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Viscoelastic Properties of Pharmaceutical Semisolids I: Ointment Bases

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Abstract ☐ The rheological evaluation of semisolids by continuous shear methods is limited in its application. However if materials are viscoelastic, their properties can be assessed in creep testing where fundamental parameters are provided and rheological behavior can be represented by mechanical models. Measurements have been made on a number of ointment bases over a range of temperature. The addition of small quantities of complex materials to paraffin ointment bases changes their behavior from elastic to viscoelastic. As many of the materials show a characteristic change in viscoelastic spectrum with temperature it is hoped that creep testing will provide a suitable method for the correct rheological evaluation of many important materials.

Keyphrases ☐ Viscoelastic properties—ointment bases ☐ Ointment bases—creep testing ☐ Creep compliance—ointment ☐ Temperature effect—viscoelastic properties ☐ Shear, continuous, creep—ointment viscoelasticity

The rheological evaluation of pharmaceutical semisolids is useful in that it provides both a method of quality control during and after manufacturing processes (1–3) as well as information as to the structures of the phases present in a material and the influence of various agents used in its formulation. Continuous shear-rheology has been a popular approach (4, 5) and in particular the Ferranti-Shirley viscometer, with automatic flow-curve recording unit, has been much utilized (6–10). However many pharmaceutical semisolids demonstrate complex rheological behavior that is difficult to characterize in this way (11). If the semisolids are viscoelastic in nature it is more valuable, both theoretically and practically, to examine them in their rheological ground state where the method of testing does not significantly alter the structure.

The importance of viscoelasticity in pharmaceutical materials has been discussed briefly by McVean and Mattocks (12) and Berneis and Munzel (13). A detailed study of the viscoelastic system, sodium lauryl sulfate, cetyl alcohol, water (with and without the addition of oil) has been made by Barry (6, 14). The theory of linear viscoelasticity (15) can be applied to

pharmaceutical materials (2, 16) and recently a number have been examined by oscillatory methods.

One of the simplest methods of examining viscoelasticity in a semisolid is the creep test where a stress is suddenly applied and then maintained constant, sometimes for a considerable period of time. The time-dependent strain response is known as the creep curve. If the strain is in the linear region, where the ratio of stress to strain is a function of time alone and not strain magnitude (17), the creep curve can be analyzed using the theory of viscoelasticity. The strain response on removal of the stress is know as the recovery curve. A typical creep curve is shown in Fig. 1. The creep curve can be split up into three separate regions each of which can be represented by a mechanical model (18). The region A-B represents an instantaneous elastic component which can be associated with an uncoupled Hookean spring. Region B-C is where the flow is viscoelastic and can be represented by a Voigt unit(s). This is a spring in parallel with a dashpot. Region C-D is that of viscous flow and can be associated with an uncoupled residual Newtonian dashpot. In recovery, the regions A-B, B-C, are recov-
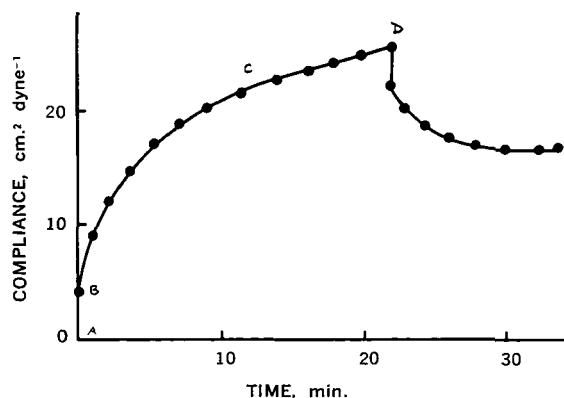

Figure 1—*Typical creep curve for a viscoelastic material. A–B, instantaneous elastic region; B–C, Voigt region; C–D, region of viscous flow.*

ered completely and in part, respectively, while the region C-D is not recovered. The change of creep compliance with time [$J(T)$] can be expressed as

$$\text{Region} \quad \underset{\text{A-B}}{J(T)} = J_0 + \underset{\text{B-C}}{\sum J_i (1 - e^{-t/\tau_i})} + \underset{\text{C-D}}{t/\eta_0}$$

where $J(T) = \gamma(t)\sigma$, where $\gamma(t)$ is the shear strain at time t, σ the shear stress, J_0 the instantaneous shear compliance, η_0 the residual viscosity, and τ_i the retardation time of the ith model. $J_i = 1/G_i$ where G_i is the modulus of rigidity.

Alfrey and Gurnee (18) have emphasized that the use of models does not necessarily imply anything concerning the molecular mechanism responsible for the observed behavior; however, individual elements can sometimes be qualitatively identified with definite processes at a molecular level. For a semisolid, Barry (6) considers that the instantaneous contribution represents bonds being stretched elastically and is due to a network structure in the system. The Voigt units represent that part of the structure in which secondary bonds are breaking and reforming during the test. The retardation time τ is the time during which bonds break and reform and as all bonds do not do this at the same rate a spectrum of retardation times exists. When the stress has been applied for sufficient time to ensure that all the Voigt units are extended, further deformation is in the nature of viscous flow. In this region the system is flowing as a solid dispersion in a liquid medium of high viscosity.

In the present work a number of pharmaceutical ointment bases of the British Pharmacopoeia have been examined over a range of temperature. Their behavior in continuous shear has also been investigated.

EXPERIMENTAL

Materials—A number of commercially available ointment bases were selected for examination. These are listed in Table I together with their compositions.

Apparatus—*(a) Continuous Shear*—A Ferranti Shirley cone and plate viscometer was used for continuous shear studies (19). It was fitted with a flow curve recorder unit and X-Y plotter, the apparatus dimensions and constants have been given by Davis *et al.* (11).

(b) Creep Testing—Creep experiments were performed using a concentric cylinder modification of the Weissenberg rheogoniometer (2). Samples for examination were allowed to remain in the apparatus for at least 24 hr. before testing so that any stresses in the material produced by loading were able to relax. For lanolin the sample was enclosed in a water-saturated environment to prevent changes due to evaporation.

RESULTS

The ointment bases were examined in creep over the temperature range 26–50°. The upper temperature in each case was limited by the materials becoming nonlinear in their viscoelastic properties. Continuous-shear rheograms were obtained at 25° only. The maximum shear rate was in the region of 1,700 sec.$^{-1}$, a value close to that which has often been used before for pharmaceutical systems (6–9).

The creep curves were analyzed by a computer modification (20) of the procedure discussed by Warburton and Barry (2). The derived viscoelastic parameters, at different temperatures, are given in Table II.

(a) White Soft Paraffin—The rheogram for white soft paraffin has been described in detail previously (7, 8, 11). It is
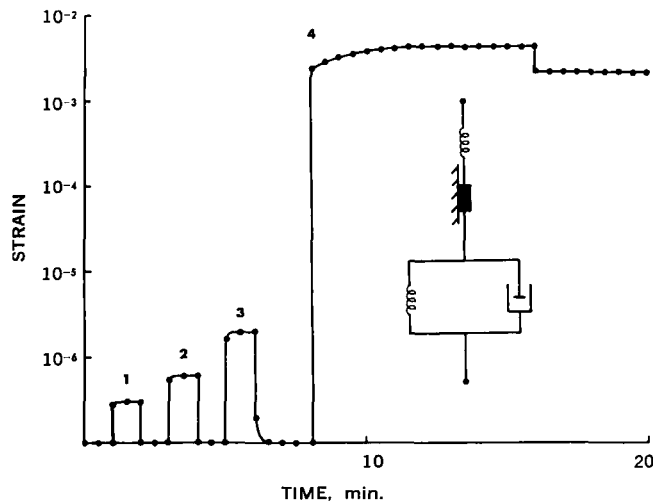

Figure 2—*Creep curve for white soft paraffin. Key: shear stress, dyne* cm.$^{-2}$: 1, *157;* 2, *314;* 3, *628;* 4, *722.*

of the hysteresis-loop type, with a static yield value and a number of shear stress maxima and minima (21). In creep, white soft paraffin shows no evidence of viscoelastic behavior (Fig. 2). For shear stresses below 700 dyne cm.$^{-2}$ it behaves as a Hookean solid (*i.e.,* an uncoupled elastic spring) with strain proportional to stress. On removal of the stress there is complete recovery. If higher stresses are used the material yields, *i.e.,* becomes nonlinear, and demonstrates slight viscoelastic behavior but without residual viscosity. On removal of stress there is only slight recovery. A model for this behavior is shown in Fig. 2.

(b) Wool Fat and Lanolin—In continuous shear, wool fat gives a relatively simple rheogram (Fig. 3) with no evidence of a yield value. The same is true of lanolin but at high shear rate (850 sec.$^{-1}$) the up curve shows a sudden change in gradient due to expulsion of material from the gap between the cone and plate, behavior that is often shown by viscoelastic materials (22). At shear rates below this point lanolin is shown to be more viscous than wool fat.

In creep, the compliance at a given time, for a given temperature, is smaller for lanolin than for wool fat (Fig. 4) and the derived viscoelastic parameters, Table I, are greater except for G_0 at higher temperatures. Wool fat can be represented by a simpler mechanical model than lanolin at all temperatures in the range 26–41° (Fig. 5). At 41° it eventually becomes an elastic liquid, *i.e.,* a spring in series with a dashpot. The variation of the residual viscosity (η_0 with
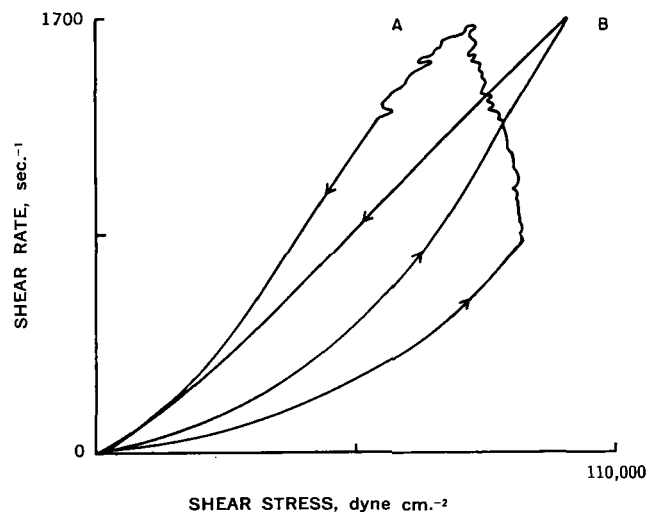

Figure 3—*Rheograms for wool fat and lanolin. Key: A, lanolin; B, wool fat. Temperature, 25°; sweep time 240 sec.*

Table I—The Composition of Ointment Bases

System	Constituents, %								
	Liquid Paraffin	White Soft Paraffin	Hard Paraffin	Wool Fat	Beeswax	Cetostearyl Alcohol	Sodium Lauryl Sulfate	Wool Alcohols	Water
White soft paraffin	—	100	—	—	—	—	—	—	—
Wool fat	—	—	—	100	—	—	—	—	—
Lanolin	—	—	—	70	—	—	—	—	30
Paraffin ointment	—	90	3	—	2	5	—	—	—
Emulsifying ointment	20	50	—	—	—	27	3	—	—
Wool alcohols ointment	60	10	24	—	—	—	—	6	—
Simple ointment	—	85	5	5	—	5	—	—	—

temperature for both materials can be represented by an equation of the Arrhenius type (23) $\eta_0 = Ae^{E/RT}$ where A is a constant, E is the activation energy, R the gas constant, and T the temperature (°K.). A plot of log η_0 versus $1/T$ is shown in Fig. 6. Activation energies for the two materials can be obtained from the gradients of the lines.

(c) Paraffin Ointment—A yield value is obtained in the rheogram of paraffin ointment (Fig. 7) but immediately after, the shear stress falls rapidly to zero due to expulsion of material from the gap. The creep behavior (Fig. 8, Table II) is different from that in (b) above in that the compliance due to the uncoupled spring disappears at 35° instead of increasing with temperature. The model representation for this is shown in Fig. 9.

(d) Emulsifying Ointment—As for the case of lanolin the rheogram of emulsifying ointment demonstrates a sudden

change in gradient of the up curve due to loss of material from the gap. In creep the material shows a progressive fall in the values of the viscoelastic parameters, and the number of models for representation, with temperature, and appears to be similar in behavior to lanolin.

(e) Wool Alcohols Ointment and (f) Simple Ointment— Wool alcohols ointment is one of the few ointment bases that has a rheogram in which there is no evidence of loss of material from the gap (Fig. 7). In comparison simple ointment has a very large yield value after which the shear stress decays rapidly to zero [cf. (c)]. At temperatures below 30° both materials give creep curves that can be analyzed. However, above 30° nonlinear behavior is clearly evident (Fig. 10). Wool alcohols ointment shows a yielding phenomenon where the compliance suddenly increases after which the curve resumes its previous gradient. Simple ointment gives creep curves that are irregular in shape. Complete analysis of both
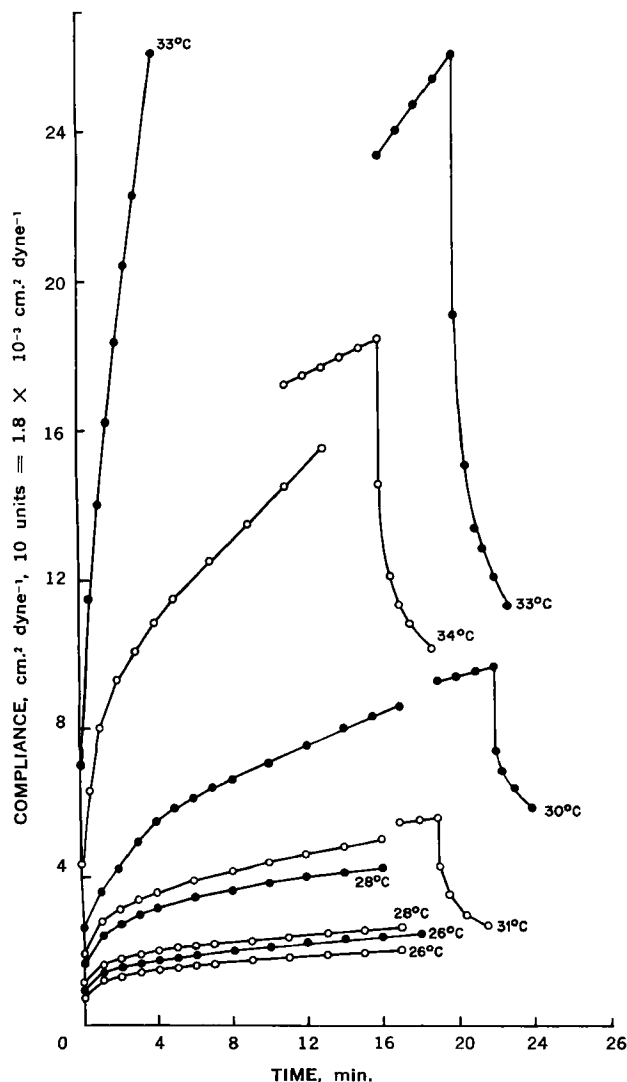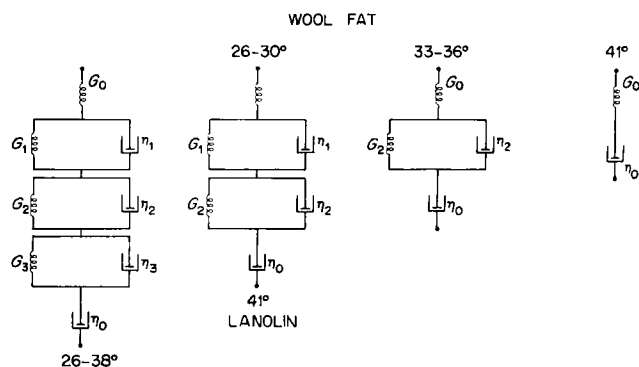
Figure 5—Model representation for wool fat and lanolin over the temperature range 26-41°. Temperatures at top refer to wool fat, those at bottom to lanolin.

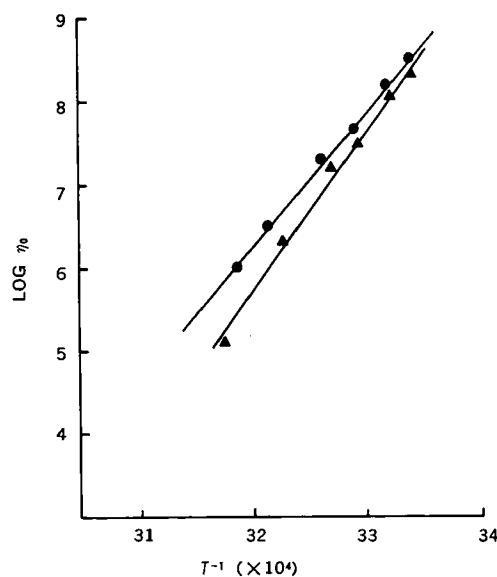Figure 4—Effect of temperature on the creep behavior of wool fat and lanolin. Key: ●, wool fat; ○, lanolin.

Figure 6—Plot of log residual viscosity against the reciprocal of the absolute temperature (Arrhenius plot). Key: ▲, wool fat; ●, lanolin.
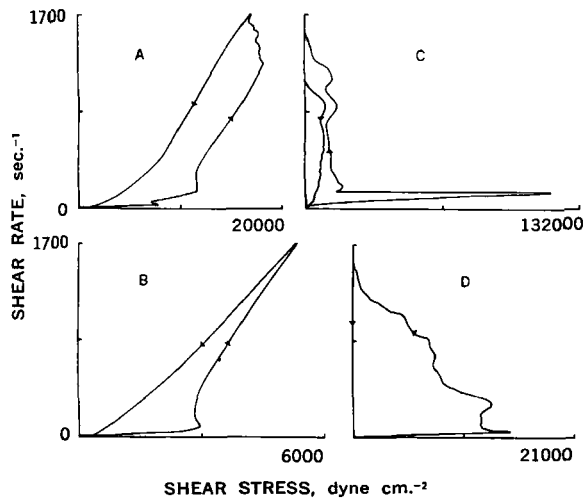
Figure 7—Rheograms of four ointment bases. Key: A, emulsifying; B, wool alcohols; C, simple; D, paraffin. Temperature, 25°; sweep time, 240 sec.

types of curve is not possible and only values for G_0 and η_0 can be obtained.

The change of η_0 and G_0 with temperature is shown in Figs. 11 and 12 for ointment bases (a–e). There is a linear relationship between log G_0, log η_0, and temperature for wool fat and lanolin. Emulsifying ointment has a similar linear relation between log η_0 and temperature but the log G_0 relation is curved. Wool alcohols ointment and paraffin ointment both demonstrate a sudden fall in η_0 and G_0 in the region of 32°.

DISCUSSION

The limitations of testing semisolids with a cone and plate viscometer are clearly shown in the continuous shear experi-
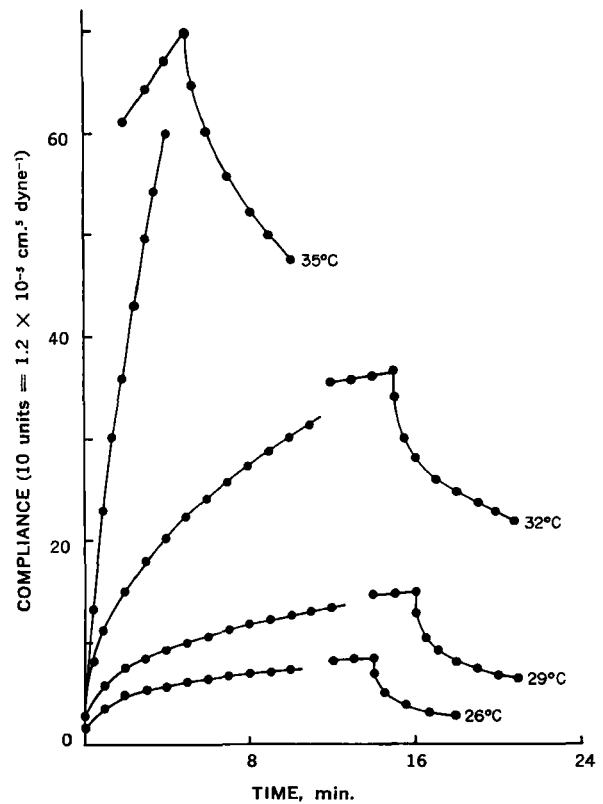

Figure 8—Effect of temperature on the creep behavior of paraffin ointment.

ments (Fig. 7). The majority of the ointment bases demonstrate loss of material from the measuring gap of the instru-

Table II—Viscoelastic Parameters of the Ointment Bases[a]

Temp., °C.	G_0[b]	η_0[c]	τ_2[d]	G_2[e]	η_2[f]	τ_1[g]	G_1[h]	η_1[i]	τ_3[j]	G_3[k]	η_3[l]
				White Soft Paraffin							
26.0	1.37, +7	—	—	—	—	—	—	—	—	—	—
				Wool Fat							
26.0	5.54, +4	2.01, +8	8.46	6.66, +4	3.39, +7	8.35, −1	1.46, +5	7.31, +6	—	—	—
28.5	3.62, +4	1.22, +8	8.51	6.07, +4	3.10, +7	9.18, −1	1.40, +5	7.71, +6	—	—	—
30.2	2.73, +4	3.11, +7	5.23	1.44, +4	4.52, +6	2.21, +1	5.44, +4	7.22, +5	—	—	—
33.0	1.28, +4	1.47, +7	2.02	8.73, +3	1.15, +6	—	—	—	—	—	—
36.0	6.82, +3	2.03, +6	6.66, −1	3.48, +3	1.25, +5	—	—	—	—	—	—
41.0	2.50, +3	1.32, +5	—	—	—	—	—	—	—	—	—
				Lanolin							
26.0	1.45, +5	3.30, +8	8.20	1.83, +5	8.99, +7	8.61, −1	5.15, +5	2.27, +7	1.55, −1	5.72, +5	5.32, +6
28.4	6.02, +4	1.49, +8	11.15	7.12, +4	4.77, +7	1.39	2.44, +5	2.05, +7	2.93, −1	2.46, +5	4.33, +6
31.5	2.82, +4	4.41, +7	12.50	3.50, +4	2.62, +7	1.36	9.38, +4	7.66, +6	2.01, −1	1.44, +5	1.73, +6
34.0	1.32, +4	2.01, +7	19.21	7.13, +3	8.27, +6	1.16	1.98, +4	1.37, +6	2.51, −1	3.75, +4	5.63, +4
37.8	2.26, +3	3.05, +6	11.76	1.98, +3	1.40, +6	9.57, −1	4.29, +3	2.46, +5	6.67, −2	4.88, +3	1.95, +4
41.0	8.73, +2	1.04, +6	7.96	2.39, +2	1.14, +5	1.16	2.15, +2	1.94, +4	—	—	—
				Paraffin Ointment							
25.0	9.70, +5	8.11, +8	12.51	2.50, +5	1.87, +8	9.55, −1	6.08, +5	3.52, +7	4.33, −1	2.59, +6	6.84, +7
26.0	7.02, +4	7.05, +8	14.31	1.40, +5	1.20, +8	1.34	3.98, +8	3.20, +7	3.00, −1	1.04, +6	1.87, +6
28.8	5.22, +5	2.58, +8	11.19	1.51, +5	1.06, +8	1.36	2.06, +5	1.68, +7	2.14, −1	5.35, +5	6.84, +5
31.8	4.37, +5	7.75, +7	9.49	4.32, +4	2.45, +7	1.16	1.04, +5	7.26, +6	1.08, −1	4.38, +5	2.83, +5
35.1	—	8.48, +6	14.82	1.16, +4	1.03, +7	1.21	5.25, +4	3.80, +6	—	—	—
37.5	—	1.82, +6	1.17	5.89, +3	4.06, +5	—	—	—	—	—	—
				Emulsifying Ointment							
26.0	8.02, +5	4.95, +8	10.99	2.42, +5	1.60, +8	9.25, −1	1.63, +6	9.79, +7	2.95, −1	1.31, +6	2.38, +7
32.0	5.23, +5	1.46, +8	9.27	1.38, +5	7.70, +7	8.53, −1	3.45, +5	4.37, +7	3.20, −1	6.57, +7	1.27, +7
44.5	6.70, +4	8.48, +6	10.03	1.68, +4	1.02, +4	8.81, −1	1.74, +5	9.21, +6	—	—	—
49.5	3.45, +3	3.61, +6	1.51	1.07, +3	9.12, +4	—	—	—	—	—	—
				Wool Alcohols Ointment							
26.0	1.06, +5	9.23, +7	19.63	5.26, +4	6.61, +7	1.51	2.38, +5	2.15, +7	4.35, −1	1.75, +5	4.53, +6
28.6	1.07, +5	5.57, +7	14.4	3.59, +4	3.10, +7	1.57	1.66, +5	1.57, +7	5.55, −1	1.12, +5	3.72, +6
30.5	1.09, +4	1.63, +7	?	?	?	?	?	?	?	?	?
32.4	—	5.06, +4	?	?	?	?	?	?	?	?	?
				Simple Ointment							
26.0	9.91, +5	4.91, +8	20.26	1.28, +5	1.56, +8	1.62	1.80, +5	1.75, +7	2.71, −1	3.25, +5	5.67, +6
28.5	7.40, +5	1.98, +8	14.89	2.06, +5	1.84, +8	6.00, −1	3.06, +5	1.10, +7	3.31, −1	6.68, +4	1.33, +6
32.0	1.45, +5	4.18, +6	8.52	6.48, +4	3.18, +7	?	?	?	?	?	?

[a] Numbers greater than 100 or less than 1 are expressed in floating point notation, i.e., 1.37, + 7 = 1.37 × 10^{7}. —, Contribution nil. ?, Poor creep curve, nonlinear behavior. [b] G_0, Modulus of rigidity of uncoupled Hookean spring, dyne cm.$^{-2}$. [c] η_0, Viscosity of uncoupled Newtonian dashpot, poise. [d] τ_2, Long retardation time, min. [e] G_2, Modulus of rigidity of Voigt unit 2, dyne cm.$^{-2}$. [f] η_2, Viscosity of Voigt unit 2, poise. [g] τ_1, Short retardation time, min. [h] G_1, Modulus of rigidity of Voigt unit 1, dyne cm.$^{-2}$. [i] η_1, Viscosity of Voigt unit 1, poise. [j] τ_3, Shortest retardation time, min. [k] G_3, Modulus of rigidity of Voigt unit 3, dyne cm.$^{-2}$. [l] η_3, Viscosity of Voigt unit 3, poise.
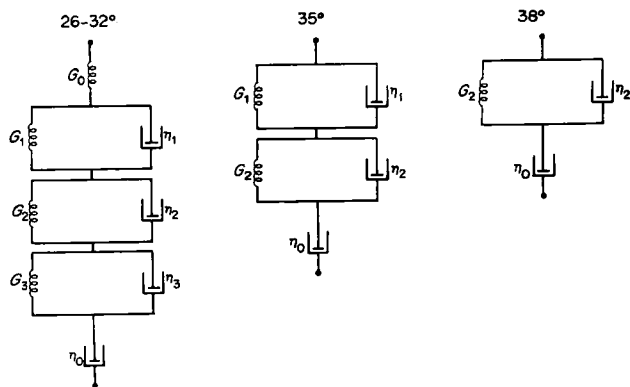
Figure 9—*Model representation for paraffin ointment over the temperature range 26–38°.*

ment. In some cases this is only noticeable at high shear rates but there is no guarantee that the effect is not occurring to a smaller extent at lower shear rates. For two of the systems (c and f), expulsion occurs immediately after the yield point where the shear rate is low. As a result very little quantitative significance can be given to continuous shear experiments on semisolid materials (11).

A viscoelastic liquid in a state of flow will possess elastic energy so that when shear is stopped the liquid recoils due to the release of this energy. When the total energy exceeds a critical value the material will fracture and the shear stress will fall. In an extreme case material will be expelled from the viscometer (22).

The creep results show that all the ointment bases studied, except white soft paraffin, have considerable viscoelastic properties which change, often in a characteristic way, with temperature. At 26° most systems can be represented by an eight-unit model consisting of three Voigt elements. Theoretically a very large number of retardation times could exist, however resolution of retardation times is difficult if their number is greater than ten and the smallest spacing between any two adjacent times is less than five times the value of the smaller retardation time (2).

The absence of viscoelastic behavior below the yield value for white soft paraffin is typical of many lubricating greases. Bogie (24) has reported that soap and synthetic base greases are nonlinear viscoelastic in response over a large range of strain amplitude, frequency, and temperature when tested in oscillatory mode, due to yielding of the grease structure. At very small strain amplitudes the response was mainly elastic (Hookean). In comparison Criddle (25) has concluded that some soap greases are linear viscoelastic in nature. White soft
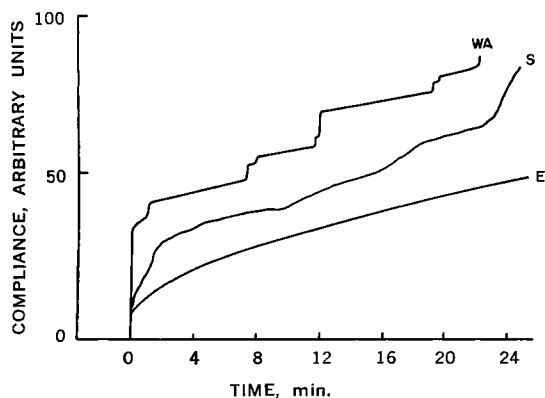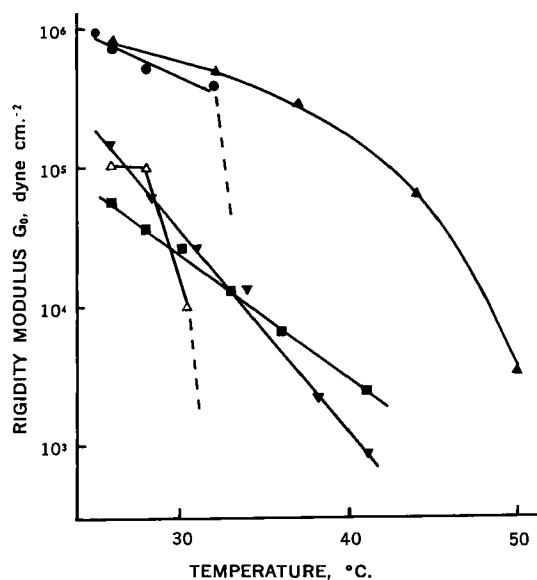

Figure 11—*Variation of rigidity modulus* (G_0) *with temperature. Key:* ▲, *emulsifying ointment;* ●, *paraffin ointment;* △, *wool alcohols ointment;* ■, *wool fat;* ▼, *lanolin.*

paraffin is a two-phase colloidal system of oil and wax (26). The latter is responsible for the crystalline gel nature of the material and this fine crystalline structure is very sensitive to mechanical strain. Schulte and Kassem (4) separated white soft paraffin into n-, iso-, and cyclic paraffin fractions and found that the rheological properties were determined by the ratios of the constituents.

In contrast wool fat and lanolin are highly viscoelastic materials. The presence of 30% water in wool fat increases its viscosity in continuous shear and the magnitude and number of viscoelastic parameters. Lanolin is essentially a water-in-oil emulsion and certain samples of wool fat are able to absorb up to 200% of their weight of water. Lanolin shows less breakdown in structure with temperature than wool fat although it is interesting to note that the value of G_0 is an
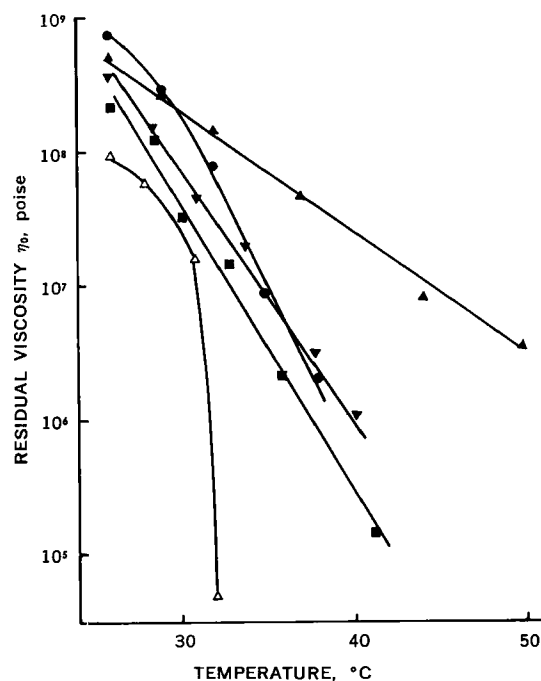

Figure 10—*Creep curves for three ointment bases. Key:* WA, *wool-alcohols ointment, 30.5°, 100 compliance units = 2.15 × 10^{-3} cm.^{2} dyne^{-1};* S, *simple ointment, 32°, 100 compliance units = 1.15 × 10^{-4} cm.^{2} dyne^{-1};* E, *emulsifying ointment, 37°, 100 compliance units = 5.65 × 10^{-5} cm.^{2} dyne^{-1}.*

Figure 12—*Variation of residual viscosity* (η_0) *with temperature. Key:* ▲, *emulsifying ointment;* ●, *paraffin ointment;* △, *wool alcohols ointment;* ■, *wool fat;* ▼, *lanolin.*

exception. Viscoelasticity in materials can be associated with long thread-like molecules that can withstand mechanical strain, e.g., polymer solutions. In some cases chains of molecules can build up to form a viscoelastic network. The structure of wool fat is ill-defined (27) but it is known to be made up of esters of sterols, terpene alcohols, and long-chain aliphatic alcohols. The cholesterol content is 15–20% (28). There has been much discussion as to the emulsifying agents in lanolin/wool fat but it appears that free alcohols are the most important constituent (29–31).

Paraffin ointment, although composed mainly of white soft paraffin and hard paraffin, is viscoelastic. The change of model representation with temperature is different from that of wool fat/lanolin. Mutimer et al. (26) found that the addition of paraffin wax (a completely crystalline material) to a mineral oil resulted in a granular mixture but with no gel structure. The addition of an amorphous wax (e.g., beeswax) led to a thickened and plasticized oil that was a stringy mass, i.e., viscoelastic in nature. A three-dimensional gel structure was postulated in which small crystallites were surrounded by long filaments or fibers that intermeshed to give a sponge-like structure. It is therefore most likely that paraffin ointment obtains its viscoelastic properties from the small quantity of beeswax (and possibly cetyl alcohol) both of which are made up of long-chain alcohols and their esters (32).

The behavior of an emulsifying ointment is similar to that of lanolin in that the Voigt models of shorter retardation time disappear as the temperature rises. This ointment base contains 30% emulsifying wax, a mixture of cetostearyl alcohol, and sodium lauryl sulfate with a small quantity of bound water. It is known that alkyl alcohols and sodium alkyl sulfates can combine to form 1:2 complexes, either when prepared by the melt method or in aqueous solution (33, 34). For the cetyl alcohol, sodium lauryl sulfate, water system, Barry (6) has postulated that threads of frozen liquid crystal form a submicroscopic network to give a gel-like structure which is viscoelastic. It therefore seems probable that even in the oily environment of emulsifying ointment, the alcohol-sulfate complex can give rise to viscoelastic properties.

Wool alcohols ointment and simple ointment are difficult to analyze due to nonlinear effects. These are probably caused by a lack of homogeneity in these materials, due to the presence of small lumps of the higher melting point constituents formed in preparation by uneven cooling of the system. Wool alcohols ointment in particular often has a variable consistency and contains lumps (35). The viscoelastic nature of wool alcohols ointment can be attributed to the wool alcohols, which are similar in nature to the constituents of wool fat, and that of simple ointment to wool fat, and cetostearyl alcohol.

In continuous-shear systems, c–f have yield values, i.e., there appears to be a minimum shear stress below which no flow occurs. However, from the creep results they have a residual viscosity, i.e., any stress however small will cause flow providing the period of observation is long enough, so that the yield values obtained in continuous shear are a function of the method of testing rather than a fundamental property of the material. In Table III the yield values of the oint-

ments are listed with the values of G_0, η_0, and τ_2 obtained from creep. There does not appear to be any correlation between the magnitude of the yield value and the values of G_0 and η_0; however, some correlation is shown between yield value and the retardation time; the greater the retardation time the greater the yield value. It must be remembered though, that when a material reaches its yield point it will be behaving in a nonlinear manner so that correlation between continuous shear and creep must be treated with reserve. Lanolin and wool fat have no yield effect. These materials are the only ones studied that do not contain crystalline material in the form of white soft paraffin or paraffin wax. As mentioned above, yield phenomena can be associated with crystalline materials that are susceptible to mechanical strain.

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Table III—Comparison Between Continuous Shear and Creep, 25 °C.

System	Yield Value, dyne cm.$^{-2}$	G_0 dyne cm.$^{-2}$	η_0, poise	τ_2, min.
Simple ointment	1.18,+5	9.91,+5	4.91,+8	20.26
Paraffin ointment	1.53,+4	7.02,+5	7.05,+8	14.31
Emulsifying ointment	7.62,+3	8.02,+5	4.95,+8	10.99
Wool alcohols ointment	3.01,+3	1.06,+5	9.23,+7	(19.63)
Lanolin	—	1.45,+5	3.30,+8	8.20
Wool fat	—	5.54,+4	2.01,+8	8.46
White soft paraffin	2.0,+3	1.37,+7	∞	∞

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Viscoelastic Properties of Pharmaceutical Semisolids II: Creams

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Abstract ☐ Oil-in-water and water-in-oil pharmaceutical creams have been examined using creep testing. Particular attention has been paid to systems stabilized by long-chain alcohol-surfactant complexes and the effect of temperature on their viscoelastic spectrum. The results show that there is a distinct difference between the behavior of complexes made from ionic and nonionic soaps.

Keyphrases ☐ Viscoelastic properties—creams ☐ Creams—creep testing ☐ Temperature effect—viscoelastic parameters, creams ☐ Ionic, nonionic soap complexes—creams

In the second part of this investigation the viscoelastic properties of some pharmaceutical creams of the B.P. and B.P.C. are investigated. A number of them are made by mixing a molten ointment base with water, *e.g.,* aqueous cream from emulsifying ointment (o/w) and oily cream from wool alcohols ointment (w/o). Creams may be considered as high-volume fraction oil-in-water or water-in-oil emulsions of high viscosity.

Recently much interest has been shown in creams that are stabilized by long-chain alcohol–surfactant complexes which, besides forming a protective film at the oil-water interface, provide a considerable "self-bodying" effect. Continuous-shear studies on such systems have been described by Talman *et al.* (1) and Groves (2), while Barry (3–5) has used creep and continuous-shear methods to investigate the ternary system: sodium lauryl sulfate–cetyl alcohol–water, with and without the addition of oil.

In the present work four pharmaceutical creams and the ternary system described above have been investigated using creep and continuous-shear methods over the temperature range 24–51°. The theory of creep testing and model representation for viscoelastic materials have been discussed in Part I(6). The limitations of continuous-shear methods for semisolids have previously been dealt with fully by Davis *et al.* (7).

EXPERIMENTAL

Materials—The creams were commercial samples of B.P. and B.P.C. formulations. Details are given in Table I. The ternary System R8 was prepared using the materials and method of Barry and Shotton (3).

Apparatus—Details of creep and continuous-shear apparatus and procedure have been given by Davis (6). During testing the samples were enclosed in a saturated water vapor atmosphere to minimize effects due to evaporation.

RESULTS

The creams were examined in creep over the temperature range 24–54° while continuous-shear rheograms were obtained at 25° only. All the systems studied were viscoelastic in nature. The creep curves were analyzed as before (8) and the viscoelastic parameters at the different temperatures are given in Table II.

(a) **Oily Cream**—In continuous shear the rheogram for oily cream (Fig. 1) demonstrates a yield value and a hysteresis loop and there is no evidence of expulsion of material from the measuring surfaces of the viscometer (7). The curve, however, is unusual in that the up curve lies to the left of the down curve implying some kind of dilatant behavior. Creep studies show (Table II) that there is a progressive fall in viscoelastic parameters over the temperature range 26–45°. At
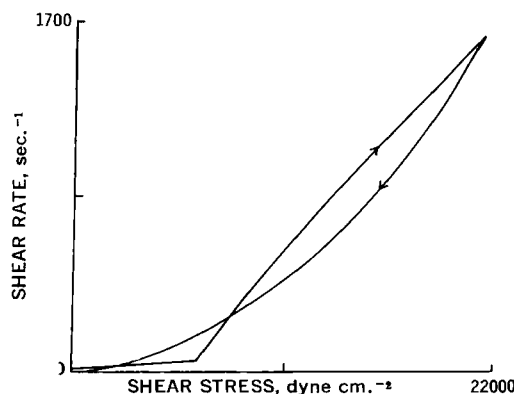
Figure 1—*Rheogram for oily cream. Temperature, 25°C.; sweep time, 240 sec.*