{dt} = \frac{\mu R}{4}\left(\frac{RP}{2l} - \frac{4}{3}f\right) \qquad (3)$$

Now the x-intercept equals 4/3 of the yield shearing stress and the slope the mobility times one-fourth the radius. To get the mobility directly from the slope we must put the equation in the form:

$$\frac{4}{R}\frac{dl}{dt} = \mu\left(\frac{RP}{2l} - \frac{4}{3}f\right) \qquad (4)$$

and plot $4/R\ dl/dt$ as a function of $RP/2l$.

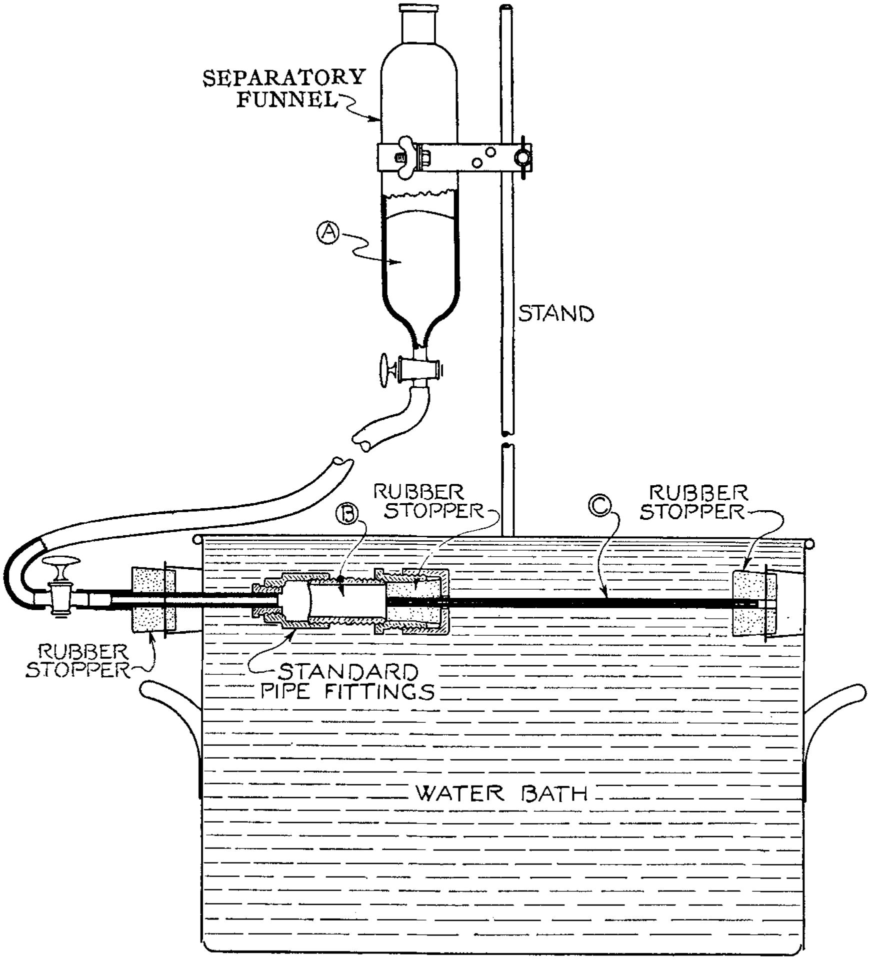

Fig. 3.—Assembled set-up.

APPARATUS AND METHOD.

Figure 3 shows a view of the whole set-up, and Fig. 4 gives the details of the plastometer proper. This is constructed entirely of standard pipe fittings, as shown. The capillary is held in a rubber stopper which is kept in position and at the same time compressed against the capillary by the drilled pipe cap shown. The apparatus is easily taken apart and can be readily washed, dried and reassembled.

In making a run, say with dental cream, the apparatus, not including the capillary with its rubber stopper and the drilled cap and reducing bushing in which this is held, is connected as shown to the rubber tube leading from the mercury reservoir, and the mercury level adjusted by holding the apparatus in a vertical position. The stop cock on the rubber tube is now closed. The dental cream is placed in the Reservoir B by squeezing it out from a collapsible tube through a 3-inch long glass tube attached to the mouth of the collapsible tube; the filling is done from the mercury surface upward, care being taken that no air-spaces or voids are left in the mass of the dental cream. Next, the apparatus is placed in a horizontal position, pushed through the opening in the wall of the water-bath, and the capillary is screwed on tightly by means of the bushing. The whole is then placed in the water-bath as shown, covered with water, and the temperature is adjusted to 25° C., and kept there for ten minutes. The run is then started by opening the stop cock and taking the proper readings, keeping the temperature of the bath at 25° C., throughout the run. The capillary can be calibrated by finding the weight of mercury required to fill a known length of the capillary.

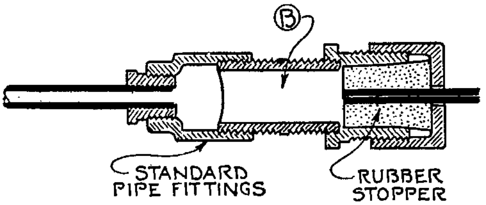

Fig. 4.—Plastometer.

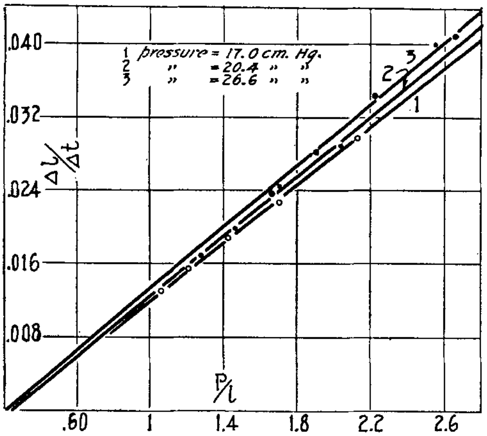

Fig. 5.—Plasticity curves for Dental Cream using varying pressures.

The first design (Type I) used an oil-cup as the body of the plastometer, the pressure being applied through a tube soldered into the top thereof. With this outfit the mercury channelled through the dental cream to the capillary, frequently entering this before the end of the run. When air pressure was used, the same thing happened. To prevent this, a 3" x $^1/_4$" copper tube was inserted between the oil-cup and the capillary (Type II). Duplicate determinations with this checked poorly, due to the mercury entering the tube varying distances. The oil-cup was then omitted, the mercury pressure being applied directly to the copper tube, the pressure thus being exerted over the whole area of the dental cream (Type III). This gave runs which checked satisfactorily, but when the applied pressure was increased the values of the slope also increased:

Pressure (cm. Hg).	Slope.	Pressure (cm. Hg).	Slope.
18.9	0.0076	25.8	0.0101
22.6	0.0096	30.2	0.0128

This seemed to be due to flow-resistance not in the capillary, but in the reservoir, which had the effect of an additional length of capillary. We therefore modified the instrument to the form first described. Runs with varying pressures gave the following results:

Pressure (cm. Hg).	Slope.	x-Intercept.
17.0	0.0156	0.24
20.4	0.0162	0.24
26.6	0.0166	0.22

The curves of these runs are shown in Fig. 5.

It will be noticed that even here the effect of the internal resistance of the reservoir shows itself somewhat. It should be pointed out that it will be impossible to eliminate this entirely with any type of capillary tube instrument. With more fluid materials its effect is less noticeable. In working with fairly thick aqueous emulsions we were able to use the Type III instrument with entire satisfaction; varying the applied pressures did not affect the slopes:

Pressure (cm. liquid).	Slope.	x-Intercept.
29	0.0175	1.2
58	0.0175	1.5

The apparatus and method outlined above have certain drawbacks and limitations which it is well to keep in mind: First, it appears that not all plastic substances give equally good results: for instance, we have found it impossible to use this method for the determination of plasticity of cold cream. This has a strong tendency to move through the capillary by slippage rather than by plastic flow. It is therefore difficult to get results which when plotted will give a straight line, or to get checking results. But it is equally true that the method in which the cold cream is allowed to flow out of the capillary under different pressures and the volumes of flow measured gives little better results.

Second, in running the same plastic material by the two methods outlined above, that is, by the "penetrivity" and the "extrusion" methods, we obtain results which do not check. The reason for this lack of agreement is still obscure, and there is as yet no real reason to consider one method better justified than the other. The results obtained by either method show any differences in consistency between samples, and this is what is desired in control work.

We have also obtained relative values for the yield shearing stress of plastic materials by allowing the plastic to flow through an orifice instead of a capillary, and plotting volume of flow against applied pressure. Straight lines are obtained in such plots, and while no values for mobility can thus be obtained, the intercept of the straight line on the X-axis is a measure of the yield value. Such a run can be easily carried out with our apparatus by holding it vertically, and attaching to it a street ell, to the mouth of which is screwed a cap with an orifice of about 2 mm. The plastometer, the street ell and the cap are full of the plastic. Since the plastometer is in a vertical position, correction for drop in pressure for each point of the run must be made. Very nicely checking results are thus obtained.

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