Applying the Low-Temperature Scanning Brookfield Technique to Analysis of Lubricants, Transmission Fluids, and Fuels

Gregory C. Miiller
Tannas Co.

Theodore W. Selby
Savant, Inc.

ABSTRACT

Adequate flow response can be a problem with lubricants, transmission/differential fluids, and fuels at low temperatures. In developing lubricants or fuel formulations expected to function well at low temperatures, it is critical to study their behavior over the broadest temperature range likely to be encountered. This can prove to be a complex task using the full scale equipment or even with instruments requiring single point measurements.

This paper discusses a simple scanning approach using rotational viscometry that provides a broad temperature range yet specific evaluation of potential flow problems in lubricants and fuels.

INTRODUCTION

Engine oil pumpability at low temperatures has been considered a threat to engine durability for many years [1,2]. However, in 1980 the threat became an event with the failure of many automobile engines in the upper midwest during an unusual winter cooling cycle. It was not that the weather was very severe -- it was, in fact, not unusual for the region.. The difference was that the temperature dropped slowly instead of rapidly during one day and dropped even more that night. One of the oils used happened to be vulnerable to these cooling conditions and became gelated or semi-solid in the crankcase. The next morning many cars with engines carrying this oil were harmed when the oil pump could not provide oil to the bearings.

This strong field experience brought about a new level of understanding and perspective concerning the importance of low-temperature engine oil pumpability as well as a need to measure it effectively. One of the instrumental tools developed which correlated well with cold-room engine tests and low-temperature field failures was the Scanning Brookfield Technique (SBT). It was first presented in 1982 after considerable development and testing [3] immediately after failing oils were available for research.

Subsequently, the value of the method was recognized and required in some automotive specifications. Still later, the SBT was a source of study and round-robin evaluation in the ASTM where it became an ASTM Test Method (D 5133). The correlation reported in the literature [4,5], is shown in Figure 1 and indicates the high level of correlation with the two forms of pumping failure encountered in the field -- **flow-limited** behavior in which the oil is simply too viscous to flow adequately to the bearings and **air-binding** behavior in which the oil forms a gelated mass in the crankcase which, in turn, permits air pressure to develop an air vortex reaching to the pump inlet.

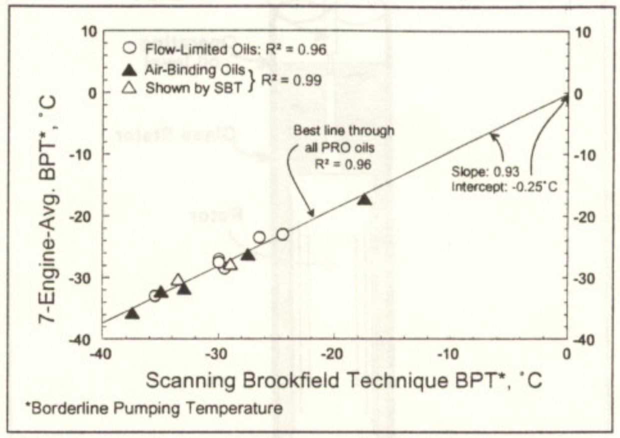

Fig. 1 - Correlation of SBT-determined borderline pumping temperatures with those obtained in cold-room engine

INSTRUMENTATION

General

Ideally, a low-temperature study of a lubricant or fuels behavior should reveal the viscosity at all desired temperatures, any unusual flow behavior and the temperature at which the unusual behavior occurs. This ideal was the aim of the effort in developing the Scanning Brookfield Technique.

The Scanning Brookfield Instrument

The Scanning Brookfield Technique (SBT) makes use of a special adaptation of the well-known Brookfield Viscometer. This form of the basic rotational viscometer utilizes a motor working through a coil of spring wire to turn a rotor. Viscous resistance to the rotor is measured by the deflection of the spring either visually or analog electrical output.

Recognizing that the analog output could be used for continuous recording of viscosity, the developers of the SBT determined that a rotor turning within a relatively close-fitting glass stator would be able to measure the viscosity of a liquid over a wide low-temperature range.

The resulting rotor/stator assemblage is shown in Figure 2 and indicates the use of hooks to couple the rotor to the special Tannas/Brookfield Viscometer head.

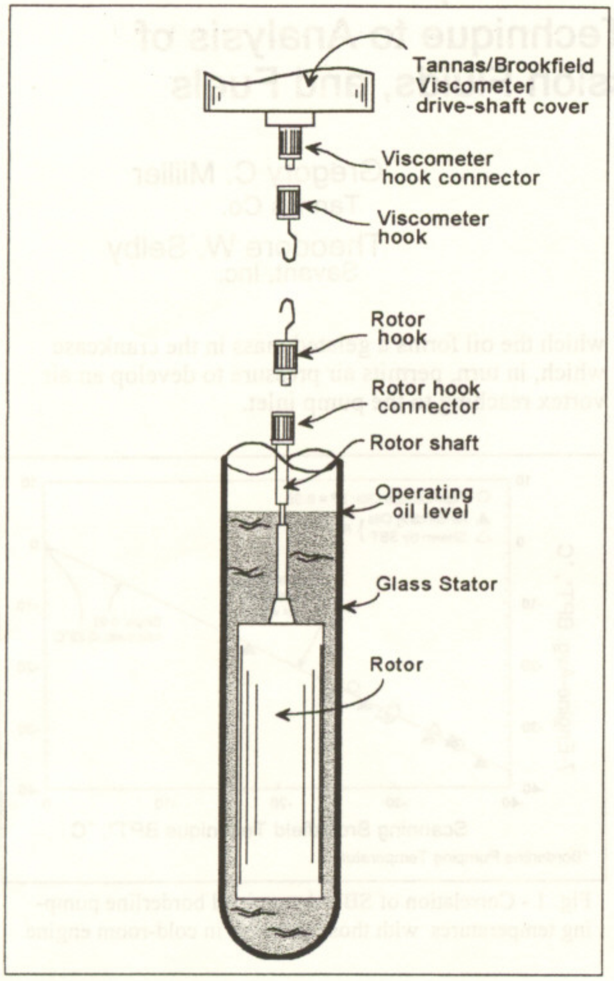

Fig. 2 - Sketch of Scanning Brookfield Viscometer rotor/stator assemblage.

The close fit of the rotor in the stator requires control of the position of the rotor in the stator. This is done by a special adapter for coupling the stator tube to the viscometer head. These adapters are shown in Figure 3 in use on one of the SBT low-temperature baths. Just under the viscometer head of each unit will be noted a white Teflon™ adapter. One of the eight heads still on the assembly stand prior to bath immersion also shows the stator coupled to the viscometer head.

While the primary purpose of the adapters is to carefully and repeatably align the rotor in the stator, the adapters also have a port to allow dry gas to flow into the stator to limit condensation on the inside wall.

As previously noted, the analog torque signal from the viscometer can be used to record the continuous viscosity data produced by the technique as the temperature is changed. If the analog signal is converted to a digital signal, a computer can be used to receive and later analyze and plot the data. The computer interface became the standard of analysis for the technique. In automatically collecting and analyzing the data, the Scanning Brookfield Technique comes very close to meeting the ideal toward which it was developed.

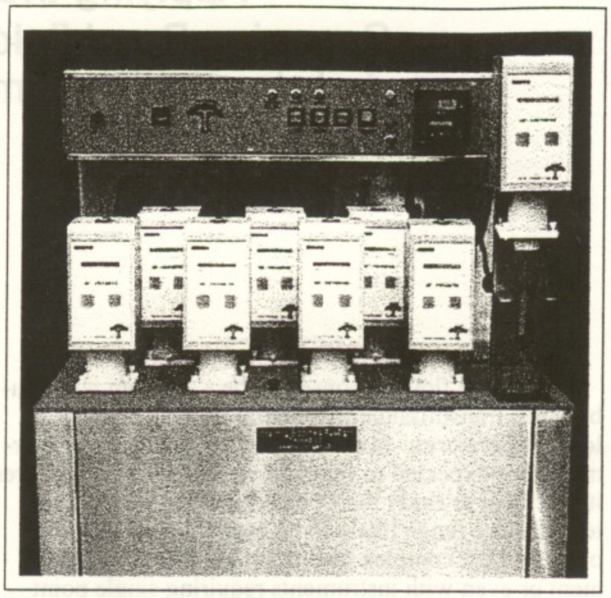

Fig. 3 - Scanning Brookfield Viscometers set up on a temperature programmable Tannas PlusEight bath. Note the unit being assembled on the right.

DEVELOPMENT OF METHOD

General

There are several factors that should be considered in the development and application of a low-temperature, viscosity-scanning technique. Temperature range, resultant viscosity range, cooling rate (linear or variable), potential degree of structure or gel formation in the oil or fuel, etc. are all critical to the data generated.

Engine Oils

As previously noted, the Scanning Brookfield Technique was originally developed around the characteristics of engine oils -- particularly engine oils having a tendency to form an internal structure (gelate) at low temperatures.

Continuous Viscosity-Temperature Information

In collecting thousands of viscosity-temperature curves over a broad low-temperature range it has been found that many mineral oil-based engine oils are considered 'well-behaved' since the viscosity changes exponentially with temperature as shown in Figure 4 (p. 3). Other engine oils are found to be exceptions in exhibiting a repeatable 'Z'-shaped irregularity in the exponential viscosity-temperature curve as shown in Figure 5 (p. 3).

The nature and repeatability of this irregularity both in degree and in temperature, suggests the presence of structural elements in the oil -- termed gelation -- at the temperatures of occurrence. Such gelation may be so extensive and strong as to exceed the capacity of the viscometer head to measure it completely or the gelation process may be limited to relatively few molecules and the distortion may only continue to the point where the minor structure-building is complete. Among the factors found to influence the formation of gelation were

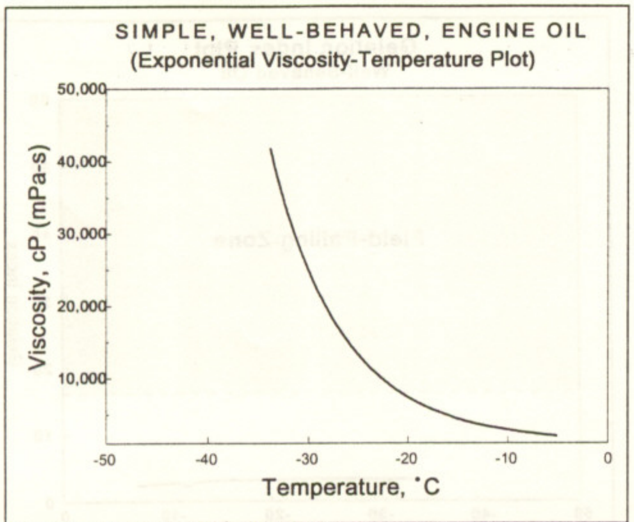

Fig. 4 - Scanning Brookfield Technique analysis of a simple Newtonian oil showing an exponential viscosity-temperature relationship

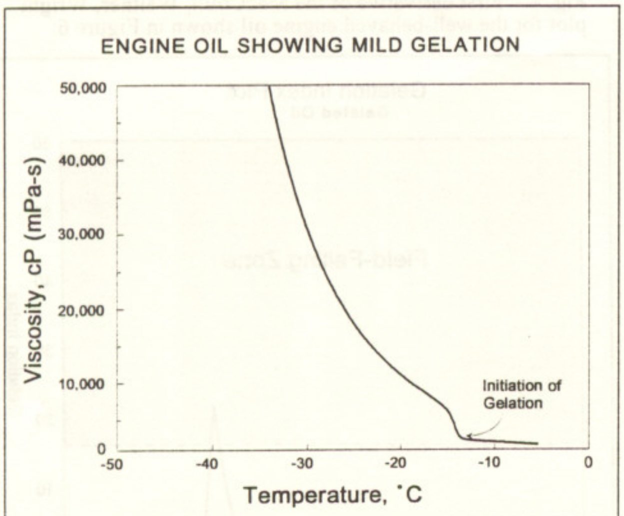

Fig. 5 - Scanning Brookfield Technique analysis of a non-Newtonian oil showing some gelation in the viscosity-temperature relationship at ~-12°C.

rate of cooling, concentration of gelating components, and temperatures to which the oil had previously been exposed.

Preheating the Oil - An interesting factor in repeatably measuring the presence of gelation was the need to preheat the oil to 90°C. Without this step a given oil might or might not show gelation. It was reasoned that preheating was necessary to remove any tendency to 'remember' previous gelation. That is, it was necessary to dissolve prior gel structures to prevent them from reducing response to the method.

Importance of Cooling Rate - Cooling rate was found to be critical. In general, faster rates limited structure formation in the oil. It is thought that the formation of gelated structures is a molecular transport phenomenon working in which the molecules capable of forming the structure are working against the viscosity of all of the other molecules. If the optimum temperature of structure formation is passed through too rapidly, the increasing viscosity of the remaining molecules may inhibit or completely prevent gelation.

Influence of Concentration of Structure-Building Molecules - Molecular transport theory would also predict that the higher the concentration of structure-forming molecules the more pervasive and evident the structure. Moreover, the higher the concentration, the more likely the structure will be formed and found despite differences in cooling rates. This has been found to be the case experimentally. Oils showing higher gelation, show it at faster, as well as slower, cooling rates.

Analysis of Gelation

Development of the Concept of Gelation Index

Early Work - It was found that many different degrees of gelation could be found in engine oils. Gelation could range from a barely noticeable distortion of the exponential viscosity-temperature curve to an off-scale sudden rise in viscosity. What was required was a method of putting a value on the severity of gelation.

Use of the MacCoull, Walther, Wright Equation - Since the early 1920's it has been known [ ] that the relationship between temperature and viscosity for mineral oils and their blends is defined by the empirical equation

$$\text{LogLog}\,(\eta+0.7) = m(\log\,°K) + b \qquad \textbf{Eq. 1}$$

where η is viscosity, **m** is the slope, **°K** is temperature in degrees Kelvin, and **b** is the intercept.

Thus, a well behaved oil would give an inclined straight line whose negative slope reflected the viscosity-temperature relationship of the oil. Equation 1 has proven effective and useful over the years and defines a straight line for a 'well-behaved' engine oil, as shown in Figure 6.

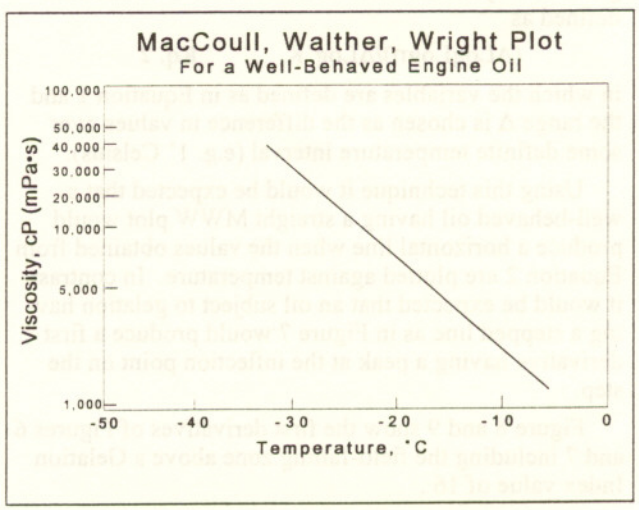

Fig. 6 - Scanning Brookfield Technique analysis of a non-Newtonian oil showing some gelation in the viscosity-temperature relationship at ~-12°C.

In contrast, the MWW plot of an oil which gelates to some degree will show this more or less evidently in a stepped line as shown in Figure 7. The MWW plot in this figure is that of the same oil whose viscosity-temperature curve was shown in Figure 5.

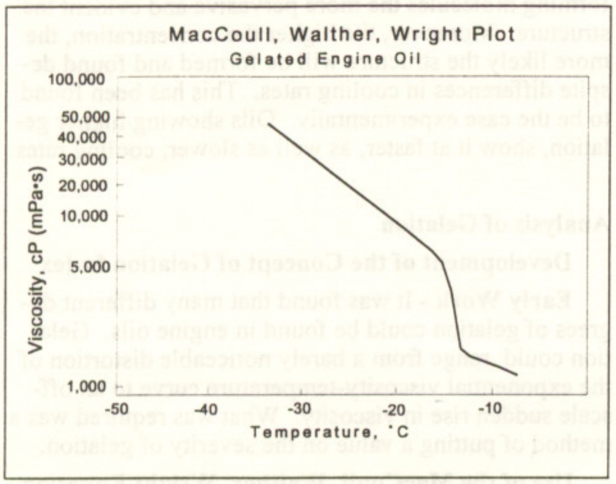

Fig. 7 - MacCoull, Walther, Wright plot of the viscosity-temperature data of a mildly gelated engine oil.

It is clear from this figure that even mild gelation will produce an evident step in the MWW viscosity-temperature plot.

The Gelation Index

At this point in the continued development of the Scanning Brookfield an important step was taken. In response to the need to distinguish among different levels of gelation, it was hypothesized that the first derivative of the MWW viscosity-temperature data produced by the SBT might be helpful in distinguishing between subtly differing degrees of gelation [9].

The first derivative of an empirical equation can be generated by definite incremental ratios -- in this case defined as

$$(\Delta \text{LogLog}\eta)/\Delta \text{Log}^{\circ}\text{K}. \qquad \textbf{Eq. 2}$$

in which the variables are defined as in Equation 1 and the range Δ is chosen as the difference in values over some definite temperature interval (e.g. 1° Celsius).

Using this technique it would be expected that a well-behaved oil having a straight MWW plot would produce a horizontal line when the values obtained from Equation 2 are plotted against temperature. In contrast, it would be expected that an oil subject to gelation having a stepped line as in Figure 7 would produce a first derivative having a peak at the inflection point on the step.

Figure 8 and 9 show the first derivatives of Figures 6 and 7 including the field-failing zone above a Gelation Index value of 16 .

The Critical Gelation Index for Engine Oils - The establishment of a value of 16 as the critical Gelation Index value was based on the field-failing oils available from the ASTM.

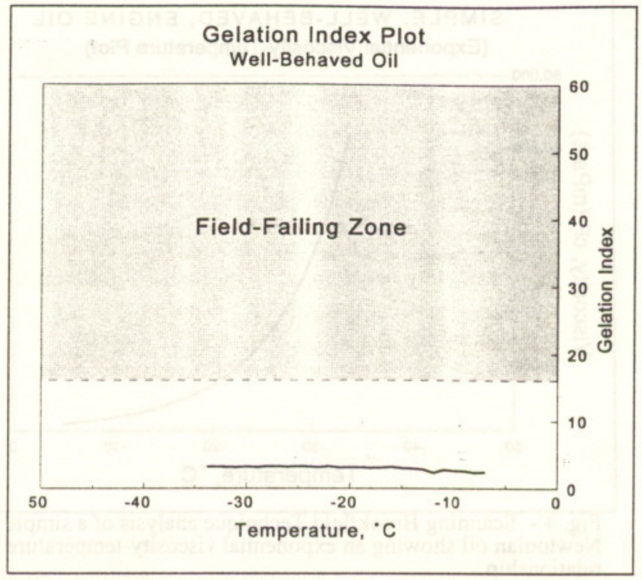

Fig. 8 - First derivative of the MacCoull, Walther, Wright plot for the well-behaved engine oil shown in Figure 6.

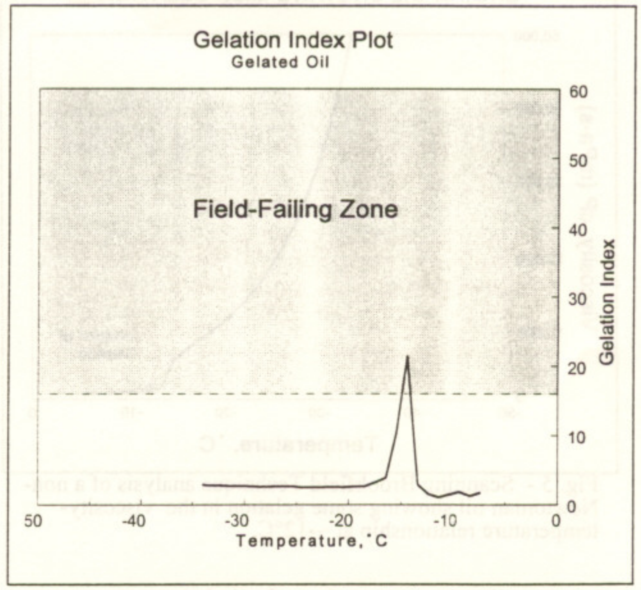

Fig. 9 - First derivative of the MacCoull, Walther, Wright plot for the gelated engine oil shown in Figure 7.

At the time of the development of this SBT equipment and method, the ASTM had obtained samples of the field-failing oils and identified them as the second Pumpability Reference Oil, PRO, series, PRO 21 to 29a. (The first PRO series had been developed and measured in cold-room engine tests during the early 1970's [10]). With these oils it was possible to determine how their Gelation Indices corresponded to the field failures.

In the process of this work it was found that the borderline-failing reference oil, PRO 29a, had the lowest Gelation Index of the field-failing oils [9], a value of 15.8. Moreover, in an early test of repeatability of the Gelation Index approach, the borderline PRO-29a SBT results were compared to a much earlier SBT test which data were reanalyzed to obtain the Gelation Index.. Results of both analyses are shown in Figure 10.

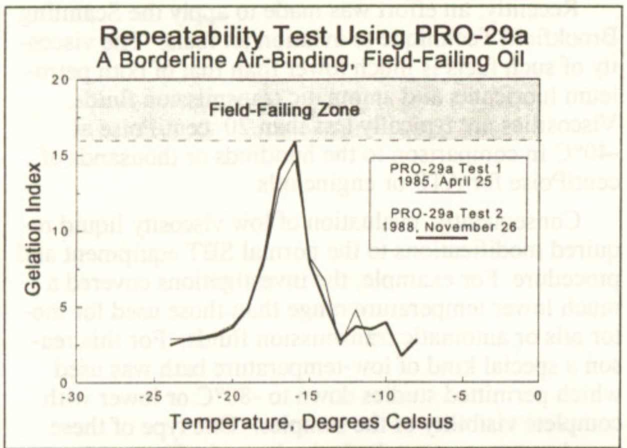

Fig. 10 - Gelation Index curves for a borderline, field-failing oil run twice by different operators on different instruments three and one-half years apart.

The results were surprisingly close considering all of the variables associated with time between analyses.

As a further, direct test of repeatability, another oil, obtained at the same time as Pro 24 (a well-defined, field-failing oil), was chosen. This oil had a Gelation Index of 45. Seven samples of the oil were analyzed by the SBT at the same time in a Tannas PlusEight bath. The results are presented in Figure 11.

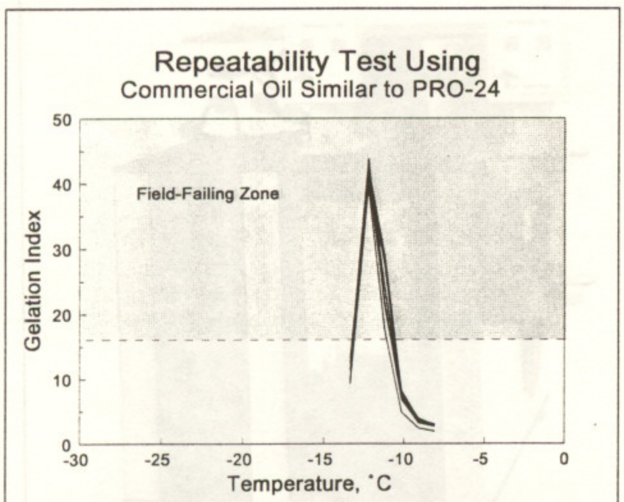

Fig. 11 - Gelation Index curves for a field-failing oil run simultaneously in seven different test cells by the same operator show good repeatability.

Both the data of Figures 10 and 11 show good repeatability -- particularly the latter which was a more exacting test. Essentially, the Gelation Index technique has been shown to have the capability of easily distinguishing among different levels of gelation and to do this in a repeatable manner.

TESTING LIQUIDS OTHER THAN ENGINE OIL

General Observations

The Scanning Brookfield Technique provides a versatile instrumental tool. Capabilities include variable temperatures and temperature ramping rates, rotor speeds, shearing stresses, and a range of liquids. For example, the method can be, and has been, applied to hydraulic fluids, glycol solutions, power steering fluids, automatic transmission fluids, and fuels such as Bunker C and jet fuels.

As in the case of engine oil, the benefit of SBT analysis on other liquids is that the viscosity over the full range of temperatures of interest can be tested. This is especially interesting and valuable in spotting and analyzing problem points or changes which may occur at uncertain temperatures. Temperatures at which icing, crystallization, gelation and other forms of thickening occur can be determined by such scanning techniques. Moreover, the SBT also provides the viscosities of the liquids over the whole range investigated for further use.

SBT Analyses of Automatic Transmission Fluids

Automatic transmission fluids (ATFs), for example, contain certain additives to help in meeting the needs of the automatic transmission. One of these needs is to have adequate flow at low temperatures. Any characteristic of the ATF which prevents this must be eliminated or transmission damage will occur [11]. In addition, the viscosity of the ATF is, in itself, important since even without any other adverse rheological effect, the viscosity must permit the ATF to move rapidly enough to satisfy the transmission functions.

Automatic transmission fluids must endure much exposure to oxidizing conditions. As a consequence, the base oils used in their manufacture are chosen from highly paraffinic stocks. However, highly paraffinic stocks are also prone to forming waxes and, when in contact with some additives, forming gelated structures. Other additives -- pour point depressants -- can correct this tendency but must be present at the right concentration.

As an example of these remarks, Figure 12 shows an ATF which develops gelation. This fluid was believed to be responsible for low-temperature transmission malfunction because of blockage of the ATF cooler located in the engine radiator areas during cold-room dynamometer tests.

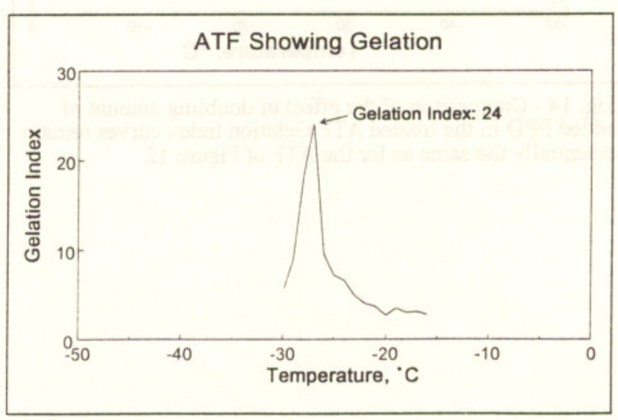

Fig. 12 - Gelation Index curve for an ATF. Gelation shows evident peak of 24 at -27°C.

With this information available, addition of a pour point depressant (PPD), seemed appropriate to lower the amount of gelation that occurred. The first experiment was to add a small amount (0.05%) percent of PPD to the transmission fluid. With this added PPD the gelation problem was reduced considerably from 24 at -27°C to 11 at -24°C. Results are shown in Figure

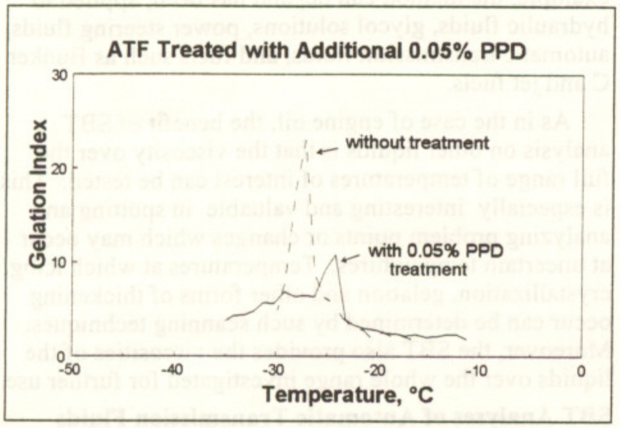

Fig. 13 - Comparison of the treated and untreated ATF Gelation Index curves for the ATF of Figure 11 after addition of 0.05% PPD.

13.

As is often the case with PPDs, after a certain level of effectiveness, additional quantity of PPD does not have an effect. This is shown in Figure 14. It is apparent that the gelation has not been significantly reduced by doubling the PPD content added. So, in retrospect, the minimal amount of 0.05 percent PPD served the purpose of resolving the problem. This is the type of viscometric and rheological information which is helpful in solving problems of low-temperature flow.

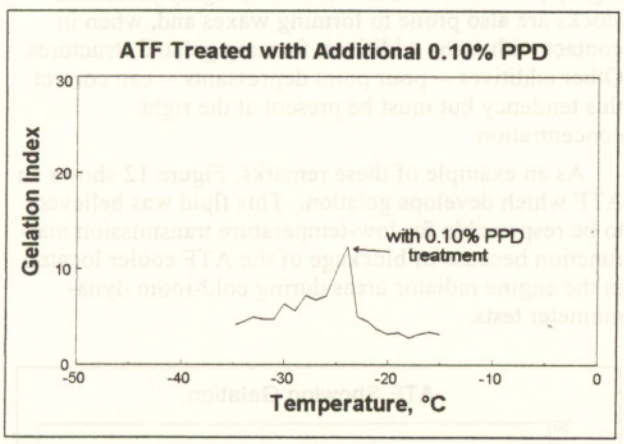

Fig. 14 - Comparison of the effect of doubling amount of added PPD in the treated ATF Gelation Index curves remain essentially the same as for the ATF of Figure 12.

SBT Analyses of Jet Fuels

Background

Recently, an effort was made to apply the Scanning Brookfield Technique to aviation jet fuels. The viscosity of such fuels is much lower than that of both petroleum lubricants and automatic transmission fluids. Viscosities are typically less than 20 centiPoise at -40°C in comparison to the hundreds or thousands of centiPoise for ATF or engine oils.

Consequently, evaluation of low viscosity liquid required modifications to the normal SBT equipment and procedure. For example, the investigations covered a much lower temperature range than those used for motor oils or automatic transmission fluids. For this reason a special kind of low-temperature bath was used which permitted studies down to -80°C or lower with complete visibility of the samples. One type of these very low-temperature baths is shown in Figure 15. While this table-top bath would hold two samples, an eight-head unit floor unit capable of -80°C temperatures was also used although direct observation of the samples was not possible.

In addition to other modifications in the method for jet fuel studies at very low temperatures, the cooling ramps used were 3° to 10°C/hour instead of 0.3°C/hour.

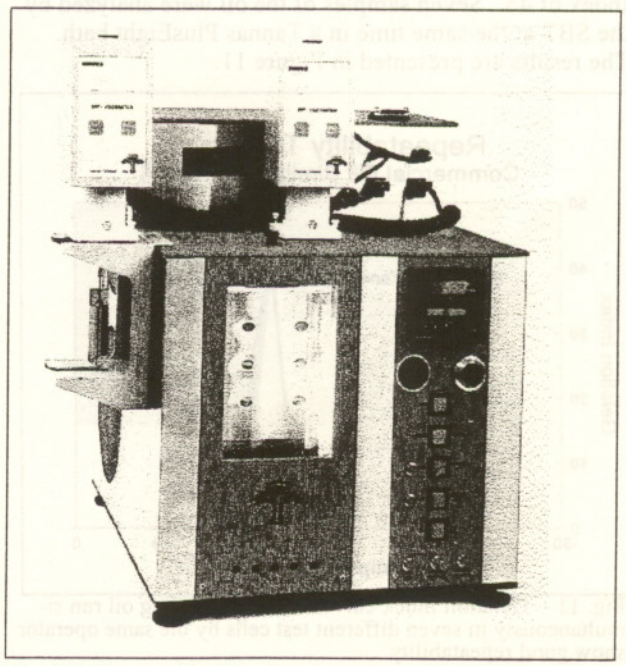

Fig. 15 - Tannas PlusTwo low-temperature bath for very low temperatures and direct observation of samples under analysis.

Results of Modified SBT Analyses

Jet fuels from three different sources were analyzed. These were commercial fuels currently being used in jet engines. Figures 16 and 17 show the results response of Jet A to the SBT. The cooling rate was -3°C per hour.

Figure 16 presents the viscosity-temperature curve of Jet A fuel. As evident, the viscosity increase down to about -52°C is fairly smooth and reaches a viscosity

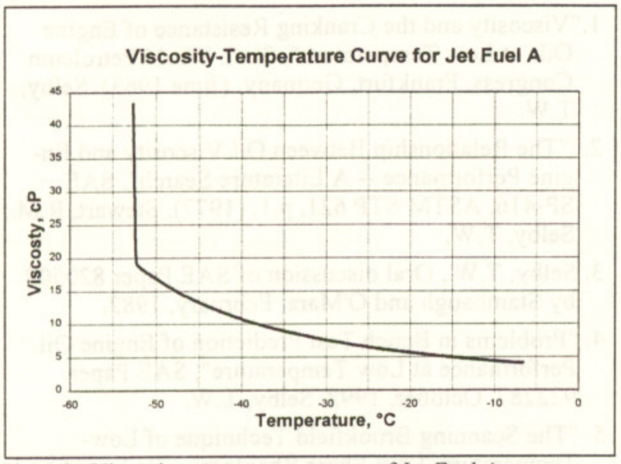

Fig. 16 - Viscosity-temperature curve of Jet Fuel A

value of about 19 cP. At that temperature, the fuel shows a sharp and continuing increase in viscosity which may reflect mass crystallization of the fuel.

Figure 17 shows the corresponding Gelation Index curve for Figure 16. The Gelation Index curve is flat until the structural change at about -52°C. It will be noted that the Gelation Index value is indicated to be greater than 70 since the inflection point on the curve had not been reached before the viscosity level went off scale. It is believed that such a strong Gelation Index without an end is related to the crystallization of a sig-

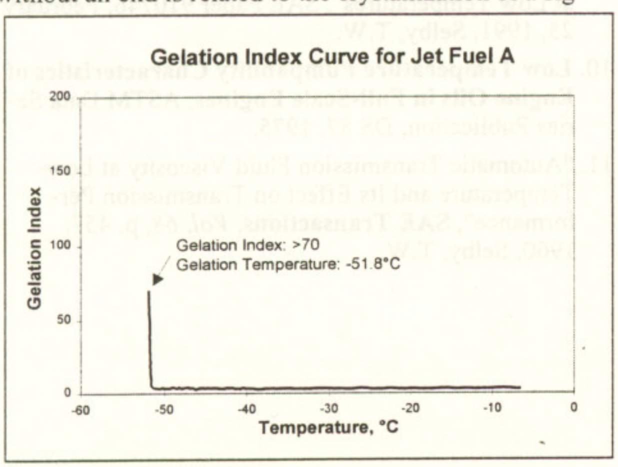

Fig. 17 - Gelation Index curve of Jet Fuel A. Also shown is the Gelation Temperature.

nificant part of the fuel composition. At this very low temperature of -52°C, such behavior is probably not a matter of concern.

The second commercial jet fuel analyzed using the modified Scanning Brookfield Technique was Jet Fuel B. Figures 18 and 19 show the viscosity-temperature and Gelation Index curves, respectively.

In most respects, the curves are similar to Jet Fuel A. with a slightly higher viscosity of 22 cP just before the viscosity begins to rise sharply. It will also be noted in

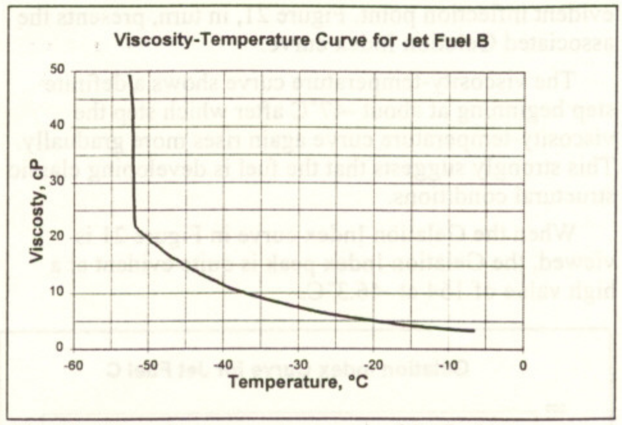

Fig. 18 - Viscosity-temperature curve of Jet Fuel B

Figure 18 that there seems to be an inflection point in the rapidly rising viscosity-temperature curve at about -52°C.

The corresponding Gelation Index curve of Jet Fuel

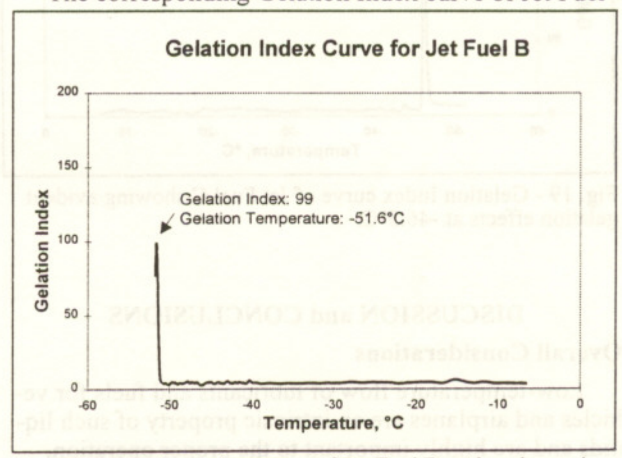

Fig. 19 - Gelation Index curve of Jet Fuel B. Also shown is the sharp Gelation Index of 99.

B shown in Figure 19 gives the expected response but, moreover, shows a sharp Gelation Index peak with a value of 99 at -51.6°C.

The third jet fuel evaluated using the modified SBT was different from the previous two jet fuels shown. Figure 20 (immediately below) presents the familiar viscosity-temperature and this curve shows a more

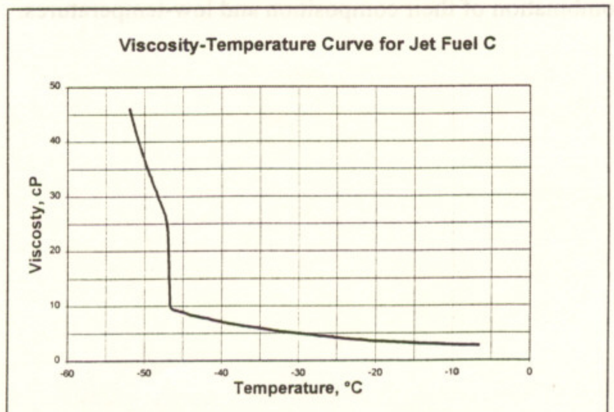

Fig. 20 - Viscosity-temperature curve of Jet Fuel C

evident inflection point. Figure 21, in turn, presents the associated Gelation Index curve.

The viscosity-temperature curve shows a definite step beginning at about -47°C after which step the viscosity-temperature curve again rises more gradually. This strongly suggests that the fuel is developing classic structural conditions.

When the Gelation Index curve in Figure 21 is viewed, the Gelation Index peak is quite evident at a high value of 164 at -46.3°C.

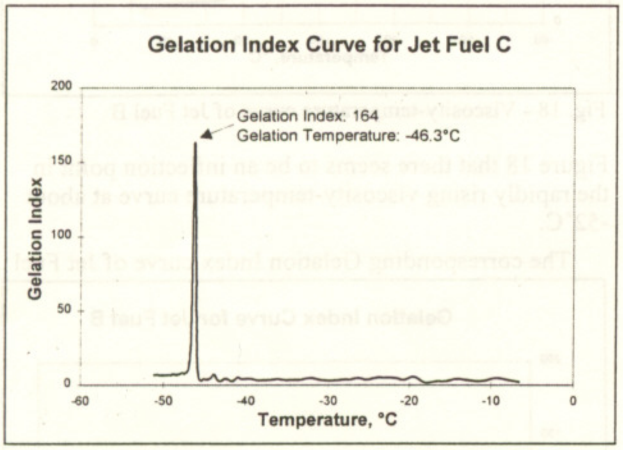

Fig. 19 - Gelation Index curve of Jet Fuel C showing evident gelation effects at -46.3°C.

DISCUSSION and CONCLUSIONS

Overall Considerations

Low-temperature flow of lubricants and fuels for vehicles and airplanes are an intrinsic property of such liquids and are highly important to the proper operation, and even the longevity of these modes of transportation. Having a suitable and relatively rapid mode of determining these properties is of considerable value in selecting these lubricants and fuels.

The Scanning Brookfield Technique has been shown to be a useful and quick means of determining low temperature viscometric and rheological properties. In addition, the viscosity-temperature data produced can be further analyzed to determine the severity of structural components induced in such lubricants and fuels by a combination of their composition and low-temperatures.

BIBLIOGRAPHY

1. "Viscosity and the Cranking Resistance of Engine Oils at Low Temperature", Sixth World Petroleum Congress, Frankfurt, Germany, (June 1963) Selby, T.W.
2. . "The Relationship Between Oil Viscosity and Engine Performance -- A Literature Search", SAE SP-416, ASTM STP 621, p.1, (1977). Stewart, R.M.; Selby, T.W.
3. Selby, T.W., Oral discussion of SAE Paper 820509 by Stambaugh and O'Mara, February, 1982.
4. "Problems in Bench Test Prediction of Engine Oil Performance at Low Temperature", SAE Paper 922287, October, 1992, Selby, T.W.
5. "The Scanning Brookfield Technique of Low-Temperature, Low-Shear Rheology -- Its Inception, Development, and Applications", ASTM STP 1143, Ed. Robert B. Rhodes, p. 33, December 1992, Selby, T.W.
6. MacCoull, N., **Lubrication**, Publ. Texas Co. N.Y, N.Y., p. 85, 1921.
7. Walther, C., **Erdöl und Teer**, *Vol. 4*, p. 510, 1928.
8. Wright, W.A., "An Improved Viscosity-Temperature Chart for Hydrocarbons", **J. Materials**, *Vol. 4*, #1, p.19, 1969.
9. "The Use of the Scanning Brookfield Technique to Study the Critical Degree of Gelation of Lubricants at Low Temperatures", SAE Paper 910746, February 25, 1991, Selby, T.W.
10. **Low Temperature Pumpability Characteristics of Engine Oils in Full-Scale Engines**, ASTM Data Series Publication, DS 57, 1975.
11. "Automatic Transmission Fluid Viscosity at Low-Temperature and Its Effect on Transmission Performance", **SAE Transactions**, *Vol. 68*, p. 457, 1960, Selby, T.W.