

Controlled Stress Rheometry as a Tool to Measure Grease Structure and Yield at Various Temperatures

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Greases are important lubricating systems that are very interesting to a rheologist since they often exhibit strongly time-dependent behavior [thixotropy], and are able to shear thin by several orders of magnitude in terms of their viscosity. This shear thinning is of course vital if they are to function as lubricants, and keep moving surfaces apart from each other, even at high relative velocities. Traditionally greases are measured in terms of base oil viscosity, pumpability [Lincoln Ventmeter] and via a penetrometer [amongst other tests!]. These test types all provide a single number or data point that is indirectly related to viscosity. Multiple data points can be obtained under varying circumstances of say temperature or in that an unworked sample is compared with a worked sample, but too often the results form only a relative measure of the grease. In an ideal situation, a profile of data points should be obtained for any given sample, showing its absolute response to stress at a variety of relevant temperatures. Controlled stress rheometry can fill this need by subjecting a small sample of grease to a defined stress field. In this paper, two groups of four related greases are studied to obtain viscosity data and viscoelastic information.

Gow¹ presented a useful review comparing penetration data on greases of a wide range of NLGI grades to controlled rate viscometry, controlled stress viscometry and stress relaxation data. The thixotropic nature of greases gives an investigator a "moving goalpost" problem if the viscoelastic structure or the viscosity is to be measured, in that the results obtained will be profoundly influenced by the sample's shear history. The method of sample loading into a cone and plate or parallel plate measuring system can affect the results obtained, and the time constants associated with certain greases may mean that minutes or hours have to pass before the "at rest" structure is regained. It is important therefore to minimize variation in this shear history of the sample prior to measurement.

The maximum resistance to flow [viscosity] of a sample at a given temperature, will be encountered after it is allowed to rest and thixotropic effects have time to build the maximum gel structure. An investigation of the at rest structure can give the "apparent yield stress"². This is of great importance, as it determines whether a material will pump successfully. The Lincoln Ventmeter can be used to determine pressure-flow relationships in a tube [or pipe] but again the results can be affected by the amount of time an operator is prepared to wait. Gow¹ presented stress relaxation data that monitored the decline in relaxation modulus [or less precisely "structure"] with time. The problem with a stress relaxation test is that the acquired data [stress] is by definition dropping steadily into the noise as the test proceeds. Controlled stress rheometry with its step change test equivalent, the creep test, is better suited to long timescale experiments since the strain data grows with time until steady state is reached, whereupon the test may be stopped.

The steady state condition is defined as the slope of the output strain or compliance [strain/stress] line reaching a constant value. This gradient is used to directly calculate the viscosity and the shear rate at which it is measured *Figure 1*.

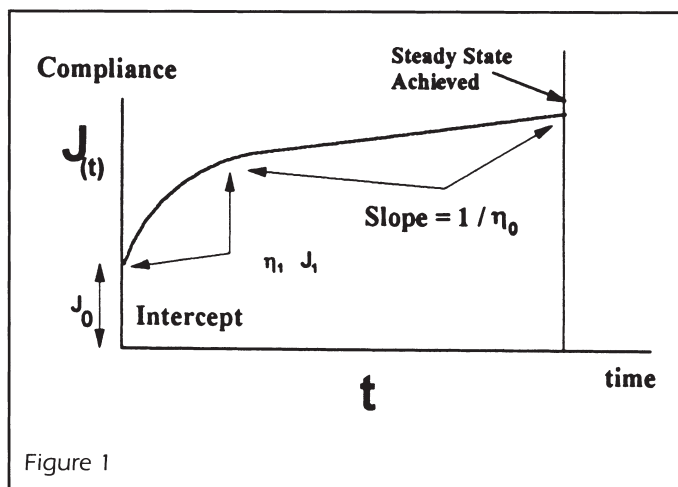


Figure 1

By automating this technique and using software parameters to define when steady state is attained at a particular stress, a series of equilibrium viscosity data points can be measured at very low to medium shear rates [10^{-7} - 0.1 s^{-1}]. This technique is sometimes referred to as equilibrium flow, and can be employed to great effect in order to generate flow curves that reveal when “yield” occurs. This technique has the added attraction that it evades the problems of thixotropy, by allowing the sample to fully accommodate a particular stress prior to moving forward.

In this study two sets of greases are evaluated using a controlled stress, rotational rheometer, both at ambient and sub-ambient temperatures. Viscoelastic data from dynamic tests is shown, along with equilibrium flow data.

Methods and Materials

Two sets of commercial greases were evaluated. The first set of four [A - D] were either production or experimental greases formulated for the aerospace market. The second set [P - S] were general purpose greases for heavy equipment in a variety of industrial settings. Where possible the grades [NLGI] or specifications of ASTM tests are included for reference.

The controlled stress rheometer used [TA Instruments CSL² 500] is a high torque instrument using a drag cup motor capable of applying 500 g.cm or 50,000 micro N.m. Displacement sensing is achieved via an optical encoder system with a resolution of 2.5 microradians, and all tests are performed through a WindowsTM software system. Gap setting between the rotor [cone or plate] and the stator [plate] is controlled via the software using a motor and gear system coupled to a precision micrometer. Coarse position control is via a pneumatic ram that has a fixed travel distance, and moves the lower platen into close proximity to the upper platen. Software options allow the gap set motor to compensate for expansion/contraction in temperature ramps, and apply slow closure routines to minimize structure damage during loading of the sample. This can reduce the recovery time required before measurements start. The appendix describes the principles of operation in some detail for the interested reader. The rheometer can operate as a controlled strain device via a feedback loop system, this can be useful for controlling strain amplitude in oscillation and emulating a shear rate in flow.

Figure 2 shows a schematic of the rheometer including its major components: drive system, temperature control system, displacement sensor etc.

The geometries used in the measurements were either cone and plate or parallel plate [for oscillation]

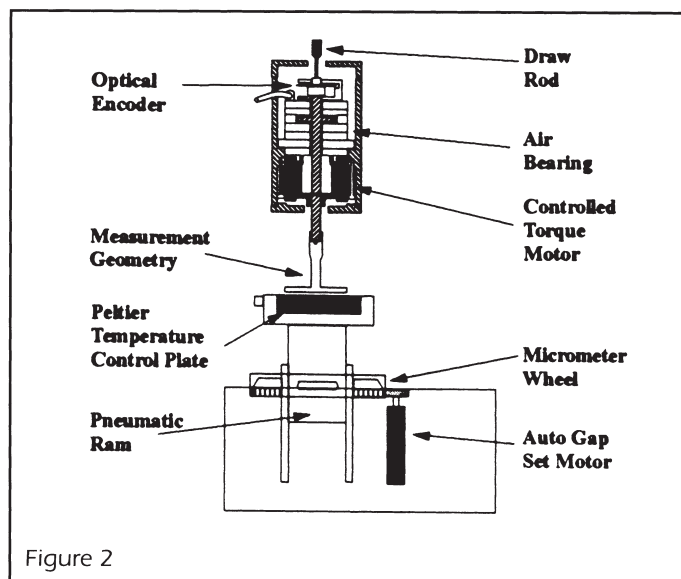


Figure 2

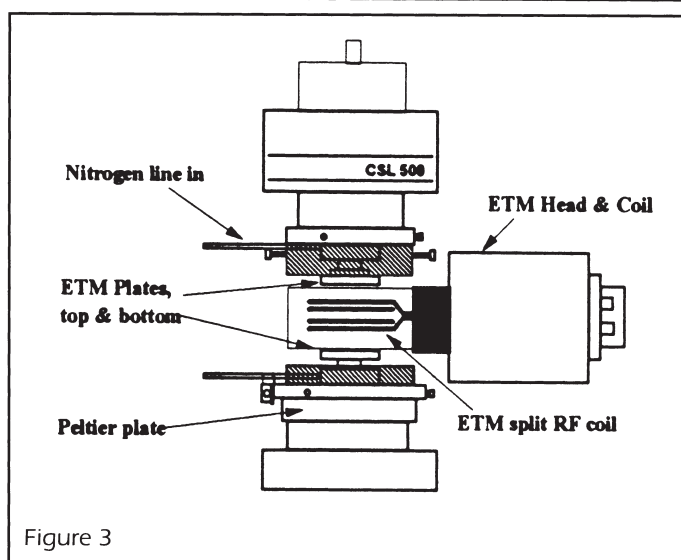


Figure 3

using steel or acrylic rotors at ambient temperature and special composite flat plates at sub-ambient. These special geometries are required for the extended temperature module [ETM] that in one mode allows for temperatures from -100 C up to 400 C to be attained. The important feature of the ETM used in these experiments was the cooling gas system. Here cold nitrogen gas from a source of liquid nitrogen in a dewar is passed through jets onto both upper and lower flat plates *Figure 3*. The flow of gas is modulated by a solenoid valve connected to external electronics, using three term [P.I.D.] control. Using this system a lower limit of -100 C can be achieved. Temperature is measured via a PRT in the lower plate [stator].

The normal temperature control system is a Peltier plate, giving active heating and cooling over a temper-

ature range of - 25C to 99C. This system was also used where feasible.

In the data tables that follow, incomplete or unavailable data is indicated by N/A in the appropriate cell, some of the thickeners are not specified, so the listed additives are included.

Results

Thixotropic Recovery [A - D]

These greases were pre-sheared at ambient temperature [25 C] for 30 minutes at 500 s⁻¹, prior to an oscillatory test [time sweep] to monitor recovery of G' [storage or elastic modulus] for another 30 minutes.

The storage modulus is chosen to monitor recovery processes, since it is the most sensitive of the parameters to small changes in viscoelasticity. The results are shown on the following page in *Figures 4 & 5*.

As can be seen the three greases all show some recovery over the time period, and all can be conveniently ranked in terms of elastic structure : [C] > [B] > [A]. This ranking agrees with the expected order of the greases from the Load Wear Index [ASTM D2596], which might be expected to relate to structure from the amount of filler used to make a grease robust. [N.B. the Y axis is a log scale.] The fourth grease [D] is an experimental formulation and showed a lag in response to the shear treatment that meant it lost structure after a brief recovery.

In terms of comparing its structure to the other greases, it can be seen that the initial climb in modulus was around 20,000 Pa - about the same as for [C] before collapse occurred. Under similar ASTM tests, the grease might therefore be expected to perform similarly to C, but no data is available to confirm this. The subsequent rise in structure, some 4 - 5 minutes later is of interest, in that it reveals something of the recovery mechanism. Apparently during pre-shearing, the structural elements that can reversibly gel were displaced to such an extent that a significant rearrangement was required before the interactions could begin to build back structure.

If the base oil or suspending phase viscosity of the grease is relatively high, then this could account for the time lag observed in the rebuilding of the gel. This response was found to be repeatable, and a subsequent test even monitored the same collapse after loading the sample between the plates, a low stress phenomenon. From its initial modulus value, the sample would be expected to build to a high level of structure, similar to grease C. It is known that the grease did not contain clays as part of the thickener

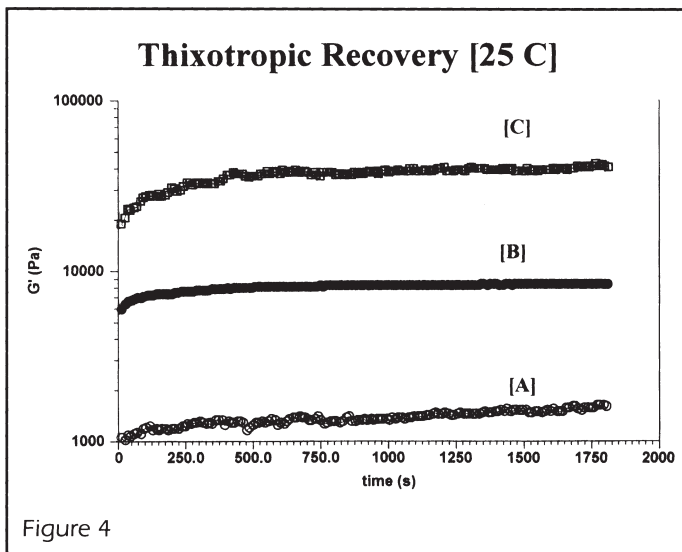


Figure 4

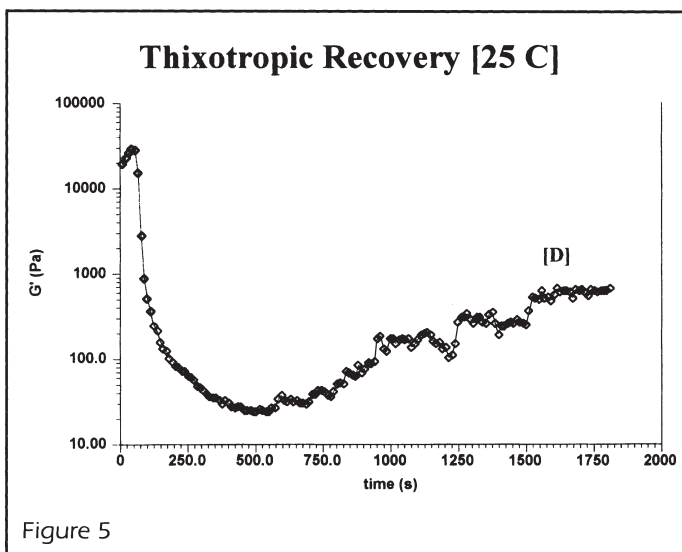


Figure 5

system, and other fillers may have been used to add to its structure. The presence of fillers in excessive quantities may distort a rheological response in polymer systems and this could be the factor responsible for the unusual and probably undesirable response.

Low Temperature Response [- 73 C]

Figure 6 shows equilibrium flow data for the four samples at low temperature. A wide range of viscosities and shear rates are covered in the plot, and good separation of the four samples is seen.

As can be seen from the equilibrium flow data, sample B really doesn't even flow much, and the data resembles noise. The greases can be ranked as follows : B > C > D > A. Samples C, D and A all shear thin somewhat and can more easily be ranked. At these temperatures the material is likely to become glassy, and therefore is

not seen to “yield”. The next figure replots the data as a function of the applied stress to amplify that concept. Even though greases B and A contain clays that can give rise to a sharp drop in viscosity associated with the “yield” phenomenon, this is not seen, probably due to the immobility of the base oil system.

The only noticeable difference in B from *Table 1* is that mineral oil is present in the base oil fraction. It is not specified as to how viscous a mineral oil is present, but it is likely that this component would be responsible for the excessively high viscosity seen at these low temperatures. The lighter fractions present in the base oil components of the other three are probably still somewhat mobile even at such a low temperature. Differences in the gelling mechanism and level of filler material will of course also contribute to a grease’s overall structure.

One way of investigating the cause of the discrepancy would be to do a more thorough examination of the base oil fraction alone. Measurement of its viscosity profile is a useful beginning, generating points at multiple shear rates for a variety of temperatures.

In *Figure 7*, there is no decline in viscosity for sample B, and the decline for the other samples is apparently less pronounced when plotted as a function of stress. The viscosity of the base suspending phase is almost certainly dominating the response, and the samples are not showing any sharp decline in viscosity that could be associated with a yield stress.

Dynamic data [a frequency sweep] shows a similar pattern for the four samples in terms of their ranking by complex viscosity [η^*] a parameter comprising both viscous and elastic components. For some polymeric samples, oscillation data of this type can be directly overlaid onto flow data using the Cox-Merz

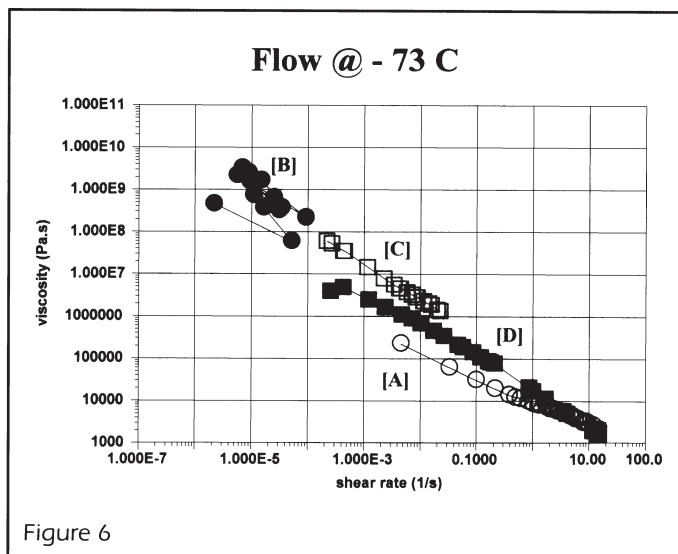


Figure 6

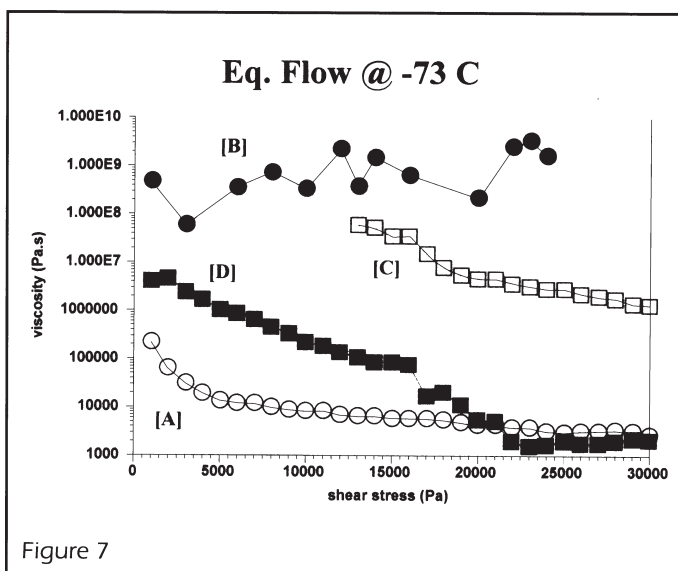


Figure 7

Table 1

| Grease | Op. Temp[C] | Base Oil | Thickener | Min. Load ASTM D2596 | Usage |
|--------|-----------------|--------------------------------------|--------------|-------------------------|--|
| A | [-73] to [+121] | Syn. Diester | Li Soap/Clay | 30 kg | Airframe bearings, gears sliding/rolling surfaces and mechanical actuators |
| B | [-54] to [+177] | Syn. Polyolester with mineral oil | Clay | 57 kg | Carbon steel cables, hinges and some bearings |
| C | [-75] to [+120] | Syn. Ester | Li Complex | 80 kg | Similar to A |
| D | N/A | N/A | Li Soap | N/A | [Experimental] Similar to A |

rule³, but the fillers in greases tend to disrupt that empirical relationship. *Figure 8*.

The responses of B and C are better separated in the dynamic test and the ranking is clearly $B > C > D > A$. There is no physical disruption of the structure required in this type of test, and the input stresses and resulting displacement amplitudes are lower. Such tests can be described as “non-invasive” tests, while flow tests are of necessity “destructive”. While the dynamic test successfully predicts the ranking found in the flow test, it gives more or less equal separations for the four materials. The flow test shows a questionable response for B, but it is likely that the stress limit of the rheometer was reached in the equilibrium flow tests for this sample.

From the table, B is seen to differ in two ways, firstly in that mineral oil is listed as an additional base component, and second that clay is listed as a thickener, and it is apparently not a Li soap system. The application of the grease is somewhat different too, and its properties include being a barrier protectant against water and other corrosive agents on the cables in aircraft. Specific mention is made of the high structure of the grease at low temperatures, and that such low temperatures should be avoided. It is also noted that the grease performs better at high temperature [177 C vs 120 C] than its counterparts, and so falls into a more specialized category. Thus the comparison of B with the other samples at this temperature is perhaps inappropriate.

Ambient [25 C] Temperature Properties

The flow data *Figure 9* appears superficially similar to the low temperature results, except that C now has the highest viscosity, B having slipped below C. All the greases are now within their operating temperature range, and so this ranking is expected to be more realistic. The ranking also agrees with the thixotropic recovery order [$C > B > A$] and the experimental grease - D lies between A & B.

In *Figure 9*, the samples all approach a common viscosity at high shear rate, just as at the low temperature study. The value of this asymptote is around two orders of magnitude lower at ambient temperature, however. It is of interest to observe whether any classical yield behavior can be seen in the greases at ambient, and so the data is replotted as a viscosity vs. shear stress curve in the following figure.

Different yield behaviors can be seen for C vs. A, B & D in *Figure 10*. Sample C seems to preserve its structure beyond 1000 Pa and the viscosity decline is gradual, whereas the other samples show sharp drops below even 500 Pa.

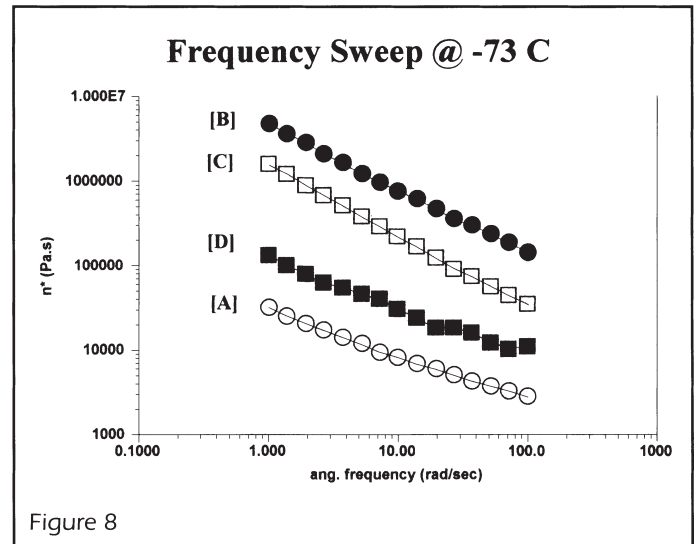


Figure 8

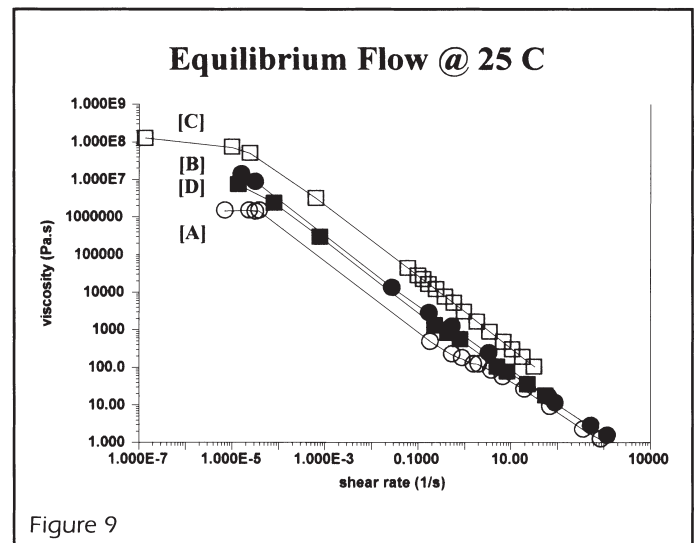


Figure 9

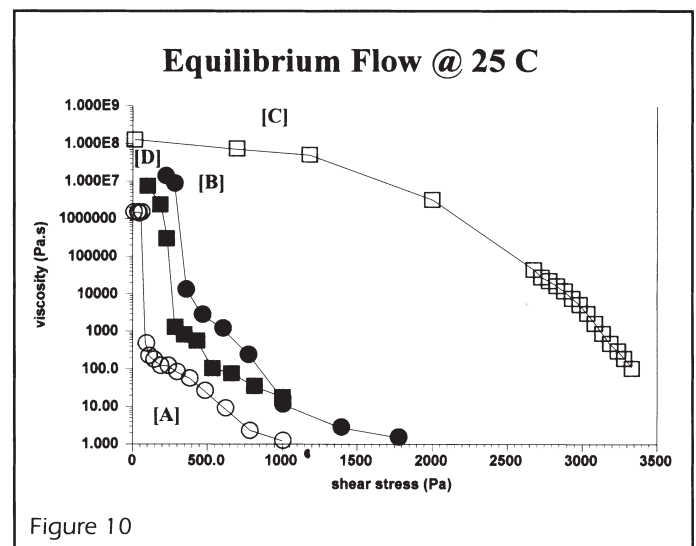


Figure 10

The responses of A, B & D sharply “break” at ~ 80 Pa, 250 Pa & 320 Pa respectively. The sharp decline is accompanied by a biphasic drop in viscosity that is far more gradual. It is noteworthy that both A & B are listed as clay thickened products and thus their response is consistent with this component. It would not be unreasonable to suppose that D contains a similar system, even though it is not listed as such due to its experimental nature.

Materials that are thickened with bentonite clays for example are often reported to break down sharply due to the collapse of their gel structure⁴. A “house of cards” configuration caused by the association of the clay platelets [edge - to - face] was originally used to explain the dramatic nature of the breakdown, but this model has been discredited in the eyes of some workers. A more generalized stabilization model is preferred, in which the details of the association are unclear, but the clay platelets are charge stabilized to form an extensive network.

Another way to consider this data is to plot angular velocity against stress, and see the growth in speed of rotation. Although it can be seen where the greatest change in properties occur, a sample may still not be considered to have “yielded” until it is moving within an observer’s frame of reference.

In the diagram below, the responses of A, B & D change slope for the second time at an angular velocity [ω] of ~ 0.01 rad/s. this corresponds to a rotational speed of ~ 0.1 rpm [conversion factor is $60/2\pi = 9.55$]. Since a 2cm cone and plate was used in this experiment, the equivalent translational velocity [v] can be calculated from $v = r\omega$.

Thus $[0.01 \text{ rad/s}] [0.01\text{m}] = v = 1 \text{ E}^{-4} \text{ m/s}$ $[0.1\text{mm/s}]$

This translational speed is probably undetectable to the naked eye, but 1 -10 mm/s is not. Thus a rotational velocity for this geometry that can be associated with movement in our frame of reference is about 0.1 - 1.0 rad/s.

Figure 11 shows the results of plotting the ambient temperature data in this way. The difference between sample C and the other greases is still clearly defined, but any chosen velocity line can be used to define the “Yield”. Hence A certainly yields first, with D either yielding before or at the same time as B [depending where in our range you look] and C yields last. Of course the stress in Pa can be converted directly to pressure in a pumping situation $[1 \text{ Pa} \sim 1.4 \text{ E}^{-4} \text{ psi}]$.

Finally, the dynamic data in Figure 12 shows frequency sweeps performed at 25 C that confirms the ranking

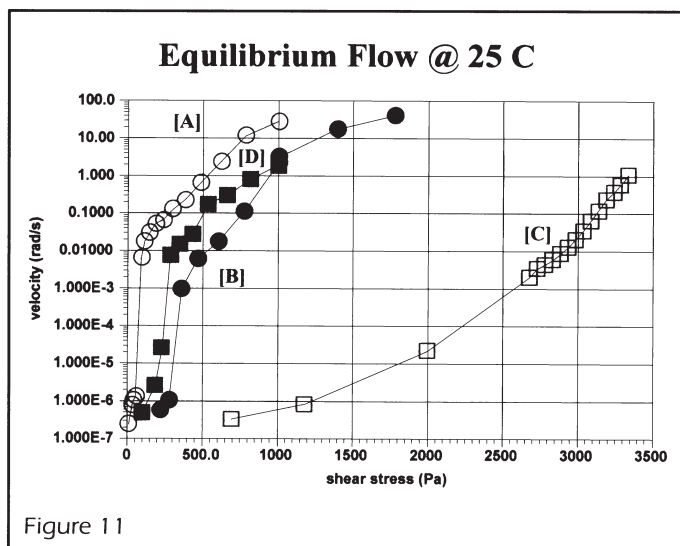


Figure 11

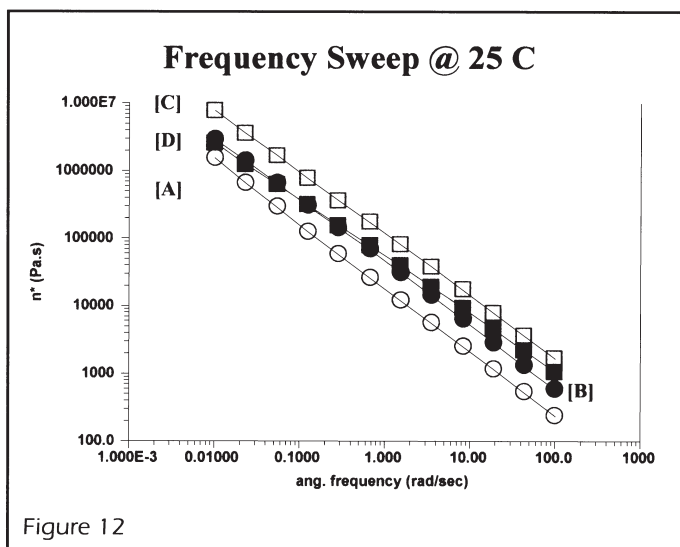


Figure 12

seen in the flow data in terms of complex viscosity. It can be seen that the large difference between C and the other samples is somewhat masked, although the close agreement between B & D is seen.

Results for Greases P - S

This group comprises more general purpose systems, designed to coat cable and bearing surfaces in harsh conditions [temperature extremes and dust/dirt]. None of them list clay or organoclay as being part of the thickener system, but 2 are described as soaps [P & Q] and the four may be divided into two pairs by the make up of the base oil. P & R are listed as containing severely treated naphthenic distillates, while Q & S are described as containing petroleum [paraffinic] bases or blends. The samples were tested by equilibrium

flow at 4 temperatures: - 25 C, - 15 C, 0 C and 20 C. The data from these tests is presented as viscosity vs shear stress graphs and then as velocity vs shear stress plots. The idea is to examine the shape of the former, and collect “yield stress” values from the latter, based on the velocity criteria used above.

As can be seen, the samples group themselves into pairs at - 25 C. In terms of viscosity, P & R are closely related, as are Q & S, with about 1 decade of viscosity between the pairs. The *shape* of the curves divide the samples into different pairings however, even though the viscosity values at low and high shear seem similar. P and Q seem to step between their viscosity extremes over a longer stress region, while for R and S the step down is itself smaller but steeper in terms of the stress range. The samples rank as follows :

R&P>Q&S

From the table data, it is seen that for both Q and S, the Lincoln Ventmeter data is quoted at lower temperatures [- 32 to - 34 C] than for the other greases. It is possible then, that they are specifically formulated with lower temperatures in mind, which accounts for their lower viscosity at -25 C. The aliphatic nature of the base oil components probably aids this performance, by making them less stiff at low temperatures.

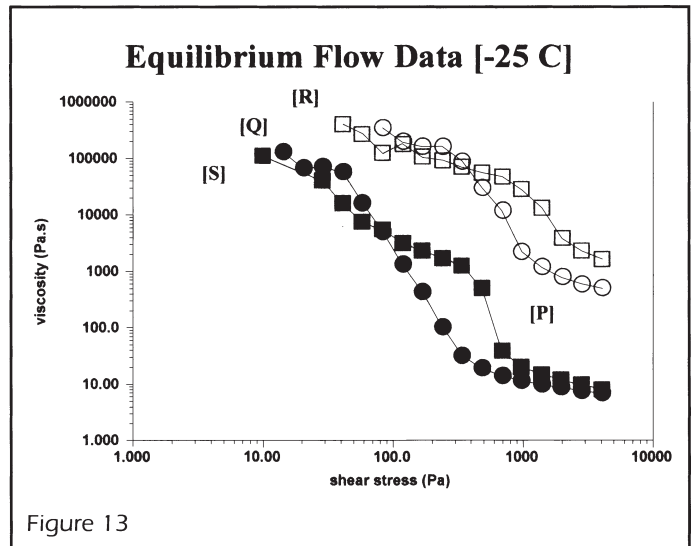


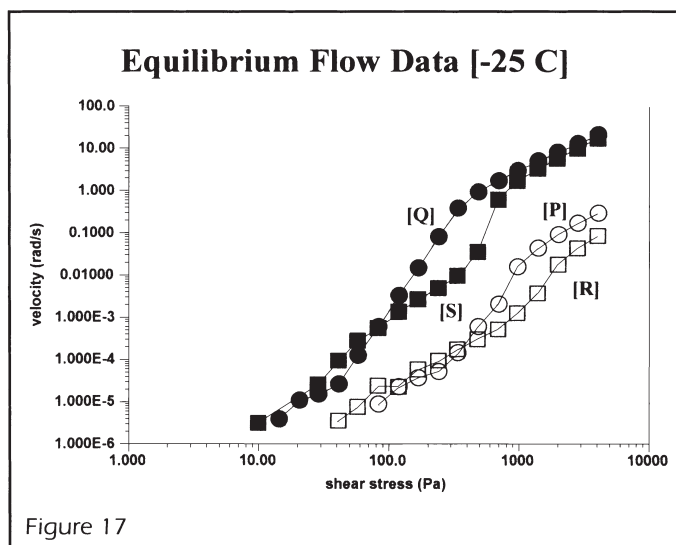
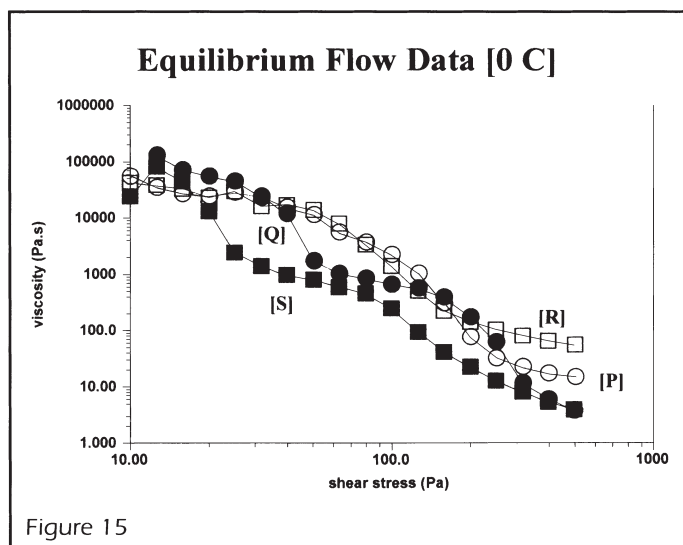
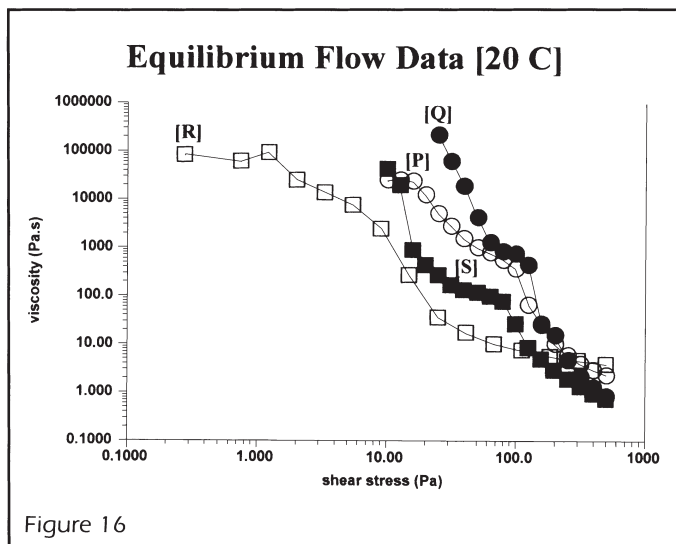
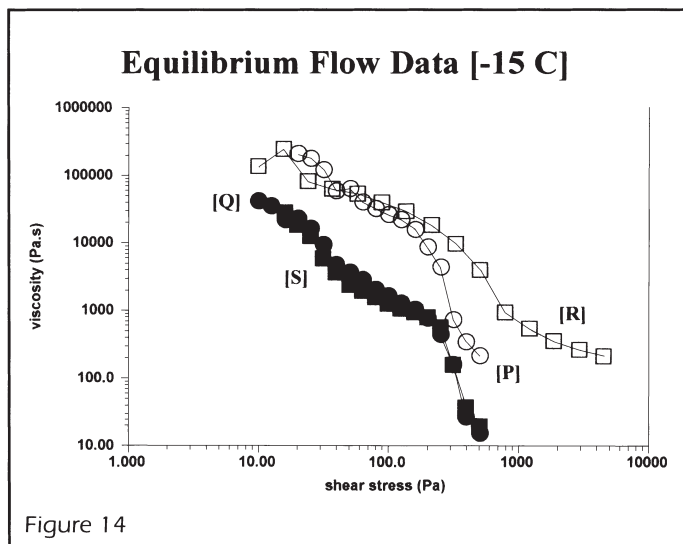
Figure 13

The shape relationship coincides with the NLGI ratings for the samples [0 and 1] as well as the similarity in penetration data and to a lesser extent 4 ball weld results. Without further testing however, it is difficult to attach great importance to that pattern.

The data at the next temperature [-15 C] shows the same pairings in terms of viscosity itself, but the shapes of the curves are all more closely related [see Figure 14]. In fact Q and S seem to be identical, while

Table 2

| Grease | Op. Temp[C] | Base Oil | Thickener | Usage | NLGI grade | Ventmeter Pumpability | Four Ball Weld Test | Penetration ASTM D217 |
|--------|---------------|--|--|--|------------|---------------------------------------|---------------------|-----------------------|
| P | N/A | severely treated naphthenic distillates [-85%] | Li soap | multi-purpose, heavy duty all-weather for mining, forestry app. | 1 | 400 psi @ [-18C] | 315 kg | 310-340 |
| Q | [-40] to [60] | petroleum/ synthetic blend to ISO 68 visc | Ca [12 H] soap | multiservice bearing lubricant:bushings/ bearings of draglines, shovels, drills | 1 | 300 psi @ [-18C] 400 psi @ [-34C] | 400 kg | 310-340 |
| R | [-18] to ? | severely treated naphthenic distillates [-50%] | Graphite [6-12%] coll. carbon [2-5%] bitumen [6-12%] | large open gears, e.g. industrial, mining & marine | 0 | ,100 psi @ [-7C] <300 psi @ [-12C] | 800+ kg | 355-385 |
| S | N/A | paraffinic petroleum base | Graphite [1-3%] coll. carbon [1-3%] olefin sulphide [1-5%] | open gears, rack & pinion, rails & rollers dipper sticks low velocity semi-enclosed gears | 0 | 500 psi @ [-32C] | 620 kg | 370 |



P is showing a much more pronounced drop in viscosity at a similar stress [200 -300 Pa].

The data at 0 C [see *Figure 15*] shows that P & R are most closely related in behavior, each of them showing a single step change in viscosity over a broad stress range. Samples Q & S show double step changes and follow similar courses, but are offset horizontally from one another. It would also seem that the viscosity at higher shear stresses are likely to diverge, such that the in use performance at this temperature might rank them as follows:

$R > P > [Q \& S]$.

Finally, the data at ambient temperature is reported [20 C] in *Figure 16* below. In this figure, the four samples do not separate as before into the two pairs of

base oil systems. Presumably, the aromatic system in P & R is indistinguishable from the paraffinic system in Q & S once a high enough temperature is reached.

The samples rank as follows: $Q > P > S > R$.

At this point the same data at the four temperatures is replotted to compare angular velocity and stress. The samples do not show sharp breaks in the data that are characteristic of clay thickened systems, but a threshold value of angular velocity [already established above] can be used to measure a pragmatic yield stress. The angular velocity used is 0.1 rad/s.

In the preceding figure, the order in which the samples cross the 0.1 rad/s line is as follows:

Q, S, P & R.

The values for shear stress at the crossover point once derived from the graph can be found in *Table 3*, designated as yield stress.

The next figure shows the data for -15 C, where the order of crossing is S+Q, P & R, i.e. the two samples S & Q are impossible to separate adequately.

In the figure below *Figure 19*, the data for the 0 C runs are presented. Here the order runs:

S, P, Q & R.

The last of the angular velocity vs stress graphs *Figure 20* shows the data at 20 C, in which the ranking is: R, S, P & Q. *Table 3* summarizes the Yield Stress data as a function of temperature and two ASTM tests. No attempt is made to correlate the Yield stress with these parameters. It is seen that they tend to form paired groupings, [ASTM D217 or NLGI rating], or else they do not follow the same pattern as the Yield data at any temperature [4 ball weld ASTM D2596]. Plotting Yield stress against temperature for the four samples does produce some interesting results, however.

In *Figures 21 - 24*, the four samples are displayed on individual graphs of Yield Stress as a function of temperature. An attempt is made to fit the data, using an exponential regression model, the results of which are displayed on each graph.

For sample P, the four values of Yield Stress are seen to fall on a regular smooth curve. While there is unlikely to be a statistical significance to the exercise [4 points!], a correlation can be made to the exponential line fit. The regression coefficient in the line equation displayed are seen to be small, but some of this is due to the small number of points.

Sample Q does not seem to follow a similar pattern, unless some doubt is cast at the low temperature point [-25 C]. Of course, slip is most likely to occur at low temperature if sample shrinkage is a problem. The exponential fit here is the worst of the four, although ignoring the first point would probably improve things.

Table 3

| Sample | Temperature [C] | Yield Stress [Pa] | 4 Ball Weld ASTM2596 | Penetration ASTMD217 | NLGI Grade |
|--------|-----------------|-------------------|----------------------|----------------------|------------|
| P | -25 | 2200 | 315 | 310-340 | 1 |
| Q | -25 | 250 | 400 | 310-340 | 1 |
| R | -25 | 4200 | 800 | 355-385 | 0 |
| S | -25 | 555 | 620 | 370 | 0 |
| P | -15 | 550 | 315 | 310-340 | 1 |
| Q | -15 | 330 | 400 | 310-340 | 1 |
| R | -15 | 1366 | 800 | 355-385 | 0 |
| S | -15 | 330 | 620 | 370 | 0 |
| P | 0 | 200 | 315 | 310-340 | 1 |
| Q | 0 | 230 | 400 | 310-340 | 1 |
| R | 0 | 280 | 800 | 355-385 | 0 |
| S | 0 | 150 | 620 | 370 | 0 |
| P | 20 | 135 | 315 | 310-340 | 1 |
| Q | 20 | 150 | 400 | 310-340 | 1 |
| R | 20 | 45 | 800 | 355-385 | 0 |
| S | 20 | 95 | 620 | 370 | 0 |

Sample R gives a very good fit to an exponential model, and the range of the Yield Stress data is perhaps the widest of all.

Finally, the data from sample S also shows a very good fit, leading one to suppose that this type of modeling is at least appropriate, if not particularly significant to a purist! Samples R & S share some similarities in their make-up in that they both contain graphite, colloidal carbon and some heavy hydrocarbons, rather than soap.

There is precedence to support the use of an exponential relationship between yield behavior and temperature is found in the Arrhenius relationship between viscosity and temperature:

$$\eta = A * \exp (E_a / R*T)$$

In the expression, E_a is defined as the "Activation Energy" for flow, a concept not unlike the Yield Stress, and this is seen to relate to temperature as part of an exponent. The critical tests for such a relationship is normally a single stress or shear rate, maintained during a temperature ramp. Further study in this area is indicated, either using the aforementioned technique, or by repeating the equilibrium flow data at more temperatures. The latter is of course more time-consuming, but would give more data to work with, since multiple stresses and shear rates would be covered.

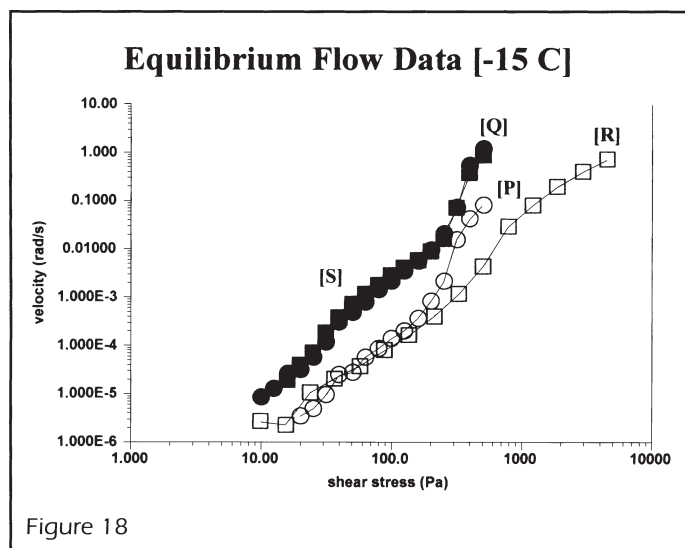


Figure 18

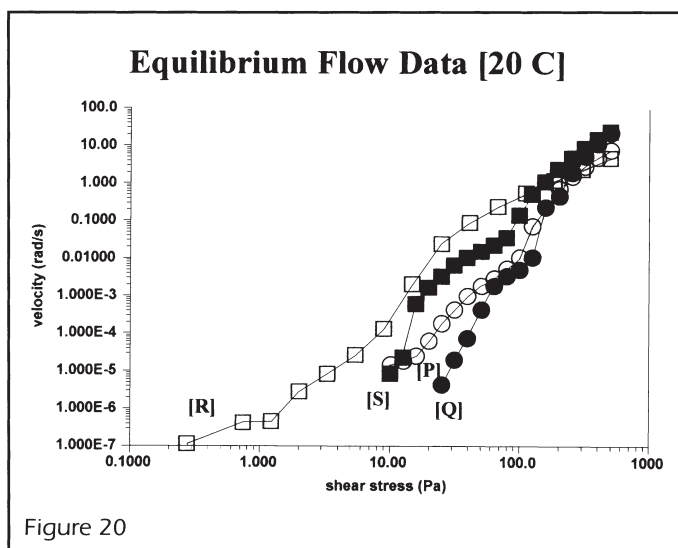


Figure 20

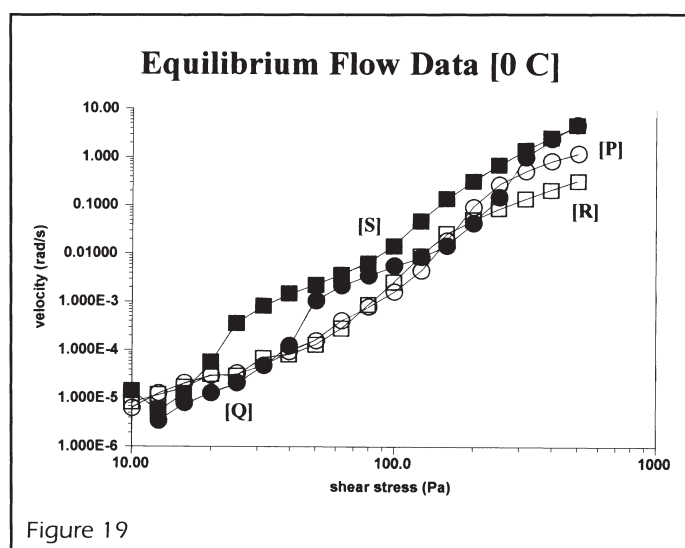


Figure 19

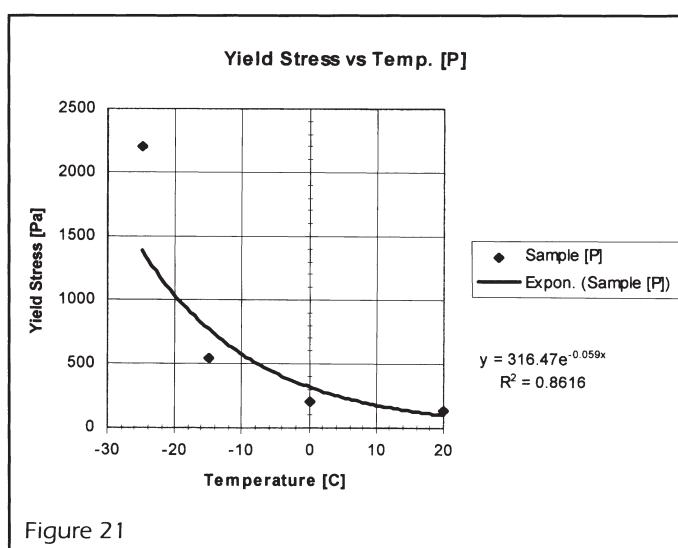


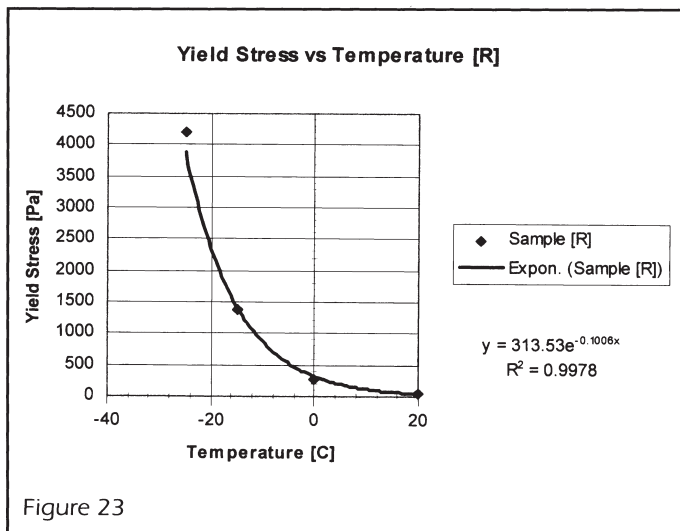
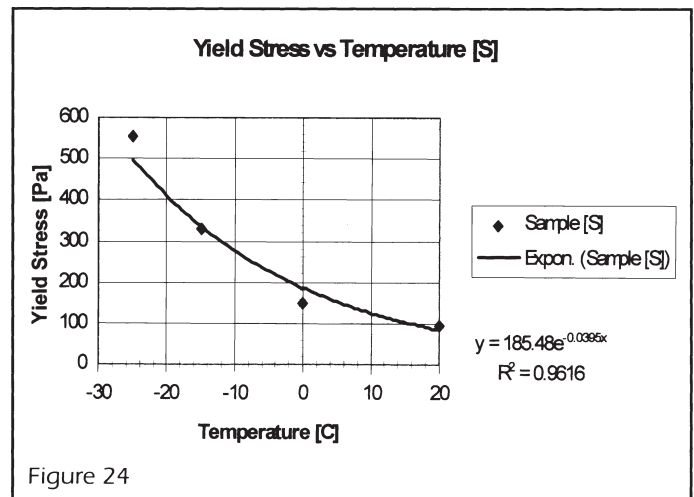
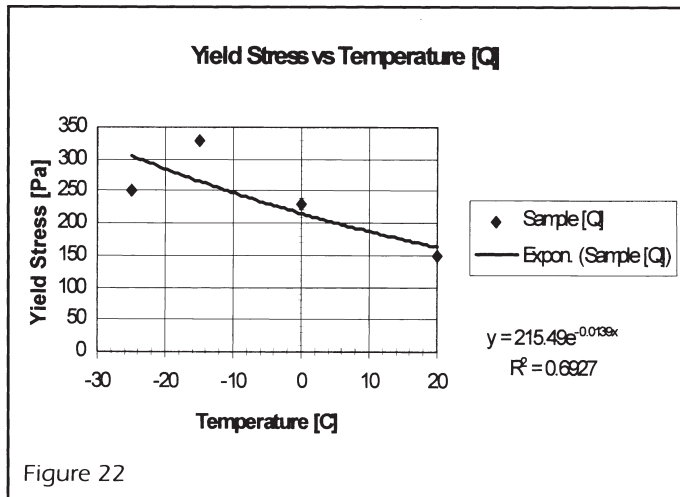
Figure 21

Conclusions

Two sets of related greases were examined using controlled stress rheometry. Dynamic [oscillatory] and equilibrium flow tests were performed to examine viscoelastic structure and "Yield Stress" respectively, at various temperatures. The first set of aviation greases were examined for thixotropic recovery using an oscillatory time sweep after a pre-shear step. Three out of the four greases responded as expected, by a rebuilding of "gel" structure reflected by the elastic modulus $[G']$. These samples could be ranked in terms of their modulus $[C > B > A]$ and they all seemed to recover with similar profiles of modulus as a function of time. The samples' ranking seems to fit with the available data. The fourth sample behaved somewhat unusually, by recovering and then showing a structural breakdown before the eventual rebuilding began. This

experimental grease showed the same kind of delayed collapse of structure when loaded onto the rheometer, even though a delicate closure mode was used. Although the grease might be expected to rank with the highest structure sample $[C]$ it is possible that an injudicious use of fillers led to this presumably undesirable characteristic.

Low temperature data for the four greases was also presented $[-73\text{ C}]$, both equilibrium flow data [shear viscosity] and dynamic frequency sweep data [complex viscosity]. The techniques are similar in what they show, but do not give truly overlapping data as can happen for simple, unfilled thermoplastics or polymer solutions⁵. At the low temperature the samples ranked somewhat differently in the two tests. The descending order of shear viscosity was $B > C > D > A$. When the operating temperature data is examined, sample B is



not rated to below - 54 C, and this may account for its apparent immobility at this temperature in flow. The oscillation data, with its small amplitude, allows more sensitive data to be generated confirming that grease B had the highest structure. The replot of the flow data as a function of stress shows that B does not move at all for the stress range applied. In the table B is noted to contain mineral oil as an additive to the base system which may account for the difference. All the samples showed a rather gradual decline in shear viscosity, not the characteristic sharp break associated with clay thickened systems. The dynamic data showed parallel traces for the complex viscosity, indicating similar frequency dependence for the samples.

Thus, if a simple ranking of several samples is required, the dynamic test is seen to give the same results as the equilibrium flow, but takes a shorter time and is less disruptive of the sample. It appears to be insensitive to the yield concept however. A dynamic test that pro-

gressively disrupts structure is known as a stress or amplitude sweep. Application of these tests may narrow the gap between equilibrium flow and dynamic tests in terms of convenience versus usefulness.

Data collected at 25 C was also presented in similar plots for the flow and dynamic data. The major difference was that the ranking of B slipped below C, a change consistent in both types of test. When the data was plotted as viscosity vs stress, the samples showed a yield in three out of four cases. Only C showed a smooth decline in viscosity, without the sharp drop typical of clay thickened systems. In the specifications of the grease samples, only A & B were listed as containing clays, while the details for D were largely unknown other than it was intended to fill the same role as A. It is not unreasonable to suppose then that those three are clay based, and that C is not.

Replotting the data as an angular velocity vs stress graph allowed the derivation of a useful frame of reference for yield, i.e. how fast does the sample have to be moving before it can be considered to have yielded? From the calculations, a translational velocity of 1 - 10 mm/s was established, which corresponded to a rotational velocity range for that geometry of 0.1 - 1.0 rad/s. The four samples were then ranked in terms of this velocity as: A > D/B > C. The dynamic data at the same temperature gave the same ranking, but did not show the same separation of C compared to the others. In this sense it can be considered to be somewhat less sensitive, just as for the low temperature data.

The data for the second set of greases [P-S] was presented in the form of equilibrium flow data only at various temperatures: -25 C, -15 C, 0 C and 20 C. The samples were detailed in a table that included some ASTM test data, NLGI grades, as well as base oil chemistry etc. The make up of the greases could be divided

into two categories, depending upon the aromatic or aliphatic character of the base oil.

The samples as plotted out graphically tended to follow the same pattern at the various temperatures. Samples P & R tended to pair up, as did samples S & Q, the former being consistently higher in viscosity than the latter. The high viscosity pair comprised the naphthenic distillate base oil system, while the paraffinic petroleum systems formed the low viscosity pair. At the two lowest temperatures [-25C & -15C], the pairs were well separated, but at the higher temperatures the pairs lay closer together. None of the greases showed a sharp breakdown in viscosity, consistent with a true "Yield Stress" but using the technique of a threshold velocity [0.1 rad/s], the yield point can be calculated from each graph.

The yield data as a function of temperature was presented in *Table 3* along with the ASTM test results and NLGI grade information. All four graphs were replotted as angular velocity vs. stress and then four more graphs of yield stress as a function of temperature were plotted [one for each sample]. Three out of the four samples produced data that could be fitted to an exponential curve with moderate to very good standard values for R^2 [0.86 - 0.998] with the fourth [Q] showing a less ordered data set. It is possible that the low temperature data was subject to artifact [e.g. slip] since the other points appeared to form a similar curve by eye. The curve fitting routine is not a serious statistical exercise however, since the number of data points is very small [$n = 4$]. It is interesting that the exponential fit does give passable results, since the Arrhenius equation relates viscosity and flow with the *activation energy* [E_a], similar in concept to the "Yield Stress". Further work is suggested in order to support the relationship between yield stress and temperature by interpolating more temperature points. The advantages of being able to predict useful viscosity and temperature ranges are clear.

The use of controlled stress rheometry is seen to be able to rank grease samples in terms of flow curves at a given temperature, as opposed to a single point result. The flow curves allow an observer to predict which samples will perform best at a given temperature and whether it will pump, by converting stress in Pascals to appropriate units [e.g. p.s.i.]. A further advantage is the ability to directly measure angular velocity and, from the geometry factors, calculate translational velocity. Any relevant reference frame of velocity can be chosen to determine when the sample is responding to the stress. Both dynamic and equilibrium flow

curves can be used to simply rank the samples as a screening procedure, but the latter is the preferred method, albeit a more longwinded one. While controlled stress rheometry is not expected to replace the ASTM protocols, it is a useful tool to provide absolute information about the viscosity of a sample under defined conditions of shear and temperature.

References

1. Gow G., Judges 5 : 5, The Time Factor in Rheology, Paper Presented at the 55th NLGI Annual Meeting in Tampa 1988
2. Barnes H.A. and Walters K., The Yield Stress Myth?, *Rheol. Acta* 24 323 - 326 1985
3. Cox W.P. and Merz E. H. , Correlation of dynamic and steady flow viscosities., *J. Polym. Sci.* 28 619 - 622 1958
4. Van Olphen H., "Clay Colloid Chemistry", John Wiley & Sons. NY 1963

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Editor's Note: Peter Whittingstall was presented the NLGI Author award for this paper at the annual meeting in Carlsbad, California.