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Some limitations of continuous shear methods for the study of pharmaceutical semi-solids

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The limitations of the Ferranti Shirley viscometer are reviewed and discussed. An experimental study of four pharmaceutical materials indicates that the apparatus is restricted to a qualitative use for semi-solids because of effects due to evaporation, sweep time selection and shear fracture. When the above effects are gross, the rheograms demonstrate obvious peculiarities. If they are slight, they could escape unnoticed physically and yet lead to incorrect interpretation. The rheograms obtained for such materials are not reproducible for a once sheared sample and hence their quantitative interpretation would be meaningless. Transient tests or oscillatory studies are suggested as alternative methods of examination.

A WIDE range of gels and ointment bases (Schulte & Kassem, 1963, 1964) as well as aqueous solutions of surfactants (Gohlke & Hoffman, 1967) have been examined by continuous shear methods. In this field, the Ferranti Shirley cone and plate viscometer, available with an automatic program unit, enables continuous rheograms to be plotted at varying sweep times and maximum shear rates. This instrument has been used to study a range of ointment bases (Boylan, 1966, 1967), creams stabilized by complex films (Groves, 1967; Talman, Davies & Rowan, 1967) and soap, water amphiphile mixtures (Barry & Shotton, 1967a).

All these workers reported rheograms of the hysteresis loop type of varying degrees of complexity, including maximum and minimum shear stresses, which indicated that the systems studied were complex. The loop test method of analysis using the Ferranti Shirley viscometer, however, has a number of disadvantages and limitations. These are as follows:

(*a*) Continuous shear methods do not provide any fundamental rheological parameters (Warburton & Barry, 1968). These authors considered it more valuable, both practically and theoretically, to examine a system in its rheological ground state. Creep analysis, based on theories of linear viscoelasticity (Ferry, 1961) was suggested as an alternative.

(*b*) With the Ferranti Shirley instrument different combinations of sweep times and maximum shear rates will affect the shape of the resultant hysteresis loop and make comparisons difficult:

Reference	Sweep time (sec)	Maximum shear rate (sec^{-1})
Boylan (1966)	120	1074
Groves (1967)	600	188
Barry & Shotton (1967a) ..	600	1632

(*c*) Slippage effects have been considered by Jefferies (1965), and by Boylan (1967) who recommended that long sweep times should be used

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with semi-solids to avoid "serious slippage artefacts", the cause of these was not explained.

(*d*) At high shearing speeds viscous heating of the sample can become considerable (McKennell, 1956) and as a result of this, a hysteresis loop occurs under cyclic testing even for non-time dependent materials. To reduce the heating effect Cheng (1965) recommends that the time of shearing should be as small as possible.

(*e*) When the Ferranti Shirley viscometer is used with the large (3·5 cm radius) cone at short sweep times the large peripheral skirt can produce a "fly wheel" inertia effect resulting in a hysteresis loop even for Newtonian materials. This loop differs from that due to time effects in that the down curve lies closer to the torque axis than the up curve. Cheng (1965, 1967) has pointed out that the cone is driven by the motor via a torsion spring and that at small sweep times unsteady conditions will result in which the cone is subjected to accelerating forces; thus the Y plot will not be a true measure of shear rate. The X plot also is not a true measure of shear stress. Such errors can be corrected by procedures that involve first and second derivatives of the X–Y curve and by taking into account whether the material has a yield value or not.

(*f*) The placing of the sample in the viscometer disturbs the structure and it is generally not practicable to leave the sample between the cone and plate long enough before examination so that the structure may be built up once more (See (*g*) below).

(*g*) Difficulty arises in the determination of reversibility for aqueous systems which have a thixotropic structure that builds up slowly after cessation of shear, as evaporation effects limit the time a sample can be left in the viscometer.

(*h*) Acceleration variations of up to 10% during the up and down sweeps have recently been reported by Barry & Shotton (1968).

(*i*) In some materials fracture of the sample can occur at certain shear rates with an attendant fall in shear stress due to a decrease in the effective shearing radius. Such an effect can be erroneously interpreted as thixotropy as the fractures can heal (stress recovery) unless the shear rate has been such that material is ejected from the shearing zone (Hutton, 1963).

The phenomenon, also known as cavitation or tensile failure, can occur in liquids that are nearly Newtonian although is more common in pigment suspensions and materials with high elastic component (Hutton, 1963, Lammiman & Roberts, 1961). An optical method has been suggested for observing the phenomenon (Stiggles, 1965), whilst Lenk (1965) avoids spurious effects due to fracture by a preliminary determination of the shear rate at which it first occurs.

(*j*) For viscoelastic materials containing particulate matter the particles migrate to the outside of the cone due to normal force effects; this leads to a fall in viscosity (Highgate & Whorlow, 1967).

In the present work a critical evaluation of the Ferranti Shirley viscometer is made using a range of pharmaceutical materials.

Experimental and results

Materials. White soft paraffin, lanolin and paraffin ointment (white) were B.P. ointment bases. The emulsion system was a 60% dispersion of liquid paraffin stabilized by potassium laurate (2·5%) prepared as described by Shotton & Davis (1968).

Apparatus. A Ferranti-Shirley cone and plate viscometer with automatic flow curve recorder unit* was used according to Barry (1967). The manufacturers' anti-evaporation unit, consisting of a solvent trough and vapour hood, was fitted in an attempt to prevent evaporation effects with aqueous systems. Cone sizes of 3·5 cm, 2·0 cm and 1·0 cm radius with cone angles, 0·0062 radians, 0·0064 radians and 0·0061 radians respectively were used. A 200 g cm torque spring was fitted; this had a constant of 549 dyne cm/division.

A wide ended pipette was used for the fluid samples and a small spatula for semi-solids; samples were disturbed as little as possible. The calibration of the viscometer was checked using a N.P.L. viscometry standard (liquid paraffin B.P.—1·572 poise at 25·00°).

Hysteresis loop areas were measured by planimeter.

RHEOLOGICAL ANALYSIS

Evaporation effects. Rheological structure can be studied by following the change in a rheological parameter, usually relative viscosity, with temperature (Reiner, 1960). This has been done with the Ferranti Shirley viscometer by Lenk (1965) and by Barry & Shotton (1967a). Davis (1967) found a slight increase in viscosity, apparently due to evaporation, even though the apparatus was fitted with an anti-evaporation unit. The effect of evaporation, caused by increases in temperature, or long sweep time, on an emulsion of known rheological properties using the 3·5 cm radius cone has therefore been examined. The results (Fig. 1) show that at 40° and with a 60 sec sweep time, a simple pseudoplastic flow curve is obtained. A similar curve was obtained at the same temperature using a Couette viscometer where evaporation effects are negligible. Use of a 600 sec sweep time gave rise to a large hysteresis loop that differed from that normally found with time-dependent systems in that the down curve lay nearer the torque axis than the up curve. For the long sweep time, evaporation effects at 40° become evident after the sample has been in the viscometer for about 3·5 min. The lack of an evaporation loop at the 60 sec sweep time is thus explained.

Sweep time effect. The effect of sweep time on the shape of the hysteresis loop was investigated using white soft paraffin B.P. The eight sweep times available on the autoplotter (from 10 to 600 sec up curve sweep) were used and the maximum shear rate was 1692 sec^{-1} in each case. Fig. 2 shows that at low sweep times the shape of the loop is markedly dependent on sweep time. As the sweep time increases, the static yield value (Levy, 1962) and maximum shear stress both decrease as does the loop area and the shear stress at the maximum shear rate. A plot of the

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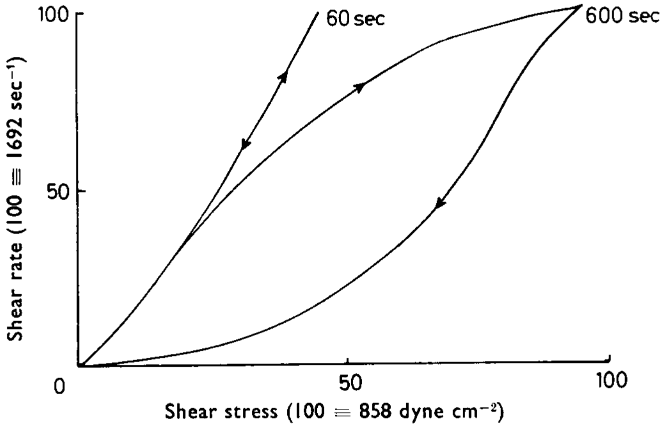

FIG. 1. The effect of temperature on the flow curve of an emulsion of liquid paraffin in potassium laurate (40°). Figures on curves are sweep times.

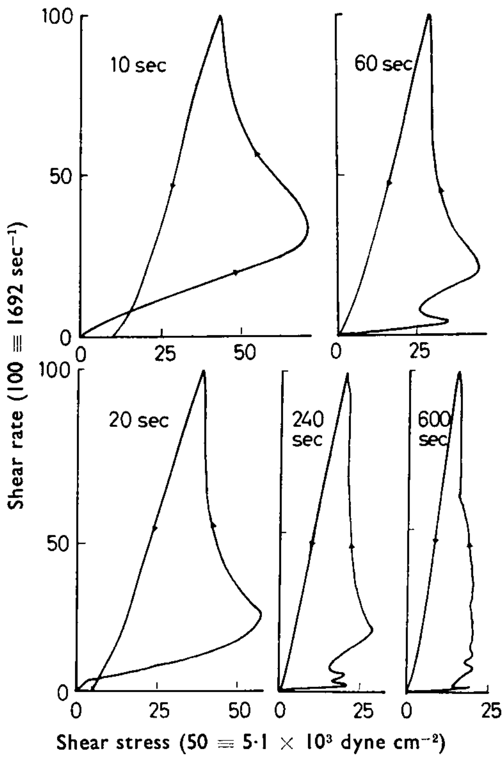

FIG. 2. The effect of sweep time on the shape of the hysteresis loop for white soft paraffin.

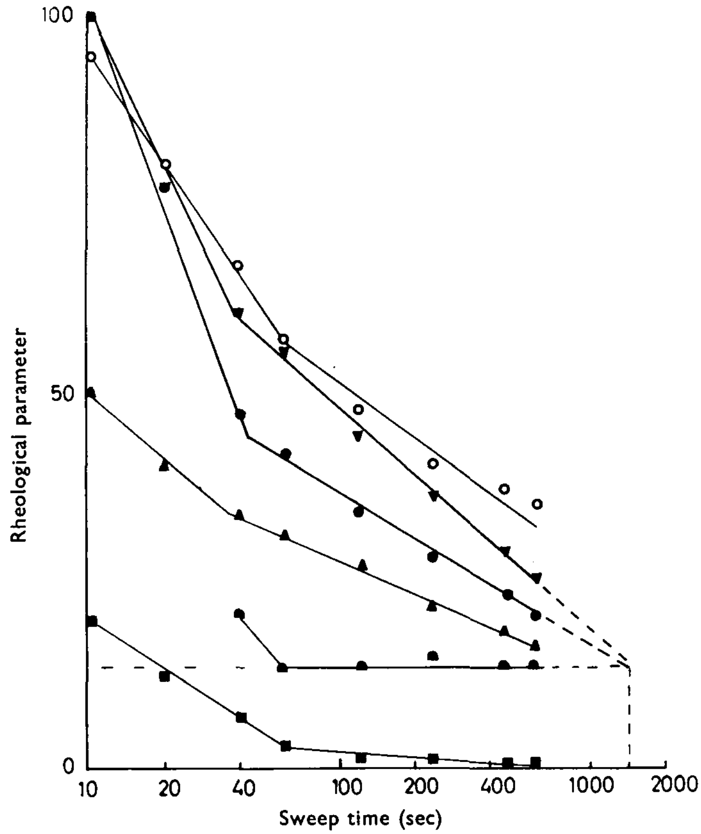

FIG. 3. The change in rheological parameter with sweep time for white soft paraffin. ● Static yield value. ▼ Shear stress maximum. ■ Dynamic yield value. ▲ Extrapolated static yield value. For all: $100 \equiv 7{\cdot}5 \times 10^3$ dyne cm^{-2}. ▲ Loop area ($100 \equiv 600$ cm^2). ○ Apparent viscosity ($100 \equiv 3{\cdot}0$ poise).

selected rheological parameter against log of sweep time (up curve) indicates that a discontinuity exists in the region of 60 sec (Fig. 3). The lowest static yield value (at 600 sec/sweep) is in the region of 1700 dyne cm^{-2}, whereas the extrapolated static yield value at sweep times greater than 40 sec has a value that is independent of sweep time and is in the region of 10^3 dyne cm^{-2}. This is close to a yield value of 995 dyne cm^{-2} found by the successive addition of weights to two scale pans attached to the inner cylinder of the concentric cylinder viscometer described by Warburton & Barry (1968). An extrapolation of shear stress maximum, static yield value and extrapolated static yield value to higher sweep times indicates that all these have an identical value at 1400 sec sweep (up curve).

Shear fracture. The up curve of the rheogram for lanolin B.P. at 25° showed a sudden fall in shear stress at a critical shear rate whilst for paraffin ointment B.P. at 25°, once the static yield value had been reached,

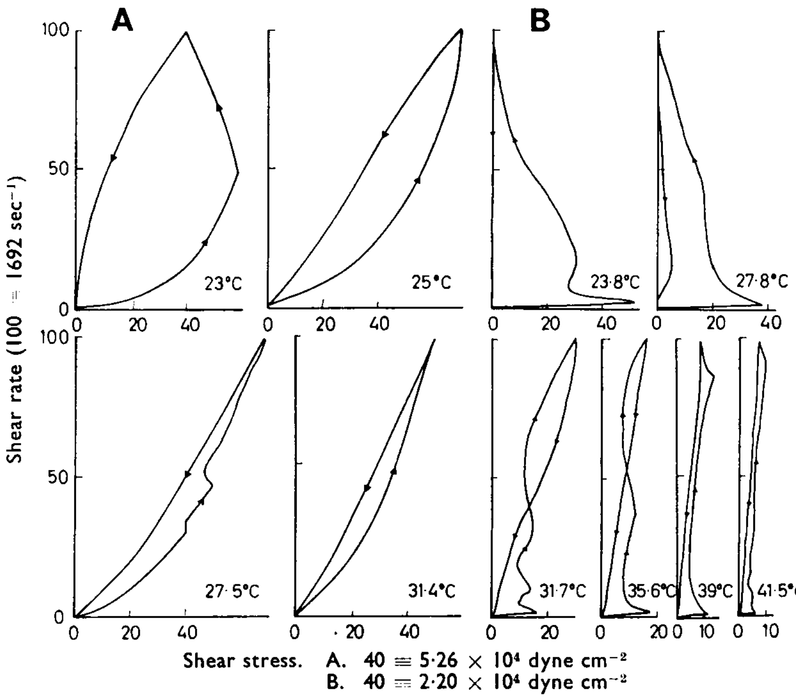

FIG. 4. The effect of temperature on the hysteresis loop of A. Lanolin, B. Paraffin ointment. Sweep time = 600 sec.

the shear stress decayed rapidly to almost zero. On separating the cone and plate, after the materials had been sheared, very little of the sample remained in the gap. This effect is due to fracture of the sample and its subsequent ejection from the gap. No loss was observed with white soft paraffin.

The effect of temperature within the range 20–42° on the loss of shear stress due to fracture was investigated for lanolin, paraffin ointment and white soft paraffin (Fig. 4A and B). Changes in loop area, and apparent viscosity at maximum shear rate, with temperature, for lanolin and paraffin ointment are different from the changes shown by white soft paraffin (Figs 5 and 6). The three materials all show a linear relation between yield value, or shear stress at low shear rate, and temperature.

Thixotropy. A test for thixotropy was made on white soft paraffin (Fig. 7). A sample was subjected to the loop test at 25° (curve 3) and then resheared after a 10 min rest period (curve 2). The up and down curves in the second cycle are close to the down curve in the first cycle indicating negligible build up of structure. A third cycle after a two day period (curve 1) demonstrated some build up of structure, but the initial loop was not completely recovered.

Creep analysis. The three ointment bases were examined by the creep method using the apparatus of Warburton & Barry (1968). The applied

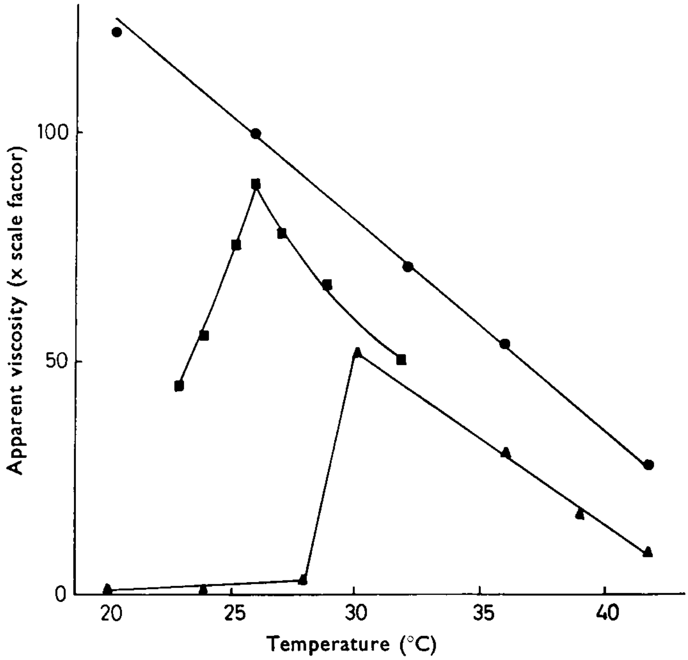

FIG. 5. The change in apparent viscosity with temperature for three ointment bases. Sweep time = 600 sec. ● White soft paraffin (100 = 1·2 poise). ■ Lanolin (100 = 76·5 poise). ▲ Paraffin ointment (100 = 19 poise).

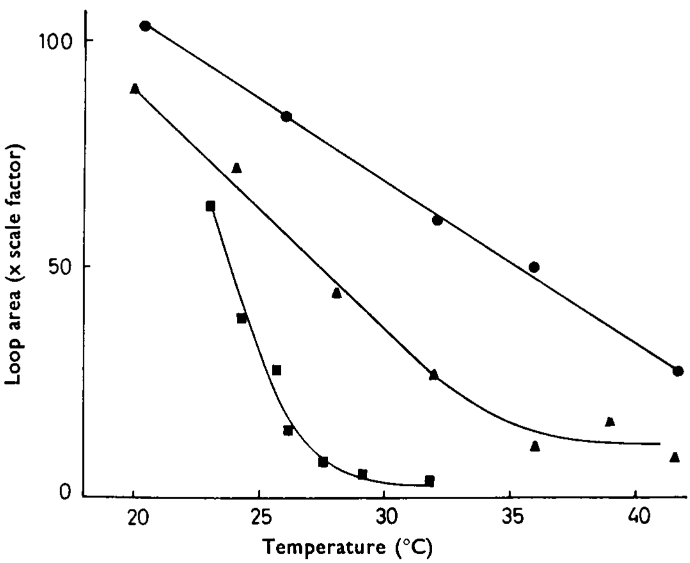

FIG. 6. The change in hysteresis loop area with temperature for three ointment bases. Sweep time = 600 sec. ● White soft paraffin. ▲ Paraffin ointment (100 = 180 cm^2). ■ Lanolin (100 = 1400 cm^2).

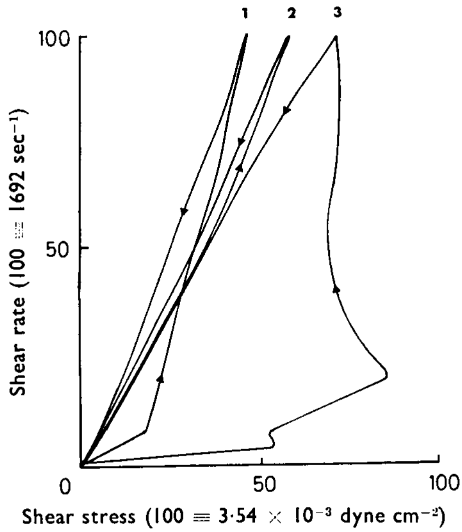

FIG. 7. White soft paraffin thixotropy test. Sweep time = 600 sec. (1) After two days rest. (2) After 600 sec rest. (3) Original curve.

stress was adjusted so that the strain response was in the linear region (Ferry, 1961). The results were analysed by the method of Barry & Shotton (1967b) and Warburton & Barry (1968) in which shear behaviour is described in terms of series Voigt model elements. The creep curves for lanolin and paraffin ointment were typical of viscoelastic behaviour and may be represented as a Maxwell unit in series with two Voigt units. The values of the individual components are given in Table 1. White soft paraffin gave a curve typical of an elastic (Hookean) solid with the strain independent of time after the instantaneous shear component. For all three materials, removal of the stress gave immediate recovery of the instantaneous shear component.

TABLE 1. THE VISCOELASTIC PARAMETERS OF THREE SEMI-SOLIDS

System	Voigt unit	Values of viscoelastic parameters		
		τ (sec)	G dyne cm^{-2}	η poise
White soft paraffin	0	—	$1\cdot37 \times 10^7$	—
Lanolin	0	—	$6\cdot72 \times 10^4$	$7\cdot87 \times 10^7$
	1	$5\cdot98 \times 10^2$	$4\cdot80 \times 10^4$	$2\cdot87 \times 10^7$
	2	$5\cdot91 \times 10$	$1\cdot08 \times 10^5$	$6\cdot40 \times 10^6$
Paraffin ointment	0	—	$7\cdot28 \times 10^5$	$6\cdot42 \times 10^8$
	1	$4\cdot46 \times 10^2$	$2\cdot40 \times 10^5$	$1\cdot07 \times 10^8$
	2	$5\cdot65 \times 10$	$5\cdot16 \times 10^5$	$2\cdot92 \times 10^7$

τ = retardation time
G = shear modulus of Voigt model
η = shear viscosity of Voigt model ($\eta = G\tau$)

Discussion

The use of the Ferranti Shirley viscometer for aqueous systems can lead to spurious results due to evaporation at elevated temperatures, even when the viscometer is fitted with the manufacturers' anti-evaporation unit. For a simple emulsion system of known rheological properties, the use of lower sweep times provides a correct rheogram. With time dependent materials however, the breakdown of the material due to thixotropy or irreversible shear thinning will be opposed by the effect of evaporation. Lower sweep times may result in a radical change in the shape and area of the hysteresis loop and in the values of rheological parameters. Although evaporation effects are greatly reduced in concentric cylinder geometry, this apparatus is limited to non time-dependent materials, since no apparatus of this geometry is available with the automatic programming facilities of the Ferranti Shirley viscometer.

The choice of sweep time greatly affects the values of the rheological parameters that can be calculated from the hysteresis loop. A decrease in all the measured parameters occurs with increase in sweep time (Fig. 3) and more detail in the up curve is resolved. An extrapolation of the static yield values and shear stress maximum to higher sweep times shows they have an identical value of 10^3 dyne cm^{-2} at a sweep time of 1400 sec (up curve). This value is very close to that obtained by a successive loading test in concentric cylinder geometry and it may well be that at a sweep time of 1400 sec white soft paraffin will give the up curve of a typical plastic (Bingham) material without shear stress minima or maxima.

The acceleration of the cone at different sweep times will affect the loop size and shape by several mechanisms. (1) At low sweep times the apparatus will constitute an oscillatory system (Cheng, 1965) introducing effects due to inertia and the torsional stiffness of the spring (Ferry, 1961, Van Wazer, 1963). (2) The yield value of a material is not independent of time (Houwink, 1958). It has been found (McVean & Mattocks, 1961) that the static yield value is a function of the rate of strain and is associated with viscoelasticity and retardation behaviour. With a cone and plate apparatus, Bauer, Shuster & Wiberley (1960) found that the yield stress was affected by the rate of increase of stress. Fischer, Bauer & Wiberley (1961) have pointed out that the measurement of yield stress may give values dependent on the apparatus design, as well as the nature of the test material and the time scale of the test procedure.

The cause of shear stress minima in flow curves for concentric cylinder geometry was suggested by Enneking (1958) to be a combination of slippage and variation of shear rate across the gap. Although the shear rate is independent of radius for cone and plate, a similar explanation can be advanced if it is assumed that there are regions in the material which act as "stress raising points". We suggest that at the static yield value the material flows only in the region of the cone surface and not throughout the whole gap because of the formation of a slippage plane of the type described by Wood, Giles & Catacalos (1964). As the cone accelerates, further structure breakdown occurs and the effective cone angle will increase. Since the shear rate is proportional to the reciprocal of cone angle, the actual shear rate will decrease even though the speed of rotation of the cone increases. Because shear stress is related to shear rate it shows a decrease and the process continues until flow occurs in the whole gap and the stress minimum is reached. When the whole of the sample is sheared, the effective cone angle will be the true cone angle and the shear rate and rev/min (given by the Y axis of the autoplotter) will be directly proportional. The true flow curve will thus be obtained. In support of this theory it has been found for white soft paraffin that if the up curve after the stress minimum is extrapolated back to the shear stress axis, the yield value so obtained is close to that obtained by the loading test method, i.e. 10^3 dynes cm^{-2}.

Lanolin and paraffin ointment both demonstrate loss in shear stress due to fracture and subsequent expulsion of material from the shearing zone of the instrument due to the viscoelastic nature of these materials. This is characterized by a *fall* in shear stress with increase in shear rate. An increase in temperature causes viscoelastic structure to be broken down, resulting in less expulsion from the gap and a rise in apparent viscosity. The rheograms become simpler until eventually the classical type of loop, with shear stress increasing with shear rate, is obtained. Fracture of fluids in shear has been linked with elasticity (Hutton, 1963). A viscoelastic liquid in a state of flow will possess elastic energy so that when shear is stopped the liquid will recoil due to release of this energy. Hutton has postulated that when the total elastic energy exceeds a critical value the liquid will fracture. Initially such breakdown is believed to be localized as a conical fracture surface that starts at the periphery and grows radially inwards. The shear stress falls as the effective shearing radius decreases as the fracture grows. On reduction of shear the fracture can heal and the whole effect may be erroneously interpreted as some form of thixotropy or structural breakdown. Gross fracture, i.e. loss from the gap, is clearly shown in the present work by a negative gradient in the shear stress/shear rate relation. Difficulty will still arise however, even if lower shear rates are used, in ascertaining whether a fall in consistency is due to thixotropy or shear failure and subsequent stress recovery.

White soft paraffin, which appears to be a Hookean solid below its yield point, does not exhibit noticeable shear fracture, and the selected rheological parameters decrease linearly with temperature (Figs 5 and 6). The final part of the up curve for white soft paraffin shows an abrupt change in gradient and is then almost vertical (Fig. 7). Some form of shear fracture or even slight ejection may be occurring. In the test for thixotropy the incomplete build up of structure after two days may be a real effect but equally well it could be due to slight loss of material from the gap during the initial shearing cycle. This of course cannot be recovered on resting.

CONCLUSIONS

It is concluded that the value of continuous shear methods using the Ferranti Shirley apparatus with pharmaceutical semi-solids is strictly limited. Problems arise due to evaporation, sweep time selection, shear fracture and wind up of the torque sensing spring, and at best it should be used as a *qualitative* measurement of rheological structure. Analysis methods where the material is kept in its rheological ground state, such as creep (Warburton & Barry, 1968) or oscillatory testing (Warburton & Davis, 1968) are more suitable for semi-solid materials.

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