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Grade variation in the rheology of white soft paraffin B.P.

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The rheology of six grades of white soft paraffin B.P. at 25° has been investigated using continuous shear viscometry and a creep viscometer. Temperature effects between 25° and 50° have been measured in continuous shear, and activation energies from 14·0 to 25·3 k cal mol^{-1} (58·6 to 105·9 k J mol^{-1}) have been determined. Working the samples on a triple roller mill at 25° was found to decrease the apparent viscosity and, initially, to increase the yield stress. Five of the grades were linear viscoelastic, one was non-linear viscoelastic. The nature of ductility and its relation to measured rheological parameters have been discussed. Creep viscometry data gave a better correlation with the manufacturer's data than did continuous shear measurements.

White soft paraffin, which consists mainly of n-paraffins, iso-paraffins, and naphthenes (Nelson & Stewart, 1949; Asinger, 1968; Meyer, 1968), forms a colloidal gel type of structure containing oil, microcrystalline waxes and discrete crystals (Franks, 1964; Longworth & French, 1969). Its physical nature is influenced by the ratios of the component fractions of the material, and the constituents within the fractions, and thus depends on the source of the crude petroleum, the type and degree of refining, and possibly on subsequent blending processes (Mutimer, Riffkin & others, 1956; Schulte & Kassem, 1963).

There is controversy about the rheological properties of white soft paraffin which may be derived using continuous shear and small strain experiments, as well as semi-empirical methods such as penetration techniques. The soft paraffins and similar paraffinic materials have been variously reported as (*a*) elastic (Davis, 1969a), (*b*) non-linear viscoelastic (Bogie, 1968) and (*c*) linear viscoelastic (Hutton & Mathews, 1953; Criddle, 1965; Barry & Grace, 1970) in small strain experiments. Continuous shear viscometry causes either irreversible shear breakdown (Weltmann & Kuhns, 1957) or thixotropic shear breakdown (Bondi, 1951; Barry & Grace, 1970).

The purpose of this work is to investigate a series of soft paraffins of pharmacopoeial standard, using continuous shear and creep viscometers, to indicate the variation in rheological properties which may occur in white soft paraffin B.P. A more detailed rheological profile of a single sample of white soft paraffin has already been made (Barry & Grace, 1970).

EXPERIMENTAL

Materials. Samples of white soft paraffin (B.P.) were obtained from two sources. One grade (sample 1) from J. M. Loveridge Ltd. (Southampton), and five grades from Dalton & Co. Ltd. (Silkolene Oil Refinery, Belper). The manufacturer's data on these grades are given below.

Grade 783/L (Sample 2), the basic paraffin from which the others in the range are derived, is resistant to shear breakdown, and is a general use petroleum jelly; Grades 892 and 910 (Samples 3 and 4 respectively) are soft paraffins with low stability to shearing stress; Grade 944 (Sample 5) has a medium stability to shearing stresses; Grade 783/L/40A (Sample 6) is highly resistant to shear breakdown, with low ductility and viscosity. Samples 5 and 6 are produced for use in ointment manufacture. Further physical data supplied by the manufacturer are given in Table 1.

Table 1. *Manufacturer's data on the physical properties of samples* 2 *to* 6, *and activation energies for viscous flow and apparent viscosity data derived from the curves in Fig.* 1

	Manufacturer's data		Experimental data	
Sample No.	Drop point* (I.P. 31/57)°C	Unworked penetration No.* at 25°	Activation energy for viscous flow k cal mol^{-1}‡	Apparent viscosity at 25° and 1754 s^{-1} poise
1	—	—	21·9	10·2
2	46–50	155–175	21·3	6·8†
3	43–49	170–190	15·1	1·2
4	46–50	150–170	22·4	4·2†
5	47–51	200–220	14·0	4·8
6	44–48	155–175	25·3	6·2†

* Standards for Petroleum and its products, 23rd Edn (1964) part 1, pp. 266–268.
† Values derived by extrapolation of the curves.
‡ 1 k cal = 4·1868 kJ.

Continuous shear experiments. A Ferranti–Shirley cone and plate viscometer, with automatic flow curve recorder unit, was employed for continuous shear investigations (Boylan, 1967; Barry & Shotton, 1968). The viscometer, with medium cone, was used in the automatic mode and 600 s sweep time for two test regimes: (1) rates of shear varied from 0·0 to 1754·0 s^{-1} and (2) rates of shear varied from 0·0 to 175·4 s^{-1}. The temperature range was 25° to 50° (±0·1°).

The test samples were melted on a water bath at 70° and cooled for 2 h at 25° (±1·2°), as a standard procedure before comparative rheological testing (Kinsel & Phillips, 1950; Weltmann, 1960; Ackroyd & Aubrey, 1964). Apparent viscosity values were determined from the apex of the continuous shear curves (Boylan, 1967); the value obtained is equivalent to that of the Newtonian fluid whose flow curve would pass through the point used in the determination. Yield stresses were derived from the spur points in the curves where the slope of the curve became infinite for the first time. The apparent viscosity and yield stress data derived in continuous shear are given in Table 2. Fig. 1 is an Arrhenius-type plot of apparent viscosity at 1754 s^{-1} for each sample. The activation energies derived are given in Table 1.

To investigate the effect of working the samples, these were worked in an arbitrary manner using a triple roller mill (Erwerka-apparatebau Gmbh) of three ceramic rollers with axes of rotation parallel. The central roller rotated in the opposite direction to the end rollers, and each roller rotated at a different speed. A sample of material was placed on one of the end rollers and was forced into a thin film and momentarily stressed at a high rate of shear as it passed between the rollers. The sample was then carried through the second gap by the central roller. The maximum

Table 2. *Apparent viscosity and yield stress data derived by continuous shear viscometry.* η' is apparent viscosity at apex of loop (poise), σ is yield stress derived from spur points (dyne cm^{-2} or $Nm^{-2} \times 10^{-1}$). Regime 1, 0·0 to 1754·0 s^{-1} in 600 s; Regime 2, 0·0 to 175·4 s^{-1} in 600 s. The asterisks indicate gross ejection of the test sample from the measuring gap of the viscometer

	25°		30°		35°		40°		45°		50°
Regime 1 Sample No.	η'	σ	η'	σ	η'	σ	η'	σ	η'	σ	η'
1	10·2	7700	5·7	5200	3·3	2100	2·2	1300	1·2	700	0·6
2	*	3550	*	2700	2·1	1300	0·9	600	0·7	200	0·4
3	1·2	2300	1·0	1600	0·7	900	0·4	400	0·3	175	0·2
4	*	4200	2·2	2300	1·2	1900	0·7	600	0·4	250	0·2
5	4·8	2100	3·4	1400	2·2	650	1·5	450	1·1	200	0·9
6	*	4500	3·3	1600	1·5	1200	0·6	400	0·4	150	0·3
Regime 2 Sample No.											
1	61·1	5100	15·8	2900	9·2	1800	5·2	770	2·5	—	—
2	12·1	2600	10·2	1500	6·4	850	3·2	200	0·5	—	—
3	6·5	2150	5·2	950	3·3	550	2·3	200	1·0	—	—
4	10·8	3200	7·6	2100	4·4	1050	2·0	950	1·9	87	—
5	12·7	1250	8·8	910	5·7	500	4·0	200	1·8	—	—
6	19·0	2800	13·8	2700	3·6	550	2·7	300	0·6	—	—

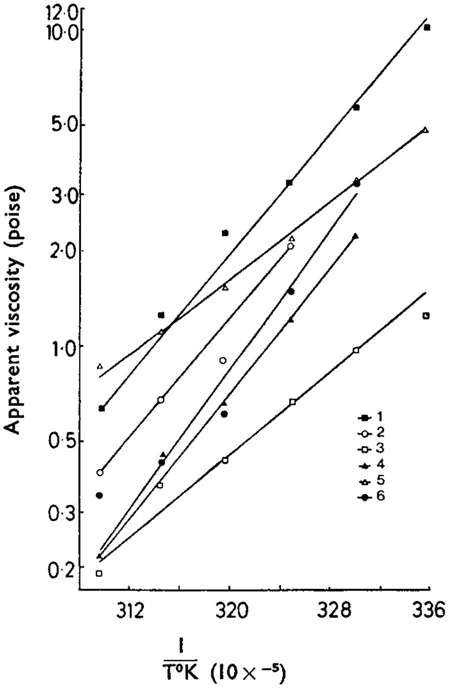

Fig. 1. Arrhenius-type plots of apparent viscosity of soft paraffin samples determined at 1754 s^{-1} using continuous shear viscometry.

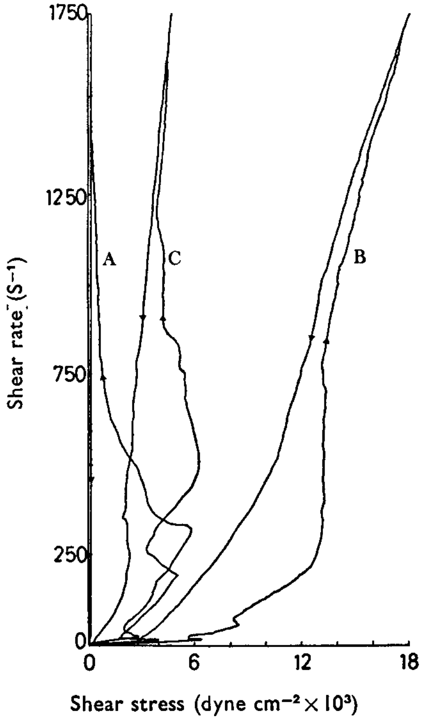

FIG. 2. Continuous shear rheograms for sample 2, obtained using Regime 1 (0·0 to 1754·0 s^{-1} n 600 s). Curve A is an unworked sample; B, worked once; C. worked four times.

shear rates in each gap were approximately 6300 s^{-1} and 10300 s^{-1}, calculated by dividing the linear velocity differences at the roller surfaces by the gap distances between them, assuming plane laminar flow in the gap.

One working thus consisted of two very short periods of shearing stress at high rates of shear.

Creep experiments. Fig. 3a is a diagram of the creep viscometer which is a modification based on a Westwind PCB III reaction air turbine (Davis, Deer & Warburton, 1968; Davis, 1969b) calibrated by the method of Barry & Saunders (1969). The inner cylinder of the viscometer was machined to the dimensions of the Haake Rotovisko MVII cylinder. The outer cylinder and water bath were adapted from those used on the Rotovisko viscometer. The water bath and enclosed cylinder were made concentric with the inner cylinder by means of a centering ring with lockable adjustable screws, and a dial gauge attached to the bearing in place of the inner cylinder. The turbine pressure, which applied the torque, was measured by mercury and water manometers at high and low pressures respectively. An air bearing pulley wheel and weights were used to supply torques in excess of those available from the compressed air supply (Barry & Saunders, 1969). The temperature was controlled by circulation of an ethylene glycol-water mixture using a Shandon Circotherm unit. A Grant CC20 cooler unit was available for temperatures below ambient.

The creep viscometer was loaded by heating the test sample to 60° in a water bath, and pouring the molten material into the outer cylinder. The inner cylinder

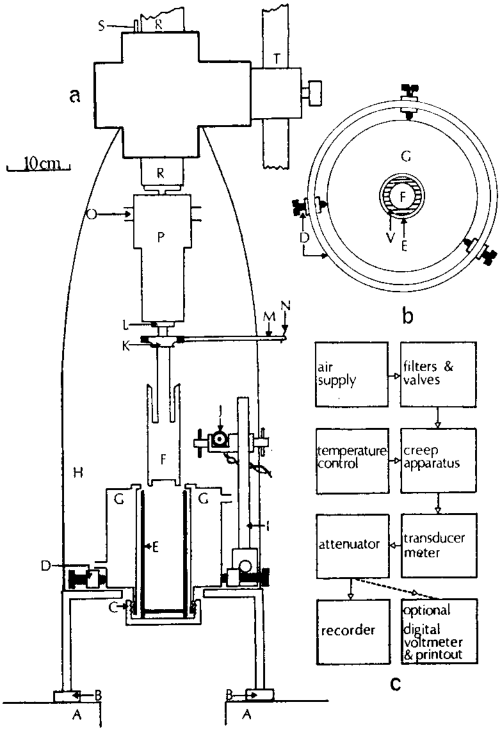

FIG. 3. (a) Sectional diagram of the creep apparatus, with transducer armature free of transducer coil, and inner cylinder in the raised position. The scale is expanded laterally to show the viscometer elements with greater clarity. A, bench; B, antivibration mounting; C, screwcap holding (E) in position; D, centering ring with adjustable lockable screws; E, outer cylinder; F, inner cylinder; G, waterbath; H, mandrell press; I, magnetic stand; J, transducer coil; K, boss; L, chuck screw; M, arm, bearing the transducer armature, N; O, ducts for air supply; P, Westwind PCB III reaction air turbine; R, operating arm; S, locating pin; T, cranking arm. (b) Plan of centering arrangement. Key as in Fig. 3a, with V as sample gap. (c) Flow chart, indicating relation between creep apparatus and ancilliary equipment.

was lowered into the liquid, and the sample left overnight at the test temperature for stresses to relax, crystallization to occur, and for temperature equilibration. As crystallization of soft paraffins has been shown to be time dependent (Kato & Saito, 1967), the samples used in creep viscometry may be considered to be one day old.

Each sample was checked for linearity and a creep test performed at 25° (±0·2°) in the linear region. The curves were analysed by the method of Warburton & Barry (1968) using the equation for a line spectrum of retardation times,

$$J(t) = J_0 + \sum_{i=1}^{n} J_i \left(1 - e^{-t/\tau_i}\right) + \frac{t}{\eta_0} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where J(t) is the compliance at time t, J_0 is the initial elastic compliance, J_i is an elastic compliance associated with a viscous element, τ_i is a retardation time, and η_0 is the residual Newtonian viscosity.

A computer program was written which reconstituted the original creep curve when the derived parameters were used as input data. Analyses were accepted if the reconstituted curve lay within 2% of the experimental curve. Fig. 4 contains

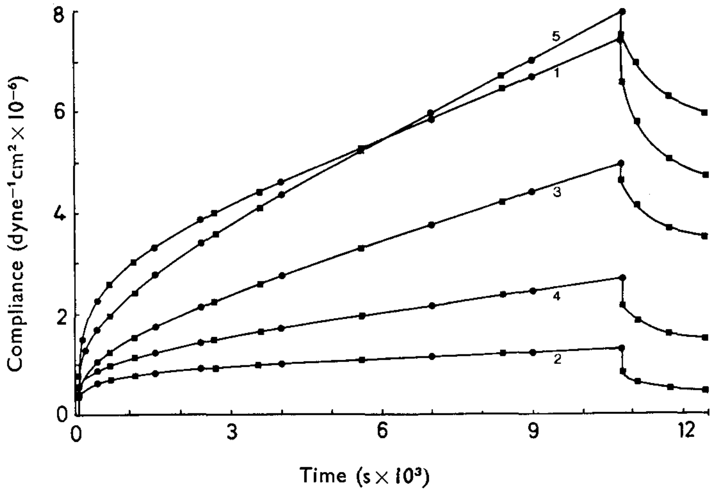

FIG. 4. Creep curves of linear viscoelastic soft paraffins. ■ Experimental data, ● reconstituted data.

creep curves for samples 1 to 5, with typical original and reconstituted coordinates, which indicate the agreement between the two sets of data.

The data derived by creep viscometry are given in Table 3. Samples 1 to 5 exhibited linear viscoelastic properties, and sample 6 was non linear (minimum stress applied 3·03 Nm^{-2}, resulting strain 4×10^{-6}). Fig. 4 indicates the differences in the flow properties at very low rates of shear. Samples 1 and 5 are similar, with

Table 3. *Rheological parameters derived for soft paraffins using creep viscometry.* The value of J_0 for sample 6 is derived from a non linear creep curve at a shear stress of 120 dyne cm^{-2}

	Sample No.					
	1	2	3	4	5	6
Compliance (dyne^{-1} cm^2 $\times$ 10^{-8})*						
J_0	75·7	35·5	42·6	47·3	51·0	34·9
J_1	98·0	31·5	75·0	37·0	105·0	
J_2	45·2	10·0	23·0	14·6	39·3	
J_3	38·8	6·20	2·40	12·5	34·7	
J_4	46·0	5·50	10·4	9·90	—	Exhibits non-linear visco-elastic behaviour
Retardation time (s)						
τ_1	1360	1424	1495	2059	1413	
τ_2	236	238	104	487	38	
τ_3	45	38	12	52	2	
τ_4	8	5	2	7	—	
Viscosity (poise $\times$ 10^8)						
η_1	13·9	45·2	19·9	55·7	13·5	
η_2	5·2	23·8	4·54	33·4	0·98	
η_3	1·16	6·13	5·00	4·18	0·06	
η_4	0·18	0·83	0·20	0·75	—	
η_0	24·6	278	31·5	73·5	19·0	

* dyne^{-1} cm^2 = N^{-1} m^2 $\times$ 10^1.

large elastic compliance and low residual Newtonian viscosity. Sample 2 had a high residual viscosity and low elastic compliance. The total elastic compliance of sample 1 is over three times that of sample 2, and their residual viscosities differ by a factor of ten. The mechanical representation of the linear viscoelastic properties of the samples of soft paraffin used in this work consists of one Maxwell unit in series with four Voigt (Kelvin) units, except for sample 5 which has three Voigt units.

DISCUSSION

The continuous shear flow curves determined for these samples are anticlockwise hysteresis loops, each containing a spur point indicating a yield stress. At higher temperatures the extent of hysteresis, as measured by the area of the loop, was reduced, and the magnitude of the yield stresses decreased. The anticlockwise loops indicate either irreversible shear breakdown or thixotropy. It has been shown that sample 1 may undergo partial thixotropic breakdown (Barry & Grace, 1970).

The apparent viscosity of some of the soft paraffins could not be determined at low temperatures as test samples were ejected from the cone-plate gap; this may be due to elastic recovery or fracture of the material, or both (Hutton, 1963; Davis, 1969a). Application of a cone and plate instrument to routine testing procedures is severely limited when the phenomenon occurs. Sample 2 was almost completely ejected immediately after the spur point (see Fig. 2); with sample 1 there was no visible ejection of the test material, but the possibility exists that a small amount is lost, causing errors in viscosity determination.

The Arrhenius-type plots of apparent viscosity at 1754 s^{-1} versus inverse absolute temperature, Fig. 1, are approximately linear (c.f. Barry & Grace, 1970). The values of apparent viscosity derived using regime 2 also give linear plots, although the data are more scattered. Extrapolation of the curves in Fig. 1 indicates that there is not a large difference in the apparent viscosity between samples at 25°, see Table 1. The expulsion of the test samples from the measuring gap of the cone and plate viscometer is thus probably not a function of viscosity alone.

Activation energies for viscous flow of the samples were derived from Fig. 1 using equation 2, which is a viscosity modification of the Arrhenius equation (Arrhenius, 1912), and these are listed in Table 1.

$$\eta = \mathrm{K}e^{\mathrm{E}/\mathrm{RT}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

Where η is the apparent viscosity, K is a constant, E is the activation energy for viscous flow, R is the gas constant, and T the absolute temperature. Although controversy exists about the validity of activation energies derived using this equation (Jobling, 1953; Bondi, 1956)—the data may not be of fundamental significance—they are given to indicate the differences which may occur in the flow properties of the soft paraffins. Activation energies for viscous flow derived by continuous shear viscometry are in the form of an overall average (Barry & Grace, 1970) and they are concerned with the energy necessary to cause the individual components of the paraffin to move from one equilibrium position to another in the direction of flow (Glasstone, Laidler & Eyring, 1947; Eyring, 1956). The difference between the upper and lower values is approximately 10 k cal mol^{-1} (42 kJ mol^{-1}), which indicates that the sizes of the flowing entities vary considerably. A possible cause of such variation is the differences in the ratios of solid to liquid paraffins within the different samples. A high percentage of solid paraffins would increase the mean size of the flow units. These would have to overcome a higher potential energy barrier in order to flow, and therefore require a higher activation energy.

Arrhenius-type plots of the yield stresses determined in continuous shear were linear for each sample, as previously reported for sample 1 (Barry & Grace, 1970) and in agreement with earlier work on similar materials (Ramaya, 1944; Berneis & Münzel, 1964).

When the soft paraffins were milled, structure broke down. This was indicated rheologically by a lower value of apparent viscosity at high rates of shear, see Fig. 2. The unworked sample was ejected from the cone-plate gap at high rates of shear. After one passage through the triple roller mill the material gave a full rheogram with a *larger* yield stress than in the unworked test sample. The single working damaged the fibrous crystal matrix (Jones & Tyson, 1952; Van der Have & Verver, 1957) and ruptured secondary valence bonds within the material (Münzel, 1968). Two possible causes for the increase in yield stress are: (*a*) a thin film of soft paraffin forms on the roller mill which may cause orientation of the large acicular crystals thus superimposing further structure upon that remaining in the sample, and (*b*) it is possible that ejection of unworked sample from the measuring gap begins to occur while the spur point is forming. The reduction in the elastic modulus of the material caused by milling would tend to allow the material to remain in the measuring gap for a longer period, thus increasing the stress reading. After the test sample was milled four times, it gave a rheogram with a much lower apparent viscosity, and the yield stress was less than after one working, but still larger than in the unmilled sample. This decrease indicates a gross breakdown of the three dimensional matrix within the test sample of soft paraffin.

The continuous shear investigations indicate that sample 1 differs from samples 2 to 6. The apparent viscosity and yield stress for temperatures up to 40° are generally higher than those of samples 2 to 6, although the activation energy is comparable with those of samples 2 and 4.

Yield stresses measured in continuous shear viscometry are a function of some property of the material, and not due solely to instrumental effects, although these may contribute to the magnitude of the yield stresses (Barry & Grace, 1970). Davis (1969a) has suggested that yield phenomena are associated with crystalline materials which are susceptible to mechanical strain, and has correlated long retardation times determined in creep with high yield stresses determined in continuous shear. Comparison of the continuous shear and creep data derived for samples 2 to 5 indicates a similar correlation, especially with the second and third retardation times. Sample 6 is not considered as it is non-linear viscoelastic and the creep curve cannot be represented by the equation used in this work. Sample 1 is exceptional (c.f. continuous shear work) as it has large yield stresses, but only moderate retardation times.

Ductility, a rheological property of soft paraffins, is concerned with the capacity of the material to form filaments when subjected to a tensile stress and depends on the variation in viscosity which occurs during elongation of the filament (Bikerman, 1960). Stefan's equation (Stefan, 1874) indicates that the initial force necessary for filament elongation in a Newtonian material is directly proportional to the shear viscosity of the material. The behaviour of non-Newtonian materials cannot readily be treated mathematically, but is quantitatively similar. The ductility, or fibre length, of soft paraffins is variable (Warth, 1956) and is usually determined subjectively, although a physical test has been proposed (Kinsel & Schindler, 1948). In our work there is no clear relation between ductility and the continuous shear data. In creep, with the exception of sample 6, which is non-linear, the total compliance at any given time is greater the more ductile the sample. For example, sample 2 has a low compliance, indicating a high residual viscosity, and the manufacturers' data indicate that it is resistant to shear breakdown. Under such conditions the force necessary to cause filament elongation exceeds the cohesive strength of the material and fracture occurs. The material is thus of low ductility, or short fibre length. Sample 5 is compliant in creep, and is less resistant to stress than is sample 2. Thus an applied tensile stress causes formation and elongation of filaments, and the material is highly ductile. The creep curve of sample 6, which has a low ductility, could not be analysed, but it indicated a large total compliance, that is, a low apparent viscosity, at 120 dyne cm^{-2} (12·0 Nm^{-2}). The manufacturer reports that this sample is highly resistant to stress. Thus, in elongational strain, fracture occurs despite the low apparent viscosity of the material.

When soft paraffins are used in cold working procedures, the apparent viscosity of the material needs to be considered, as more energy is required to manipulate a highly viscous material. The determination of apparent viscosity of the soft paraffins at 25° using continuous shear viscometry was inconclusive, due to expulsion of the material from the cone-plate gap. Creep viscometry indicated that sample 2 is highly viscous, but samples 5 and 6, which are derived from it, are both of low viscosity, which confirms their suitability for ointment manufacture with respect to low energy consumption. However, sample 5 is highly ductile, which is a disadvantage in cold working. Sample 6, which has a low ductility and a low apparent viscosity, is therefore best suited for cold working procedures.

When soft paraffins are used in ointments manufactured by fusion, the apparent viscosity and ductility have little effect on the efficiency of manufacture, whilst factors such as melting and congealing points become important.

This work has shown the rheological variation which may occur between different grades of white soft paraffin of pharmacopoeial quality. Interbatch variations have not been studied, although they may be considerable, since the blending of soft paraffins with other paraffinic petroleum derivatives to specific requirements is an empirical procedure. Subsequent grading depends on physical tests such as melting point, worked and unworked penetration tests, and complex parameters determined subjectively. The investigation indicates that rheological techniques may be utilized, and that whilst creep viscometry uses very low rates of shear, the data derived show the pattern of the grade properties (as indicated by the manufacturer) far better than do those data derived in cone and plate continuous shear viscometry at high rates of shear.

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