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## RESEARCH ARTICLES

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# Investigation of Semisolid Lipophilic Preparations by Small Strain and Continuous Shear Viscometry and Their Application to Texture Profile

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**Abstract** □ The effects of grade variation of white soft paraffin on the rheological properties of paraffin ointment BP, simple ointment BP, and some nonpharmacopoeial paraffinic and emulsion preparations were investigated by continuous shear and creep viscometry. The creep curves were analyzed to determine discrete and continuous spectra of retardation times and transformed mathematically to determine dynamic parameters such as storage and loss compliances. The elastic properties of the white soft paraffins influenced the properties of preparations made with these paraffins. There was no general correlation between viscosity data for the preparations, possibly due to some specific interaction such as that described for hard paraffin and liquid paraffin. Dilution of white soft paraffin with liquid paraffin shortened the retardation times but did not significantly alter the type of retardation spectrum involved (bimodal), while emulsification radically altered the retardation mechanisms. The utility of the types of viscometry and various analyses of the creep curves is discussed in terms of correlation with sensory data for texture profile evaluation. It is concluded that small strain experiments are important in texture profile evaluation.

**Keyphrases** □ Ointments—paraffin effect on rheological properties □ Paraffin, soft—rheological effect, ointments □ Rheology—ointments, emulsions, soft paraffin □ Viscometry—continuous shear, creep, oscillatory □ Viscoelasticity—ointments, soft paraffin, emulsions

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Manufacturers of therapeutic and cosmetic semisolid preparations must be able to reproduce the consistency of their products and to ensure that new products are of a consistency acceptable to the consumer. By correlating sensory data with rheological data, a texture profile may be determined, an important concept which has been developed in recent years in the food industry. Many of the parameters, such as viscosity, elasticity, and ductility, which contribute to a subjective assessment of consistency may be measured rheologically. Sherman (1) recently discussed the textural profile and evaluation

of pharmaceutical products for external application, and he reviewed the published data correlating instrumental and sensory evaluations of textural properties.

Many rheological techniques are available for evaluation of pharmaceutical materials. Continuous shear viscometry has been a popular approach (2–4); in particular, the Ferranti-Shirley cone and plate viscometer with an automatic flow curve recorder unit and X-Y plotter has been used (5–9). However, the information derived from continuous shear experiments is of limited use in characterizing complex rheological properties such as viscoelasticity, because the high rates of shear involved often cause breakdown of the viscoelastic structure of the sample. To examine a viscoelastic material in its ground state, approximating to zero shear conditions, it is usual to employ small strain experiments such as creep (10) and oscillatory (11) methods.

It was shown that the rheological properties of white soft paraffin BP may vary considerably from grade to grade (10), and a brief discussion of the effect of such variation on the industrial use of the materials was given. The properties of a sample depend on the source of the crude petroleum, the type and degree of refining, blending processes, and the mechanical and thermal history of the material (12–14). Such variation in the properties of white soft paraffin is reflected in the properties of formulations containing significant amounts of this material. The purposes of the present work are: (a) to investigate the effects of grade variation of white soft paraffin on the rheological properties of selected lipophilic formulations, and (b) to indicate various rheological techniques and methods of experimental data treatment that are available and may be of use in texture profile studies of pharmaceutical preparations.

Table I—Composition of Ointment and Emulsion Bases

System	Constituents, %							
	Liquid Paraffin	Hard Paraffin	Wool Fat	Beeswax	Cetostearyl Alcohol	Water	Sorbitan Monooleate <sup>a</sup>	White Soft Paraffin <sup>b</sup>
White soft paraffin	—	—	—	—	—	—	—	100.0
Simple ointment BP	—	5.0	5.0	—	5.0	—	—	85.0
Emulsion of simple ointment	—	2.5	2.5	—	2.5	49.75	0.25	42.5
Paraffin ointment BP	—	3.0	—	2.0	5.0	—	—	90.0
Dilutions of soft paraffin with liquid paraffin:								
A	20.0	—	—	—	—	—	—	80.0
B	40.0	—	—	—	—	—	—	60.0
C	60.0	—	—	—	—	—	—	40.0
D	80.0	—	—	—	—	—	—	20.0
E	90.0	—	—	—	—	—	—	10.0
Emulsions:								
A	—	—	—	—	—	50.0	2.0	48.0
B	9.6	—	—	—	—	50.0	2.0	38.4
C	19.2	—	—	—	—	50.0	2.0	28.8
D	28.8	—	—	—	—	50.0	2.0	19.2
E	38.4	—	—	—	—	50.0	2.0	9.6
F	43.2	—	—	—	—	50.0	2.0	4.8

<sup>a</sup> Span 80. <sup>b</sup> The preparations made with the different samples of white soft paraffin are distinguished in the text by the sample number in parentheses.

## EXPERIMENTAL

**Materials**—The materials used were of BP standard, except the surface-active agent<sup>1</sup> which was a commercial sample. Three grades of white soft paraffin were used, designated I, II, and III<sup>2</sup>. The compositions of the various preparations used are given in Table I, and in the text they are identified by name with the white soft paraffin sample number in parentheses.

**Procedure**—*Continuous Shear*—A Ferranti-Shirley cone and plate viscometer, with an automatic flow curve recorder unit and X-Y plotter, was used for continuous shear studies. The viscometer was used in two modes: (a) rates of shear varied from 0.0 to 1754.0 sec.<sup>-1</sup>, and (b) rates of shear varied from 0.0 to 175.4 sec.<sup>-1</sup>, using a 600-sec. sweep time in each case. The performance of the instrument was described previously (15). The test samples were prepared as described later and stored at 25 ± 1.2° for 24 hr. before use.

**Creep Testing**—Creep experiments were performed using a modification of a Westwind P.C.B. III pneumatic bearing and reaction turbine (10). The ointment bases were loaded into the viscometer at 60°; the emulsions, except emulsions of simple ointment, were mixed at 60°, using a Silverson mixer, and loaded into the viscometer while still warm. The simple ointment emulsions were made as described, but when cool they were milled using a triple-roller mill. Unless treated this way, the emulsions were unstable when large concentrations of water were incorporated, as reported for emulsions of hydrophilic petrolatum by Kostenbauder and Martin (3). The laboratory scale mill (Erwerka Apparatebau GMBH) had calculated maximum shear rates in the roller gaps of 6300 and 10,300 sec.<sup>-1</sup>. All samples were left in the creep viscometer overnight at 25 ± 0.1° for stresses to relax, for temperature equilibration, and for crystallization to occur. Since crystallization of soft paraffins has been reported to be time dependent (16), the samples should be considered as 1 day old.

Approximate linearity checks were performed on each sample, and a creep curve was obtained in the linear region. All the curves were analyzed by the method of Warburton and Barry (17) to obtain discrete spectra. The accuracy of each analysis was checked by a computer program, which regenerated the curve when the analyzed parameters were used as input data. The analyses were accepted if the reconstituted data were within 2% of the experimental curve. Selected curves were also analyzed to obtain continuous retardation spectra. Dynamic, or oscillatory, data were derived from the creep curves using a computer program which employed Schwarzl's approximations for the transformation of transient into dynamic data (18).

## RESULTS AND DISCUSSION

**Continuous Shear**—The continuous shear investigation of some preparations was inconclusive due to ejection of the test sample from the measuring gap of the viscometer. This phenomenon is concerned with the elastic recovery and/or fracture of the test sample during shear (8, 9, 19) and may also occur in concentric cylinder viscometers. The viscometer design of Kostenbauder and Martin (3) is evidence that they were aware of this problem.

White soft paraffin (I) and all the preparations containing hard waxes were ejected, to some extent, from the cone-plate gap of the viscometer, and apparent viscosity data could not be derived. The yield values obtained were higher for preparations of the soft paraffins and hard waxes than for the soft paraffins themselves. The yield stresses (Table II) are probably dependent upon the nature of the crystalline matrix (8), which was reinforced by the addition of the hard waxes. However, the validity of the yield stress data for these materials is questionable, because it is not known whether ejection of the test sample begins to occur during or after the formation of the spur point in the flow curve.

Continuous shear studies on the emulsions and paraffinic dilutions of soft paraffin (III) (Table II) indicated that the flow curves were anticlockwise hysteresis loops which sometimes contained spur points. The hysteresis may have been due to thixotropy or to irreversible shear breakdown; both the extent of hysteresis and the magnitude of the spur points decreased with a decrease in the percentage of white soft paraffin.

Figure 1 shows that the apparent viscosity at 1754.0 sec.<sup>-1</sup> of the emulsions and liquid paraffin dilutions of white soft paraffin (III) decreased as the percentage of soft paraffin decreased, but that the apparent relative viscosity of the emulsions increased [apparent relative viscosity is apparent viscosity of emulsion/apparent viscosity of liquid paraffin dilution, at any given concentration of white soft paraffin (III)]. Plotting the apparent viscosity data on semi-logarithmic axes yielded linear graphs, indicating that the variation in apparent viscosity of the emulsions and paraffinic dilutions with the percentage of white soft paraffin (III) could be represented by an Arrhenius-type equation (20, 21). The data derived at 175.4 sec.<sup>-1</sup> were similar.

The inverse relationship between apparent relative viscosity and concentration of white soft paraffin (III) in the continuous phase of the emulsions indicated that as the percentage of white soft paraffin (III) was decreased, the contribution of the emulsified water to the apparent viscosity of the emulsion increased, especially when less than 20% white soft paraffin was present.

**Creep: Discrete Spectra**—The rheological behavior of a viscoelastic material that shears under a constant stress in the linear region, that is, where the stress-strain ratio is a function of time alone and not stress magnitude, may be expressed by the equation:

<sup>1</sup> Span 80, Atlas Chemical Industries.

<sup>2</sup> Samples I and II are grades 783/L and 892/2/148 produced by Dalton & Co. Ltd., England. Sample III was produced by Plantar Industries.

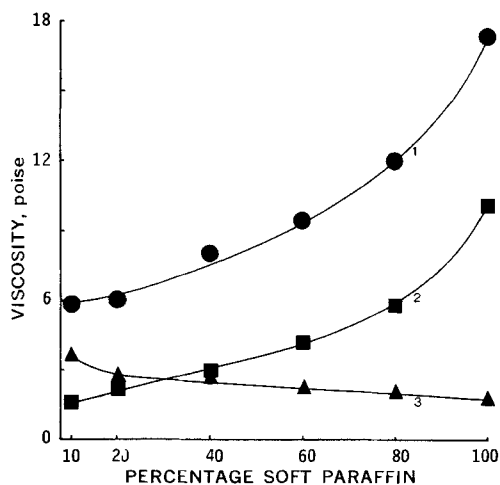
**Table II—Continuous Shear Data**

Preparation	0.0-1754.0 sec. <sup>-1</sup>		0.0-175.4 sec. <sup>-1</sup>	
	Ap- parent Vis- cosity, poise	Yield Stress, dynes cm. <sup>-2</sup>	Ap- parent Vis- cosity, poise	Yield Stress, dynes cm. <sup>-2</sup>
White soft paraffin				
I	* <sup>a</sup>	3,550	12.1+	2,600
II	1.2+	2,300	6.5	2,450
III	10.1+	7,700	33.4	5,100
Paraffin ointment				
I	*	8,150	*	6,100
II	*	5,150	1.3+	7,200
III	13.7+	15,500	8.8+	5,550
Simple ointment				
I	*	9,500	*	5,200
II	*	4,600	*	2,850
III	13.3+	22,300	31.6+	5,500
Simple ointment emulsion				
I	21.3+	22,500	62.4+	10,300
II	*	8,800	*	6,750
III	*	20,300	*	9,600
Emulsion				
IA	13.1	5,500	26.8	3,450
IIA	4.3	5,050	14.4	2,750
IIIA	17.4	6,750	37.9	4,600
IIIB	11.9	2,650	23.9	1,850
IIIC	9.4	1,300	16.5	850
IIID	8.1	—	14.2	450
IIIE	6.0	—	10.6	—
IIIF	5.8	—	7.9	—
Dilution of white soft paraffin III with liquid paraffin				
IIIB	5.9	4,200	14.2	1,650
IIIC	4.2	2,900	10.0	700
IIID	3.1	481	6.6	—
IIIE	2.2	—	3.3	—
IIIF	1.6	—	1.8	—

\* Indicates total sample ejection, + indicates some sample ejection, data may be invalid. Rates of shear varied from (a) 0.0-1754.0 sec.<sup>-1</sup>, and (b) 0.0-175.4 sec.<sup>-1</sup> in 600 sec., apparent viscosity determined at apex of flow curve.

$$J(t) = J_0 + \sum_{i=1}^n J_i(1 - e^{-t/\tau_i}) + t/\eta_0 \quad (\text{Eq. 1})$$

where  $J(t)$  is the total compliance (strain-stress ratio) at time  $t$ ,  $J_0$  is an initial elastic compliance,  $J_i$  is a time-dependent elastic compliance,  $\tau_i$  is a retardation time, and  $\eta_0$  is the residual Newtonian viscosity. Using the method of Warburton and Barry (17), a creep curve may be analyzed to determine the values of the param-



**Figure 1—Effect of concentration of white soft paraffin (III) on the apparent viscosity, at 1754.0 sec.<sup>-1</sup>, of: (1) emulsions, (2) liquid paraffin dilutions of the soft paraffin, and (3) the apparent relative viscosity of the emulsions [apparent relative viscosity is apparent viscosity of emulsion/apparent viscosity of paraffinic dilution at any given concentration of white soft paraffin (III)].**

eters  $J_0$ ,  $J_i$ ,  $\tau_i$ , and  $\eta_0$ . All the data derived by discrete spectrum analysis are given in Tables III and IV.

The three soft paraffins used represent the median and upper and lower extremes of a range of soft paraffins recently investigated (10). The total elastic compliance,  $[J(t) - t/\eta_0]_{t \rightarrow \infty}$ , of Sample III was more than three times that of Sample I, and their residual viscosities differed by more than a factor of 10. The ratio of the total elastic compliance (derived by summation of individual elastic compliances) of white soft paraffins (I, II, and III) is given in Table V, with the corresponding ratios for simple and paraffin ointments and simple ointment emulsion. In each case the preparation of soft paraffin (I) was the least compliant, and its compliance was considered as unity in the calculation of the ratio. The ratio between the total elastic compliances of soft paraffins (I and II) was approximately maintained for each of their preparations, but there was greater variation between the ratios of preparations of white soft paraffins (I and III). The conclusion derived is that the elastic properties of white soft paraffin are of importance in formulation, because they may affect the elastic properties of the final product.

The effect of grade variation of the soft paraffins was not so apparent when the residual viscosities of the preparations of the soft paraffins were compared (Table III). The paraffin ointments maintained the same order of magnitude of residual viscosity as the soft paraffins, but the difference between the values was reduced. With the simple ointments and their emulsions, the order

**Table III—Discrete Spectra Data for Ointment Bases and White Soft Paraffins**

Parameter	White Soft Paraffin			Paraffin Ointment			Simple Ointment			Simple Ointment Emulsion		
	I	II	III	I	II	III	I	II	III	I	II	III
$J_0$	35.0	44.0	76.0	32.0	46.0	47.0	40.0	46.0	43.0	41.0	56.0	50.0
$J_1$	31.0	52.0	98.0	19.0	29.0	22.0	7.8	12.0	10.0	96.0	180.0	520.0
$J_2$	10.0	19.0	45.0	2.7	7.9	9.4	—	7.0	6.0	23.0	54.0	59.0
$J_3$	6.2	14.0	39.0	4.0	7.7	8.6	—	5.8	15.0	48.0	43.0	80.0
$J_4$	5.5	2.4	46.0	6.2	12.0	11.0	—	6.1	—	—	43.0	56.0
Total elastic compliance, $JT^a$	87.7	131.4	304	63.9	102.6	98.0	47.8	76.9	73.9	208	376	765
$\tau_1$	1424	2059	1360	1282	655	1175	20	546	424	743	890	1442
$\tau_2$	238	425	236	328	96	248	—	82	28	120	150	374
$\tau_3$	38	25	45	60	19	7	—	7	6	18	35	80
$\tau_4$	5	3	8	5	3	1	—	1	—	—	9	9
$\eta_1$	45.2	39.6	13.9	65.7	22.7	53.4	2.5	44.4	44.2	7.74	4.81	2.77
$\eta_2$	23.8	22.2	5.20	120.0	12.2	26.4	—	11.6	5.13	5.22	2.78	6.34
$\eta_3$	6.13	1.86	1.16	15.1	2.44	7.55	—	1.15	0.43	0.36	0.82	1.00
$\eta_4$	0.83	1.30	0.18	0.85	0.27	0.70	—	0.16	—	—	0.21	0.16
$\eta_0$	278.0	35.0	24.6	286.0	137.0	107.0	24.1	148.0	9.84	8.07	4.58	7.37

<sup>a</sup>  $JT = [J(t) - t/\eta_0]_{t \rightarrow \infty}$

**Table IV**—Discrete Spectra Data for Emulsions and Liquid Paraffin Dilutions of White Soft Paraffin (III)

Parameter	Emulsion IA	Emulsion IIA	Soft Paraffin III	Emulsion IIIA	Dilution IIIB	Emulsion IIIB	Dilution IIIC	Emulsion IIIC	Dilution IIID	Emulsion IIID	Emulsion IIIE	Emulsion IIIF
$J_0$	0.71	0.49	0.76	1.7	1.4	3.8	2.4	8.4	17.0	30.0	180.0	1600.0
$J_1$	0.78	0.41	0.98	4.5	0.6	8.0	5.5	18.0	13.0	14.0	66.0	910.0
$J_2$	0.36	0.22	0.45	1.5	1.1	2.9	2.4	66.0	4.5	12.0	33.0	540.0
$J_3$	0.31	0.18	0.39	1.4	1.0	1.2	1.2	51.0	19.0	11.0	16.0	780.0
$J_4$	0.24	—	0.46	0.9	—	2.0	—	2.4	—	—	—	—
$\tau_1$	1369	1360	1360	1638	2440	1638	661	1470	222	354	180	305
$\tau_2$	190	147	236	229	212	200	43	116	69	28	13	53
$\tau_3$	26	5	45	31	19	62	1	21	12	5	4	7
$\tau_4$	7	—	8	4	—	7	—	3	—	—	—	—
$\eta_1$	1750.0	3320.0	1390.0	364.0	4190.0	204.0	120.0	80.4	17.1	25.3	2.7	0.3
$\eta_2$	527.0	208.0	520.0	148.0	198.0	69.5	17.8	18.7	15.2	2.3	0.4	0.1
$\eta_3$	84.0	26.2	116.0	22.2	19.5	51.3	1.2	18.2	0.6	0.4	0.2	0.01
$\eta_4$	31.3	—	18.0	4.3	—	3.7	—	1.4	—	—	—	—
$\eta_0$	1760.0	2870.0	2460.0	617.0	1690.0	482.0	239.0	109.0	177.0	54.4	30.9	2.0

of magnitude of the residual viscosities did not correspond with that of the soft paraffins. Slippage effects did not occur significantly during the experiments, as confirmed by the creep recovery curves; the reasons for the lack of correlation between the data are not known, but some specific interaction between the components of the preparations may affect the viscosity. Such a phenomenon may be observed when a mixture of liquid paraffin and 5% hard paraffin is heated to 60° and cooled and the Newtonian viscosity of the mixture is measured. The addition of 5% hard paraffin causes a significant decrease in the viscosity of liquid paraffin (1.6-1.4 poise). This has been confirmed using a Haake Rotovisko viscometer and is, thus, not an instrumental effect due to cone and plate geometry. The decrease in the viscosity is thought to be due to entrapment or cocrystallization of the higher paraffin fraction of liquid paraffin with the crystals of hard paraffin. The removal from solution of the higher paraffins reduces the viscosity of the liquid paraffin more than it is increased by the suspended crystals of hard paraffin; therefore, there is an overall decrease in viscosity.

The three-dimensional crystal matrix which exists in soft paraffins and similar materials (22) was reinforced by the addition of crystalline waxes such as hard paraffin and beeswax, as shown by the decrease in the total elastic compliances of the paraffin and simple ointments in relation to the respective white soft paraffin. The reverse occurred with the simple ointment emulsions, because the milling process disrupted the crystalline matrix of the continuous phase.

**Creep: Continuous Retardation Spectra**—Analysis of creep curves into discrete viscoelastic spectra leads to mathematical data which

may not always be easy to understand or compare, although the data may be such that they can be plotted to determine additional parameters. For example, the residual viscosity may be employed in Arrhenius-type curves to obtain the activation energy for viscous flow (8, 9). Analysis of creep curves to obtain continuous retardation spectra is simpler and yields graphical results which are often easier to use, because the spectra represent the viscoelastic behavior of materials in a more general way than other functions such as  $J(t)$ . The retardation spectrum,  $L$ , is defined by the continuous analog of Eq. 1:

$$J(t) = J_0 + \int_{-\infty}^{\infty} L(1 - e^{-t/\tau}) d \ln \tau + t/\eta_0 \quad (\text{Eq. 2})$$

and has the nature of a distribution function with the dimensions of a compliance (23). Maxima in the curves indicate a concentration of retardation processes (time-dependent elastic strain mechanisms at molecular level) measured by their contribution to compliance. Several approximation techniques are available to determine retardation spectra (24, 25); the one used here is due to Schwarzl and Staverman (26-28) and was developed from a method proposed by Alfrey (29). The value of the distribution function at any given time may be derived using Eqs. 3 and 4:

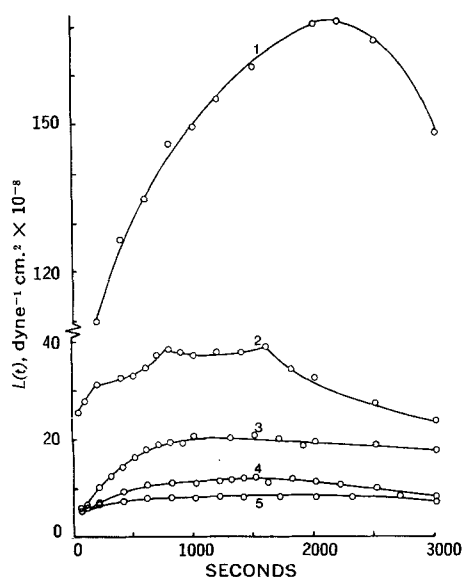
$$L(t) \sim \frac{d}{d \ln t} [J(t) - t/\eta_0] \quad (\text{Eq. 3})$$

$$L(t) \sim \frac{d}{d \ln t} \left[ J(t) - \frac{dJ(t)}{d \ln t} \right] \Big|_{t=2\tau} \quad (\text{Eq. 4})$$

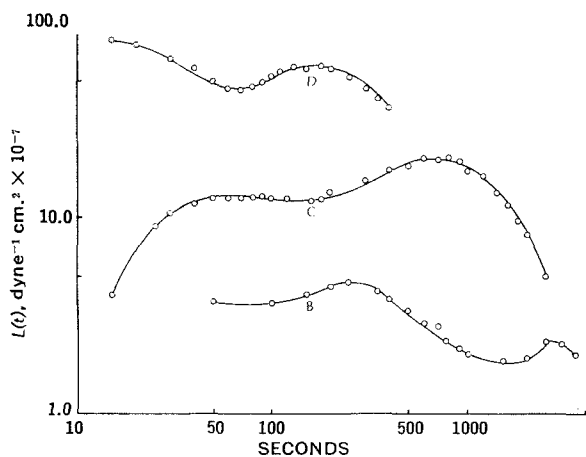
The values of  $J(t)$  and  $t/\eta_0$  may be determined directly from an experimental curve or obtained from the discrete spectrum data by using the reconstitution program. Equations 3 and 4 were used by Sherman in the study of water-in-oil emulsions (30) and food products (31, 32). They may be used to investigate aging and temperature effects and to compare different formulations of a preparation or material.

Figure 2 indicates that while the retardation spectra of white soft paraffins (I and II) determined by Eq. 3 were broad and smooth, that of white soft paraffin (III) had two maxima. Paraffin ointment BP (III) in the same figure appears to have a very broad and flat distribution; however, expansion of the ordinate showed that it was bimodal, although the maxima were depressed. Emulsion (IIIA) had a single maximum, and the retardation processes involved appeared not to correspond with those of white soft paraffin (III). The continuous retardation spectra of dilutions of soft paraffin (II) with liquid paraffin were all bimodal, although the relative magnitude of the maxima varied and the spectra became narrower, with the peaks shifting to shorter times as the dilution increased (Fig. 3). Thus, emulsification of white soft paraffin (III) radically altered its retardation mechanisms, but dilution with liquid paraffin, although affecting the time scale of the spectrum, did not change the bimodal distribution of the retardation processes.

**Creep: Transformation to Dynamic Parameters**—Dynamic, or oscillatory, small strain experiments consist of imposing a sinusoidal



**Figure 2**—Continuous retardation spectra. Key: 1, emulsion (IIIA); 2,3,4, white soft paraffins (III), (II), and (I), respectively; and 5, paraffin ointment BP (III).



**Figure 3**—Continuous retardation spectra of liquid paraffin dilutions (IIB–IIID, Table I) of white soft paraffin (III).

stress or strain on a test material and measuring the resultant strain or stress, respectively. By using small amplitudes of oscillation, the structure of the test material changes far less than when it is sheared continuously, even at low rates of shear. Takano (33) compared the effects of oscillatory and continuous shear viscometry. For studying viscoelastic materials which are linear only at low stress, a dynamic system of testing has the advantages that: (a) at low amplitudes the information obtained approximates closely to the zero shear condition, and (b) properties of the test material may be determined over a wide range of frequency of oscillation. The complex compliance determined in dynamic experiments may be resolved into parameters descriptive of the elastic and viscous characteristics of the material, the storage and loss compliances, respectively. A suitable instrument for oscillatory testing of pharmaceutical semisolids is the Weissenberg rheogoniometer with transfer function analyzer (11). This sophisticated instrument is expensive and would be available only in specialized laboratories. Alternative methods for obtaining dynamic information are either to convert a continuous shear viscometer to oscillatory mode (34) or to transform creep data into dynamic data.

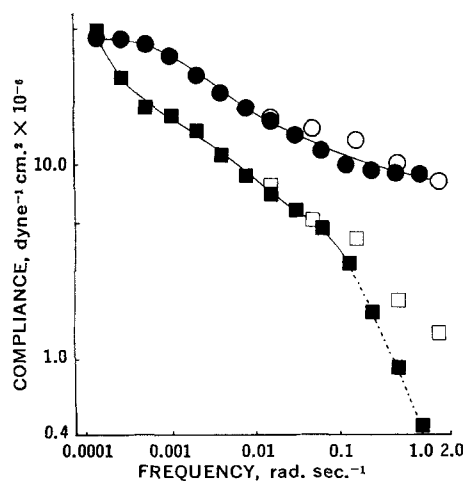
This transformation is feasible if the test material is linear in its viscoelastic behavior, but the procedure is mathematically difficult (23, 35). Many approximation methods have been proposed for the interconversion of dynamic and transient viscoelastic data (23, 35, 36). The approximation due to Schwarzl (18) for calculation of dynamic compliances from creep data involves using values of  $J(t)$  at various times in creep; for example, Eq. 5 is the most accurate for the determination of the storage compliance,  $J'(\omega)$ :

$$J'(\omega) \sim J(t) + 0.0007[J(32t) - J(16t)] - 0.0185[J(16t) - J(8t)] + 0.197[J(8t) - J(4t)] - 0.778[J(4t) - J(2t)] - 0.181[J(t) - J(t/2)] - 0.049[J(t/4) - J(t/8)] \quad (\text{Eq. 5})$$

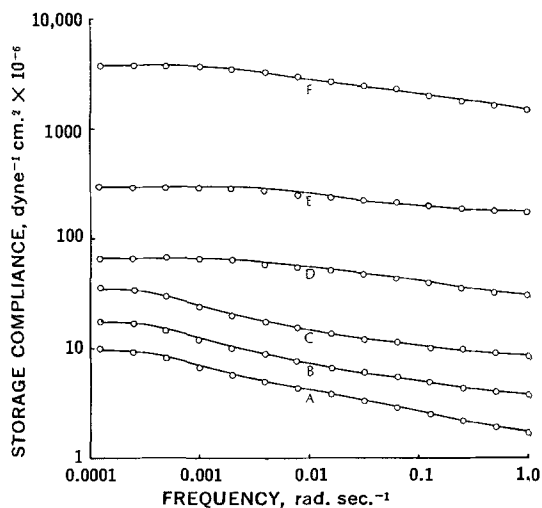
where  $\omega = 1/t$ . The loss compliance is calculated using a similar type of equation. The values of  $J(t)$  required may be measured directly from an experimental creep curve. However, a computer program has been written to convert transient data derived by discrete spectrum analysis into dynamic data for linear viscoelastic materials. The advantage of such a method, as opposed to reading  $J(t)$  directly, is that it facilitates the transformation over a wider range of frequency, especially at higher frequencies which correspond to creep times too short to be measured directly from the experimental curve.

A brief preliminary investigation was carried out to determine the accuracy of the approximation technique and this application of it. Experimental dynamic data were obtained using a Weissenberg rheogoniometer with transfer function analyzer. Creep curves were obtained for samples loaded into the viscometer while cold to simulate the loading procedure used with the rheogoniometer. The curves were analyzed graphically by the method of Warburton and Barry (17), the analyses were checked by computer, and the data were transformed by computer. Theoretical and experimental data for emulsion (IIIA) are plotted in Fig. 4. The agreement between the experimental storage compliances and those determined from the creep curve was satisfactory, the maximum difference between the values being  $3.5 \times 10^{-6} \text{ cm.}^2 \text{ dyne}^{-1}$  at approximately 0.1 rad.  $\text{sec.}^{-1}$ . The agreement between the experimental and theoretical loss compliances was also satisfactory, except at higher frequencies. While the two loss compliance curves are similar, they diverge at frequencies of oscillation greater than 0.1 rad.  $\text{sec.}^{-1}$ , although the difference between their values is only  $1.1 \times 10^{-6} \text{ cm.}^2 \text{ dyne}^{-1}$  at 0.5 rad.  $\text{sec.}^{-1}$ . This frequency corresponds qualitatively with a creep test of 2-sec. duration, and calculation of the loss compliance involves  $J(t)$  at times less than 0.01 sec. As the short time values of  $J(t)$  are important in the calculation of the loss compliance, the errors involved may be large and are unavoidable. It is probable that 0.1 rad.  $\text{sec.}^{-1}$  represents the maximum frequency at which this method of data treatment should be used to calculate the loss compliance from any given creep curve.

The preparations used to indicate the application of this method of data transformation were the emulsions (IIIA–IIIF) of white soft paraffin (III). The curves for the storage compliances of emulsions (IIIE and IIIF) (Fig. 5) attain a maximum at frequencies below approximately 0.002 rad.  $\text{sec.}^{-1}$ , indicating that the emulsions attained the equivalent of transient steady-state flow. With reference to the model representation of viscoelastic behavior (37), the equilibrium attained by the storage compliance indicates maximum extension of the Voigt units and Hookean spring. Emulsions (IIIA–IIIC) attained a similar state at frequencies a power of 10 lower. The slopes of the curves before the plateau region was reached were



**Figure 4**—Dynamic compliances for emulsion (IIIA). Key:  $\circ$ ,  $\square$ , experimental storage and loss compliances, respectively, derived using a rheogoniometer; and  $\bullet$ ,  $\blacksquare$ , theoretical storage and loss compliances, respectively, derived by transformation of creep data.



**Figure 5**—Variation of storage compliance with frequency of oscillation for emulsions of white soft paraffin (III). See Table I for details of emulsion formulations.

similar, showing that the elastic structures within the materials were similar. The loss compliances (Fig. 6) decreased as the frequency increased, and the slopes of the curves were similar at low frequency. The increase in the loss compliance slopes at frequencies greater than approximately 0.1 rad. sec.<sup>-1</sup> was found to occur experimentally using the rheogoniometer, but the error involved may be large.

**Texture Profile Evaluation**—The relationship between instrumental and sensory data has been studied for many years (38). Stevens (39) defined two types of sensory stimuli, prothetic and metathetic. The former may be represented by a double logarithmic equation and are quantitative (how much? how viscous? *etc.*). The latter are qualitative stimuli (of what kind?) and may be represented with simple logarithmic equations. Katz (40) found that psychological properties such as body and elasticity do not correspond directly to the physical parameters of viscosity and elasticity but are the result of a complicated cooperation of different senses. Thus, the sensory property called elasticity does not correspond to physical elasticity but is more accurately expressed by the viscosity/elasticity ratio. Therefore, in a sensory evaluation of rheological properties, there is a complex interrelationship between stress, strain, and time as the consumer cannot always differentiate the properties that are measured instrumentally, and it may be necessary to use power equations involving all three parameters (41, 42). Examples of textural studies on food and cosmetic products are those of Szczesniak (43), Matz (44), and Fryklöf (45).

Continuous shear viscometry would appear, initially, to be a suitable method for rheological investigation in texture profile studies, because the conditions, such as shear rate, involved in a subjective assessment of consistency may be simulated on a continuous shear viscometer. However, certain materials are not amenable to such a procedure, due to, for example, ejection of sample in a cone-plate viscometer or fracture and slippage in a couette viscometer. With suitable materials, information may be derived concerning the variation of apparent viscosity with rate of shear, temperature, and age of sample, and also the types of flow curve of the materials. Yield stresses may also be determined; while their cause is not always known, they are due, in part at least, to some property of the material (9). Davis (8) suggested that in some materials they are concerned with crystalline structures which are susceptible to mechanical strain. The parameters determined by continuous shear viscometry are only of use in textural studies if they can be correlated with sensory data. Difficulties arise in attempts to measure shear forces and rates of shear in a sensory evaluation, since certain parameters, such as hardness, may be assessed rapidly, while others, such as ductility, require a longer time. It is also necessary to know exactly what the consumer is assessing, a psychological problem, because there is overlap in property identification.

Small strain experiments to measure viscoelastic properties of test materials are useful in many ways. While the underlying mechanisms of the ultimate properties of a material (properties during structural breakdown) are not fully understood, they involve to some degree the same molecular mechanisms that are reflected in simpler viscoelastic properties (23). This correlation may be applied to the spreading of viscoelastic emulsions, ointments, gels, and creams, as spreading causes rupture of the viscoelastic structure within the material. Small strain experiments may also give an indication of the ductility (fiber or strand length) of a material (10), a parameter that is usually assessed subjectively, although a physical test has been proposed (46). The difficulty, as in continuous shear studies, is to correlate experimental and sensory data. The discrete spectrum analysis of creep curves yields detailed data by representing the time-dependent elastic properties of the test material by the algebraic sum of a set of hypothetical series compliances which may, or may not, have a direct physical significance in the system studied (23, 47).

The data may be useful in comparative studies, especially when they can be plotted against a controlled variable (48). For example, by extrapolation it may be shown that plots of creep parameters such as  $J_0$  and  $\eta_0$  of the emulsions and paraffinic dilutions of white soft paraffin (III) against soft paraffin concentration intercept at 20% or more of white soft paraffin. By correlating this with the apparent relative viscosity data derived in continuous shear, it is reasonable to propose that for concentrations of white soft paraffin (III) less than 20% of the continuous phase of the emulsions, the contribution of the emulsified water dominates the rheological properties of the emulsions, and the effect of white soft paraffin is minimal. However, correlation between small strain and continuous

**Table V**—Comparison of Ratio (I:II:III) of Total Elastic Compliance of Preparations of Soft Paraffins (I, II, and III)

Preparation	I	II	III
White soft paraffin	1.0	1.5	3.5
Paraffin ointment	1.0	1.6	1.5
Simple ointment	1.0	1.6	1.5
Simple ointment emulsion	1.0	1.8	3.7

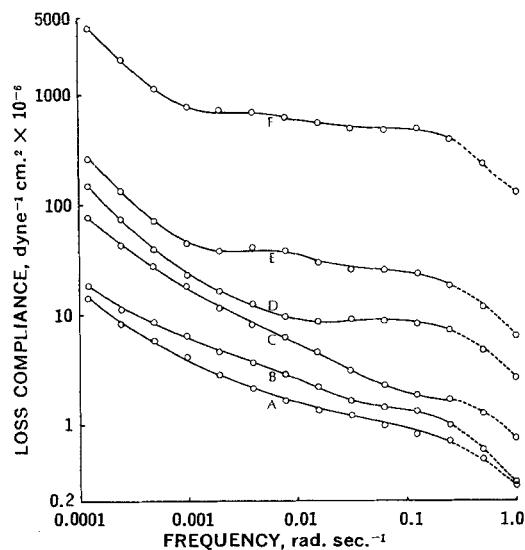
shear data is often difficult to achieve because most complex materials become non-Newtonian at higher rates of shear. For example, in creep, emulsion (IIIA) has a lower residual Newtonian viscosity than white soft paraffin (III), while in continuous shear the paraffin has a lower apparent viscosity than the emulsion. The utility of discrete spectra data in texture profile evaluation is difficult to assess. It is possible that the compliance (the inverse of the elastic modulus) or residual Newtonian viscosity may be correlated with some sensory information in a complex manner, as shown by Katz (40).

A retardation time is the product of a compliance and its associated viscosity:

$$\tau = J\eta \quad (\text{Eq. 6})$$

and discrete spectra analyses produce retardation times which may not have a basic physical significance. Therefore, when the sensory situation reported by Katz (40) is known to exist, it may be more useful to analyze creep curves to obtain continuous retardation spectra. For example, while discrete spectra analyses indicated that soft paraffins (I, II, and III) were dissimilar as regards compliance and residual viscosity, the retardation data did not show any large difference between the materials. However, the continuous spectra indicated that soft paraffin (III) possessed retardation mechanisms different to those of samples (I) and (II). Similarly, although discrete spectra analyses indicated that emulsion (IIIA) was weaker than soft paraffin (III), they did not show that emulsification altered the type of retardation mechanisms. That emulsification does alter the gel structure of white soft paraffin was recently shown by other workers (49), and the results derived here are thus not due to errors in the methods of analysis applied. Such differences in the retardation mechanisms of viscoelastic materials, which are not easily detected using discrete analyses, may possibly be correlated with sensory data when a consumer's subjective property identification concerns both viscosity and elasticity.

The maximum rates of shear involved in a sensory evaluation depend inversely on the general consistency of the samples being assessed. Furthermore, different sensory parameters are determined at different rates of shear. For example, the sensory evaluation of consistency of water-in-oil and oil-in-water semisolid emulsions was correlated with initial shear stress (a parameter derived using a vis-



**Figure 6**—Variation of loss compliance with frequency of oscillation for emulsions of white soft paraffin (III). See Table I for details of emulsion formulations.

cometer with discontinuous shear rate variation, and equivalent to a yield stress at a low rate of shear), while *spreadability* was correlated with apparent viscosity at 400 sec.<sup>-1</sup> (50, 51). Barry and Grace (52) found a relationship between the sensory evaluation of consistency of work softened and unworked white soft paraffin and the yield stresses determined in continuous shear. Apparent viscosity data at rates of shear below 30 sec.<sup>-1</sup>, but after the formation of a spur point in the flow curves, were not correlated with the sensory data. However, a linear relationship was found using discrete viscoelastic parameters determined in creep at very low rates of shear. It is thus apparent that: (a) small strain data may be correlated with sensory data, and (b) for a full texture profile evaluation, experimental data should be derived at various rates of shear. Dynamic small strain experiments may thus be of use in textural studies as measurements may be made over a wide range of frequency (rate of shear) in conditions that approximate to the rheological ground state. Transformation of creep data into oscillatory data is less accurate at high frequencies, especially for the loss compliance. However, by taking creep measurements at various temperatures and employing the method of reduced variables (23), it may be possible to extend the range of accurate transformation of data to higher frequencies.

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