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## Rheological and Sensory Evaluation of Work Softening and Recovery of Pharmaceutical White Soft Paraffins

B. W. BARRY and A. J. GRACE

**Abstract** □ Continuous shear and creep viscometry were used to investigate the effect of work softening and recovery on the rheological properties of four grades of white soft paraffin BP. In continuous shear, using a cone and plate viscometer, the apparent viscosities of two samples increased with recovery time after working, which indicated partial structural recovery. Apparent viscosities of unworked samples were generally lower than those of the worked samples due to elastic recovery and/or sample fracture of the unworked samples during shear in the viscometer. Viscoelastic results were analyzed to obtain initial elastic compliances and residual viscosities. These data indicated that the loss of consistency during working and recovery after working were mainly viscous phenomena. Continuous spectra of retardation times derived for worked and unworked soft paraffins showed that working caused little irreversible structural breakdown. Structural recovery, indicated by concentrations of retardation mechanisms in the continuous spectra, occurred for at least 240 hr. after work softening. A sensory evaluation of white soft paraffin in different states of working was correlated with discrete viscoelastic parameters and continuous shear yield stresses of the material; no correlation was found with continuous shear apparent viscosity data.

**Keyphrases** □ White soft paraffin, rheology—work softening and recovery effects □ Rheological properties, white soft paraffin—continuous shear and creep viscometry □ Viscometry, continuous shear, creep—white soft paraffin rheology □ IR spectrophotometry—structure, work softening of soft paraffins

White soft paraffin BP, which is used as an excipient in many pharmaceutical and cosmetic ointments, consists of a three-dimensional crystalline matrix embedded in a colloidal gel of liquid and amorphous hydrocarbons (1). When the material shears, whether during manu-

facture, viscometry, or in application to the skin, the structure is broken down by rupture of bonds within the material and the consistency decreases as the material work softens. Few experiments have been reported concerning the effect of work softening on the rheological properties of white soft paraffin. Haighton (2) and Shama and Sherman (3) investigated work softening of margarine and butter, which are similar in consistency to white soft paraffin. Tsagareishvili *et al.* (4) reported that work softening of soft paraffin caused up to 90% breakdown of bonds within the material, that it reduced the viscosity, and that the cycloparaffin content, measured by IR spectroscopy, increased.

In manufacturing processes involving cold working of materials containing significant amounts of white soft paraffin, the final product will not have its maximum possible structure because of the working procedure. The product consistency will vary, depending on: (a) the initial structural condition of the material, for example, melted and cooled or worked when cold; (b) the degree of work softening; (c) the type or grade of material; and (d) the age of the finished product. The first two variables are, to some extent, under the control of the manufacturer. The effect of grade variation on the rheological properties of unworked white soft paraffin has been investigated by continuous shear and creep viscometry (5). The present study investigated the effect of work softening and recovery on the rheological properties of four grades of white soft paraffin (factors c and d).

## EXPERIMENTAL

**Materials**—Four grades of white soft paraffin of BP quality were used<sup>1</sup>. For previous work on these samples, see Barry and Grace (5, 6).

**Procedure**—The white soft paraffins were worked in the standard manner using a grease worker (7). This consisted of one double stroke per second for 1 min. at approximately 25°, in a cup 6.35 cm. deep and 7.60 cm. in diameter, using a perforated plate 7.45 cm. in diameter containing 51 apertures of diameter 0.635 cm.

A Ferranti-Shirley viscometer with automatic flow curve recorder unit and X-Y plotter was employed for the continuous shear investigation. The viscometer, with medium cone, was used in two test regimes; rates of shear varied linearly from: (a) 0.0 to 1754.0 to 0.0 sec.<sup>-1</sup>, and (b) 0.0 to 175.4 to 0.0 sec.<sup>-1</sup>. Each cycle was 1200-sec. duration at 25 ± 0.1°. Apparent viscosity data were derived by point determinations (8) at 1754.0 and 175.4 sec.<sup>-1</sup>, and shear stresses were derived from the spur points where the slopes of the flow curves became infinite for the first time.

Creep experiments at 25 ± 0.2° were of short duration (1200 sec.) except with unworked samples, because restricted time studies were necessary with work-softened materials due to their rapid rate of recovery. Discrete parameters,  $J_0$  (initial elastic compliance) and  $\eta_0$  (residual viscosity), were derived from each curve. Since the creep curves of worked samples did not reach a steady-state flow condition, an approximate residual viscosity was obtained using the terminal 300 sec. of each curve. Such approximate values are represented in the text by the symbol  $\eta_0'$ .

Continuous spectra of retardation times were determined from each creep curve using the second approximation method of Schwarzl and Staverman (9):

$$L(\tau) \approx \frac{d}{d \ln t} \left[ J(t) - \frac{dJ(t)}{d \ln t} \right] \Big|_{t=2\tau} \quad (\text{Eq. 1})$$

where  $L(\tau)$  is the value of the retardation spectrum and  $J(t)$  is the total compliance at time  $t$ .

IR spectra were determined with a Perkin-Elmer 257 grating spectrophotometer with materials mounted between rock salt plates. Worked white soft paraffin samples were prepared in the grease worker, using one double stroke per second for 300 sec. at approximately 25°.

In the sensory evaluation of worked and unworked white soft paraffin, 12 persons were required to assess samples of soft paraffin by rubbing them into the skin of the back of the hand and ranking the materials in order of ease of rubbing in. A point system was used, 4 points for the easiest and 1 point for the most difficult. The materials were all Sample 1: (a) unworked; (b), (c), and (d), worked and aged 0.5, 24.0, and 240.0 hr., respectively. To avoid the subjects gaining sensory impressions during removal of material from containers, each subject was given 0.2-ml. samples of the materials using a disposable syringe modified so that the sample was not sheared on delivery. The panel members were academic and technical staff of the School of Pharmacy with no previous experience of this type of test; they were given no training in this type of evaluation so that they would react as typical consumers.

## RESULTS

**Continuous Shear**—Table I contains the continuous shear data for worked and unworked white soft paraffins. Samples 3 and 4 in the unworked state were grossly ejected from the cone-plate gap of the viscometer during shearing, and their apparent viscosity data were derived by extrapolation of Arrhenius-type curves (5). Sample 4 was grossly ejected from the viscometer gap after work softening, and apparent viscosity data were not obtained. Apparent viscosity data for Samples 1 and 3 indicated that structural recovery occurred to some degree after working, which is further evidence for partial thixotropic breakdown in white soft paraffin (6). Little recovery of apparent viscosity was detected for Sample 2. The manufacturers stated that this sample was susceptible to shear breakdown (*cf.*, viscoelastic results). Thus, any recovered structure was probably

<sup>1</sup> Sample 1 was produced by Printer Industries; Samples 2, 3, and 4 were, respectively, grades 892/2/148, 783/L, and 783/L/40A produced by Dalton & Co. Ltd.

**Table I**—Continuous Shear Data for White Soft Paraffins at 25°<sup>a</sup>

Sample	Recovery Time after Working, hr.	—0.0–1754.0 sec. <sup>-1</sup> —		—0.0–175.4 sec. <sup>-1</sup> —	
		$\eta'$ , poise	$\sigma$ , dyne cm. <sup>-2</sup>	$\eta'$ , poise	$\sigma$ , dyne cm. <sup>-2</sup>
1	0.5	10.0	5550	28.9	2150
	24.0	10.2	5600	28.4	2700
	120.0	10.6	5750	29.9	3400
	Unworked	10.2	7700	61.1	5100
2	0.5	1.9	1250	8.5	700
	24.0	2.0	1500	8.4	750
	Unworked	1.2	3550	6.5	2600
3	0.5	6.3	3000	19.0	1550
	24.0	7.5	3800	20.9	1850
	Unworked	6.8	3350	12.1	2600
4	0.5	—	1850	—	1750
	24.0	—	2150	—	2600
	Unworked	6.2	4500	19.0	2800

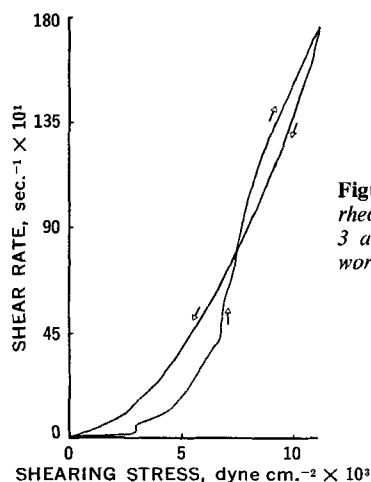
<sup>a</sup> Apparent viscosity,  $\eta'$ , and yield stress,  $\sigma$ , determined as stated in the Experimental section. Unworked apparent viscosity data for Samples 3 and 4 were determined by extrapolation of Arrhenius-type curves of  $\eta'$  versus  $1/T^\circ\text{K}$ .

destroyed during development of the upcurve in viscometry. The yield stresses of each sample increased with age after working.

The apparent viscosities of unworked samples at 1754.0 and 175.4 sec.<sup>-1</sup> were often lower than those of the worked samples after 24 hr. recovery, although the yield stresses were greater. The flow curves obtained for Sample 3 were complex, as shown in Fig. 1, and indicated that some shear thickening may occur at high rates of shear, which correlates with the low ductility of this sample (5).

**Discrete Viscoelastic Parameters**—Figure 2 indicates the changes that occurred in the viscoelastic properties of Sample 1 with aging after work softening. A plot of total compliance [ $J(t)$ ] at 1200 sec. after onset of stress against recovery time was linear on double logarithmic axes. Discrete viscoelastic parameters derived from the creep curves are given in Table II. The decrease in consistency after working was shown by an increase in total compliance. The largest relative initial compliance,  $J_{rel}(\infty/0.5)$ , after working occurred in Sample 2;  $J_{rel}(0.5/\infty)$  is defined as  $J_0$  at 0.5 hr. after working/ $J_0$  of the unworked sample (Table III). The largest relative residual viscosity,  $\eta_{rel}'(\infty/0.5)$  (defined as  $\eta_0$  of the unworked sample/ $\eta_0'$  at 0.5 hr. after working) occurred in Sample 3. Recovery of  $J_0$  and  $\eta_0'$  after working is shown in Table III, using relative parameters similar to those above but defined as  $J_0$  for sample aged 0.5 hr./ $J_0$  for sample aged 24.0 hr. [ $J_{rel}(0.5/24.0)$ ], and  $\eta_0'$  for sample aged 24.0 hr./ $\eta_0'$  for sample aged 0.5 hr. [ $\eta_{rel}'(24.0/0.5)$ ]. The relative recovery of  $J_0$  and  $\eta_0'$  was greatest for Sample 2; the other samples were similar. The increase in  $\eta_0'$  with recovery time after working was linear when plotted on double logarithmic axes, but no simple relationship was found for recovery of  $J_0$ . Sample 4, which was nonlinear viscoelastic in the unworked state (5), was still nonlinear after working.

**Continuous Retardation Spectra**—The continuous retardation spectra for worked and unworked white soft paraffins are shown in Figs. 3 and 4. Unworked Samples 2 and 3 had bimodal retardation



**Figure 1**—Continuous shear rheogram for worked Sample 3 at 25 ± 0.1°, 0.5 hr. after working.

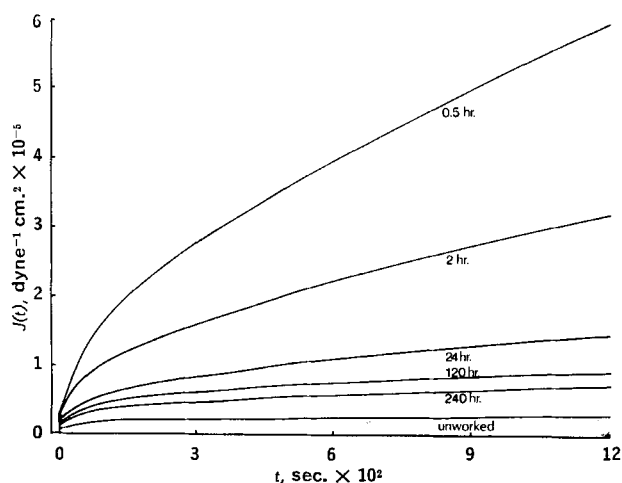
**Table II—Discrete Viscoelastic Data for Worked and Unworked White Soft Paraffins at 25°<sup>a</sup>**

Sample	Recovery Time after Working, hr.	$J_0$ , dyne <sup>-1</sup> cm. <sup>2</sup> × 10 <sup>-7</sup>	$\eta_0'$ , poise × 10 <sup>7</sup>
1	0.5	28.7	3.4
	2.0	20.9	7.5
	6.0	18.6	8.1
	24.0	16.4	19.8
	72.0	16.3	22.0
	120.0	14.7	43.4
	240.0	8.4	50.6
	Unworked	7.6	246.0
2	0.5	51.9	4.1
	2.0	43.5	6.5
	6.0	29.9	13.5
	24.0	9.5	40.9
	Unworked	4.3	315.0
3	0.5	28.5	3.4
	2.0	16.4	6.2
	6.0	13.3	10.6
	24.0	12.5	19.9
	Unworked	3.5	2780.0
4	0.5	16.2	1.0
	2.0	12.9	1.7
	6.0	11.7	2.5
	24.0	9.6	5.9
	Unworked	3.5	104.0

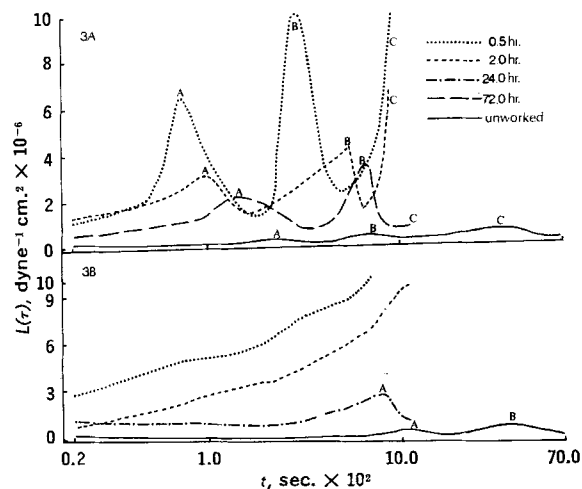
<sup>a</sup> Sample 4 (nonlinear viscoelastic): unworked, creep shearing stress, 120 dynes cm.<sup>-2</sup>; and worked, creep shearing stress, 15 dynes cm.<sup>-2</sup>.

spectra, while the curves for unworked Samples 1 and 4 contained three maxima. In general, the largest peak was broad and occurred at large values of  $t$  (2000–4000 sec.). The retardation spectrum curves for the worked samples decreased in height with recovery time after working and, with one exception, the peaks moved to larger values of  $t$ . Worked Samples 1 and 4 exhibited three maxima in their retardation spectra. Only part of the terminal peak, C, at large values of  $t$  was determined due to the restricted time of the creep tests (see *Experimental* section). The movement of the maxima to larger values of  $t$  with recovery time after working may be seen easily (e.g., Fig. 3A).

Sample 2 was exceptional because the retardation distribution of the worked material did not initially show any distinct maxima but sloped up toward one general peak at large values of  $t$ . After 24.0 hr. recovery, a single peak appeared in the spectrum which was correlated with a peak in the unworked sample spectrum. Work-softened Sample 3 had three maxima in its retardation spectra compared to two in the spectrum of the unworked sample. Two maxima, B and C, of the worked Sample 3 behaved normally since they decreased in height and moved to larger values of  $t$  as the recovery time



**Figure 2—Creep compliance curves, indicating changes in the viscoelastic behavior at 25 ± 0.2°, of white soft paraffin Sample 1 with working. Aging time after working is shown in the figure.**



**Figure 3—Continuous spectra of retardation times,  $L(t)$ , for worked and unworked white soft paraffins. Key: A, Sample 1; and B, Sample 2. Aging time after working is shown in the figure.**

increased. Peak A decreased in height with recovery but moved to smaller values of  $t$  as the material aged after work softening. Peak B was not resolved by analysis for the 0.5-hr. sample, but its presence was indicated by the shoulder on peak C.

**IR Spectroscopy**—No significant differences were found between IR absorption spectra for unworked and heavily worked white soft paraffins.

**Sensory Investigation**—The mean panel score derived in the sensory evaluation of Sample 1 in various states of work softening gave a linear plot against  $\eta_0'$  data using semilogarithmic axes (Fig. 5). A similar linear relationship was found with  $J_0$ , but the data were more scattered. When the test was repeated using fresh samples, the slopes of the linear plots differed by 9 and 3%, respectively, for  $\eta_0'$  and  $J_0$ . A linear relationship was found between the logarithms of the yield stresses determined in continuous shear and the sensory data (Fig. 6). No correlation was found between the sensory data and the apparent viscosities of the materials used (apparent viscosities determined at various rates of shear from less than 30 to 1754 sec.<sup>-1</sup>). The linearity of the single logarithmic graphs is in accord with the Weber-Fechner equation described by Scott Blair (10).

## DISCUSSION

The continuous shear viscosity data derived concerning the effect of work softening and recovery of white soft paraffin were of limited practical use; changes which were determined were generally small. An increase in apparent viscosity with age after work softening occurred for Samples 1 and 3. Barry and Grace (6) previously

**Table III—Relative Compliance and Relative Viscosity Data for White Soft Paraffins<sup>a</sup>**

Sample	Worked		Recovered	
	$\frac{J_{rel}(0.5)}{(\infty)}$	$\frac{\eta_{rel}'(\infty)}{(0.5)}$	$\frac{J_{rel}(0.5)}{(24.0)}$	$\frac{\eta_{rel}'(24.0)}{(0.5)}$
1	3.8	72.3	1.7	5.8
2	12.0	76.8	5.5	10.0
3	8.1	817.0	2.3	5.8
4	4.6	104.0	1.7	5.9

<sup>a</sup> Derived from Table II, where:

$$J_{rel}\left(\frac{0.5}{\infty}\right) = \frac{J_0(0.5 \text{ hr.})}{J_0(\text{unworked})}$$

$$\eta_{rel}'\left(\frac{\infty}{0.5}\right) = \frac{\eta_0'(\text{unworked})}{\eta_0'(0.5 \text{ hr.})}$$

$$J_{rel}\left(\frac{0.5}{24.0}\right) = \frac{J_0(0.5 \text{ hr.})}{J_0(24.0 \text{ hr.})}$$

$$\eta_{rel}'\left(\frac{24.0}{0.5}\right) = \frac{\eta_0'(24.0 \text{ hr.})}{\eta_0'(0.5 \text{ hr.})}$$

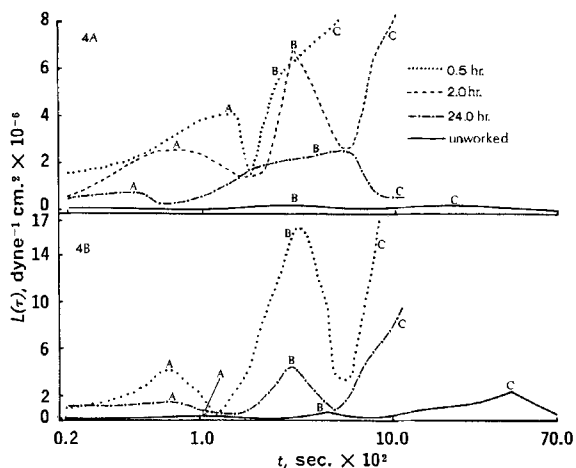


Figure 4—Continuous spectra of retardation times,  $L(\tau)$ , for worked and unworked white soft paraffins. Key: A, Sample 3; and B, Sample 4. Aging time after working is shown in the figure.

reported that Sample 1 may undergo partial thixotropic breakdown during shear. The manufacturer states that Sample 2 is susceptible to shear breakdown, a fact confirmed by the small strain experiments, which also indicated that Sample 2 recovered considerably with time after working. The lack of measured recovery detected using continuous shear viscometry was probably due to breakdown of any recovered structure during development of the upcurve of the rheogram. This indicates that continuous shear rheological testing is too drastic a technique for materials containing labile structures.

The continuous shear viscometry data (Table I) seem to indicate that work-softened materials aged 24 hr. often increased in apparent viscosity when compared with unworked samples. This anomalous result is probably in part an instrument artifact and may be explained by: (a) elastic recovery or fracture of the sample during shear, causing ejection of sample from the cone-plate gap of the viscometer; or (b) fracture of the material in the sample gap of the viscometer during shear but with no visible ejection of the material from the cone-plate gap; or (c) fracture of the adhesive forces between the sample and the viscometer elements leading to slippage (11–13). For example, gross expulsion of sample occurred during viscometry of unworked white soft paraffins 3 and 4, and apparent viscosities were derived indirectly. No noticeable expulsion of material occurred for unworked Samples 1 and 2, but it is possible that the samples fractured in the viscometer gap during shear and/or a small amount of each sample was ejected from the gap. Loss or fracture of the samples during shear in the viscometer would reduce the measured torque and, hence, the derived apparent viscosities at any given rate of shear. Apparent viscosity data derived would thus be lower than their correct values. Work-softened materials with lower elastic moduli would not be expelled or fractured to the same extent, and derived data would be nearer to the correct apparent viscosity values. Using this theory, it is apparent that a degree of fracture and/or sample ejection may have occurred with Samples 1 and 2, although there was no indication of the phenomena in the rheograms obtained or at the cone-plate gap. Preliminary experiments showed that a concentric cylinder viscometer (Rotovisko) could not be used because the initial shear stress often exceeded the capacity of the torque scale and sample cleavage occurred at higher rates of shear. This situation clearly indicates one disadvantage of continuous shear viscometry of viscoelastic semisolid materials.

In general, the yield stresses obtained in continuous shear were lower after work softening than in the unworked state, even after recovery. This indicates that sample ejection from the viscometer gap or fracture within the gap occurs after formation of the spur point in the rheogram. It is thus possible that yield stresses derived from spur points may be utilized in quality control procedures, especially if they can be correlated with other parameters such as sensory data (Fig. 6) or viscoelastic retardation times (5, 12).

The discrete viscoelastic parameters derived from the creep curves (Table II) were mainly of qualitative value, although correlations were found with sensory data. The elastic properties of Sample 2 were the most affected by working, in agreement with the manufacturer's data, but this sample also recovered to a greater extent, or

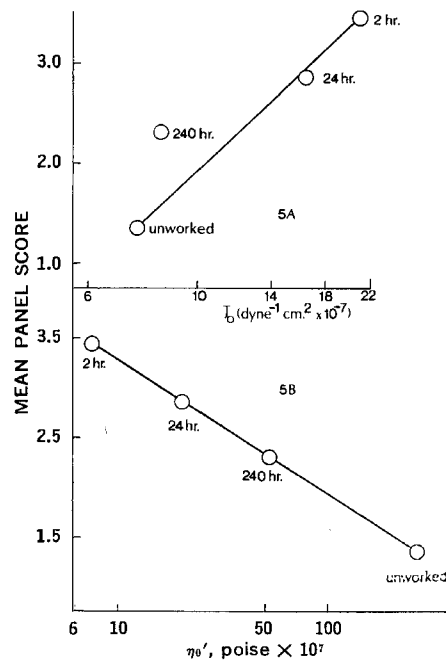


Figure 5—Correlation of sensory assessment test data with discrete viscoelastic data; mean panel score versus: A, logarithmic initial elastic compliance,  $J_0$ ; and B, logarithmic residual viscosity,  $\eta_0'$ . Aging time after working is shown in the figure.

at a faster rate, within 24 hr. than the other materials. Thus, worked and unworked penetration tests (7) may yield misleading data since the official method does not include penetration after recovery. Sample 4, which was nonlinear viscoelastic before working (5), was still nonlinear viscoelastic after working because the material work hardened in creep. This correlates with the short fiber length of the material (5). The comparison of worked and unworked Sample 4 is complicated; the materials were sheared at different stresses, because the compliance of the unworked sample was too small to be measured at the lower shearing stress employed for the worked sample. The parameters quoted for this nonlinear viscoelastic sample are thus specific for the shearing stresses given in Table II.

The relative residual viscosity data are not fundamental because the method used to derive  $\eta_0'$  was an approximation. The accuracy of the approximation depended on the degree of work softening, that is, on how near to a steady state of flow the material was be-

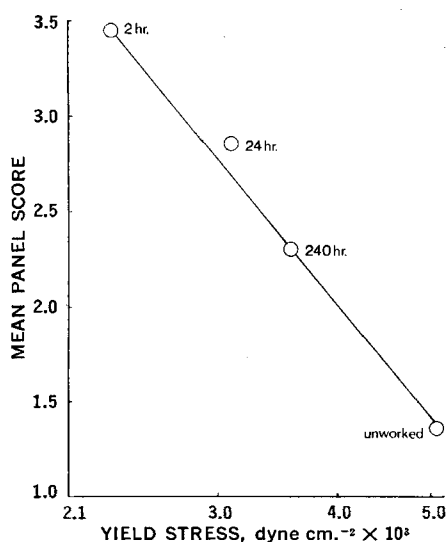


Figure 6—Correlation of sensory assessment test data with the logarithm of yield stresses determined in continuous shear viscometry using shear rate regime (b). Aging time after working is shown in the figure.

tween 900 and 1200 sec. after the onset of stress, since the part of the curve obtained during this time interval was used in the determination of  $\eta_0'$ . The large variation between relative residual viscosities after working,  $\eta_{rel}' (\infty/0.5)$ , may thus correctly represent material variations or be due to varying degrees of approximation in the determination of  $\eta_0'$ . The similar values obtained, except for Sample 2, for the relative residual viscosity on recovery,  $\eta_{rel}' (24.0/0.5)$  (Table III), indicated that variation in the degree of approximation between worked samples was small. Comparison of residual viscosity data for worked and unworked samples of white soft paraffins is not as useful as comparing the recovery data.

The continuous retardation spectrum,  $L$ , is defined by Eq. 2 (14, 15):

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

where  $J(t)$  is total compliance at time  $t$ ,  $J_0$  is the initial elastic compliance,  $\eta_0$  is the residual Newtonian viscosity, and  $\tau$  is a retardation time. Although  $L$  has the dimensions of a compliance, it is in the nature of a distribution function of retardation times. Maxima in the distribution indicate concentrations of retardation processes (time-dependent reversible strain mechanisms at molecular level) measured by their contribution to compliance.

The three maxima in the retardation spectra of Samples 1 and 4 probably represent similar retardation mechanisms; indeed, the terminal peak,  $C$ , at large values of  $t$  is common to each sample, which indicates that they have at least one type of retardation mechanism of a similar nature. The three maxima in work-softened Samples 1 and 4 (Figs. 3A and 4B) relate to those in the unworked samples since they approach to the size and position of the maxima of the unworked samples with recovery time after working. It is possible that the maxima represent three distinct types of molecular interactions or retardation processes within the materials which are removed from an equilibrium state by the working process. This leads to an increase in the elastic compliance, indicated by the height of the curves, and an increase in the rate at which strain occurs, indicated by the shifting of the maxima to smaller values of  $t$ . The gradual recovery to an equilibrium state (which is not necessarily identical with the former state, as primary bonds may have been irreversibly ruptured during working) begins immediately after working ceases. The actual molecular retardation mechanisms are not known; however, the recovery of the samples indicates that the majority of work softening was due to reversible rupture of weak secondary bonds. An almost infinite array of such bond strengths is possible within white soft paraffin because the strength of the bonds depends on particle size and shape (16), the distance between particles, and the medium separating them (17).

Examples of the types of major interactions which could cause the three maxima in the retardation spectra of Samples 1 and 4 are given here. The examples are hypothetical since there is no direct evidence to suggest that the interactions cited contribute to the viscoelastic properties of white soft paraffin. Three types of material compose white soft paraffin: crystalline, liquid, and amorphous. Assuming that the liquid hydrocarbons do not contribute significantly to the elastic properties of the soft paraffin, that is, their contribution is mainly viscous, three major types of interaction may occur: (a) crystal-crystal, (b) amorphous-amorphous, and (c) crystal-amorphous. Within each group of interactions, there would be variation in bond strengths due to the factors mentioned previously. Crystal-crystal cohesive bonds, formed during cooling of a molten white soft paraffin by the crystals growing together, are examples of bonds that may rupture irreversibly during shear in a working procedure. It may prove possible in future work to alter the ratio of crystalline to amorphous material and thus deduce the contribution of the two forms to the bulk rheological properties.

The distribution of retardation times of worked Sample 2 provided a relatively smooth curve, with no distinct maxima formed until after 24 hr. recovery (Fig. 3B). Since this sample was susceptible to shear breakdown, it is probable that working altered the internal structure to such a degree that the retardation processes producing peaks in the spectra of the unworked sample were entirely disrupted. The retardation spectra thus became very broad distributions in which no distinct maxima appeared until the material aged sufficiently to reconstitute structures that caused concentrations of retardation mechanisms.

Peak  $A$  in the spectra of worked Sample 3 was anomalous in that it was not present in the spectrum of the unworked sample and moved to smaller values of  $t$  as the sample recovered after working. It is possible that a labile structure was imposed upon the natural structure of the material by the working process; a similar phenomenon was reported previously (5). Movement of the peak to shorter time intervals indicated that the structure causing it gradually decayed with age after work softening.

It was reported that mechanical treatment of white soft paraffin in a viscosimeter increased the content of cycloparaffins, as detected by IR spectroscopic analysis (4). The same authors also reported up to 95% breakdown of internal bonds among hydrocarbon molecules, which caused changes in the rheological properties of their materials. However, in the present work, the IR absorption spectra for worked and unworked white soft paraffins showed that no changes occurred during working that were detectable spectrophotometrically.

In the sensory evaluation of consistency, the simple test used correlated rheological data with sensory data (Figs. 5 and 6), indicating that the changes in consistency of Sample 1 caused by working and subsequent aging may be detected by the consumer. The material used in this test was selected because it was *not* the most affected by working and recovery; it is probable that a consumer could detect differences in other samples with equal or greater facility. Panel members were asked to rank the samples in order, using a specific test; they were not indicating a preference for a material of a given consistency. The work is of significance for manufacturers of semisolid pharmaceutical and cosmetic ointments and creams whose production involves a cold-working procedure. Katz (18) showed that consumers are unable to differentiate between elasticity and viscosity in semisolid materials but tend to measure the *ratio* of these properties. The product of an elastic compliance (inverse of an elastic modulus) and its associated viscosity is a retardation time. Therefore, it is possible that continuous retardation spectra may be useful in textural studies of semisolid viscoelastic materials where the test panel is required to evaluate products in order of preference rather than to use a simple ranking test as in this work.

The loss of consistency of white soft paraffin on working and subsequent recovery were not easily or clearly determined using continuous shear viscosity data derived by cone and plate viscometry, a method frequently employed as a routine testing procedure. However, yield stresses determined from the spur points in the continuous shear rheograms did indicate such changes, as did the viscoelastic data, and these parameters were correlated with the sensory test data (Figs. 5 and 6). The cause and significance of yield stresses are not fully known. Davis (12) and Barry and Grace (5) correlated yield stresses with retardation times determined in creep; a linear relationship was found between yield stress and temperature (6). Yield stresses are a function of some property of the test material and not simply an instrumental artifact (6). A yield stress probably represents the maximum stress that a test material may support before gross structural deformation occurs, and the spur points from which yield stresses are derived form at low rates of shear. It is thus apparent that, for the materials used here, low shear rate data are more valuable for correlation with sensory data than are high shear rate data. Continuous shear techniques at relatively high shear rates are often assumed to be more valuable than small strain experiments in textural tests, because the shearing conditions are reported to approximate closely to consumer usage (19, 20). However, the present work indicates that this correlation is not necessarily valid. The rate of shear attained during application of a material to the skin depends inversely on the consistency of the material. Thus, low shear rate studies are necessary for correlation with sensory evaluations of preparations of high consistency. For example, recent data on sensory testing of semisolid creams (21, 22) indicated that the sensory determination of consistency was best correlated with instrumental data using the initial shear stress (a parameter derived with viscometers limited to discontinuous shear rate variation and which is equivalent to a yield stress).

## SUMMARY AND CONCLUSIONS

The consistency of four grades of white soft paraffin was reduced by working and increased on aging after working. Apparent viscosity data derived in continuous shear using a cone and plate viscometer were not suitable for following such changes, partly due

to the phenomena of sample fracture and/or sample expulsion from the cone-plate gap of the viscometer. Continuous shear yield stresses, which are formed at low rates of shear, did indicate the breakdown of structure within soft paraffin caused by working and the subsequent structural recovery with time.

Significant structural-rheological changes were found after working by utilizing small strain viscometry. Discrete viscoelastic parameters,  $J_0$  and  $\eta_0'$ , were used to describe the changes in consistency of the materials and to determine whether these changes were due mainly to elastic or viscous processes. These parameters were not useful for studying changes in structure at a molecular level, but they were correlated with sensory parameters for one grade of white soft paraffin. Continuous spectra of retardation times, which are more fundamental viscoelastic functions, indicated changes that occurred in the molecular retardation processes. The advantage of continuous spectra is that they may be derived from creep curves which have not attained a steady state of flow; they may also be used as an approximate measure of the viscoelastic behavior of nonlinear viscoelastic materials. To obtain a full discrete spectrum analysis, using, for example, the method of Warburton and Barry (23), the creep curve must attain a steady state of flow, which may take up to 4 hr. for white soft paraffin under certain conditions. In systems that are changing rapidly with time, it is thus not feasible to use full discrete spectra to characterize their rheological properties.

The investigation has shown that manufacturers of semisolid materials could standardize the structural state of their products more effectively using viscoelastic techniques rather than continuous shear viscometry; thus, they could control more closely the rheological and sensory properties of their products. An alternative method for determination of viscoelastic properties of creams, ointments, pastes, and other semisolids using penetration testing has been suggested (24). The combination of viscoelastic and textural studies may be valuable for determining rheological properties of semisolids which will ensure maximum consumer acceptance of a product.

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