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The Use of the Scanning Brookfield Technique to Study the Critical Degree of Gelation of Lubricants at Low Temperatures

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ABSTRACT

Scanning Brookfield Technique (SBT) studies have provided the background for a new concept in rheological characterization of gelation in lubricating oils at lower temperatures. Using the typical SBT temperature/viscosity range, the concept requires calculation of the first derivative of the MacCoull/Walther/Wright empirical equation. The derivative values show peaks at the temperatures at which gel formation begins and these peak heights, which are termed the Gelation Index, are shown to correlate with values of yield stress from the literature. They are also shown to correlate with the presence and severity of air-binding pumpability failure in the field and in the ASTM Pumpability Studies. In regard to the latter, the study shows that the Scanning Brookfield Technique seems to be the only widely used pumpability technique to correctly predict air-binding engine response to oils which gelate below -20°C since it is the only ASTM method to impose the slow-cooling conditions necessary for gel formation below that temperature.

INTRODUCTION

Over the last 10 years, pumpability has become a major concern in the formulation of engine oils. Foremost in this concern is the possibility of an engine oil blend developing a potential for air-binding under certain cooling conditions. The disastrous winters of '80-'81 and '81-'82 in which two or three air-binding oils caused millions of dollars of engine damage in the United States and Europe, will not be forgotten but repetition is certain if causes are not understood or measured. Prevention requires knowledge, understanding, and measurement of the causes of the various forms of gelation associated with air-binding.

Interrelationships of base stock, wax levels, VI improvers, pour-point depressants, dispersant-inhibitor packages, etc., are important considerations. This is particularly the case with the availability of so many base stocks from around the world as well as the virtually continuous development and commercialization of new additive chemistries to enhance the formulated engine oil. Instrumental techniques revealing the rheology of gelation are a first line of defense against the inadvertent injection of seriously air-binding engine oils into the marketplace.

This paper, then, presents an effort to further develop predictive information concerning engine oil gelation and its rheology. To some degree, there is an air of urgency in understanding and utilizing some of the findings in the paper, as will be shown.

Scanning Brookfield Technique (SBT) data used in this paper to develop the concepts and relationships to be discussed were presented [1] to an ASTM Task Force developing the round-robin study and research report [2] culminating in ASTM Method D 5133 [3].

Instrumentation

Savant Laboratory instruments used in gathering the data presented in this paper included the commercially made Tannas Scanning Brookfield Plus Eight self-contained cooling bath shown in Figure 1. On-board temperature programming simplified both calibration and sample analyses. The eight Brookfield heads purchased with the Tannas Plus Eight bath were especially modified versions for computer use.

Each head rested on a special Pennzoil-Tannas adapter commercially available to provide precise and repeatable alignment of rotor and stator. Titanium rotors and matching precision-bore glass stators were also purchased commercially. Figure 2 is a sketch of the adapter with rotor and stator.

During most of the work reported in this paper, the analog voltage signals of the Brookfield Viscometer heads were transferred to multi-pen strip chart recorders and the traces analyzed by hand-picking points on the curves. These data were subsequently entered into a spread-sheet computer program for further analysis. However, in the later stages of these studies, a special computer program developed by the Tannas Co. to meet Savant Laboratory requirements was used to directly record and calculate the desired data. The program receives data from an analog-to-digital translator and, using the calibration information for each Brookfield head, converts the signal into a viscosity which is simultaneously stored on disk and shown on the computer monitor in a special, real-time simulation of the viscosity plotted against temperature for each of the eight viscometers. Upon completion of the run, the recorded data can be converted into any desired tabular or graphical relationship.

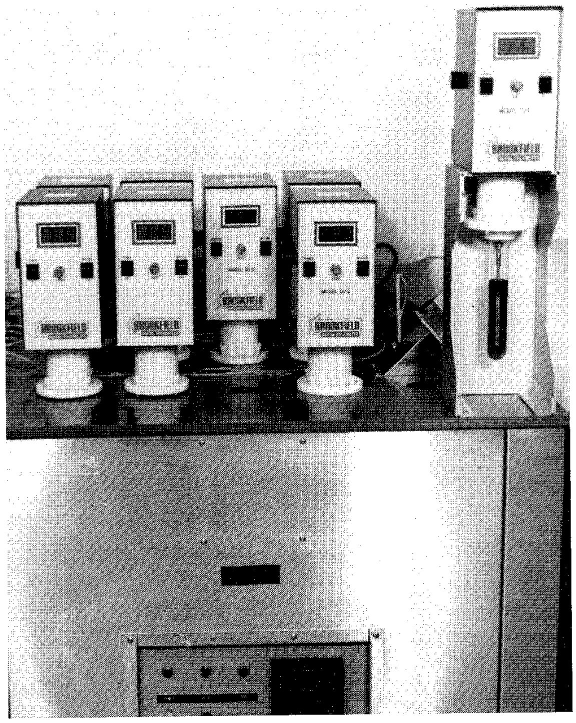


FIGURE 1
Scanning Brookfield Plus Eight

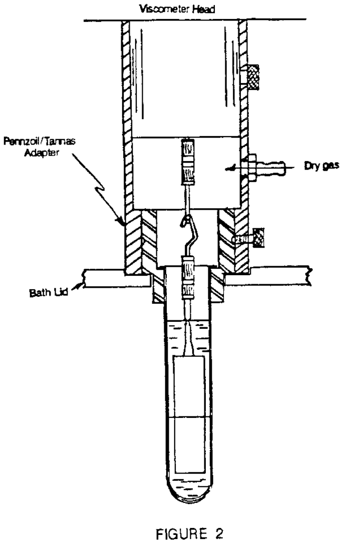


FIGURE 2

SCANNING BROOKFIELD TECHNIQUE TEST CELL
(Early Version)

Reference Oils

An engine pumpability study conducted within the ASTM [4] produced the first set of Pumpability Reference Oils (PROs) which were identified as PRO-01, 03, 05, 06, 07, 08, 09, 10, 11, 12, 13, 15, and 16 -- thirteen in all. These oils were analyzed repeatedly in sequentially lower engine cold-room tests until they exhibited one of two pumpability problem responses 1) flow-limited behavior (a predominately viscous response), or 2) air-binding behavior (a predominantly structure-building or gelation response). From this study, it was possible to determine the borderline pumping temperature (BPT) which is the highest temperature at which the engine exhibits pumpability problems.

As a consequence of serious pumpability problems from 1980 to 1982 and occasional problems afterward, another set of Pumpability Reference Oils were gathered which were associated either with engines failing in the field or engines failing under cold-room, field-simulating conditions. These later oils were identified as PRO-21 to 30. It should be noted that with these latter oils no effort was made to determine their BPT -- either because of relatively limited supplies or the lack of a coordinated program such as the earlier ASTM study.

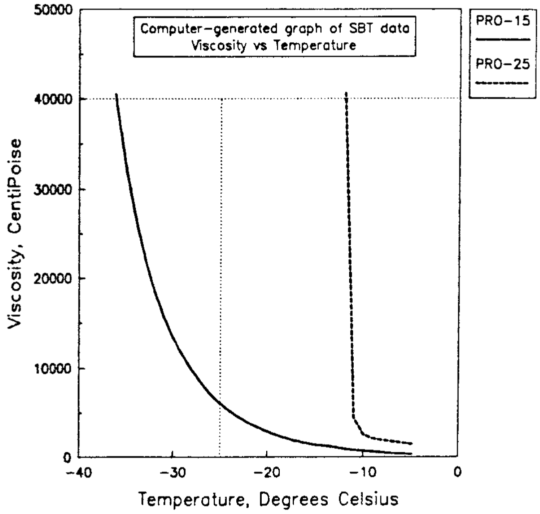
A NEW ANALYTICAL TECHNIQUE USING DATA FROM THE SCANNING BROOKFIELD VISCOMETER

As discussed in a previous paper [5], gelation of an engine oil can generate many levels and forms of structural rheological responses ranging from levels producing engine air-binding failure to innocuous levels of gelation which may have little or no influence on the pumping of the oil. Obviously, it is important to know what level of gelation is present and, if so, whether that level should be of concern. Visual inspection of the viscosity-temperature Scanning Brookfield Technique (SBT) data such as in Figure 3 can be helpful for predicting the potential for air-binding in the case of strong gelation.

In the case of Figure 3, the normal exponential viscosity/temperature curve produced by PRO-15 (an SAE 10w) is contrasted to the sharply breaking curve for PRO-25, one of the original field-failing, SAE 10w-40 engine oils. The horizontal dashed line at 40,000 mPa.s (cP) indicates the Critical Pumpability Viscosity limit established in early correlation efforts with the SBT [6-10]. On the basis of the SAE J-300 Classification System [11], both oils should have critical viscosities lower than -25°C (the vertical dashed line). It is evident that PRO-15 meets this requirement handily at about -36°C while PRO-25 abjectly fails at -11°C.

However, many structure-containing oils are not as obviously gelated as PRO-25. Gelation associated with borderline conditions of air-binding requires a more sensitive, less subjective approach for analyzing SBT data.

Figure 3
Comparison of Curve Forms for Gelating and Non-Gelating Oils



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MacCoull-Walther-Wright Equation Curves

A first step in simplifying and clarifying the viscosity-temperature comparisons, is to use the empirical, linear MacCoull-Walther-Wright relationship (LogLog viscosity versus Log absolute temperature)[12] as shown in Figure 4. Data from many previous SBT analyses show, as in Figure 4, that this empirical equation, originally developed around higher temperature viscosity/temperature relationships, continues to be useful at low temperatures. That is, it produces a linear relationship at low temperatures and low shear rates for engine oils having simple (non-gelated) viscosity response such as PRO-15 and 16. Again in contrast, the sudden, rapidly increasing viscosity in both SAE 10w-40 field-failing oils PRO-23 and 25 show evident gelation response using the MacCoull-Walther-Wright viscosity-temperature relationship.

When all the remaining air-binding, field-failing PROs (except PRO-22, the supply of which was exhausted) are plotted on MacCoull-Walther-Wright charts, the curves of Figure 5 result. While all show clear evidence of departure from linearity, clear delineation of differences among the oils is more difficult to find. Instead, there is a range of 'S' curves and one can imagine a series of other gelated conditions producing a continuum of such curves down to the point where there would be little or no distinction when compared to the straight line of a simple, non-gelated oil. Was it possible to develop an approach which would give clear distinction among oils of different degrees of gelation? More important, would such an approach agree with the response of those PROs which have been shown to be borderline field-failing oils? Lastly, which PROs give the borderline responses so necessary for instrument and technique development?

Figure 4
Walther Plot Comparisons of Gelated and Non-Gelated Engine Oils

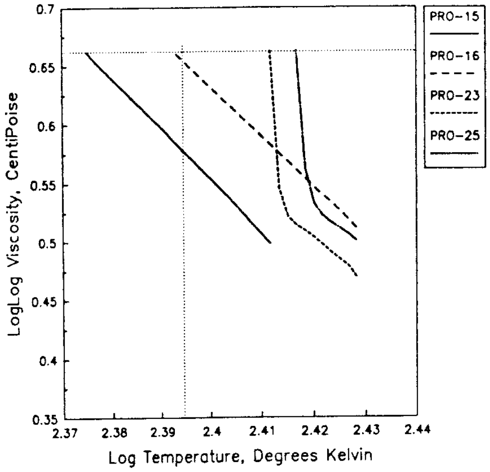

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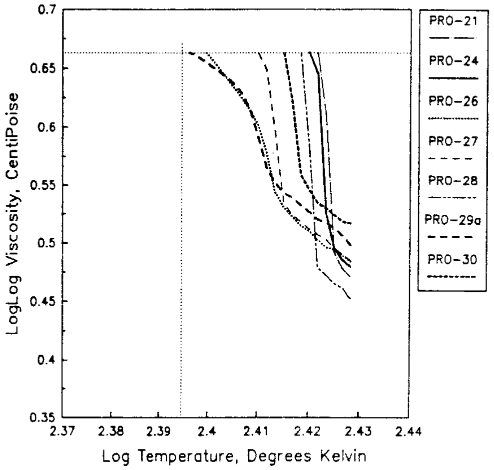
Figure 5
Walther-ASTM Plots of Gelated Field-Failing or Borderline Engine Oils



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Regarding the last question, published papers of Smith [13], Henderson and his co-workers [14], as well as unpublished work by Stambaugh [15], indicate that PRO-26 and PRO-29 gave evidence of being borderline oils. In particular, Smith [13] (whose trail-blazing work with the regeneration of the MRV after the correlation difficulties of '80-'81 gave impetus to the later investigators of MRV methods) found problems in getting both of these oils to simultaneously show failure response to different MRV methods and considered them as the real challenges to the development of a method around the MRV.

Scanning Brookfield Technique Results

Using the Scanning Brookfield Technique, Figure 5 illustrates that all of the PROs plotted show show clearly gelating behavior -- that is, all depart from the linearity expected from non-gelating oils, including PRO-26 and PRO-29. However, the curves shown do not clearly answer the question of whether these two oils show less gelation tendency -- more borderline response -- than the other oils tested. One indication that PRO-26 and 29 might have milder gelation characteristics is indicated in that both oils are closer to the SAE -25°C minimum for the Critical Pumpability Temperature than the other oils. However, this fact is not evidence that their structural properties are less potent -- one can certainly imagine oils having strong, engine-damaging gelation response but still passing the viscosity criterion simply because their gelation response was near or below -25°C. What, then, might be effective in characterizing gelation/air-binding potential?

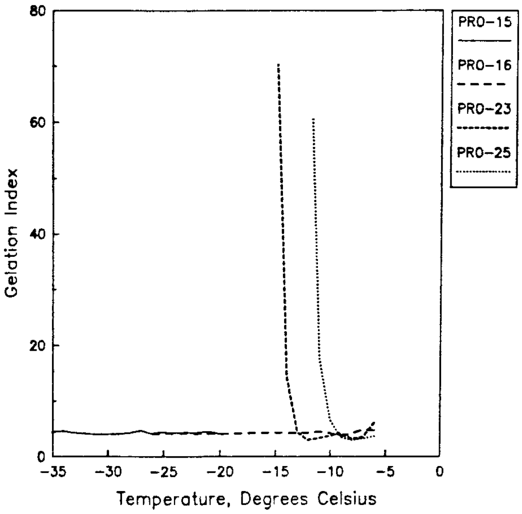
Definition of Gelation Index

From calculus, the incremental ratio (or approximation of the derivative) of the empirical MacCoull-Walther-Wright equation should produce horizontal straight lines when non-gelated oils like PRO-15 and 16 in Figure 4 are plotted against temperature. In contrast, oils showing evidence of gelation when plotted with the aforementioned equation, such as in Figures 4 and 5, should show peaks at their viscosity-temperature inflection points unless the viscosity of the oil exceeds the upper limit of the viscometer/rotor/stator combination (ca. 50,000 mPa.s) before reaching the viscosity/temperature inflection point (such as evident with PRO-23 and PRO-25 in Figure 4). It is reasonable to imagine that the height of these peaks would be related in some way to the strength and/or concentration of the gel-forming components as well as related to the ameliorating effects of those additives suppressing gelation such as pour-point depressants.

In practice, the technique required obtaining the incremental ratio Δ LogLog viscosity $\div$ Δ Log Temperature(Kelvin) from the viscosity-temperature data generated by the SBT. This value was plotted against temperature in degrees Celsius for clarity. The temperature increment used was one degree Celsius as an initial, but not critical, choice. In the remaining portion of this paper, the term "derivative" will be used to mean "incremental ratio". Moreover, since the value of the incremental ratio of the MacCoull-Walther-Wright equation will be shown to be an index of the degree of gelation, the absolute value of this ratio is given the term "Gelation Index". Obviously, the maximum value of Gelation Index reached by a given oil is the most important value of Gelation Index and the term will also be used to identify the maximum value.

Derivative curves for PRO-15, 16, 23, and 25 from the MacCoull-Walther-Wright plots of Figure 4 are shown in Figure 6 as a first example of the application of the method. As expected, PRO-15 and 16 plot as horizontal lines. The curves are extensions of one another as a consequence of their MacCoull-Walther-Wright slopes being essentially the same. In contrast, both PRO-23 and 25 show a sharp break after a short, roughly horizontal period. Their rate of gelation development is such that neither of these oils reach their inflection points in Figure 4 and, thus, neither reach their gelation peak before passing out of viscometer range. The maximum value for their Gelation Index is in the 60-70 region.

Figure 6
Gelation Indices of Field-Failing, Air-Binding
PRO-23 and 25 vs. Non-Gelated PRO-15 and 16



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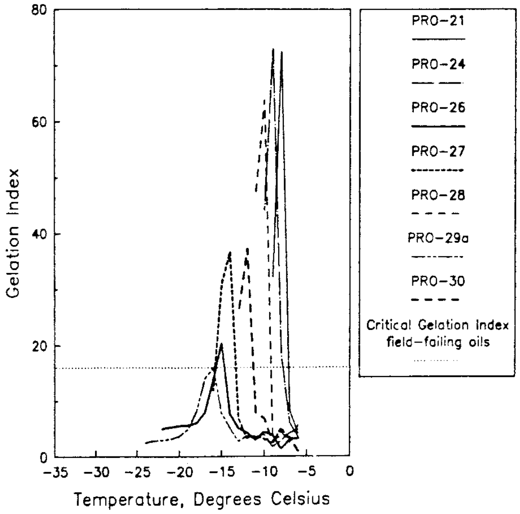
Derivative plots of the remaining field-failing oils whose MacCoull-Walther-Wright curves were given in Figure 5 are shown in Figure 7. It is evident that the plots permit clear distinction to be made among the oils on the basis of the height and breadth of their peaks and the temperatures at which the peaks occur. Again, as would be expected from their inflection points falling within viscometer range, and in contrast to the two gelated oils of Figure 6, all of the oils shown in Figure 7 show a clear peak

Figure 7
Gelation Indices of Seven Field-Failing, Air-Binding PRO Engine Oils



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and peak height (Gelation Index) value of the derivative. The Gelation Indices for the peak height range from 15.9 for PRO-29 to 73.0 for PRO-24. It should also be noted that the gelation peak temperatures vary from -7° to -15°C for this set of field-failing oils -- no gelation peak temperatures were found below -20°C. This fact will be raised as a point of interest and attention later in the paper.

Indicated Borderline Gelation Behavior

More interestingly, in response to the question posed earlier concerning finding a technique capable of distinguishing the borderline air-binding oils, PRO-26 and PRO-29, it will be noted in Figure 7 that these two oils show the lowest Gelation Indices of the group, 15.9 and 20.3, respectively. With this fact in hand, it is difficult to ignore the implication that the Gelation Index is directly related to the strength and extent of gelation.

From this point of view, if PRO-29 is considered a borderline oil on the basis of published data [5,13-15], its assigned Gelation Index of 16 can be considered a borderline or critical Gelation Index. This level is well above the level of the non-gelating oils and PRO-29 shows a sharp and well-defined peak.

Gelation Index Analyses of Original PRO-Series Oils

Having obtained clear distinction among the field-failing Pumpability Reference Oils, PRO-21 to PRO-30, and a strong suggestion of a relationship between the strength of gelation and Gelation Index, it was of interest to use the derivative technique to analyze the original group of Pumpability Reference Oils, PRO-1 to PRO-16 used in the ASTM engine pumpability studies [4].

One of the factors to be considered is that the ASTM study and the field-failing experiences differed considerably in oils and engines available as well as thoroughness of determining the borderline condition. For example, the borderline failing temperatures of all of the oils in the ASTM study were determined and these were the values used for comparison. In contrast, the field-failing oils simply were found to have failed at some temperature condition with no knowledge of whether that failure might have been similarly produced at some higher temperature.

Analyses of the original PROs whose engine results and/or SBT curves indicated gelated conditions sufficient to cause air-binding, gave the results shown in Figure 8 for those oils having gelation peak temperatures above -20°C and Figure 9 for those oils having gelation peak temperatures below -20°C. It is evident that these oils show widely varying values of gelation peak temperatures and Gelation Index. Peak temperatures range from -10 to -28°C -- a considerably broader range than the -8 to -16°C span of the field-failing PROs. Gelation Indices range from 8.6 to 61.3.

(It should be noted that two of these oils were shown to be gelating in slow-cooled bench tests typical of conditions for field-failing oils. As such, these oils, PRO-03 and PRO-11, are treated as air-binding oils in all subsequent analyses and discussions in this paper.)

Thus, the data show that the ASTM study produces a borderline gelation index of 8.5 which value is slightly below the lowest Gelation Index value shown by any of the air-binding oils tested in the study. PRO-01 gave 8.7 and PRO-09 gave 8.6. This is about half of the value shown by the less developed data from the field-failing oils and indicates that the criterion of borderline pumping temperature (BPT) is more severe than that producing field failure.

There were no flow-limited, field-failing oils reported which is a significant statement in itself regarding effects of flow-limited temperature conditions and startability. That is, will an engine start if the oil is viscous enough to produce flow-limited behavior? This was the primary reason behind the five degree lower differential for testing pumpability than cold cranking viscosity.

Analyses of the flow-limited oils from the ASTM Engine Pumpability Study [4] are shown in Figure 10. On the basis of expectations, these should show relatively flat lines when analyzed by the derivative technique. By and large, this is so with four of the six oils showing relatively horizontal lines with no significant peaks outside of instrumental variation and Gelation Indices below 5.

Two of the oils, PRO-07 and PRO-08, both indicated to be SAE 20W-20s, show small gelation peaks at -27°C and Critical Pumpability Temperatures of -30°C. Gelation Indices are 8.6 and 6.8, respectively -- the latter below the air-binding borderline Gelation Index of 8.5 and the former at a borderline level. The interesting point is

Figure 8
Gelation Indices of Original Air-Binding PROs for Gelation Peaks Above -20 C

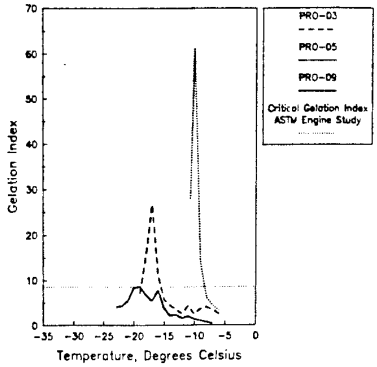

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Figure 9
Gelation Indices of Original Air-Binding PROs for Gelation Peaks Below -20 C

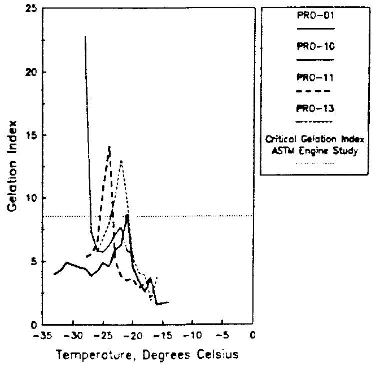

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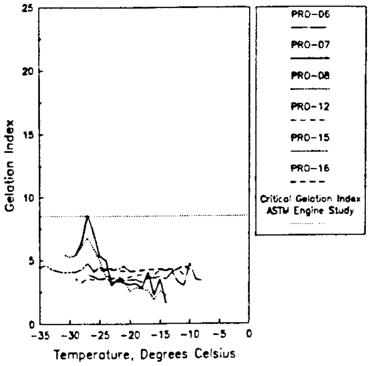
Figure 10
Gelation Indices of Original Flow-Limited PROs Used in ASTM Engine Pumpability Study, DS-57



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that, for PRO-07, the SBT would predict flow-limited failure at -30°C and air-binding failure at -36°C. The actual 4-engine average borderline pumpability temperature of PRO-07 in the ASTM study was -27°C -- the same temperature at which gel formation peaked. Apparently, at least for borderline air-binding oils, the lower the peak temperature, the more likely a forming gel will merely contribute additional viscous behavior to the already high viscosity present, resulting in a flow-limited condition for the engine. However, this speculation should be checked by cold-temperature tests.

Repeatability of the Gelation Index Value

Since the Gelation Index appeared to be a significant measure of the rheology of the engine oil, it was important to next determine the level of repeatability of the measure.

Often, the most severe test of the repeatability of an emerging method is found in a borderline oil. In this case, PRO-29, even though very limited in availability, was considered a good oil to select initially from the field-failing oils to test repeatability of the Gelation Index concept. Figure 11 shows the results of two runs of PRO-29 separated by a period of three and one-half years and run by different operators in different equipment. Repeatability appears acceptable.

However, two runs of PRO-29 do not provide statistical dependability. Considering the scarcity of PRO-29, another engine oil having a moderate but failing level of gelation was chosen for further tests of repeatability of Gelation Index, gelation peak temperature, and Critical Pumpability Temperature.

Figure 11
Repeatability Test Using PRO-29a
A Borderline Air-Binding, Field-Failing Oil

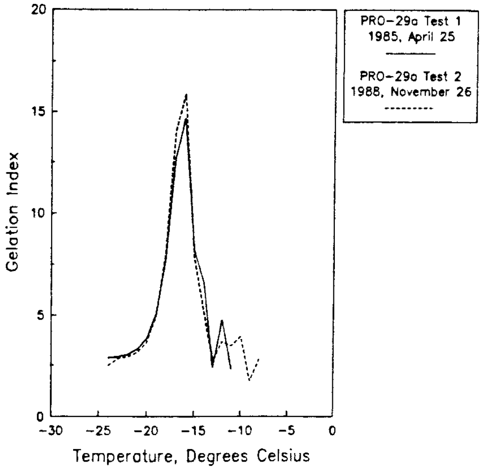

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TABLE 1

Replicate Analyses of R-1300 to Test Repeatability

Test Cell	Oil	Critical Pumpability Temperature* °C	Gelation Criteria	
			Peak Temperature °C	Gelation Index
A	R-1300	-13.0	-12.3	41.4
B	---------------- Not used --------------			
C	R-1300	-12.9	-12.3	39.5
D	R-1300	-12.6	-12.3	41.1
E	R-1300	-12.4	-12.3	40.0
F	R-1300	-12.6	-12.3	42.3
G	R-1300	-12.8	-12.3	43.7
H	R-1300	-12.8	-12.3	42.8
	Mean:	-12.74	-12.3	41.5
	Std. Dev.:	0.191	0.0	1.56
	95% Confid.:	0.374	0.0	3.07 (7.4%)

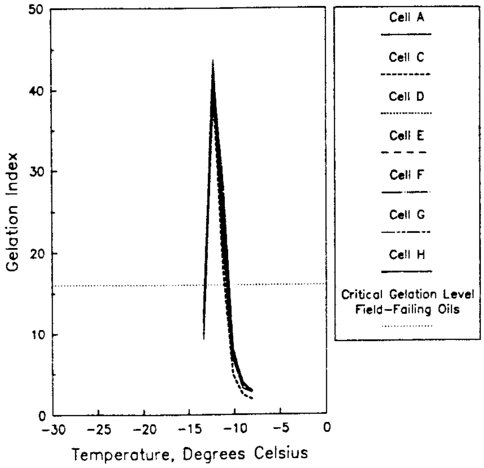
* ASTM Method D 5133 [2]

R-1300 is an internal standard use in the Savant Laboratories. This reference oil is from the same period and formulation as several of the other field-failing oils of the 1980-1982 period. Results and statistical evaluations are given in Table 1. Seven SBT runs were made simultaneously using the Tannas Scanning Brookfield PlusEight unit previously mentioned. In contrast to the previous analyses, this run was controlled by the Tannas Company's Automatic Data Collection and Analysis program. Figure 12 shows the derivative plot of the data set. The borderline Gelation Index established with PRO-29 is shown as a dotted horizontal line. The derivative was calculated every 1°C as in the 'hand-calculated' values given previously. It is evident that good repeatability is found for the derivative curve and, thus, the technique.

The data gathered in Table 1 underscore the dependability of the determination of each of the parameters: gelation peak temperature, Gelation Index, and Critical Pumpability Temperature. Such repeatability is particularly good considering the use of different cells, different Brookfield Viscometer heads with different calibration constants. Critical Pumpability Temperature at 95% confidence was -12.7 ±0.37°C, well within the repeatability limits of ASTM D 3155 (r = ±0.80°C). The constancy of the gelation Peak Temperature is partially a consequence of choosing 1°C intervals for evaluating the derivative. However, later use of the Tannas SBT Analysis Program, with choice of 1/4°C temperature intervals for the derivative values, did not change this to any significant degree. It is believed that gelation peak temperatures will be found to be quite precise depending on the thoroughness of removing sample memory by heating before analysis.

On the basis of this work, Gelation Index repeatability seems to be adequate to establish reasonably precise values for a Critical Gelation Index using PRO-29 and a Gelation Index of 16 as the borderline comparator.

Figure 12
Repeatability Test Using R-1300;
A Gelating Commercial Oil Similar to PRO-24



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GELATION INDEX AS A MEASURE OF GEL STRENGTH

To this point of the paper, it has been shown that the derivative of the MacCoull-Walther-Wright equation produces a repeatable plot of values where peak temperatures are related to the temperature of gel formation in the oil and peak heights (Gelation Indices) were tentatively assumed to be related to the strength of the structure. Assumptions, however, are unsatisfying and often enough lead to subtle or obvious error.

An appropriate test of the significance of the gelation peak height (Gelation Index) is to attempt to correlate the value to a more fundamental measure of gel strength. Such a measure is yield stress -- the amount of force necessary to initiate flow.

Fortunately, Henderson and his co-workers [14], in receiving the baton passed from Smith [13], generated yield stress measurements on the two PRO series during the Herculean task of trying to find the best correlative method for a modified procedure for the MiniRotary Viscometer in pumpability test. This work focussed on a protocol identified as TP-1. (The latter protocol, after further changes simplifying the identification of oils with yield stress, became ASTM D 4684).

Comparison of Gelation Index to Yield Stress

Table 2 compares Gelation Index data on a number of PROs with yield stress found for those oils by Henderson, et al.[14] using the TP-1 test protocol. The primary objective for Henderson et.al. study was stated as finding the shortest cooling cycle which would correspond with the field-failing oils. Their work produced a two-day (47-hour) cycle, called the TP-1 cycle, which cooled the sample from -5° to -8°C at 1/2°C/hr, from -8° to -20°C at 1/3°C/hr., and from -20° to -25°C at 2.5°C/hr. Stopping the slow-cooling at -20°C and continuing cooling at a much higher rate to lower temperatures saves considerable time. Justification for this approach was found in noting that all of the PROs had wax appearance points above -20°C, and this led to the assumption that slow-cooling below -20°C was unnecessary to run the test cycle as long as the test showed good correlation with the PROs.

Two of the PROs, PRO-01 and PRO-10, were 5W-30s and a somewhat different protocol, called TP-6, a four-day cycle, was used by Henderson, et.al.[14] for evaluation. This latter protocol cooled at 0.15°C/hr. from -5° to -20°C, at 0.4°C/hr., from -20° to -24°C/hr., and at 5°C/hr. from -24° to -30°C with an additional half-hour soak at -30°C. These yield stress data from TP-6 were used in the absence of TP-1 data on these particular PROs.

In contrast to the MRV methods studied by Henderson et.al.[14], the Scanning Brookfield Technique uses only one protocol and applies slow cooling all through the temperature range traversed during measurement. The cooling rate is 1.0°C/hr. which, with the stirring accompanying continuous measurement of viscosity, is slow enough to capture the adverse and acceptable responses of all the PROs available.

Thus, the main differences between the methods are

1. Continuous measurement of viscosity with SBT vs. one temperature value from the MRV.
2. Slow-cooling throughout the temperature range measured using the SBT at 1°/hr. vs. slow-cooling only to -20°C with the MRV TP-1 protocols at two slow-cooling rates, first at 0.5°C/hr. from -5° to -8°C and then at 0.33°C/hr. down to -20°C, followed by a fast-cooling rate from -20°C down.
3. Maximum of 20 hrs. to -25°C test time for the SBT (ASTM D 5133) vs. test time of 47 hrs. to -25°C for the MRV (ASTM D 4684).

Despite these marked differences in protocol, both instruments show reasonable correlation with the air-binding, field-failing oils. Because of this, it was thought that correlation might be found between the two methods when comparing the Gelation Index obtained by the SBT and the yield stress obtained with the TP-1 protocol.

Table 2 presents highly interesting and important relationships. Particularly notable is the fact that for those oils which generate their gelation peak above -20°C (shown in bold typeface), the values for Gelation Index and yield stress seem to mutually vary. This relationship is more clearly indicated in **Figure 13** where the yield stress and Gelation Indices of 19 of the PROs are correlated. The data of **Figure 13** are plotted in three groups, using asterisks for those whose gelation temperatures are above -20°C, filled circles for those that are between -20° and -24°C, and open circles for those that are below -24°C. (The reason for separating the data is related to the temperatures at which slow-cooling is terminated in the MRV TP test methods. As was previously noted, slow-cooling for TP-1 is ended at -20°C and for TP-6 at -24°C.)

Figure 13
Correlation of Gelation Indices by SBT to Yield Stresses Produced by MRV TP Methods

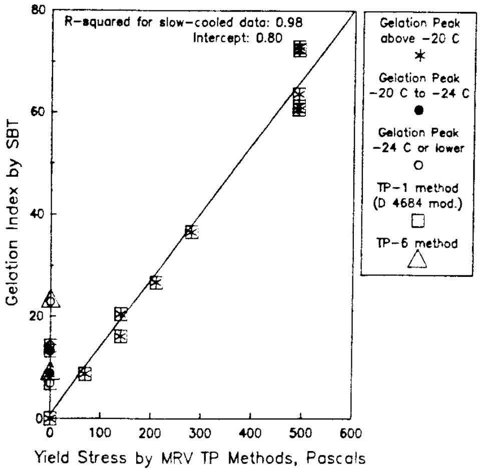

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TABLE 2

Comparison of Indices of Gelation Using the TP-1 Technique on the Mini-Rotary Viscometer vs. the Scanning Brookfield Technique (Plus Two 10W-30 oils Analyzed by TP-6 Technique)

PRO	SAE Grade	SBT Gelation Peak		MRV New Methods		
		Temp °C	Index	Yield Stress Pa	Temp. °C	MRV Method
01	5W-30	-21	8.7	0	-30	TP-6
03	**10W-40**	**-17**	**26.7**	**210**	**-25**	**TP-1**
05	**10W-40**	**-10**	**61.3**	**>490**	**-25**	**TP-1**
06	**20W-50**	**no gelation**		**0**	**-25**	**TP-1**
07	20W-20	-27	8.6	ND*	-	-
08	20W-20	-27	6.8	0	-25	TP-1
09	**10W-40**	**-19**	**8.6**	**70**	**-25**	**TP-1**
10	5W-40	-28	>22.8	0	-30	TP-6
11	10W-40	-24	14.1	0	-25	TP-1
12	10W-50	no gelation		ND	-	-
13	10W-40	-22	13.1	0	-25	TP-1
15	10W	no gelation		0	-25	TP-1
16	20W	no gelation		0	-25	TP-1
21	**10W-30**	**- 8**	**72.4**	**>490**	**-25**	**TP-1**
22	**10W-30**	**untested**		**>490**	**-25**	**TP-1**
23	10W-40	-15	>70.3	ND	-	-
24	**10W-40**	**- 9**	**73.0**	**>490**	**-25**	**TP-1**
25	**10W-40**	**-12**	**>60.6**	**>490**	**-25**	**TP-1**
26	**10W-40**	**-15**	**20.3**	**140**	**-25**	**TP-1**
27	**10W-40**	**-14**	**36.6**	**280**	**-25**	**TP-1**
28	**10W-30**	**-10**	**63.7**	**>490**	**-25**	**TP-1**
29	**10W-40**	**-16**	**15.9**	**140**	**-25**	**TP-1**
30	15W-40	-12	37.1	ND	-	-

* ND: not determined

As shown in Figure 13, for the TP-1 data whose gelation peak temperatures are above -20°C, the correlation between the Scanning Brookfield Technique Gelation Index and the yield stress is surprisingly good. The Coefficient of Determination, R^2, was 0.985. This statistical parameter is often used as a measure of co-relatedness of two variables (more simply, the ability to predict one value from the other). This relatively high correlation was coupled with a low intercept value of -0.5 (indicating little or no residual offset or correction for the best line through the data).

Equally evident in Figure 13 is the fact that, for TP-1 data, correlation is zero for gelation peak temperatures of -20°C and below -- a rather bizarre and highly unlikely overall relationship unless some other factor entered the relationship. This is shown to be the case.

In explanation of this apparent strangeness, Henderson et.al.[14] have shown the importance of slow-cooling in generating structure in the oil. Thus, it would seem reasonable that the sudden disappearance of correlation between the Gelation Index and yield stress with oils forming structure below -20°C is attributable to the fact that the slow-cooling protocol of the TP-1 method (as well as the resulting D 4684 method) ends at -20°C [14,16] and is followed by a fast cooling rate to the temperature of measurement.

It should be noted that the 0.4°C/hr. slow-cooling protocol for TP-6 ends at -24°C. Henderson et.al.[14] applied this lower-temperature variant of the TP methods to PRO-01 and PRO-10, two 5W-30s. In the SBT evaluation, both had gelation peaks below -20°C -- PRO-01 at -21°C and PRO-10 at -28°C. In both cases, no yield stress was observed. On the basis of the reasoning above, no yield stress would have been expected for PRO-10 since the MRV/TP-6 was in a high rate of cooling mode. This was not the case for PRO-01. However, as shown in Table 2, relatively low yield stress would have been expected for PRO-01 in any case, since its Gelation Index was the lowest of the air-binding oils and, in fact, established the borderline condition for the ASTM air-binding oils. Using TP-1 and TP-6 data obtained in the slow-cooling modes, an R^2 value of 0.980 and an intercept of 0.8 is produced when correlated with the Gelation Index.

It is also worthy of note that, of the four oils in Figure 9 having gelation peaks below -20°C in the SBT, three showed air-binding response in the ASTM Engine Pumpability tests. However, because of the apparent lack of measurable yield stress, these oils were identified as flow-limited by the MRV test methods TP-1 and TP-6.

Calculation of Yield Stress from Gelation Index

Since no yield stresses were shown by the MRV protocol below -20°C, it was of interest to determine what stresses might have been obtained had slow-cooling been continued with this device. On the basis of the correlation shown between Gelation Index and TP-1 yield stress above -20°C, the yield stresses of the four oils showing gelation peaks below -20°C could be estimated. These values are given in Table 3.

On the basis of the information in Table 3, the calculated yield stress values for the MRV would be high enough (>35 Pa) for this instrument to predict the air-binding problems actually found in the ASTM study. It would be of interest to check these calculated yield stress values against values determined in an extended slow-cool MRV TP-1 protocol by the laboratory or laboratories originally producing the data reported in the Henderson et.al. paper [14].

Application of Gelation Index Concept to Oils in the Field

With the information generated by the Gelation Index concept and remembering the debacle of 1980-1982, it was of interest to determine if any oils on the market showed significant Gelation Indices, particularly with gelation peak temperatures below -20°C.

A database published by the Institute of Materials (IOM) [17], among other information, contains Scanning Brookfield Technique as well as MiniRotary Viscometer D 3928 and D 4684 pumpability data. Recent reports from this database on marketed engine oils showed several having SBT curves suggesting significant Gelation Indices. As a subscriber, Savant Laboratories asked if the Institute would provide the raw SBT data on two recently purchased SAE 5W-30 oils selected from a number of oils with interesting SBT curves. Since it is a practice of the Institute to obtain replicate data on all properties considered questionable, several sets of analyses of these two oils were sent in response to the Savant Laboratories

TABLE 3
Calculation of the MRV TP-1 Yield Stress
at Temperatures Below -20°C

PRO	SAE Grade	SBT Gelation Peak		TP-1/TP-6 Yield Stress	Borderline Pumping Temperature			
		Temp °C	Level	Calculated Pascals	SBT (AB temp.) °C Resp.	7-Engine Average °C	*	TP-1 Methods °C Resp.
01	5w-30	-21	8.7	60	AB -37	-36	(4AB/7)	-38 FL
10	5w-40	-28	>22.8	>166	AB -33.5	-32.5	(5AB/7)	**ND FL
11	10w-40	-24	14.1	100	AB -33.5	-30.5	(0AB/7)	-30 FL
13	10w-40	-22	13.1	93	AB -32.5	-32	(2AB/7)	-31 FL

*: ratio of air-binding engines to total engines tested
**: ND - not determined

request.

Results from the derivative analyses of replicate SBT tests of these two oils, one of which is from Canada, are shown in Figure 14. Oil A shows Gelation Indices of 21.3 and 20.5 at a common gelation peak temperature of -26°C. Not surprisingly on the basis of the data presented earlier, results from the two ASTM MRV methods, D 3928 and D 4684, showed no yield stresses and viscosity levels of 7700 and 8400 mPa.s respectively at -30°C -- well on the 'safe' side of the borderline value of 30,000 mPa.s.

The three analyses of oil B shown in Figure 14 had an average Gelation Index of 16.7 ±0.8 with gelation peak temperatures of -22 and -23°C. Analyses using the MRV methods again showed no yield stress and viscosity values of 8800 and 8900 mPa.s for D 3928 and D 4684, respectively.

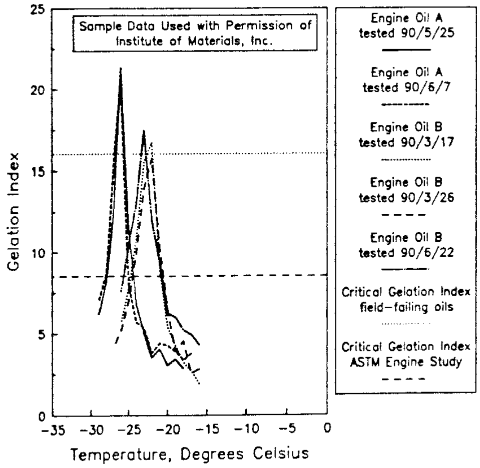
Summarizing these latter results, SBT derivative analysis indicates that some oils on the market develop evident gelation below -20°C with Gelation Indices comparable to Pumpability Reference Oils which have given air-binding responses in engines. In comparison, D 4684 results indicate that these same oils are acceptable.

Variation and Similarity in Pumpability Test Responses

The foregoing results support the opinion of Deysarkar and Clampitt [18] in which they note the variation among pumpability tests and the need for more understanding to bring this area of concern more fully into an area of understanding.

Perhaps --at least above -20°C -- the close correlation of the Gelation Index and yield stress is a step in the direction of such understanding. The differences discussed earlier between the SBT and the MRV TP-1 at temperatures below -20°C might disappear and create further understanding if slow cooling were extended in the MRV methods to temperatures of -30°C.

Figure 14
Replicate Derivative Analysis of
5w-30 Engine Oils Purchased in 1990



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CONCLUDING DISCUSSION

General

The focus of the work reported in this paper is essentially on the rheology of gelated oils. Flow-limited, or simple, oils have never constituted a problem of measurement except, perhaps, as they may have exhibited some slight aspects of gelation. Consequently, while a viscometric technique must be able to deal easily with flow-limited oils, any such technique will be challenged by the complicated rheology of air-binding engine oils.

To quote from the aforementioned paper by Smith [13]: "It is axiomatic that 'no test is better than the kinds of oils it has evaluated'." Agreeing with this, the author would like to suggest a paraphrased corollary: It is also axiomatic that no test is better than its limits -- imposed or inherent.

A further quote from Smith's paper regarding one of his conclusions from his extensive experience in developing new MRV methods, is also very appropriate in the light of this SBT study:

> "For maximum effectiveness and minimum cycle time, an optimized thermal cycle should -- cool rapidly to desired test temperature after essentially all critical species have crystallized from solution".

In the author's opinion, Smith's statement is precisely correct -- it only remains to determine what the critical species are and when they have completed crystallization. The Scanning Brookfield Technique seems to have found species of gelation-producing components that manifest themselves after slow cooling to -20°C which are not registered by the MRV D 4684 method presently used apparently because the methods have shifted into the rapid cooling mode.

Derivative of the Scanning Brookfield Technique Results

Viscosity/temperature data generated by the SBT was used to obtain the first derivative of the MacCoull-Walther-Wright empirical equation. Using the derivative gave essentially horizontal straight lines for non-gelated oils and varying degrees of peak formation with gelating oils.

The peaks were repeatable in regard to the temperatures at which they appeared and the height to which they rose. Even the shapes of the peaks are repeatable on re-analysis of a sample. This seems to indicate that the low temperature "rheogram" of a gelated oil is specific to the particular oil.

It was found that the peaks associated with the formation of gelation could occur over a relatively wide temperature range -- at least from -9 to -28°C.

The height of the gelation peaks was shown to correlate with yield stress developed under slow-cooling conditions and, thus, were shown to be associated with gelation strength. From this recognition, and the need to simplify the concept, a new term was applied: "Gelation Index" which is the absolute value of the derivative of

MacCoull-Walther-Wright equation. The term has also been used to define the value of peak height.

During the years of pumpability tests, one of the reference oils, PRO-29 was shown to be borderline in air-binding behavior. Another similar oil was PRO-26. The new derivative analytical approach showed both of these oils to be lowest in Gelation Index. As a consequence, the Gelation Index of PRO-29, a value of 16, was used to establish a critical Gelation Index for field-failing oils.

In similar work with the first Pumpability Reference Oil series associated with the ASTM Engine Pumpability study, a critical Gelation Index of 8.5 was established indicating that the ASTM study produced somewhat more demanding performance constraints on gelation limits.

Two repeatability studies, one with the borderline PRO-29, gave acceptable results using the derivative technique after an interval of more than three years. This led to a more statistically acceptable study analyzing one gelating oil using seven Brookfield Viscometers run in one bath, the ASTM Repeatability (95% confidence) was 7%.

Correlation of Gelation Index and MRV TP-1 Yield Stress

With the development of the Gelation Index as a measure of gelation level or strength, correlation was sought between Gelation Index and yield stress, a more fundamental measure of gelation strength. When the gelation peak temperatures were above -20°C, correlation between Gelation Index and yield stress gave 0.985 as a value for R^2 with an intercept of -0.5 -- a surprisingly high level of agreement between two dissimilar tests of pumpability. This was considered strong evidence that the Gelation Index is, indeed, a measure of gel strength.

Correlation between Gelation Index and yield stress disappeared completely using the MRV TP-1 protocol for PROs whose gelation peak temperatures were below -20°C because the MRV methods were not designed to accommodate oils forming gelation below this temperature.

Correlation with Engine Pumpability Tests

A more important observation was that three of the four PROs having gelation peak temperatures below -20°C (PRO-01,10,11, and 13) were shown as air-binding in both the SBT and the ASTM engine cold-room tests and should have been so identified by both the MRV methods and the SBT. Instead, as shown in Table 3, all four oils were identified as flow-limited by the MRV TP-1. The fourth oil, PRO-11, became flow-limited at -30.5°C, three degrees Celsius before air-binding was predicted by the SBT.

It is interesting, as shown in Table 3, that both the air-binding BPTs of the SBT and the flow-limited BPTs of the TP-1 agree well with the primarily air-binding BPTs of the 7-Engine Average. However, the fact that the MRV TP-1 flow-limited BPTs were close to the air-binding engine BPT in these cases, leaves open the question of whether this is adequate response when the flow-limited response does not equate with air-binding responses at temperatures below -20°C, as shown earlier with modern 5W-30 oils from the market

In contrast, the Scanning Brookfield Technique gave both reasonably close correlation with the engine BPT values and concurred with the mode of engine response.

Gelation Indices of Some Field Engine Oils

Applying the concept of Gelation Index to two marketed 5W-30 engine oils resulted in finding that both failed SBT D 5133 and developed significant gelation below -20°C. However, both passed MRV D 4684 with no difficulty. Again, the results point to the likely need for slow-cooling with the MRV methods down to the temperature of test. Of more pertinence, the results show that significantly air-binding engine oils are on the market and that some of these are to be found in climates which experience the cold weather necessary to produce engine gelation.

SUMMARY

The studies in this paper have shown the application of a new criterion of gelation termed the 'Gelation Index'. This parameter is the absolute value of the first derivative of the MacCoull-Walther-Wright empirical viscosity-temperature relationship for a lubricating oil. Two new tools for the understanding and control of gelation have been presented, the Gelation Index, and the temperature at which the gelation forms, called the 'gelation temperature'.

It was shown that the parameter of Gelation Index is closely correlated to the yield stress and can be used to determine the order of severity of gel-forming engine oils. Consequently, in testing known field-failing oils, it was shown that the critical Gelation Index associated with borderline air-binding failure is a value of 16.

Repeatability was shown to be reasonably good both in regard to the parameter of gelation temperature and Gelation Index with a value of 7.4% at the 95% confidence level. In determining the relationship between Gelation Index and yield stress obtained from the MRV TP-1 protocol, it was shown that close correlation obtained above -20°C became zero for oils whose gelation temperatures were below -20°C. This is the temperature where the TP-1 and D 4684 protocols do not continue the slow cooling associated with gel formation. Moreover, it was shown that three out of four original PRO oils whose gel formation temperatures were below -20°C and which showed air-binding in engines did not give the expected yield stress response in the MRV protocols but did in the Scanning Brookfield.

Applying the Gelation Index concept to modern oils on the market, two 5W-30 engine oils which showed questionable behavior were analyzed and found to have

Gelation Indices at or over the borderline value of 16 and had gelation temperatures below -20°C. Not surprisingly on the basis of the information in this paper, these same oils were shown to be acceptable in the D 4684 test with relatively low flow-limited values, i.e. no signs of gelation.

The information pointed out two important matters: 1) that there are potential field-failing oils on the market and 2) they may not be detected by the MRV 4684 method unless the slow-cooling protocol of that technique is extended.

Concluding Remarks

The need to bring together understanding of the low-temperature, low-shear rheology of engine oils and relate this to pumpability in engines, is quite clearly evident. Without this understanding, the related industries serving the motorist must operate with formulations requiring much analytical screening to avoid a repetition of the 1980-1982 experience.

Some progress has been made over the years by many investigators trying to pull back the curtains surrounding the subject. Of the two forms of pumpability failure, air-binding is paramount in difficulty of analysis and interpretation. This paper has presented new tools of analysis, gelation temperature and Gelation Index, to assist in the progress. The new technique has also shown that different pumpability methods may have high correlation using certain critical parameters in important areas of information and, consequently, it is possible for one instrument to be used to help evaluate and develop another by using certain technical evidence and mathematical tools.

However, the original ASTM database built on low-temperature pumpability analysis of reference oils in engines, is now ancient by technical standards and the reference oils generated by that work are in questionable supply and/or condition. The author would like to hereby make a call for 'a few good engineers' to put together the experimental design that would win the backing necessary to generate a new database relevant to today's and tomorrow's engines and engine oils.

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GLOSSARY

PRO - Pumpability Reference Oils provided through the ASTM

SBT - Scanning Brookfield Technique -- ASTM D 5133; the low-temperature, low-shear pumpability test used in the studies presented in this paper

MRV - MiniRotary Viscometer -- ASTM D 3928 and D 4684; original pumpability test device developed in ASTM and later modified to meet new pumpability requirements

BPT - borderline pumping temperature -- temperature at which engine shows critically low oil pumping ability

CPT - Critical Pumpability Temperature -- the temperature at which the SBT reaches 40,000 mPa.s -- associated with BPT data

MacCoull-Walther-Wright equation - an empirical viscosity-temperature relationship expressed at higher viscosities by: LogLog viscosity vs. Log Temperature (Absolute)

gelation peak - a peak in the first derivative of the Walther equation

gelation temperature - the temperature at which a gelation peak occurs

Gelation Index - the absolute numerical value equal to the height of the gelation peak in units of Δ LogLog viscosity $\div \Delta$ Temperature (Absolute)

air-binding - a form of oil response to cooling rate in which a gelated condition is formed. When this structure collapses under the vacuum drawn by the oils pump, air is pulled from the sump oil surface and binds the pump by an oil by which air is allowed

flow-limited - a viscous response of an oil in which the flow rate of oil to the pump is insufficient to satisfy the lubrication needs of the engine