

The Low Temperature Rheological Response of Fresh versus Used Oils Using the Scanning Brookfield Technique

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Abstract: Rheological measurements of modern engine oils have been shown to be important particularly when determining their low-temperature pumpability. Historical and recent field failures dictate that testing fresh and used oils is critical in determining whether and oil is free of the potential to form structure reported as gelation. This paper presents studies utilizing the Scanning Brookfield Technique as a powerful tool to analyze both fresh and used engine oils.

Background and Introduction

Prologue

The amount of effort that goes into developing fresh oil for the use in any vehicle is a daunting task. The types of base stock, additives and other treatments necessary to achieve success in the pre-determined testing regime is costly and requires a strong understanding of the petrochemical field. Each engine type requires proper hydrodynamic lubrication specific to its performance. This must be maintained while the changes occurring to base stocks, additives, passenger cars and heavy duty vehicles are occurring almost daily. To complicate matters, the fresh oil is only available to the engine for a short period of time. What happens after the oils becomes oxidized and soot-laden? What properties change in the oil and what effect do they have on the engine?

One aspect of vehicle operation is the ability of the engine oil pump to supply lubricant to the critical wear sites of the engine. This 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 [1]. This added dimension of cold climates creates more obstacles for the oil to overcome in order to provide proper lubrication to the engine. First, the oil has to arrive to the critical locations in the engine immediately upon starting the engine. However, that is not always the case; sometimes the oil may not pump due to various phenomena occurring in the oil caused by the lower temperatures. These will be discussed later in the paper.

The added element in this study is the effect of particulate and soot. It has been shown in a military study on diesel engines that as little as 1.0% soot can increase pumpability times substantially [2]. The combination of factors in the engine such as high temperatures and oxygen along with the reaction from a mixture of various liquids and gases and the addition of a variety of solids such as carbon-based dirt and metallic particles lead to the oil becoming sooted [3]. Investigating the oil performance in the Scanning Brookfield Technique (SBT) from fresh to used (aged) is one way that this understanding may be enhanced. The information to follow will cover the behavior of fresh oils, used oils, and aged oils in the SBT.

Pumping Attributes of an Oil at Low Temperatures

Before embarking into the research performed for this paper, a novice understanding of the background of the flow conditions of oil at low temperatures is important. There are two critical low-temperature pumping aspects of the average engine 1) flow limited and 2) air binding [4]. The flow limited response of the oil occurs when the ability of the oil to flow is restricted by the increased viscosity of the fluid due to decrease in temperature.

In other words, the oil becomes too thick to pump as it becomes colder. The pumping viscosities desired for an oil are dependent upon the engine type. For example, an electronic ignition passenger car engine designed for fuel economy may require a much lower viscosity at the same temperature than a heavy-duty diesel truck as shown in SAE specifications.

The second condition, termed air binding, is a phenomenon where the combination of viscous and agglomerated flow properties create a gelated mass allowing only a small portion of the oil to be pulled into the pump and subsequently starving the engine of oil for a period of time [1,4,5]. A moderate condition of this may retard the oil flow causing minor or even negligible damage in the short term, but possibly major damage if the same episode continues over time. An immediate and more serious case is where the engine fails, with metal on metal damage occurring, before proper hydrodynamic protection is ever obtained. There are several cases where this has occurred over the years [1, 4, 5, 6]. The test method D4684 and D6896, the Mini Rotary Viscometer (MRV), is the a part of specifications that can test these attributes but is limited to a single point temperature measurement. The Scanning Brookfield, as shown later in the paper, provides a more thorough scan of the information over a large temperature range.

The Scanning Brookfield Technique – At a Glance

In order to properly “fingerprint” the pumpability response of an oil the Scanning Brookfield Technique was developed. The model used in this paper is the SBTDC manufactured by Tannas Company in Midland, MI. Details of the test are covered later in the paper. The test is accomplished by monitoring the viscosity of a sample continuously by turning a stainless steel rotor at 0.3 rpm inside of an oil filled stator, without destroying the structure, it became evident that both flow-limited and air-binding information could be collected with one cool-ramp cycle. To accomplish this either a liquid or direct cooling (dry solid block) method can be used to lower the temperature of the sample from -5 to -40 degrees Celsius (higher and/or lower temperatures may also be tested). The cool rate is one degree Celsius per hour and by monitoring the viscosity versus temperature information the information can be valuable. At this slower rate the structure forming tendencies are greater. There will be more on this later.

First of all, the viscosity information itself is useful. The viscosity at any temperature may be determined along with the maximum viscosity obtained. Second, analyzing the response of the viscosity in respect to the change in temperature reveals the structure that may form in the oil. In other words, when a sudden change in viscosity occurs it is indicative of gelation or a structure being formed in the oil.

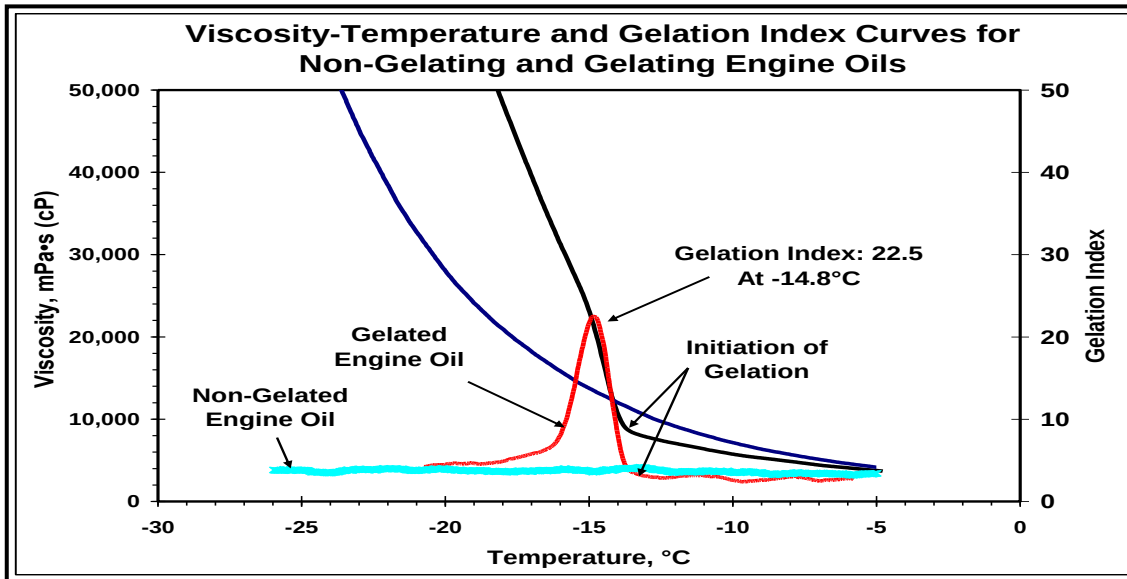
The presence of gelation can be visually evident in the recorded viscosity curves; however, it was necessary to convert the observed information into a measurable value. The MacCoull, Walther, Wright equation provided the means of calculating the degree and temperature of gelation. The empirical MacCoull, Walther, Wright (MWW) equation [7] has been used for many years as a means of interpolating and extrapolating the viscosities of mineral oils and their compositions. The equation can be expressed by:

$$\text{LogLog}(\eta + 0.7) = \text{Log}(^{\circ}\text{T}) \cdot \mathbf{m} + \mathbf{b}$$

in which η is viscosity, T is the temperature in $^{\circ}\text{K}$, $\mathbf{m}$ is slope, and $\mathbf{b}$ is intercept. At reasonably constant shear rate, oils of normal behavior produce a straight line whose slope, $\mathbf{m}$, is a measure of the effect of temperature on viscosity – the lower the slope, the less exponential change of viscosity with temperature.

Garnering this information and then applying the first derivative to the MWW reveals whether or not an inflection point exists; and how strong it occurs. In other words, if no inflection point or substantial change in the MWW slope relationship occurs then the result of the first derivative is a low value. However, if a significant or sudden change exists then the derivative will flag the larger and more evident change (Figure 1). This is recorded as the gelation index.

FIGURE 1



The higher “gelation” and “air-binding” values may cause serious issues in the engine [1,4,5,7]. The current failure level is at value of 12 gelation index (GI). However, many companies carefully monitor any gelation between 6 and 12 because of the failing potential. At what level the gelation index becomes an issue in an engine depends on the engine type, temperature ramp, final temperature, oil degradation and oil contamination; to name a few. This study is focused on the results of the oil before and after preconditioning takes place.

Initial SBT Studies of Fresh versus Used Passenger Car Engine Oils

It is first appropriate to introduce the oils tested and the protocol used for the testing. The author thought it important to investigate into both fresh and used oils. However, in the first part of this study the fresh oils were not available. As the table indicates, the name brand GF-4 oil was run in a gasoline passenger car and later aged further on the test bench. The table below summarizes the first samples tested (Table 1).

TABLE 1		
Oil Name	Oil Type	Method of Aging
Oil 1	10W30 Synthetic GF-4	Fresh – Not available for Testing

Oil 1A	Oil 1 Aged	Used in 2009 Chrysler, 3.8L V-6 for 4571 miles.
Oil 1B	Oil 1A Aged	Oil 1A after 90°C and 0.4 ml/min air exposed 1 day.
Oil 1C	Oil 1B Aged	Oil 1A after 90°C and 0.4 ml/min air exposed 2 days.

Step 1 was to run the SBT on the used sample 1A. Note that the engine is a 3.8L V6. The test was carried out utilizing ASTM Method D7110 at a cool rate of 3°C/hour [8]. However, because of the low viscosity of the samples, the testing started at -5°C versus 20°C. The result no gelation and a viscosity increase that had a mild and slowly rising curve that would be suitable for use as a typical 10W30. Because of the steady curve no gelation was flagged during the test. In order to gain more critical gelation information, the cooling rate was reduced to 1°C/hour. Here is where the data became interesting.

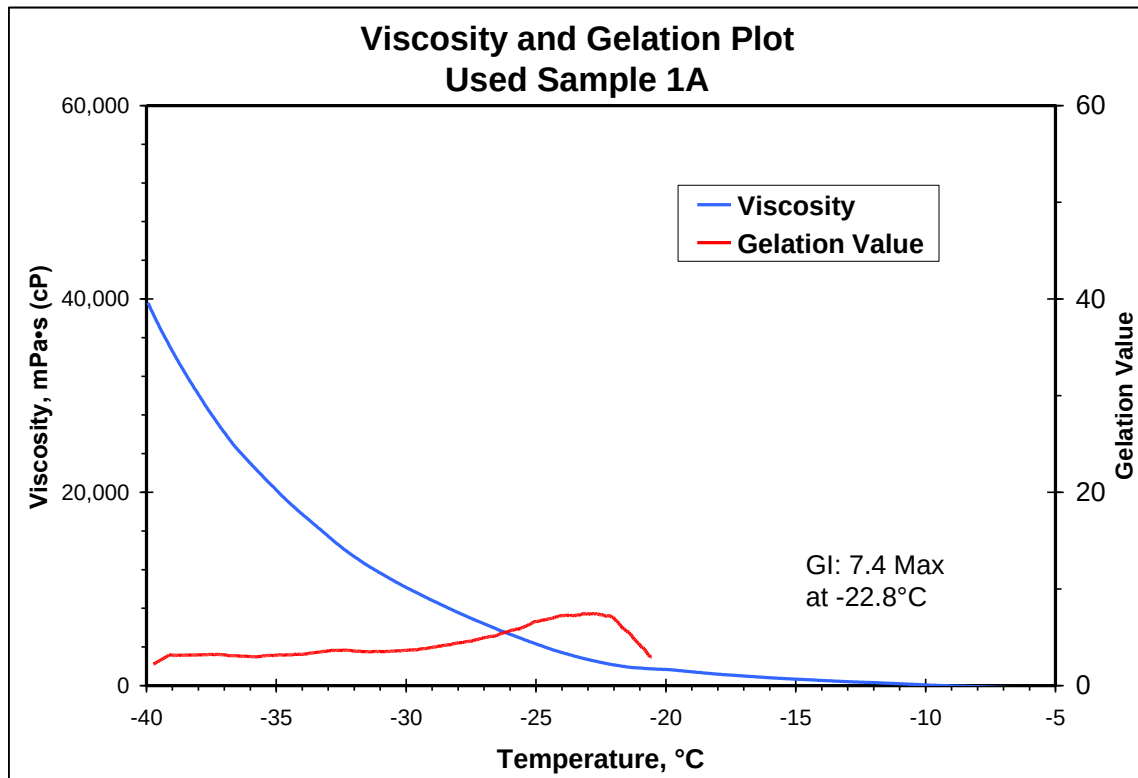


Figure 2

Sample 1A had a perceptible increase in gelation after slowing down the cool rate (Figure 2). The viscosity showed an increase only at the lower end. At the temperature of -30°C the viscosity result was 10183 centiPoise (cP). This is an increase in viscosity from 9471 cP when cooling rate of 3°C/hour was used. Conversely, the viscosity at -20°C was almost the same with a viscosity of 1698 cP at -20°C versus 1886 cP at a rate of 3°C/hour. The reason for the viscosity increase at approximately -23°C is due to the presence of gelation. The gelation index of 7.4 occurred at -23.2°C. The faster cool rate did not even show a reportable gelation index (below 6 GI). Note that the viscosity would still be well within an acceptability range for that grade; however, the gelation index value could indicate the beginning of a problem.

The fact that Oil 1A is a synthetic reveals that the contamination and/or additive types may be playing a role here. Moreover, a cool rate of $1^{\circ}\text{C}/\text{hour}$ revealed more information and was used throughout the remainder of the SBT testing. Pursuant to the results above, the aging process, induced in the laboratory, was carried out for 24 hours. The purpose was to study what would happen to the viscosity and gelation in the SBT as the oil aged. This process elevated the temperature of oil 1A to 90°C with fritted glassware lowered into the oil allowing dry air bubbles to percolate at a rate of 0.4 ml/min ; thus creating oil 1B. The aging was carried within the SBT Direct Cool unit as shown with the air diffuser (Figure 3 and 4).



Figures 3 and 4

The next interesting phenomena now occurred. The gelation that existed in Sample 1A vanished after 24 hours of aging (Figure 5). However, the viscosity increase for both Samples 1B was approximately 26% at -30°C . There are several possibilities causing the increase in viscosity and the decrease gelation. Several areas will have to be investigated to better understand this information such as volatility, TAN/TBN, HTHS and infrared spectroscopy. The oxidation process can bring about many varying factors that can play a part in the changes noted. This paper will not address all of the possibilities, just analyze the results from this testing. Since the gelation in Sample 1A was mild to begin with, the structure may be trying to form but is overwhelmed by the higher viscosity of the fluid. Other oxidative responses may also be the cause and can be revealed through infrared spectroscopy (IR). At this point it is mere speculation as it could be a combination of factors.

The same aging process was subsequently run on oil 1B creating oil 1C. Again, no gelation was detected, but the viscosity increased by 15% and 11% consecutively. The percent increase was lower at this point. Most of the light ends of the oil, along with any fuel contamination, continue to be volatilized out of the oil. At this point nothing can be concretely determined regarding the anti-oxidant of the oil. However, drastic increases or decreases in viscosity can be a concern for the oil.

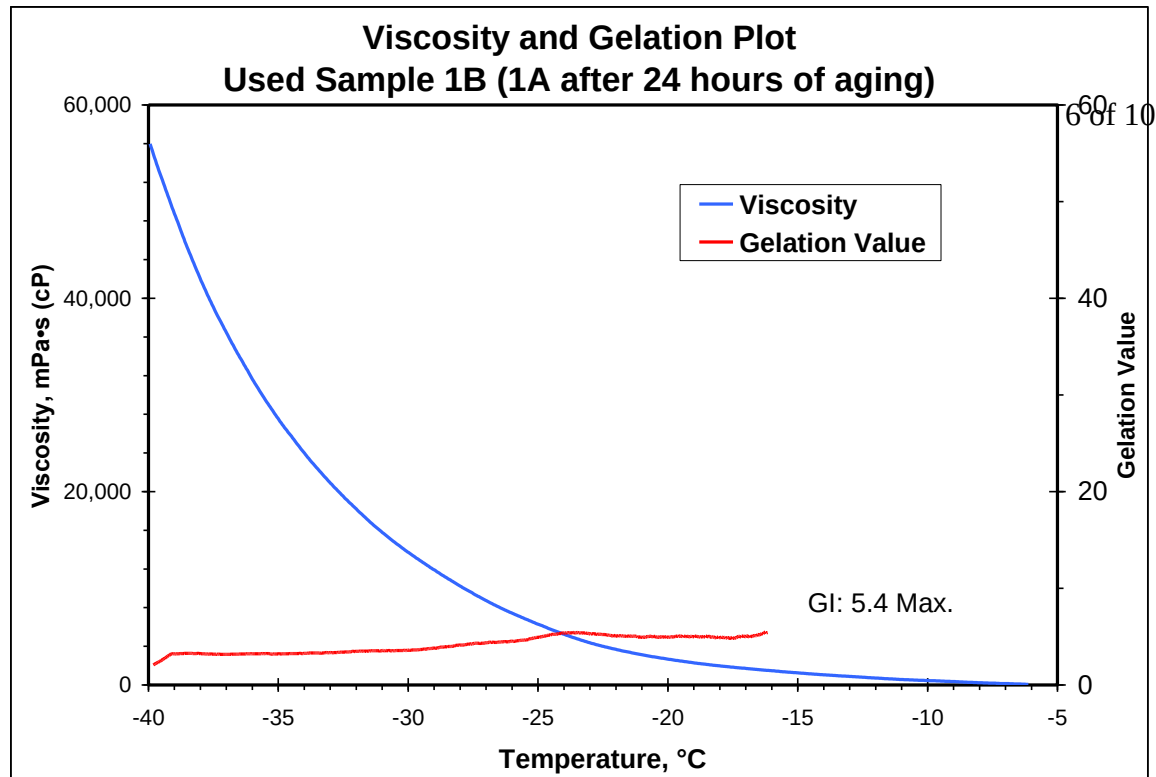


Figure 5

The Gelation vs Viscosity Experiment

The information gleaned from the above study brought about questions regarding the gelation structure such as how it is formed and how it is destroyed. The idea of having the level of viscosity change the gelation amplitude is interesting, but it does it repeat for other samples? What about the particulate or soot content and the effect on gelation?

The next experiment utilized reference oil that has been available for many years for testing instrumentation. The oil is called gelation index reference oil 150 (GIR-150). This oil has a gelation structure that forms around -16°C with an amplitude of approximately 19 GI (Fig 6).

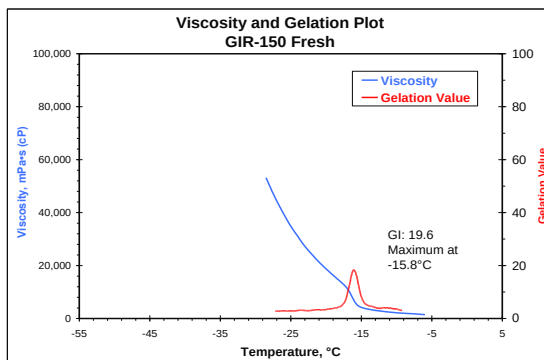


Figure 6

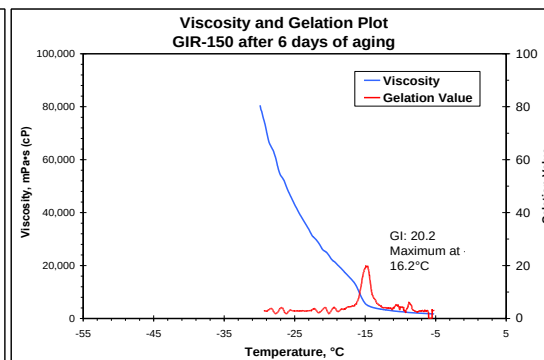


Figure 7

At first the same process of aging the oil was performed with this oil. Even though the oil showed oxidation characteristics, such as turning black, the results after six days of aging had no affect on the gelation. This graph is shown in Figure 7 and, other than a slight viscosity increase, has the same graph as the fresh oil. Then, after seven days, the viscosity increased by 22 % at -20°C and the gelation maximum decreased from 20.2 to 12.3 GI (Fig 8). The viscosity increase is not desirable at these low temperatures, but

can it be attributed to the reduction of gelation? A deeper look at the oxidation characteristics spurred investigation.

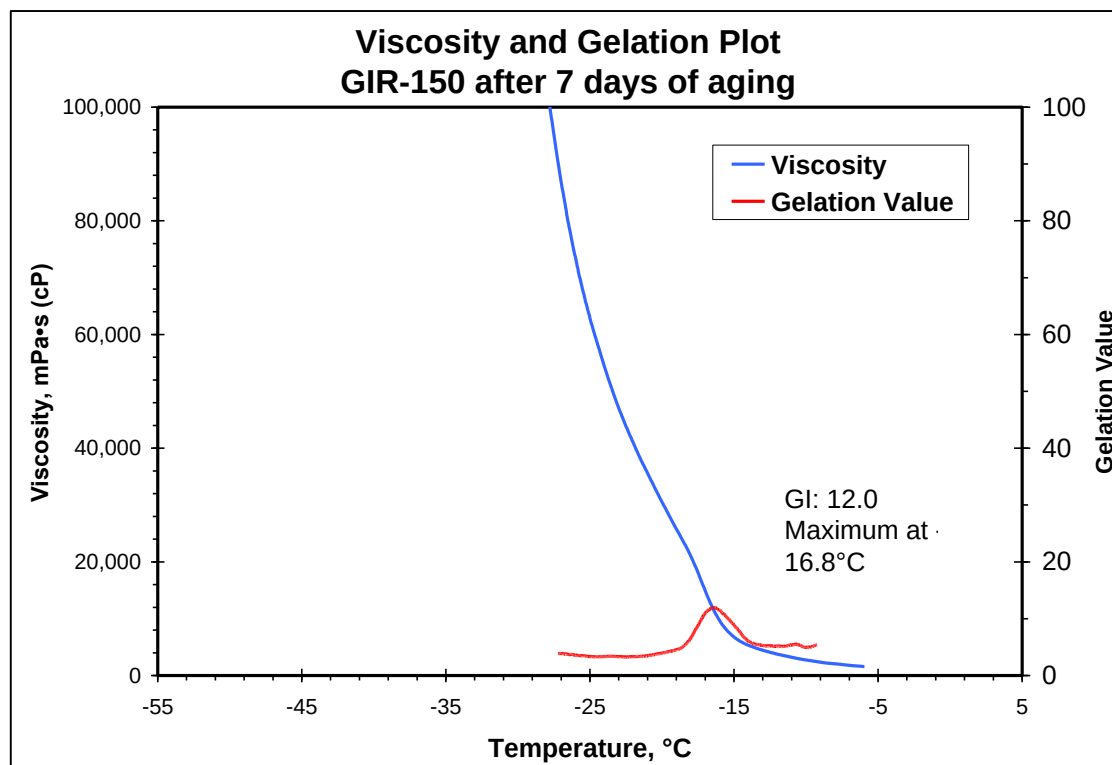


Figure 8

One of most valuable aides to look at the oxidation process is the IR. The IR was run on this oil between day 6 and day 7 of the aging process using a PerkinElmer Model 9250 Infrared Spectrometer. In order to add additional contrast, the fresh sample was also run. The results were interesting, to say the least (Figure 9). It is clear that the response of the oil from fresh to day 6 and then to day 7 showed significant oxidation changes. The top line in black is the fresh sample, the blue line is the 6 day aging and then the red line is the 7 day aging result. There is a significant change in all three samples around the 1700 cm^{-1} wavelength range. However, it is possible that the oxidation process, when the oils breaks down to a certain level, changes characteristics enough that the formation of a gel structure become less likely. The rate of oxidation and the effect on the viscosity and gelation index is dependent on the oil type and the additive package amongst other variables in the engine. More investigation in this area must take place for a better understanding.

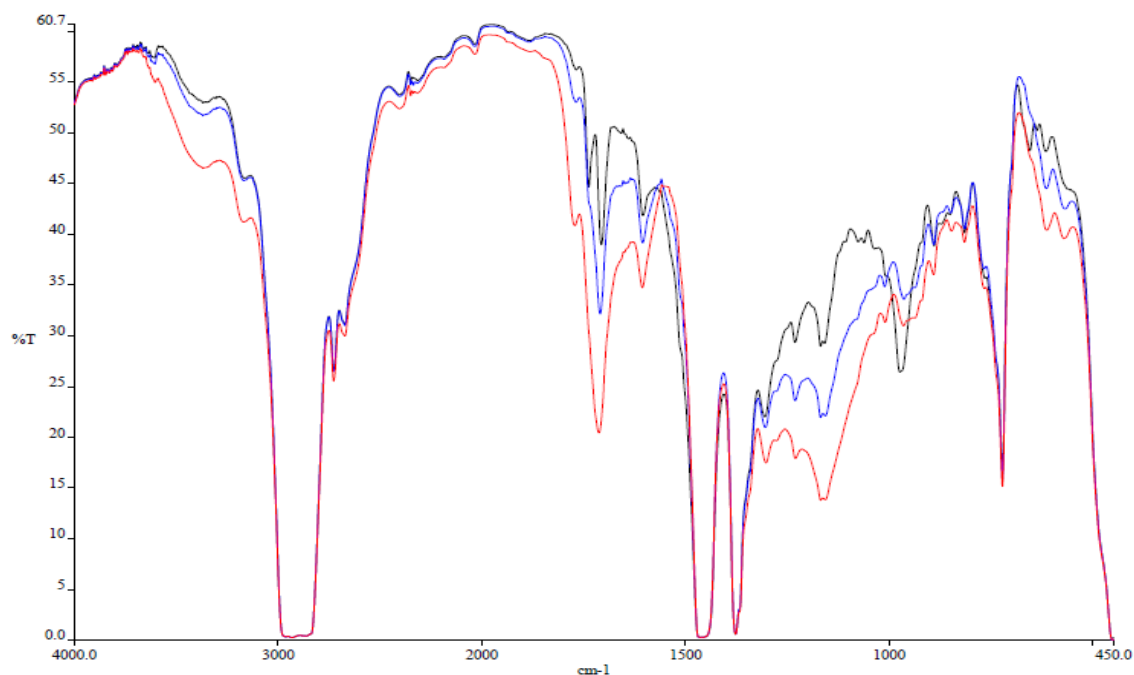


Figure 9

The question about particulate content and how it relates to gelation is also of interest. Even though particulate may cause some increase in the viscosity, it may also interfere with the formation of viscosity at low levels. The same oil, GIR-150 was used to analyze the effect of particulate content.

The Particulate Experiment

It is apparent then that the aging process has an effect on the increase in viscosity and the lowering of the gelation index. One may contemplate the various responses that are taking place during aging process and the resulting condition of the oil. Oxidation processes have proven to increase viscosity. In addition, as was recorded in some previous work by Farshid Owrang [9], it has been shown that the oxidation process of an oil at high temperatures can form a measureable amount of soot as measured in the NMR. In addition the resulting oxidized oil had similar characteristics to the combustion deposits of the same oil. Some synthetic oils had up to 25% more soot than their mineral oil counterparts. Of course, additives must be taken into account any time an analysis such as this is made. In any case, looking at the result of soot has some merit.

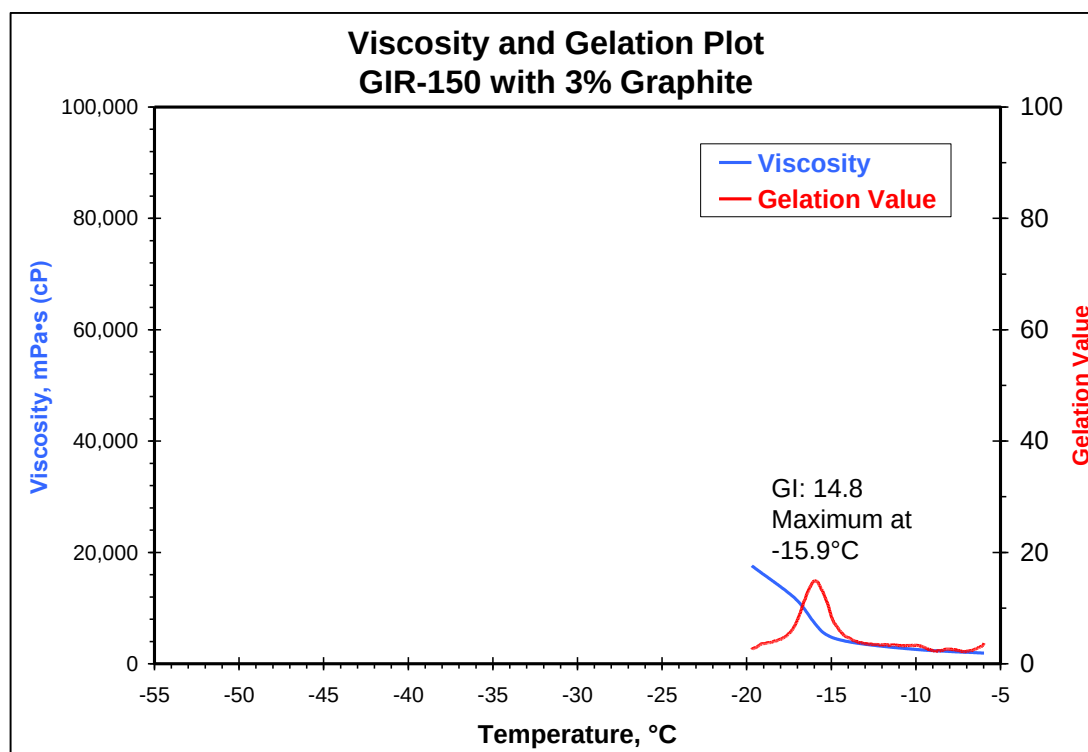
The best scenario would be to use a carbon black product to add to the fresh GIR-150. However, because of timing issues, it was decided to utilize graphite produced by AGS Company. Since graphite is similar in nanometer size and an allotrope of carbon it was the next best alternative. The first experiment was with 1% graphite. This level of graphite had no response in the gelation index. As a matter of fact, it was not until the graphite level reached 3% that any change was noted. At that point the gelation index dropped to a peak of about 12 GI. It is interesting that the viscosity level also substantially increased. The total increase percentage was 24 %. This percentage is

similar to that of the viscosity increase that lowered the gelation index earlier in the paper (Figure 10).

Figure 10

Conclusions

Low temperature pumpability is a concern in cold climates around the world. Failures have occurred and cost the industry millions of dollars over the years. As engine specifications and tolerances become tighter then subsequently oil performance will be more critical.



Fresh oils only perform with “out of the bottle” specifications for a short time. Oxidation, particulate, fuel and other contaminants quickly alter the oils performance. Testing aged and/or sooted oils is a good way to get a measure of the pumpability processes. The research information contained in this paper indicates that gelation at low levels may decrease as the oil becomes oxidized or contaminated with high levels of soot. However, the viscosity increase can also be problematic. Oxidation levels over time contribute to these issues.

Future work investigating extended drain intervals, TAN/TBN levels, IR spectroscopy, and HTHS would be interesting. It would reveal more about gelation and viscosity changes. In addition, soot levels may also change both the viscosity and gelation values. Further information is being obtained at this time to determine the response in current engine oils.

Acknowledgements

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