2006-01-3352

Low Temperature Rheology of Soot-Laden, Heavy-Duty Engine Oils Using the Scanning Brookfield Technique

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ABSTRACT

The rheology and related low-temperature pumpability of engine oils used in modern heavy-duty diesel engines are markedly affected by the presence of high levels of soot. This paper presents results of studies of the rheological condition of highly soot-laden oils using two protocols of the Scanning Brookfield Technique as investigative tools.

BACKGROUND AND INTRODUCTION

General Observations

The ability of the engine oil pump to supply lubricant to the critical wear sites of the engine is a self-evident requirement for engine life and there is a direct relationship between the rheology of oil at low temperatures and its pumpability. Earlier in automotive progress, as lower and lower temperatures were sought at which the engine could be used, the exponential increase of engine oil viscosity with decreasing temperature made startability the obstacle to be overcome. Progress was made slowly but steadily with better fuels, lower viscosity oils, and stronger starting systems until the advent of electronic ignition and fuel injection at which point startability rapidly disappeared as a matter of concern in many colder climates.

However, a new need was uncovered by easier startability – the need to have adequate pumpability of the oil once the engine was started at low temperature. This affected both the design of engine oils and engines in that order. In the former case, effects of base oils, additives, and pour point depressants took center stage – in the latter case, awareness of the effects of oil pumps; length, diameter, and bends in the pump inlet tubing; inlet screen mesh and diameter; oil galleries and orifices, etc. when handling oils formulated for lower temperatures required attention and understanding.

As it turned out, engine oil viscosity was not the only factor of the oil limiting low-temperature pumpability and was not the most troublesome. Rheology of the oil – the combination of an oil's viscosity and gelation tendency was the most critical factor. This was made manifest by an epidemic of field engine failures in Sioux Falls, South Dakota (see Appendix 1), which incident brought about the development of the Scanning Brookfield Technique and, later, the precision and discrimination of the Gelation Index (see Appendix 2).

The Critical Role of Engine Oil Gelation

Fairly extensive cold-room engine tests **[1]** had shown that pumpability failure could occur by two rheological responses of the engine oil to low temperatures:

- The first response (and most easily predictable) was the so-called 'flow-limited' response in which the oil's viscosity ultimately reached a level limiting the ability of the oil pump to circulate the oil rapidly enough and/or the ability of the oil to flow rapidly enough through the oil galleries and orifices to reach certain critical lubrication sites in the engine.
- The second was the rheological response of the fresh engine oil to various cooling profiles generating a condition termed 'air-binding' that was much more difficult to predict or measure. It was a rheological response of the oil – a combination of viscous and gelated flow properties. This gelated oil mass was shown to collapse only slowly or not at all under the influence of atmospheric pressure as the oil pump pulled an initial plug of oil reaching to the oil surface in the sump – thus starving the engine for lubrication by air-binding the oil pump **[2, 3]**.

Low Temperature Pumpability of Heavy-Duty Diesel Engine Oils

Until comparatively recently, pumpability of oil for heavy-duty diesel engines has, not been given the relatively close attention received by passenger cars over the years from about 1960. However, in 1999, heavy-duty diesel engine oils were required to carry much higher levels of soot in order to meet a mandate from the Environmental Protection Agency (EPA) requiring a reduction in the emissions of oxides of nitrogen. Among other concerns about increased wear and durability, the potential effect of the significantly increased level of soot on low-temperature engine oil viscosity and pumpability was raised **[4]**. This latter issue and the application of the Scanning Brookfield Technique (SBT) to its resolution is the subject of this paper.

The Scanning Brookfield Technique (ASTM D 5133 **[5]**) is a sensitive low-temperature pumpability test that was developed to measure both low-temperature viscosity of engine oils as well as the tendency of some oils to form a gelated condition which, as mentioned earlier, caused a condition of so-called "air-binding" of the engine oil that led to the failure of a number of engines in the Sioux Falls incident of 1980 (Appendix 1) and others in Europe in 1981.

Background of the Development and Application of the Scanning Brookfield Technique Method

For the clear understanding of interested readers, it is desirable to describe the basis of the Scanning Brookfield Technique (SBT) in order to understand its later application to soot-laden, heavy-duty engine oils as ASTM D 7110 **[6]**. However, in the interests of making the paper more readable for both those familiar and unfamiliar with low-temperature pumpability, helpful information on the background of the SBT is presented in both Appendices 1 and 2.

SBT STUDIES OF SOOT-LADEN, HEAVY-DUTY ENGINE OILS

Focus of Low-Temperature Studies in This Paper

Engine oil samples were obtained from others including both Cummins M-11 tests and Mack T-10 and T-11 tests. No other characterization of the oils were given by their sources beyond the oil having been used in highly soot-forming engine conditions producing soot levels from approximately 5 up to 10% soot. In several cases these oils were also measured by the MiniRotary Viscometer, a low-temperature pumpability test method for used oils described by ASTM D 6896 **[7]**.

The information presented in this paper was developed for three specific purposes:

1. To determine the viscometric response of the SBT to such highly soot-laden oils,
2. To determine the rheological response of these oils – if and at what temperature gelation occurred, and
3. To compare the data obtained by the SBT to that produced by the MiniRotary Viscometer using the above ASTM approach.

Preliminary Studies

In view of the need for information on the relatively unknown low-temperature rheology of soot-laden oils, first studies using the SBT protocol covered the range of temperature from +20°C to the temperature at which the viscosity of the test oil exceeded the torque capacity of the particular viscometer used. These first oils tested were generated by the 400-hour Cummins M-11 test.

Non-Gelating Viscosity-Temperature Behavior of Soot-Laden Oil – Replicate results on soot-laden, gelation-free Oil 1 are shown in Figure 1 using data from two TAV-2 viscometer heads supplied by the Tannas Company. The curves are essentially identical as shown by their indistinguishable viscosity-temperature curves. Gelation Indices of the replicate runs are not shown but, as expected (see Appendix 2), are flat with no evidence of gelation.

Gelating Viscosity-Temperature Behavior – Replicate results using two different cooling rates of 1° and 3°C/hr (SBT-XR extended range protocol) on soot-laden Oil 2 are shown in Figure 2. Departure from the normal exponential relationship of viscosity with temperature is evident. Good replication of the SBT analyses is shown even with differing cooling rates.

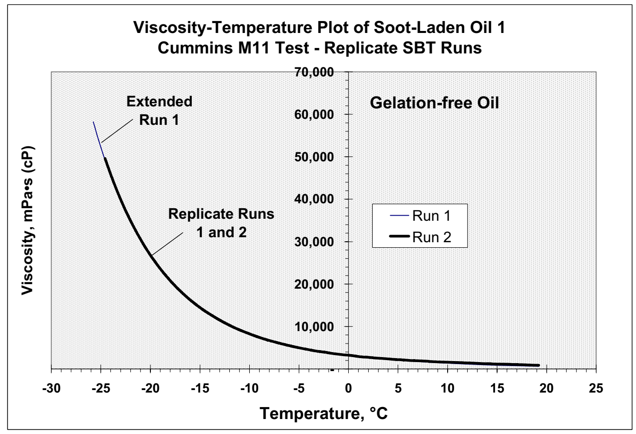

Fig. 1 – Replicate analysis of gelation-free, soot-laden, heavy duty engine oil.

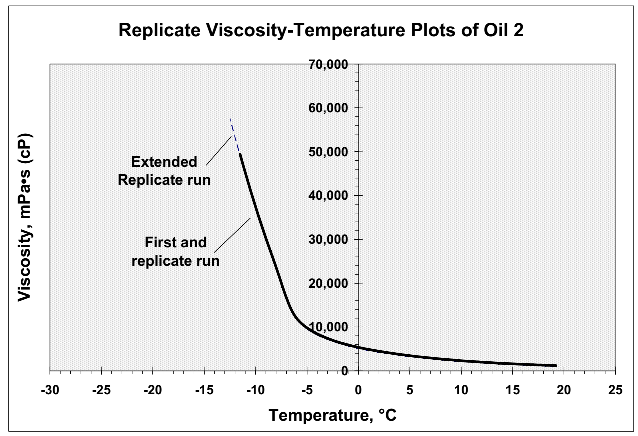

Fig. 2 - SBT analysis of gelation-prone Oil 2 using different sample cooling rates.

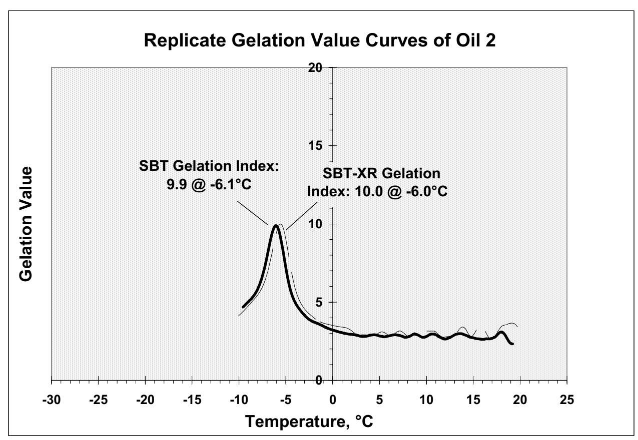

Fig. 3 – Gelation Values of replicate analyses of Oil 2 using different sample cooling rates.

Figure 3 shows the Gelation Index curves for the replicate analyses. Values obtained are quite similar at Gelation Indices of 9.9 and 10.0 and temperatures at which the Gelation Index occurs for both runs are within 0.1°C – at -4.0° and -4.1°C.

At higher temperatures, lower viscosities, and the associated lower sensitivity of the viscometer heads, the Gelation Index curves of Figure 3 become more variable but still range within ± 1 GI unit.

Precision and Characterization - Precision in determining low-temperature rheology is one of the strengths found in Scanning Brookfield Viscometry. As a consequence, the method produces viscosity-temperature and Gelation Value curves that precisely characterize a given oil. This will become evident in the following studies.

Gelation at Higher Temperatures – One of the early concerns about oils in which high levels of soot were suspended was the question of whether this soot might – itself or in concert with oil or additive components – form structures.

Figures 4 and 5 are evidence that this concern may be valid. The viscosity-temperature and gelation data of Oil 3 suggests presence of significant gelation above the +20°C temperature at which SBT measurement was begun. Re-analysis closely replicating the first test seems to confirm the presence of this phenomenon.

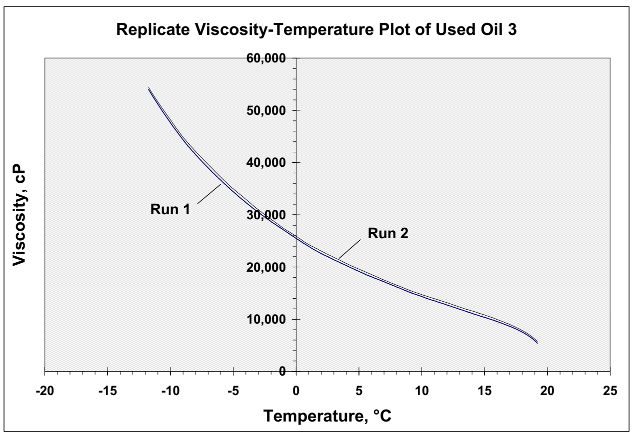

Fig. 4 – Replicate viscosity-temperature curves of Oil 3.

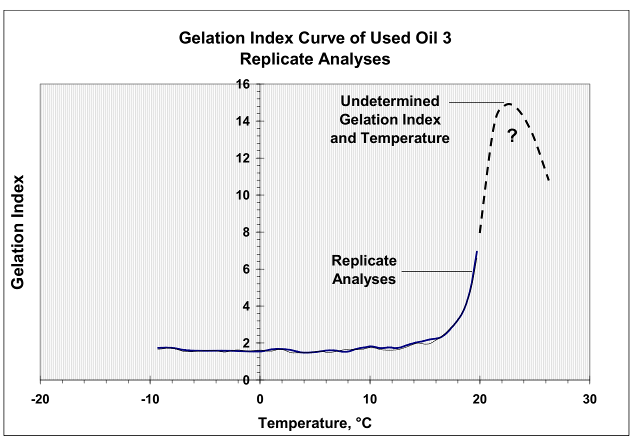

Fig. 5 – Replicate Gelation Value curves of Oil 3 suggesting a Gelation Index occurring above +20°C.

MMW Analyses of Soot-Laden Engine Oils – Comparison of the three previously discussed soot-laden Oils 1, 2, and 3 using the MWW equation is instructive.

Essentially – as is particularly evident in Figure 6 – gelation is shown to raise the viscosity level of the oil to a degree dependent on the severity of gelation. That is, once gelation has occurred, the viscosity-temperatures curve of the resulting fluid continues to manifest the rheological effects of gelation.

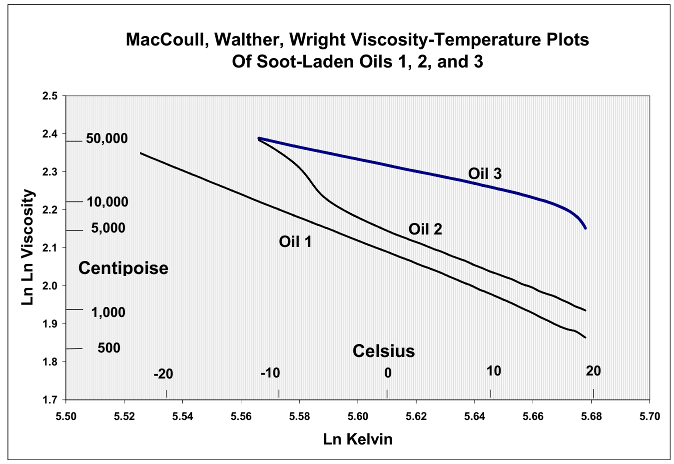

Fig. 6 – MWW plots of Oils 1, 2, and 3.

Consequently, higher viscosity levels produced by gelation would be likely to affect the rate of flow of the oil to the oil pump and, perhaps to a lesser degree, throughout the lubrication system of the engine.

The MWW values of Figure 6 also seem to further confirm the effect of some form of gelation occurring above +20°C. That is, the viscosity level of Oil 3 is initially high in comparison with Oils 1 and 2 (which have similar slopes) but Oil 3 progressively shows less increase in viscosity with decreasing temperature – less slope – as though the viscous influence of the initial form of gelation above +20°C (perhaps some form of soot agglomeration) is being mitigated by the shearing action at higher viscosity. Certainly, the rheology of Oil 3 is trending back to viscosity values of Oil 1.

In contrast, Oil 2 seems to be showing a gelation that has a permanent imprint on the rheology of the fluid as the viscosity rises with decreasing temperature.

With present information, it is not known to what degree the soot particles are the cause of, or involved, in the gelation condition observed. Moreover, it is not presently known if fresh oils might form gelated structures at temperatures as high as or higher than +20°C. Further studies are obviously of interest.

Higher Torque SBT Analyses of Soot-Laden, Heavy-Duty Engine Oils

ASTM D 7110 Protocol for Soot-Laden Engine Oils –

As mentioned earlier, one of the interesting questions that developed in the study of soot-laden engine oils was the question of their behavior at lower temperatures and higher viscosities. As a result, an SBT protocol using a viscometer head of higher torque capacity was developed and became ASTM Method D 7110 **[6,14]**. The following data were obtained on SAE 15W-40 ASTM soot-laden engine oils produced by the Mack T-10 engine test and used for low-temperature pumpability studies **[15]**. Earlier studies with soot-laden oils indicated – as shown in Figure 3 – that gelation formation with these oils could readily occur with faster cooling rates of faster cooling rates of 3°C/hour (compared to the 1°C/hour used in the SBT ASTM D 5133 protocol). This higher rate of cooling was applied in the ASTM D 7110 protocol making it possible to complete a full rheological analysis from -5° to -25°C within seven hours. A rotor speed of 12 RPM is applied briefly and immediately after the pre-heat (to simulate the operating engine) and before subsequent analysis at 3°C/hour.

Comparison of the 1°C/hour cooling rate of the ASTM D 6133 protocol to the ASTM D 7110 protocol was made using a soot-laden engine oil. These data shown in Figure 7 indicated that the two protocols yield similar viscosity-temperature results and both respond very similarly even to presence of a mild gelation tendency.

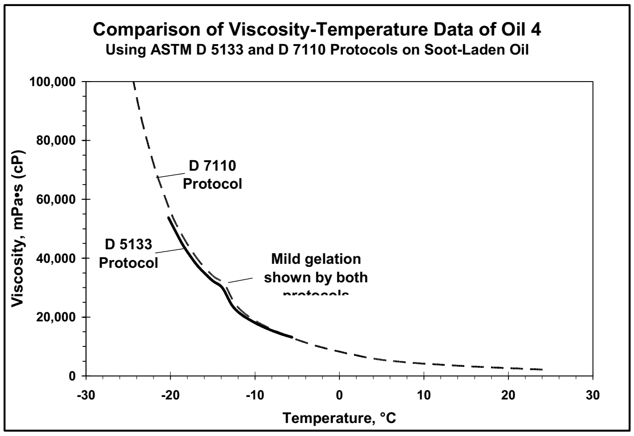

Fig. 7 – Comparison of two SBT protocols

Non-Gelating Viscosity-Temperature Behavior Using ASTM D 7110 Protocol – Using the ASTM D 7110 protocol, Figure 8 shows results on a soot-laden oil identified as Oil 5 in this paper. This oil was shown by SBT analysis to have gelation-free viscosity-temperature characteristics.

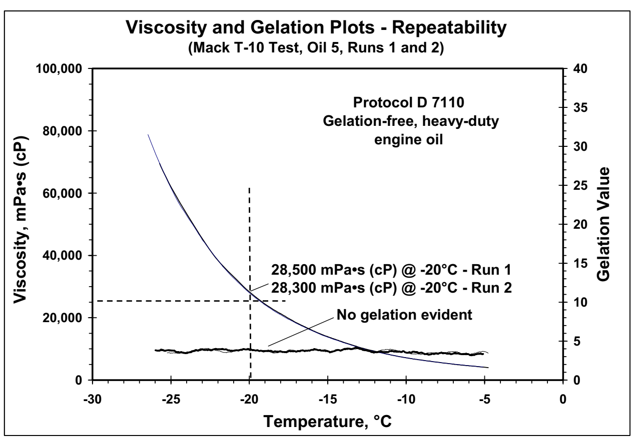

Fig. 8 - SBT analysis of non-gelating soot-laden engine oil.

As shown in Figure 8, replicate runs produced almost indistinguishable results for both the viscosity-temperature and Gelation Value curves.

The dashed lines on this and subsequent figures show the viscosity and temperature limits of 25,000 mPa•s (cP) at -20°C – specifications set for heavy-duty engine oil pumpability by the ASTM Committee D02 Heavy Duty Engine Oil Classification Panel (HDEOCP) **[16]**.

Although the oil is well-behaved regarding freedom from gelation, at 28,400 mPa•s it still fails – but marginally – to meet the specifications of 25,000 mPa•s at -20°C established.

The MWW plot of Figure 9 of Oil 5 shows the inclined straight lines expected from the flat Gelation Value curves in Figure 8. Again, repeatability is good.

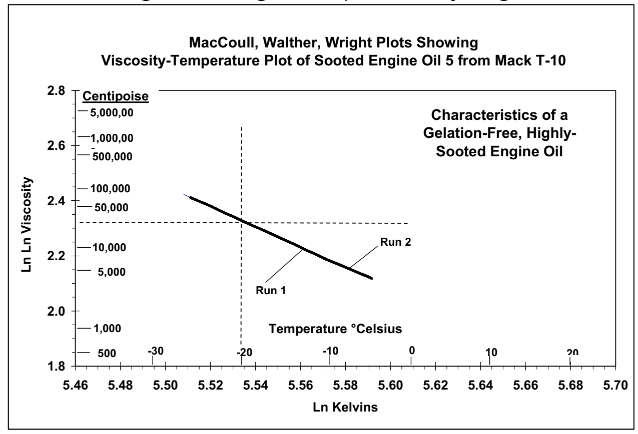

Fig. 9 – Replication of MWW plots of Oil 5.

Comparison of Data from MiniRotary Viscometry – Another low-temperature pumpability test – identified as the MiniRotary Viscometer (MRV), ASTM D 6879 **[7]** – was also applied to the soot-laden Oil 5. In some degree of similarity to the SBT, the MRV is also a rotational viscometer. However, the MRV measures viscosity at constant torque rather than at a constant shear rate as in the SBT instruments. Another difference is that the MRV produces single viscosity values at -20°C in 36 hours or at -25°C in 38 hours during which time the oil is held quiescently until analysis.

If a particular oil develops sufficient gelation, the MRV senses this as a failure of the rotor to be turned at low torque. The degree of resistance to the torque required to turn the rotor is a measure of the severity of gelation and the particular increase in mass available to turn the rotor is called the ‘Yield Stress’ (a term not quite the same as the classical definition of yield stress since the steps of increasing mass used in the MRV may somewhat overstep the true yield stress).

For comparison to the ASTM D 7110 data, values on the MRV were obtained at -20° and -25°C and (by terminating the test early – after 21 hours) also at -15°C. As indicated in Figure 10, the MRV data is in reasonably good agreement with the SBT instrument as shown by the proximity of the three MRV values to the continuous viscosity-temperature curve produced by the Scanning Brookfield Technique.

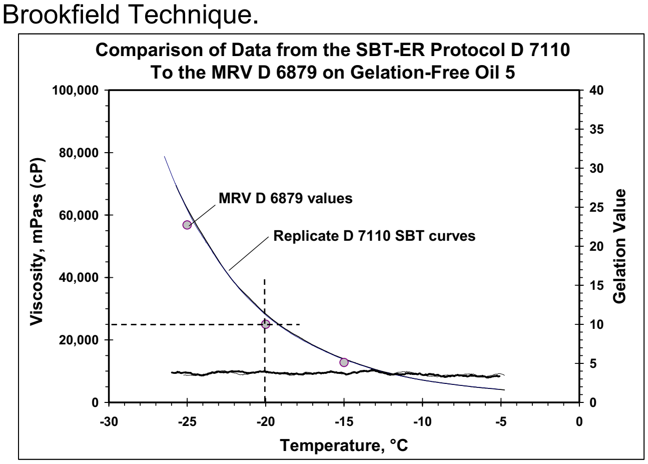

Fig. 10 – Comparison of results from SBT and MRV on Oil 5.

Rheological Behavior of Gelation-Prone Soot-Laden Oil Using ASTM D 7110 Protocol

Oil 6 – Figure 11 shows results with soot-laden Oil 6. In this case, the oil is abnormal in viscosity-temperature response and thus shows significant gelation. Again, repeatability of each set of the

1. viscosity-temperature curves,
2. Gelation Value curves, and the
3. Gelation Index values,

seem good as shown by the overlying curves and values in Figure 11.

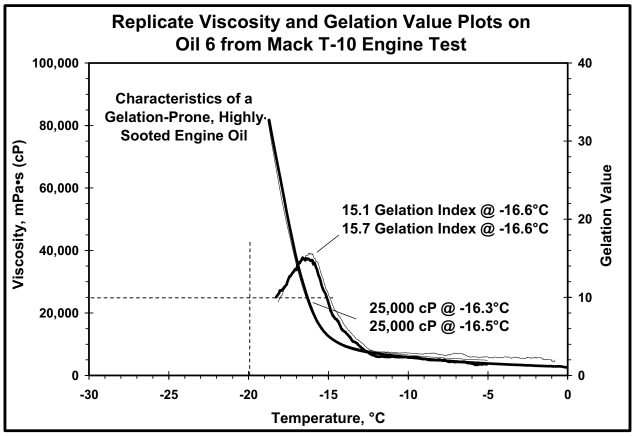

Fig. 11 – SBT analysis of gelating soot-laden engine Oil 6.

However, the viscosity-temperature values at 25,000 mPa•s (cP) were both -16.6°C and, thus, Oil 6 would fail to pass the viscosity limits established **[16]**. That is, Oil 6 would not meet the ASTM HDEOCP requirement of having a viscosity of 25,000 mPa•s at -20°C or lower. Moreover, Gelation Index values were significant at 15.1 and 15.7 at temperatures of -16.3° and -16.5°C, respectively.

Comparison with Data from the MiniRotary Viscometer on a Gelation-Prone Oil – Comparison is again made with data from the MRV ASTM D 6879 protocol as shown in Figure 12.

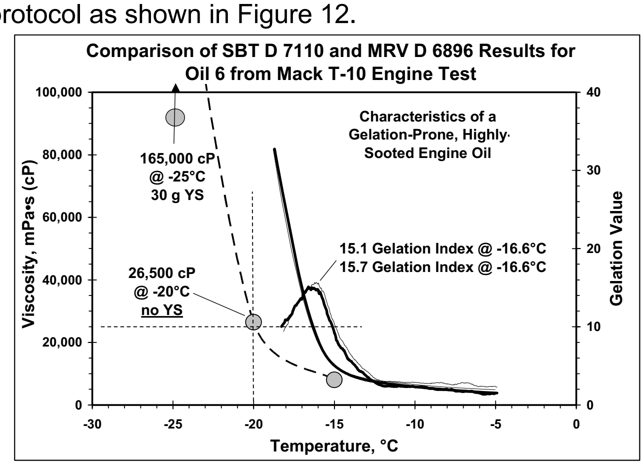

Fig. 12 – Comparison of SBT and MRV viscometers, Oil 6.

In this case involving a gelating oil, the two low-temperature pumpability methods give considerably different information. For example, for the MRV ASTM D 6896 method, Oil 6 almost meets the 25,000 mPa•s (cP) maximum viscosity at -20°C with a value of 26,500 mPa•s (cP) and shows no Yield Stress.

However, at -25°C, a viscosity of 165,000 mPa•s and a Yield Stress of 30 g is recorded.

In contrast, the SBT ASTM D 7110 method shows a Gelation Index of over 15 at -16.6, a viscosity of 25,000 mPa•s(cP) at -16.4°C, and, interestingly, a viscosity of 81,000 mPa•s(cP) at -18.8°C.

Thus, for some or perhaps most gelation-prone oils, the two methods 'see' the rheology of the oil considerably differently. This reflects a more fundamental difference in the two methods. While sensitive to viscosity, the MRV protocols are relatively insensitive go/no-go tests regarding gelation and Yield Stress.

From the viewpoint of predicting potential failure in the field both the MRV and SBT instruments respond similarly to viscometrically flow-limited behavior but when potential air-binding gelation may occur, the SBT is usually the more definitive of the two as shown with Oil 6.

Oil 7 – Figure 13 shows results of the SBT analysis of soot-laden Oil 7. Figure 13 shows that this oil develops gelation early in the SBT viscosity-temperature scan of ASTM D 7110 analysis and shows that, in such case, starting the analysis at 0°C can give further information. Even higher initiation temperatures are reasonable.

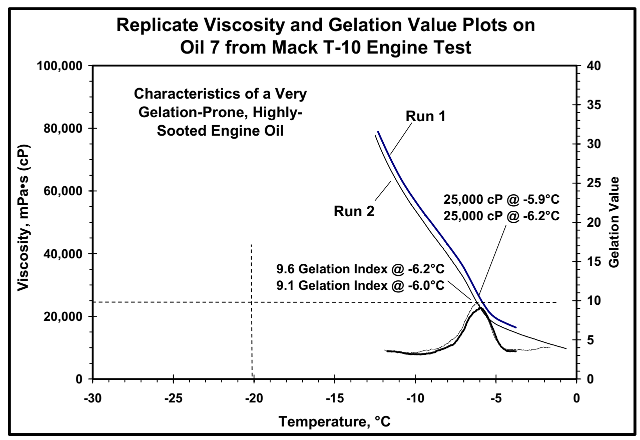

Fig. 13 – SBT analysis of gelating soot-laden engine Oil7.

In any case, the response of Oil 7 is markedly undesirable. The oil reaches the specification limit of 25,000 mPa•s at -5.9° and -6.2°C in Runs 1 and 2, respectively – approximately 14°C higher than desired. Moreover, the rapid rise in viscosity is triggered by gelation that results in a relatively modest Gelation Index (values of 9.6 and 9.1 at -6.2° and -6.0°C for Runs 1 and 2, respectively). As in the earlier data on Oil 3 in Figure 9, this shows the marked influence of gelation on viscosity even with relatively moderate levels of gelation when they occur at higher temperatures.

DISCUSSION

Factors in Scanning Rheometry

Scanning Technique Applied to Soot-Laden Engine Oils – As detailed in the Appendices, the technique of continuously determining the low-temperature rheology of oil by constant low-shear-rate rotational analysis while progressively and relatively slowly decreasing the oil temperature, as applied by the SBT was first found to be effective in the study and correlation of the pumpability of fresh engine oils. It later became part of engine manufacturer specifications of passenger car engine oils.

With the growing concern about the low-temperature pumpability of highly soot-laden, an effort has been made to apply this scanning technique to these oils as well. The studies have shown that when applied to highly soot-laden engine oils, the technique is uniquely informative and repeatable.

Effect of Continuous Shear on Inducing Gelation - It is believed **[13]** that the sensitivity and precision of the SBT protocol is related to the way in which it provides transport to crystal-forming molecules. The laminar shearing action of the rotor places these molecules in juxtaposition rather than requiring them to migrate under Brownian motion through an exponentially increasing quiescent viscous medium. In practice, this approach seems to encourages the formation of gelation that might be otherwise overlooked – gelation that Nature could, in its variety, trigger by some temperature regime as, for example, that of the Sioux Falls incident (see Appendix 1).

In the present study this gelation stimulation is shown in Figure 12 with Oil 6 where the oil develops obvious gelation in the SBT ASTM D 7110's slow rotation protocol at -16°C but does not show such gelation until -25°C in the quiescent-sample MRV ASTM D 6896 protocol.

Shorter Analytical Tests – One of the limitations of low-temperature pumpability tests has been the time required to gather information. ASTM Method D 5133 for the SBT requires a cooling rate of 1°C/hour or 20 hours from -5° to -25°C. ASTM Methods D 4684 and D 6896 both require 1/3°C/hour over the range at which they are sensitive to gelation for a total of about 44 hours to reach -25°C. In contrast, ASTM Method D 7110 requires only about seven hours reaching -25°C.

Scanning Brookfield Protocols – Two SBT protocols, ASTM D 5133 and D 7110, were used in this study – the former with viscometer heads capable of recording viscosities up to about 50,000 mPa•s (cP) and the latter having essentially double that capacity. Both were shown to be in good agreement by comparing them in application to a slightly gelating oil. Temperature ranges covered were as broad as +20° to -25°C.

Application to Soot-Laden, Heavy-Duty Engine Oils

Source of the Test Oils – The highly soot-laden oils used in this study came from two sources. One group of oils were oils from the Cummins M-11 test and were previously studied using the ASTM D 5133 protocol over the temperature range of +20° down to the temperature at which the torque capacity of the viscometer head was exceeded. The second group of oils was from the more recent ASTM round robin on soot-laden oils which included oils from the Mack T-10 engine test.

Non-Gelating and Gelating Soot-Laden Oils – The information presented on soot-laden, heavy-duty engine oils revealed that some of these oils could have low-temperature behavior free of any tendency to form gelation. In contrast, other soot-laden oils could become gelated and produce significant Gelation Indices. Of the oils tested, gelation occurred at relatively moderate temperatures of -16°C and higher.

Gelation Above +20°C – Interestingly, when the Scanning Brookfield Technique was applied to Oil 3 over the temperature range of +20° to -25° C, significant gelation was suggested above +20°C. Whether this gelation is dependent on the presence of soot or the original oil composition or both, is not, at present, known. What is evident is that the effect of the gelation increased the level of apparent viscosity of the oil considerably as was shown in Figure 6. Further study is planned particularly in regard to the effects of agitation of the oil after pre-heating.

Question of Agitation of Soot-Laden Oils Before Low-Temperature Viscometric Analysis – The finding of gelation at temperatures above +20°C raises the question of the effect of agitation of the sample presently called for in present low-temperature pumpability methods for the MRV ASTM D 6896 **[6,16]** before low-temperature viscometric analysis.

As previously noted, such higher temperature gelation has a significant effect on the viscosity-temperature relationship manifested by the progressive cooling of the oil. In contrast, in the field, soot-laden engine oil is highly agitated in engine operation after which it is quiescently exposed to low-temperatures during which it may develop gelation by either, or both, oil and/or soot response.

To emulate the engine, then, and to take into account possible soot agglomeration under quiescent heating of the sample, the question is: at what temperature – and with what degree of severity – should agitation of the sample be imposed? Whatever level of soot agglomeration may be possible, it can occur both on pre-heating and on cooling from the pre-heating step.

It would thus seem reasonable that agitation of the sample only occur during pre-heating and not afterward in order to emulate the engine response. If the oil is agitated after pre-heating and before low-temperature analysis, any soot or other form of gelation that might have increased the oil susceptibility to gelation at lower temperatures is eliminated along with any information from the instrument on this aspect of pumpability response of the oil.

The very mild shearing action of the SBT protocol is believed to encourage the development of gelation rather than interfering with or disturbing development of its rheological influence. Forcing Nature to reveal the potential for gelation is thought to be an advantage.

Test Method Differences in Viscometric and Gelation Response – In the comparison of the two pumpability test protocols, MRV ASTM D 6896 and SBT ASTM D 7110, the soot-laden Oil 6 from the ASTM program on pumpability showed early viscosity failure at -16.4°C and significant gelation – above 15 – in the SBT ASTM D 7110 test protocol. In contrast, the same oil was shown as only a borderline fail at -20°C (26,500 mPa•s) in the MRV 6896 protocol without any Yield Stress but followed by a clear failure with relatively strong Yield Stress at -25°C. Such difference with oil that has disturbing proclivity to gelation failure suggests that further studies on both instruments are in order starting with determination of the repeatability of the results on this oil.

On the other hand, heavy-duty cold-room pumpability studies of Galbraith and May **[17]** indicated that they could detect no air-binding tendencies in a number of soot-laden oils. This can be viewed as either an indication that gelation is not a problem or that cold-room pumpability tests may not be as subtle as Nature.

Conclusions

This study of the rheology of soot-laden engine oils has suggested further challenging work related to the low-temperature rheology of these oils. More than this, the study has revealed the likely formation of gelation at unexpectedly high temperatures above +20°C.

The data have shown that the Scanning Brookfield Technique provides a highly repeatable and sensitive method of delineating the presence or absence of gelation in these highly soot-laden engine oils. Moreover, over the temperature range of past concern – from -5° to -25°C – the analysis can be completed in seven hours, a considerable benefit in obtaining the desired information.

An area of concern was manifested when two different low-temperature pumpability instruments and protocols responded to an ASTM soot-laden test oil differently. Specifically, the SBT protocol indicated that the test oil was a failure at the required temperature of -20°C while the MRV protocol applied to the same oil indicated a passing result at -20°C but an apparently strong failure at -25°C.

Areas requiring further study are

1. Cause or causes of gelation above +20°C.
2. The effect of gelation in the original engine oil on the gelation of the soot-laden counterpart.
3. The progression of accumulation of soot on the rheology of soot-laden engine oil.
4. Causes of the difference between results of two different instruments for pumpability tests on a certain gelation-prone test oil.

Acknowledgements

The authors are grateful for the help of a number of associates who generated the work reported in this paper and for the comments of those who reviewed the paper.

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Appendix 1
The Sioux Falls Incident and Consequences In Low-Temperature Pumpability Development

THE SIOUX FALLS INCIDENT

History and Consequences

An unfortunate and costly epidemic of Air-Binding engine failures in Sioux Falls, South Dakota, in 1980 as well as other failures in Europe in 1981 was shown caused by oil gelation **[A1-1]**. The incidents made it evident that gelation of the oil (resulting, at worst, in a condition called Air-Binding in which the oil becomes gelated to the point where the oil pump creates a void) was considerably more unpredictable and likely to cause engine damage than the expected effects of Flow-Limited behavior (a viscosity dependent response in which oil cannot be pumped fast enough to satisfy the engine requirements. Further, the usual cold-room engine test procedures were not predictive of the many ways in which Nature could induce gelation as shown by the two-stage Sioux Falls incident.

Temperature and Gelation Development

The latter fact was proven by the seminal work **[A1-2]** of O'Mara and Stambaugh in their investigation – and cold room reproduction – of the temperature and time conditions leading to the Sioux Falls incident. They showed that starting with engine operating temperatures of at least 180°F, the cooling condition producing the field problem began with formation of a so-called 'wax nucleation' within a surprisingly high and narrow temperature range of +15° to +17°F (-9.4° to -8.3°C).

Moreover, the oil had to remain at this temperature for several hours for sufficient development of this 'wax nucleation' process. Following this stage, they found that the temperature then had to be decreased by ~10°F (~5°C) or more for failure to be generated. O'Mara and Stambaugh suggested that this necessary further temperature decrease was a crystal growth stage. However, another view is that since continued crystallization might be expected to occur at the initial temperature of +15° to +17°F as well, perhaps the increased viscosity of the oil entrained within the crystallization structure at the ~10°F lower temperature imparts added resistance to deformation of the structure. Thus, it is likely that viscosity and structure working in concert – the total rheology of the oil mass – that is involved in Air-Binding failure.

Important Aspects of the Sioux Falls Incident

There are several valuable conclusions that can be drawn from the O'Mara, Stambaugh replication of the Sioux Falls failures:

1. Crystal formation (one form of structure-building or gelation) in quiescent oil is highly temperature and time dependent and, when subtle, may require several hours to 'set up' at the critical temperature.
2. Gelation may occur at surprisingly high temperatures – i.e. +15°F (-10°C)or higher.
3. The initiation and development of gelation is strongly temperature dependent and may occur over a narrow temperature range – i.e. within 2°F (1°C).
4. In the work associated with the Sioux Falls incident, it was shown that two different temperature conditions were required – one that produced gelation but not Air-Binding and another, 5°C lower, at which the oil was sufficiently strong rheologically to result in Air-Binding.
5. Nature is likely to have many paths of producing Air-Binding but gelation formation almost certainly must precede or accompany them.

Contributing Factors to Gelation Formation

Several interdependent or independent factors have been shown to be, or are considered to be, associated with gelation formation and Air-Binding of fresh engine oil. Among these are:

1. Initial operating temperature of the engine before shutdown.
2. Ambient low temperature(s) after shutdown.
3. Residence time at gelation formation temperature.
4. Final temperature at which engine starting is attempted.
5. Base oil paraffinic content.
6. Pour-point depressant type and concentration.
7. Positive or negative effects of other engine oil additives.

RESPONSE TO THE SIOUX FALLS INCIDENT

The Scanning Brookfield Technique (SBT) pumpability bench test was developed in response to the epidemic of engine failures in 1980-81, and the method was first presented in discussion **[A1-3]** of the 1982 paper by O'Mara and Stambaugh.

A fact worth noting because of its significance in correlation with earlier low-temperature engine pumpability tests conducted by the ASTM: The SBT method showed that the temperature of development of gelation in a Sioux Falls field-failing oil occurred at the same temperature that O'Mara and Stambaugh found necessary for the eight-hour cold soak to nucleate gelation **[A1-2]**. This was early evidence of the predictability of Air-Binding tendencies of oils by the SBT.

Choice of Continuous Sample Stirring

In the process of collecting data, the SBT continuously, slowly, and laminarly stirs the oil with a cylindrical rotor in a matching glass stator with a gap of 1 mm. The approach of moving the oil gently during cooling was suggested by earlier low-temperature capillary work by one of the authors which indicated that gentle laminar movement of the oil could induce the appearance of gelation if it were potential. Thus, the Scanning Brookfield Technique can be viewed as a method of forcing occurrence of gelation – if such tendency is present in the engine oil. The SBT was thus believed to minimize the occurrence of otherwise unpredictable 'Sioux Falls' type afflictions of Nature.

Importance of Elimination of the Oil 'Memory'

In early SBT work on pour point of oils, it was found that pre-gelating associations of oil components could form at ambient temperatures. Moreover, if oil were once subjected to low-temperatures and warmed to ambient temperatures, any gelation that previously formed would incompletely re-form unless this 'memory' was removed. Heating the oil to a temperature such as 90°C that removed molecular associations was chosen as adequate to remove this 'memory' without affecting other properties of the engine oil. This pre-heating technique became part of the resulting protocol of later ASTM methods including the SBT.

Relationship of the Temperatures of Gelation and Air-Binding

As shown by the cold-room studies of O'Mara and Stambaugh, the temperature at which gelation occurs is not necessarily the temperature at which an engine would experience Air-Binding.

Using this observation in conjunction with the major ASTM cold-room engine pumpability studies of the 1970s with thirteen Flow-Limited and Air-Binding oils, Table 1 and Figure 1 were generated using the SBT **[A1-4,5]**. Correlation with the engines' Borderline Pumping Temperature is reasonably good when the 5°C difference between gelation and Air-Binding failure found by O'Mara and Stambaugh is applied The slope of the best line through the data is 1:1 and the intercept is essentially zero.

Table 1 -- Correlation of Engine and Scanning Brookfield Pumpability Data

PRO Oils	Air Binding	Flow Limited	Borderline Pumping Temperature			
			Engine BPT	Scanning Brookfield Technique		
				Viscosity	Gelation	Predicted BPT
01	Yes		-36.0		-31.0	-36.0
03	Yes*		-28.0		-22.5	-27.5
05	Yes		-17.5		-11.0	-16.0
06		Yes	-23.5	-26.5		-26.5
07		Yes	-27.0	-30.0		-30.0
08		Yes	-27.5	-30.0		-30.0
09	Yes		-26.5		-21.0	-26.0
10	Yes		-32.5		-28.5	-33.5
11	Yes*		-30.5		-27.0	-32.0
12		Yes	-28.5	-29.5		-29.5
13	Yes*		-32.0		-26.5	-31.5
15		Yes	-33.0	-35.5		-35.5
16		Yes	-23.0	-26.0		-26.0

* Oils indicated to be simulataneously air-binding and flow-liminted by SBT data

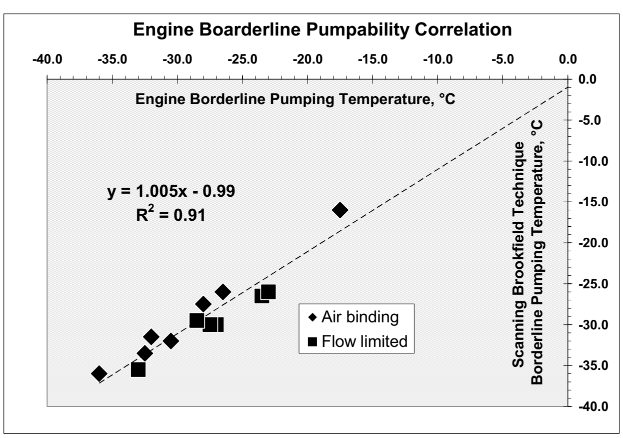

Fig. 1 – Correlation of SBT and engine pumpability.

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Appendix 2
The Scanning Brookfield Technique

Initial Development

The SBT protocol was specifically developed to continuously measure viscosity over any low-temperature range of interest. Of particular importance, the method used the viscosity scan to determine any gelation tendency of the engine oil. For fresh engine oils, a cooling rate of 1°C/hr. was found adequate to produce both viscosity and gelation tendency. The method was subjected to an ASTM round robin and became Method D 5133 **[A2-1]**.

The difference in rheological response of non-gelating oil, with its exponential viscosity-temperature relationship, and oil manifesting the developing presence of gelation as the oil is cooled from higher temperatures is shown in Figure A2-1 using the SBT protocol, D 5133.

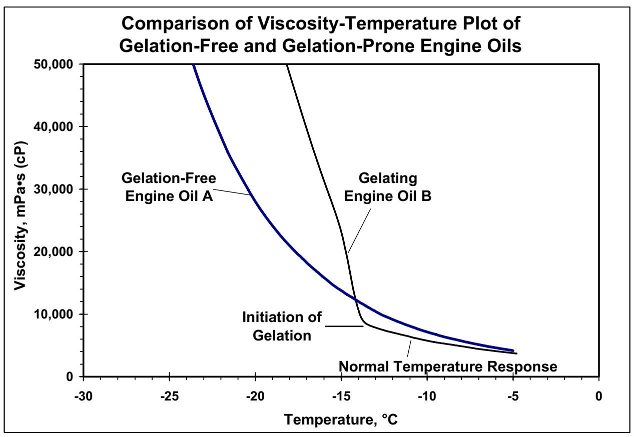

Fig. A2-1 – SBT comparison of gelation-free Oil A and gelation-prone Oil B

Although the presence of gelation in oil was visually evident in the recorded curves first generated in SBT studies, it was considered necessary to convert the observed information into measurable and comparable values. The MacCoull, Walther, Wright **[A2-2,3,4]** equation provided the means of generating a value related to the intensity of gelation and its temperature of occurrence.

The MacCoull, Walther, Wright Equation

The empirical MacCoull, Walther, Wright (MWW) equation has been used for many years as a means of interpolating and extrapolating viscosities of mineral oils and their compositions using kinematic viscometric data obtained at temperatures of 40° and 100°C most commonly. The simplest form of this empirical equation is expressed by the linear equation:

$$\mathrm{LnLn}(\eta+0.7) = \mathrm{Ln}(K)\cdot m + b \qquad \text{Eq. A2-1}$$

in which η is viscosity, **K** is temperature in Kelvin units, **m** is the slope, and **b** is the intercept.

At reasonably constant shear rate, oils having a normal viscosity-temperature relationship produce a straight line whose slope, **m**, is a measure of the effect of temperature on viscosity – the lower the slope, the less exponential change of viscosity with temperature. (Oils with lower slopes are generally more desirable for lubrication of equipment subjected to a range of temperatures.)

Application of the MacCoull, Walther, Wright Equation at Low Temperatures – In earliest studies, data obtained from the continuously-recording Scanning Brookfield Technique (which produces absolute or dynamic viscosity data rather than kinematic viscosity) showed that the empirical MWW equation also applied to low temperature dynamic viscosity and was found to be very useful **[A2-5]**.

Figure A2-2 shows the application of the MWW equation using the two oils shown in Figure A2-1. The non-gelating oil produces a straight line with a slope associated with its viscosity-temperature relationship while the gelation-prone oil manifests a clearly ogee or 'S'-shaped pattern.

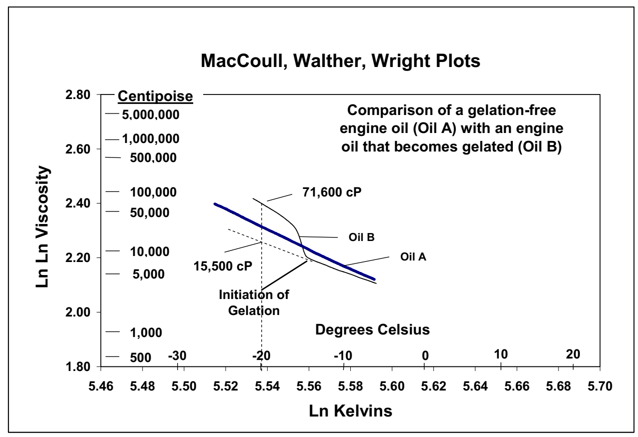

Fig. A2-2 – MWW plot of curves shown in Figure A2-1.

It should be noted that at higher temperatures, the plot of the gelating oil initially has a linear section associated with normal exponential increase of viscosity with temperature until gelation begins. At this point, the viscosity-temperature curve shows a rapidly rising apparent viscosity with decreasing temperature as a consequence of this developing gelation.

In this typical case of gelation analysis, after the rapid rise in gelation-induced viscosity, the MWW curve once more approaches a more normal exponentially linear form at considerably higher oil viscosities suggesting a return to a more normal viscosity-temperature relationship but now carrying the viscous effects of the presence of the prior gelation.

To more fully appreciate the impact that gelation has on the apparent viscosity of this gelated oil, additional data in Figure A2-2 indicate that this gelation has increased the viscosity of the oil by a factor of almost four over the viscosity the oil would have had if gelation had not occurred. This shown by extrapolation of the initial portion of the gelating oil's MWW viscosity-temperature relationship to -20°C, the viscosity value of this oil – had it not been affected by gelation – would have been about 15,500 mPa•s (cP). Instead a value of 71,600 mPa•s (cP) is generated by the effects of gelation – more than four times greater in apparent viscosity.

Gelation Index

After finding that the MWW equation could be applied at low temperatures, a simple method of measuring the magnitude and temperature at which gelation occurs was developed **[A2-6,7]**.

A so-called 'Gelation Value' was obtained by calculating the progressive slope or tangent (first derivative) of the MWW equation from the point-to-point experimental viscosity-temperature values generated by the SBT. If this were done, for example, for the gelation-free Oil A exhibiting the inclined straight line in Figure A2-2, the value of the first derivative or tangent would essentially be constant. Any change from such a linear relationship – as was, for example, shown by Oil B – would be expressed as a change in the value of the tangent of the curve. This is shown in Figure A2-3 for Oils A and B previously plotted in Figures A2-1 and A2-2.

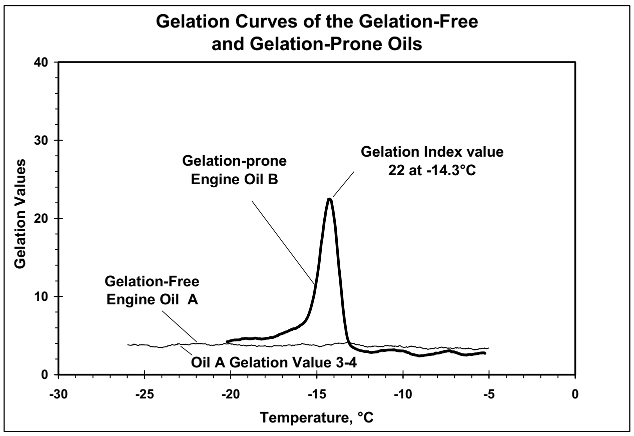

Fig. A1-3 – Comparative Gelation Indices of Oils A and B in Figures A2-1 and A2-2.

The tangents or 'Gelation Values' of the two Oils A and B are, as expected quite different. Oil A, with its constant slope shown in Figure A2-2 has an essentially unchanging Gelation Value of about 3 to 4 which reflects its viscosity-temperature relationship in the absence of gelation. In contrast, the Gelation Value of Oil B changes markedly below about -13°C finally reaching a maximum value at about -14°C called the Gelation Index. The latter value corresponds to the inflection point of the MWW equation shown in Figure A2-2. The shape of the curve produced from the first derivative of the MWW equation is itself informative concerning the nature of gelation development and strength **[A2-7]**.

In the collection of SBT and other data on over five thousand engine oils shown in the Institute of Materials Engine Oil Database **[A2-8]**, Gelation Indices range from many oil values less than 6 (corresponding to the natural viscosity-temperature relationship of the oils) to a number of values from 10 to well above 100. In fact, Gelation Value of some oils exceeds the capacity of the viscometer head before generating a peak value. (In such cases, the Gelation Index is given as the maximum obtained for the Gelation Value.)

It is important to note that Gelation Index values greater than 15 were associated with the field failure of engines in the Sioux Falls incident (see Appendix 1). Thus, the gelation-prone Oil B shown in Figure A2-3 would have likely caused failure under the Sioux Falls cooling conditions.

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