Rheological investigation of a thixotropic lotion

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Various methods of characterising the thixotropic properties of an oil in water lotion are described. Stress relaxation behaviour, which can be expressed over a range of shear rates by a single empirical equation, is shown to be more informative than the measurement of hysteresis loops. Relaxation rate depends upon previous shear treatment which suggests that more than one process occurs during breakdown.

AN important aspect of quality control of many fluid pharmaceutical preparations is the determination of their flow properties. Such measurements may be correlated with subjective assessments of consistency and in some cases with physical stability. For non-Newtonian materials it is desirable that the flow properties be investigated before an attempt is made to devise a routine testing procedure. With this object the present study was made on a corticosteroid lotion base consisting of a thixotropic aqueous dispersion of cetostearyl alcohol.

Thixotropic systems exhibit stress relaxation when subjected to a steady shear rate and afterwards recover their initial state relatively slowly. The phenomenon is considered to be due to the presence of a shear-sensitive structure containing interparticle or intermolecular links (Hauser & Reed, 1937; Goodeve, 1939; Voet, 1947). The higher the shear rate, the quicker and more pronounced the breakdown. Hysteresis is therefore observed when data obtained at increasing and decreasing rates of shear, the "upcurve" and "downcurve", are compared.

Stresses measured in a thixotropic system must be related to a particular initial structural state and to the procedures used for varying the rate of shear with time. Of the countless possible methods of making such experiments certain logical sequences facilitate the presentation and interpretation of results. Procedures used by various workers include production of hysteresis loops (Green & Weltmann, 1943, 1946; Weltmann, 1943; de Butts, Hudy & Elliot, 1957; Foernzler, Martin & Banker, 1960), measurements of stress relaxation (Hauser & Reed, 1937; Weltmann, 1943; Carver & Van Wazer, 1947) or recovery (Hauser & Reed, 1937; de Waele, 1961; Levy, 1962) and the comparison of equilibrium and initial stresses at various shear rates (Van Wazer, Lyons, Kim & Colwell, 1963). In interpreting the results two effects must be separated, namely the relaxation or recovery of stress with time at constant shear rate, and the change in stress produced by a change of shear rate only. Measurement of stress relaxation in individual samples at various shear rates is an ideal although tedious procedure. In the present work this method has been modified to obtain the same information from one sample and the results compared with those using the hysteresis loop technique.

Experimental

The composition of the lotion was (%w/w): cetostearyl alcohol, 3·0; cetomacrogol 1,000, 0·6; methyl hydroxybenzoate, 0·15; propyl hydroxy-

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benzoate, 0·08; propylene glycol, 5·0; citric acid, 0·01; and water to 100·0 (all ingredients of B.P. or B.P.C. grade). Samples were prepared as follows: The cetostearyl alcohol, cetomacrogol 1000 and propyl hydroxy-benzoate were emulsified at 70° with an equal weight of a solution of the methyl hydroxybenzoate in 85 parts of water. This concentrated emulsion was diluted with the remainder of the aqueous solution at 70°. After cooling to 50° the propylene glycol and citric acid dissolved in sufficient water to make the required weight were added. The lotion was allowed to cool undisturbed to ambient temperature: no homogenisation was necessary. The product was a translucent viscous lotion which was shown by microscopic examination to consist of a fine dispersion of solid cetostearyl alcohol. Measurements were made at 25° on two batches using the Haake "Rotovisco" and Contraves Epprecht "Rheomat" visco-meters with measuring systems MVI and B respectively. Shear rates were calculated from instrument dimensions and the speed of rotation and were therefore strictly "apparent shear rates" applicable only to Newtonian fluids. True shear rates at the measuring bob surface would in all instances be higher due to the non-Newtonian flow properties of the lotion. Samples were introduced with as little disturbance as possible and allowed to stand overnight before determining stress relaxation rates, a separate sample being used for each shear rate. Hysteresis loop measurements were made after standing for only 10 min using the method of Green & Weltmann (1943, 1946), keeping the time "t" at which readings were taken proportional to the speed of rotation and hence the shear rate, i.e. $t = \rho \times$ rpm where ρ is a constant. Recovery of structure after shear was too slow for convenient measurement in the concentric cylinder viscometers. However the reversible nature of the breakdown was confirmed in a separate experiment using the Brookfield Syncrolectric viscometer Model LVT with Helipath accessories.

Results and discussion

The stress relaxation data plotted in Figs 1 and 2 show the relationship between stress and time at each shear rate to be represented over a wide range of time by the empirical equation;

$$\log\left(\frac{\tau_a}{\tau_b}\right) = K \log\left(\frac{t_b}{t_a}\right) \quad .. \quad \quad .. \quad \quad .. \quad (1)$$

where τ_a and τ_b are the values of stress at times t_a and t_b. Values of K have been calculated for each line and are listed in Table 1. For shear rates below 200 sec^{-1} K is virtually constant for each batch of lotion. The lower values of K at high shear rates may be due to a change in true shear rate with time as the viscosity falls, or to the onset of curvature. The Rotovisco results exhibit more scatter particularly at the lowest shear rates due to unsteadiness in the readings. It is interesting to note that although stress recovery after shear has been similarly represented by de Waele (1961) for thixotropic paints, stress relaxation behaviour has been differently interpreted by other workers. Thus Weltmann (1943) found that her data on printing inks gave straight lines when plastic

TABLE 1.   VALUES OF K FOR LOTIONS A AND B AT VARIOUS SHEAR RATES

Lotion	Instrument	Apparent shear rate, sec^{-1}	K
A	Rotovisco	571	0·122
,,	,,	347	0·133
,,	,,	190	0·155
,,	,,	127	0·162
,,	,,	63·4	0·166
,,	,,	21·2	0·164
,,	,,	7·05	0·164
B	Rheomat	196	0·195
,,	,,	84·5	0·202
,,	,,	32·9	0·195
,,	,,	9·67	0·189
,,	,,	3·11	0·187

viscosity, U, was plotted against log t.   Since $U = (\tau - f)/\sigma$ and f the so-called "yield value" was taken as constant for constant shear rate, σ, it follows that $d\tau/d \log t =$ a constant.   Hahn, Ree & Eyring (1959) have contested this relationship and pointed out that the plots were sigmoidal.   They have shown from theoretical considerations that stress relaxation should be given by $\log (\tau - \tau_\epsilon) = p - at$, where τ_ϵ is the equilibrium stress, $\tau =$ stress at time t and p and a are material constants. Van Wazer & others (1963) have expressed the data of Carver & Van Wazer (1947) on a thixotropic emulsion in a similar way.
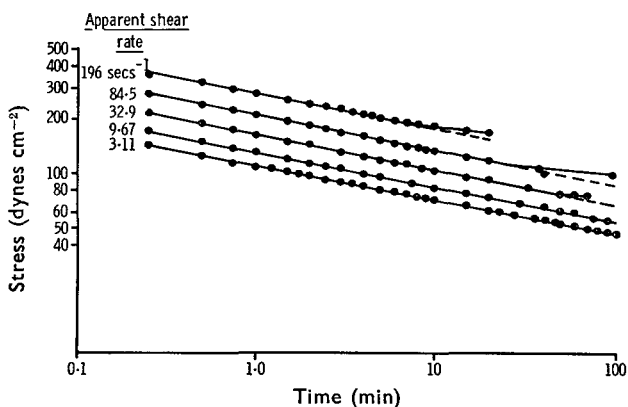

FIG. 1.   Stress relaxation at constant shear rates using Rheomat viscometer.

However, from the results in Figs 1 and 2 the value of τ_E is uncertain even at the highest shear rates used for the present system; at the lowest shear rates studied no estimate can be made even after 2 hr.   This type of relaxation behaviour has the important result that it is not possible to describe the relationship between stress and shear rate in terms of either initial or equilibrium conditions.   A practical alternative is to plot stress (after shearing the sample for some fixed time) *versus* shear rate.   Strictly, a fresh sample should be used for each determination, but an attempt was

made to overcome this requirement by making an experiment in which shear rate was progressively raised, allowance being made at each step for the loss of structure already produced.
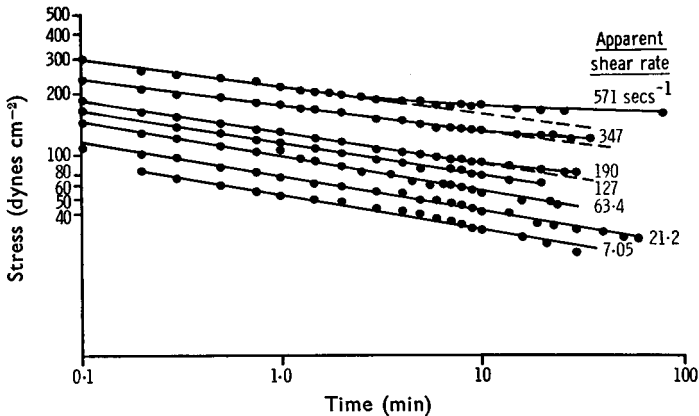

FIG. 2. Stress relaxation at constant shear rates using Rotovisco viscometer.

When stress relaxation measurements are made on samples which have already been sheared at a lower shear rate the stress values are lower than for fresh samples. To determine from measurements on a previously sheared sample how a fresh sample would behave some correction must therefore be applied. It may be considered that the breakdown in structure occurring at the lower shear rate could equally have been produced by shearing for a shorter time at the higher rate; the value of this time must be calculated and added as a correction. If the shear-induced loss of structure be denoted by Δ, and considered to be some function of the amount of shear, i.e.

$$\Delta = f(\sigma t) \qquad .. \qquad .. \qquad .. \qquad .. \qquad (2)$$

it follows that if

$$\Delta(\sigma_1, t_1) = \Delta(\sigma_2, t_2)$$

then

$$t_2 = t_1\sigma_1/\sigma_2 \qquad .. \qquad .. \qquad .. \qquad .. \qquad (3)$$

Data obtained at shear rate σ_2 after shearing for time t_1 at σ_1, where $\sigma_2 > \sigma_1$, should become identical with data on a fresh sample if an appropriate quantity, t_2, is added to each value of t. This method of correction has been applied in Fig. 3 to data obtained on a sample sheared for 140 min at 3·11 sec^{-1} before switching to 9·67 sec^{-1}. By equation (3)

$$t_2 = 140 \times 3{\cdot}11/9{\cdot}67 = 45 \text{ min.}$$

Only the three points obtained during the first 2 min after changing the shear rate are more than 5% from the line. Probably during this time some structure is broken down which can only be removed at the higher shear rate. Similar corrections applied to a sample sheared for 5 min at
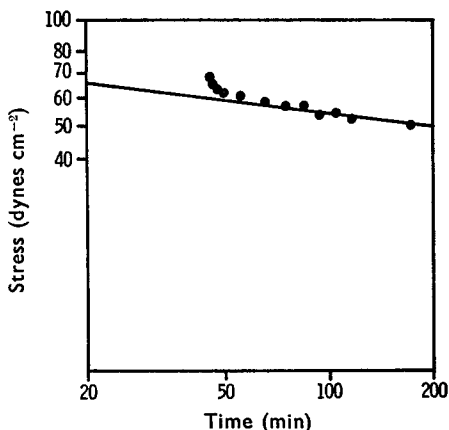
FIG. 3. Stress relaxation after previous shear at a lower rate using Rheomat visco-meter. Solid line is relaxation rate of a fresh sample at 9·67 sec^{-1}. Experimental points have been corrected for previous shear at 3·11 sec^{-1}.

5 shear rates from 3·11 to 196 sec^{-1} were equally successful, indicating equation (2) to be a useful first approximation.

Equation (3) can be used to calculate time intervals for an upcurve giving constant equivalent time at each shear rate. Table 2 lists a typical procedure for the Rheomat viscometer. In Fig. 4 such an upcurve is presented for intervals equivalent to 2 min at each shear rate. Five values determined on fresh samples are included for comparison. More

TABLE 2. PROCEDURE FOR OBTAINING AN UPCURVE UNDER CONDITIONS EQUIVALENT TO 2 MIN SHEAR AT EACH SPEED USING SINGLE SAMPLE

Speed	Apparent shear rate (sec^{-1}	t_2 (from eqn 3) = time equivalent to 2 min at next lower speed (min)	$2 - t_2$ (min)
1	3·11	0	2
2	4·18	2 × 3·11/4·18 = 1·49	0·51
3	5·50	2 × 4·18/5·50 = 1·52	0·48
4	7·33		1·50	0·50
5	9·67		1·52	0·48
6	13·9		1·39	0·61
7	18·7		1·49	0·51
8	24·6		1·52	0·48
9	32·9		1·50	0·50
10	43·4		1·52	0·48
11	62·9		1·38	0·62
12	84·8		1·48	0·52
13	111		1·53	0·47
14	148		1·50	0·50
15	196		1·51	0·49

information is imparted by a curve of this type supplemented by a stress relaxation plot than by hysteresis loops, examples of which are given in Fig. 5. The upcurves are distorted because the equivalent time at each shear rate is not uniform when p is maintained constant.

Equations for the flow curves other than in empirical terms do not seem to be possible. Most theoretically derived equations depend upon
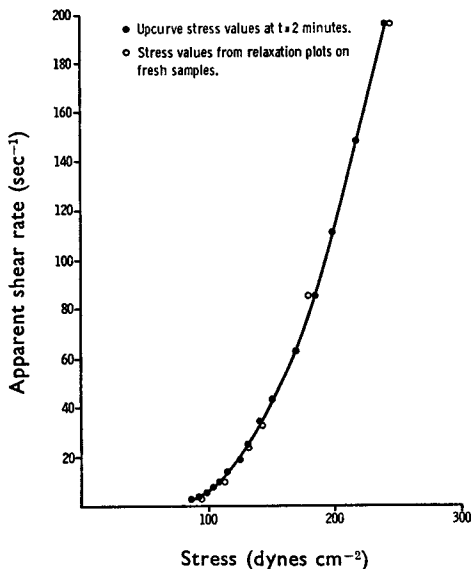
FIG. 4. Upcurve using Rheomat viscometer. Stress values were obtained under conditions equivalent to constant time at each shear rate.
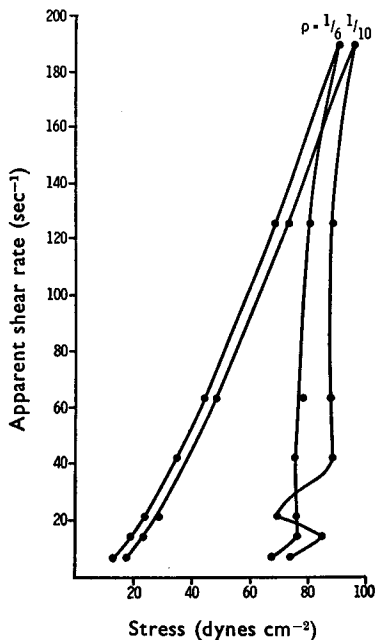

FIG. 5. Hysteresis loops obtained using Rotovisco viscometer. For explanation of ρ see text.

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steady state conditions being reached (Goodeve & Whitfield, 1938; Powell & Eyring, 1944; Casson, 1959; Gillespie, 1960a, b; Cross, 1965) whilst Green & Weltmann's upcurve equation (1943) can apply only if loss of stress is proportional to shear rate. The equation of Hahn & others (1959) for non-equilibrium conditions is applicable to simple shear-promoted transitions such as molecular disentanglement but in the present systems there is evidence that more than one process of breakdown, each with a different shear rate dependency, is involved. Thus on going from a high to a much lower shear rate there is a short period of rapid stress recovery and similarly on returning to the high shear rate some recovery is found to have occurred. Breakdown then occurs much more quickly than on the fresh sample until the point is reached again at which the high shear rate was initially interrupted. We concur with Weltmann (1960) that some structure can be broken only at high shear rates.

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