A Method of Generating and Appraising the Five Viscosity Loss Parameters of Lubricating Oils - The Viscosity Loss Trapezoid

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Information from Lubrication Savants

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ABSTRACT

A new approach to appraising the total viscous influence of VI Improvers, synthetic fluids and their combinations is presented. The technique utilizes four viscometric measurements, two at low shear rates and two at very high shear rates, to generate five different measures of viscosity loss. The technique is described and a number of applications shown for both straight grade and multigrade engine oils.

INTRODUCTION

Over the years in which oil-soluble polymers have been used to improve the viscosity-temperature properties of mineral oils, a number of efforts have been made to characterize the degree of effectiveness of these polymeric additives. Such characterizations have been known by many names and/or acronyms -- VI (for Viscosity Index) [Ref. 1], which was used earlier to distinguish among mineral oils alone; VTI (for Viscosity Temperature Index) [Ref. 2]; TVL (for temporary viscosity loss) and PVL (for permanent viscosity loss); SSI (for Shear Stability Index) [Ref. 3,4]; -- to name a few. These polymeric additives in fact took their commercial identity as VI Improvers from their ability to improve the Viscosity Index of simple refined oils.

Essentially, the development of this char-acterizing nomenclature over the years has been directed at identifying and cross-comparing two properties of VI Improvers. The two properties are:

1. Efficiency/effectiveness -- Efficiency: the amount of viscosity change imparted per percent of VI Improver added -- Effectiveness: the amount of change imparted per unit cost of the VI Improver.

2. Permanent/Temporary viscosity loss -- degree of retention of the viscosity contribution in the face of orienting and/or destructive shearing forces during the process of lubrication and flow.

Some of the characterizing techniques (VI and VTI, for example) did not require knowledge of viscometric properties of the base oil to which the VI Improver was added. Other techniques did

require such information (SSI, for example).

Low and high shear capillary data produced more than ten years ago by Alexander and Rein, and resulting in a paper [Ref. 5], led the author to consider a graphical method of presenting the gamut of viscosity loss data experienced by a lubricating oil. Over the last few years, with the availability of the TBS-Viscometer for precise, very high shear rate viscometry, the author has further developed, used, and discussed [Ref. 6,7] a new technique for appraising VI Improver viscous contribution and vulnerability to shear. He has been encouraged to develop a paper on the subject and this paper is the result.

The present paper shows the generation and application of this parameter which he has termed the Viscosity Loss Trapezoid (or VLT). This parameter has been found to be an interesting and informative method of graphically comparing the full range of viscometric responses of polymer-containing oils and/or synthetic or semi-synthetic fluids. The method does not depend on knowledge of the viscometric characteristics of the base fluid but with such knowledge, the method is even more informative. However, the determination of VLT does depend on several viscometric measurements some of which have only become generally available and dependable over the last few years.

THE VISCOSITY LOSS TRAPEZOID TECHNIQUE

Determination of the VLT requires the measurement of four viscometric values, two of these are only obtained after the fluid has been degraded by harsh shearing conditions capable of rupturing many of the polymeric chains. For the determination of a given trapezoid, all viscometric measurements are made at a chosen temperature. Two of the measurements are under very high laminar shear conditions and two are under relatively low shear conditions. For obvious reasons

of computability of values, all measurements are in terms of absolute viscosity. Moreover, all viscometric measurements must be made under steady state conditions regarding both shear rate and temperature, particularly at very high shear rates.

As noted, the particular fluid of interest is measured at both low and high rates of shear before and after shear degradation. This produces four values,

1. Undegraded low shear viscosity (ULSV),
2. Degraded low shear viscosity (DLSV),
3. Undegraded high shear viscosity (UHSV), and
4. Degraded high shear viscosity (DHSV).

When the four values are plotted versus shear rate as shown in **Figure 1**, this produces a trapezoid -- the source of the name of the technique. The actual shape of the shear rate/viscosity curve is not linear as suggested by the connecting lines but this is not important. Rather, the significance of the Viscosity Loss Trapezoid lies in the differences between and among the values actually determined as will be evident in the next section.

Figure 1
The Viscosity Loss Trapezoid
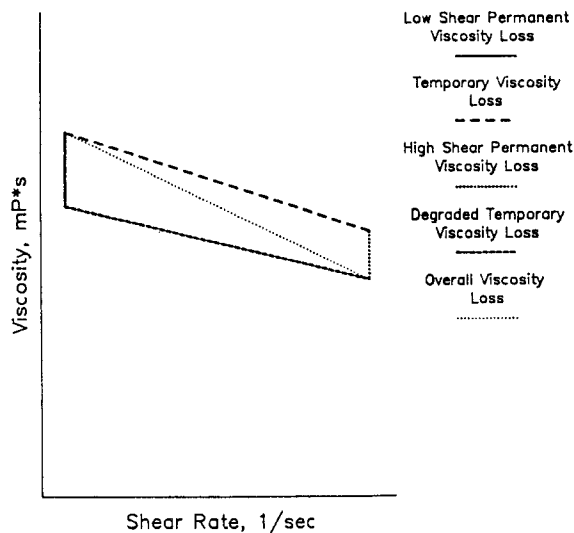
SIGNIFICANCE OF THE VISCOSITY LOSS TRAPEZOID

With the four viscosity values it is possible to determine five measures of viscosity loss each of which has a particular significance in the evaluation of a VI Improver.

LOW SHEAR PERMANENT VISCOSITY LOSS PARAMETER

The change in viscosity as a result of shear degradation has been called Permanent Viscosity Loss. In this technique it is identified as Low Shear Permanent Viscosity Loss (LSPVL) to distinguish it from the similar value at high shear. Calculation of this viscosity loss value as a percentage is as follows:

$$\%LSPVL = [(ULSV - DLSV)/ULSV] * 100 \quad \text{(Eq. 1)}$$

This value is a measure of the resistance of the VI Improver to highly disruptive shearing conditions for the fluid in which the polymeric additive is dissolved. The value varies with

1. Concentration of a given VI Improver.
2. Molecular weight of a given polymeric chemistry, (for that portion of the molecular weight distribution above the threshold shearability level of the disrupting mechanism).
3. Molecular weight distribution.
4. VI Improver chemistries and molecular arrangement.
5. VI Improver solvency in the base fluid.
6. Mode of degradation of the macromolecule under disruptive forces.

TEMPORARY VISCOSITY LOSS PARAMETER

Orientation of the dissolved polymeric molecule in the grip of the sliding fluid laminae produces a decrease in viscosity related to the degree to which the macromolecule loses its viscous influence as it deforms under laminar shearing forces. Thus, the level of temporary viscosity loss or TVL is dependent on

1. Concentration of the VI Improver.
2. Size of the macromolecular domain in solution at the temperature of viscosity measurement.
3. Molecular weight distribution.
4. Degree of branching of the macromolecules.
5. Whether or not the viscometer has a relatively constant shear gradient across the laminae of the sheared fluid.

In regard to the latter dependency, it is best to use a geometry imposing essentially a constant shear gradient across the fluid in the viscometer in order to have maximum sensitivity to the degree of temporary viscosity loss. Such geometry is exemplified by the concentric cylinder rotational geometry in contrast to the geometry of high-shear capillary viscometers which produce very non-linear shear gradients.

Calculation of the percent temporary viscosity loss (TVL) is as follows:

$$\%TVL = [(ULSV - UHSV)/ULSV] * 100 \quad \text{(Eq. 2)}$$

HIGH SHEAR PERMANENT VISCOSITY LOSS PARAMETER

When shear-degraded lubricants are measured at very high shear rates, the difference between these values and the very high shear viscosity values of the undegraded lubricants produces High Shear Permanent Viscosity Loss (HSPVL). The factors affecting this parameter are in many respects similar to the factors affecting LSPVL:

1. Concentration of a given VI Improver.
2. Molecular weight of a given polymeric chemistry, (for that portion of the molecular weight distribution above the threshold shearability level of the disrupting mechanism).
3. Molecular weight distribution.

4. VI Improver chemistries and molecular arrangement.

5. VI Improver solvency in the base fluid.

6. Mode of degradation of the macromolecule under disruptive forces.

There are also other factors which make this parameter unique in its information:

7. The relation between orientability and susceptibility to degradation

8. The concentration of orientable molecules remaining after degradation.

The percent High Shear Permanent Viscosity Loss is calculated as:

$$\%HSPVL = [(UHSV - DHSV)/ULSV] * 100$$
(Eq. 3)

DEGRADED TEMPORARY VISCOSITY LOSS PARAMETER

The difference between LSPVL and HSPVL is called the Degraded Temporary Viscosity Loss (DTVL) parameter. In several ways it is similar to TVL. However, DTVL is directly affected by the response of the lubricant to shear degradation as well as orientation effects.

The percent Degraded Temporary Viscosity Loss is calculated as:

$$\%DTVL = [(DLSV - DHSV)/ULSV] * 100$$
(Eq. 4)

OVERALL VISCOSITY LOSS PARAMETER

A fifth viscosity loss parameter comes from consideration of the effects of both permanent and temporary viscosity loss parameters. It is called the Overall Viscosity Loss (OVL) parameter and it is the maximum amount of viscosity loss related to the temperatures, shear rates, and degrading devices applied.

Percent Overall Viscosity Loss is calculated:

$$\%OVL = [(ULSV - DHSV)/ULSV] * 100$$
(Eq. 5)

USE OF ULSV AS A COMMON DIVISOR

One of the more important observations in the calculation of the various forms of viscosity loss is that ULSV is the common divisor for calculating each viscosity loss element. This approach makes all the parameters directly comparable. Moreover, if the values of TVL+HSPVL and LSPVL+DTVL are viewed as two equivalent paths to obtaining OVL, then the sums of one pair should be equal to the sum of the other. That is,

$$TVL + HSPVL = LSPVL + DTVL$$
(Eq. 6)

INSTRUMENTATION

To obtain comparative data at both low and very high shear rates for determining the various viscosity loss parameters, it is best to choose instruments capable of measuring viscosity in absolute units -- milliPascal seconds (Centipoise). Moreover, it is highly desirable for best results that the viscosity value be at the chosen constant temperature for a minimum of one minutes in order to be clearly stabilized. Temperature control should be within ±0.2°C for both the low-shear and the very high-shear viscometer. Since orientation phenomena strongly influence the results and such phenomena are highly dependent on shear rate/stress, only rotational viscometry with its constant shear gradient should be used. In contrast, capillary viscometry has a widely varying shear gradient across the annular shearing zone particularly at very high shear rate/stress which distorts the viscosity loss comparisons.

The source of shear degradation can be varied depending on the application of the information. For the work presented in this paper the instruments described in the following sections were used.

HIGH-SHEAR VISCOMETER

In studying the various Viscosity Loss Trapezoids, the author had the availability of the Tannas Model 400 Tapered Bearing Simulator-Viscometer in its automated configuration, shown in **Figure 2**, for the studies at 150°C.

This absolute automated viscometer is described in a previous paper **[Ref. 7]**. For studies at 100°C, the Tannas Model 600 TBS Viscometer was selected for its much broader viscosity range (~1 to 110 mPa*s). Temperature control was well within the desired limits at all temperatures from 40° to 180°C and beyond. The automated program configuration called for injecting 50 mL in a "chase"

technique developed for this viscometer. This relatively unique technique, uses the next sample to completely replace the previous sample by the pattern of flow into the viscometer cell.

Although the TBS-Viscometer can generate data at much higher shear rates, the shear rate chosen for this work was one million reciprocal seconds ($1*10^6$ 1/sec) and, because of the very slight taper on the mating rotor and stator and the absolute nature of the viscometer, the ability to set the desired shear rate while operating the viscometer was a great benefit.

In utilizing very high shear viscometry for purposes of determining the viscosity loss trapezoid, it is necessary to have the highest precision possible at constant temperature. The TBS-Viscometer met these criteria as indicated by ASTM Standard Method of Test D4683.

Figure 2
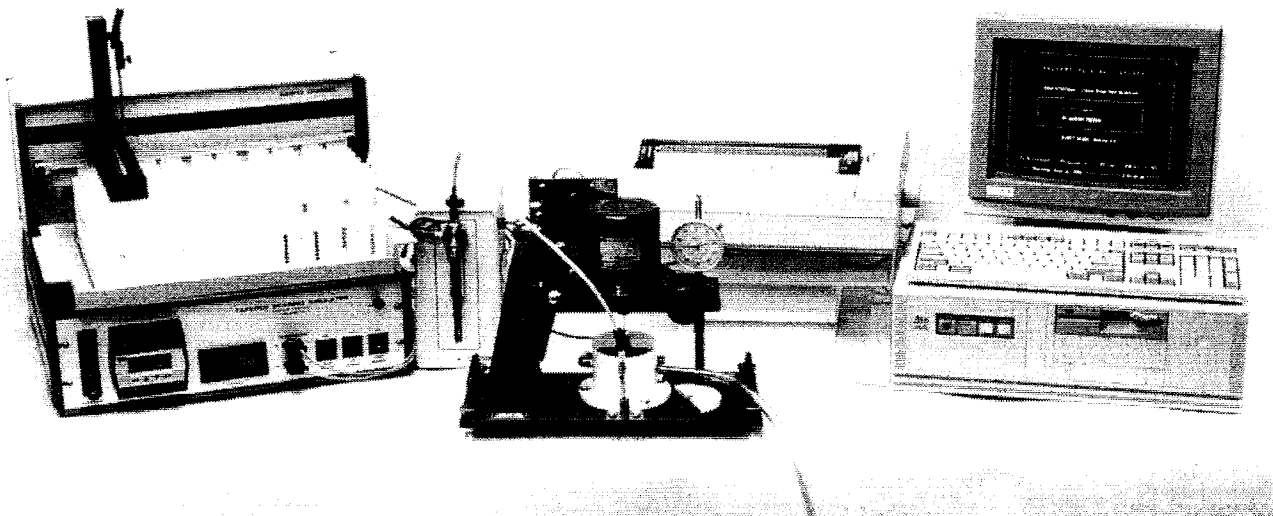
Figure 3
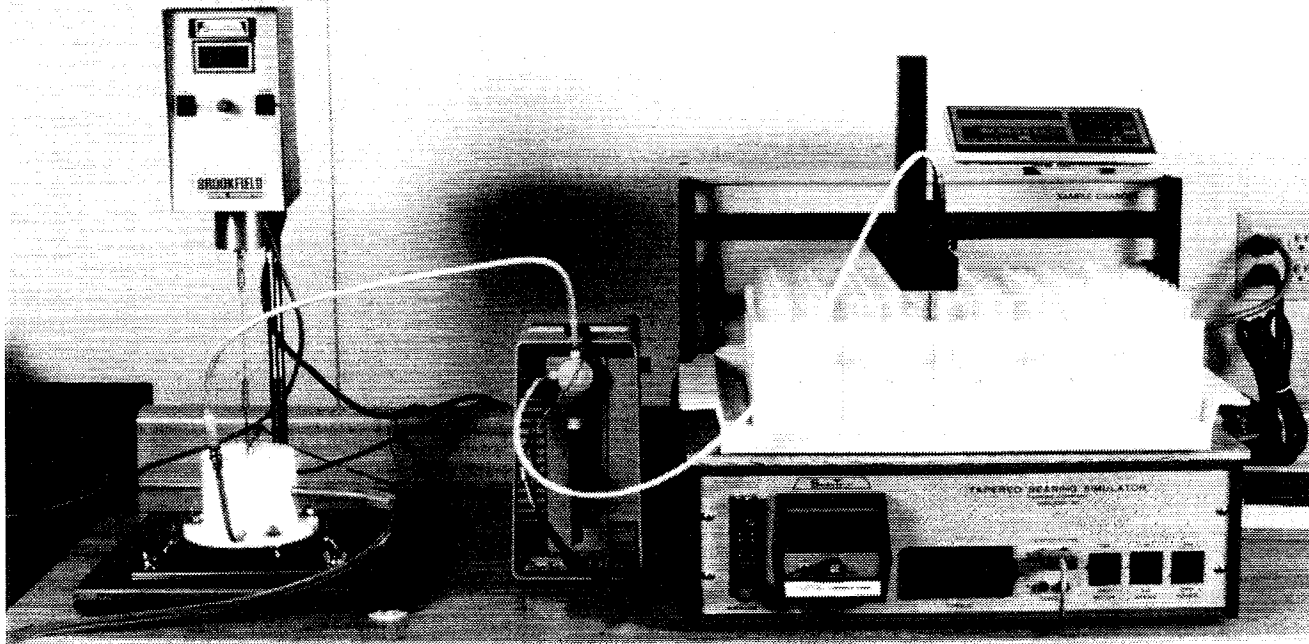
LOW-SHEAR VISCOMETER

The Tannas Co. Model 100 Low Shear Viscometer shown in **Figure 3**, was used for the low shear, high temperature studies. This instrument has been discussed in a previous paper [Ref. 8] and has been shown to follow Newtonian principles and to be precise in operation.

Temperature control is well within the desired limits at temperatures from 40° to 200°C. Sample size is about 30 to 50 cc when using the "chase" principle previously discussed wherein the next sample "chases" out and exchanges completely for the previous sample. Shear rate employed was a nominal 200 1/sec.

FUEL INJECTOR SHEAR STABILITY TESTER

Although the mode of VI Improver degradation was not critical, repeatability was. From this point of view, the FISST technique of ASTM D3945b was considered a good choice. The device used by the author and his associates is shown in **Figure 4**.

Figure 4
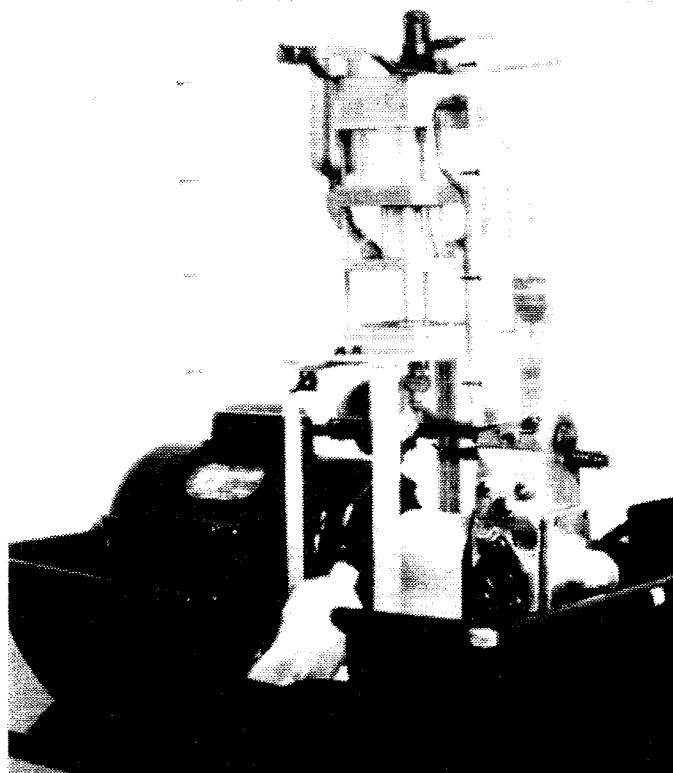
EXAMPLES OF THE VISCOSITY LOSS TRAPEZOID

NEWTONIAN ENGINE OIL

The simplest example of the Viscosity Loss Trapezoid is a Newtonian liquid and the nearest approximation to that in engine oils is a single grade oil whose only shear dependence might be in some of the additive components. In **Figure 5** is shown results on an SAE 30 oil from data in the Institute of Materials (IOM) database on engine oils. (All information presented from the IOM database in this paper is with the permission of IOM.)
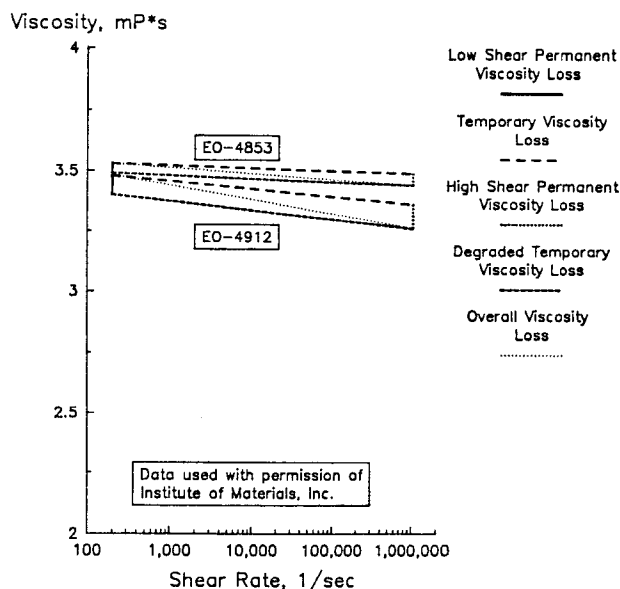
Figure 5
North American SAE 30 Engine Oil
Trapezoid Determined at 150 C

Figure 6
North American SAE 30 Engine Oils
Trapezoids Determined at 150 C
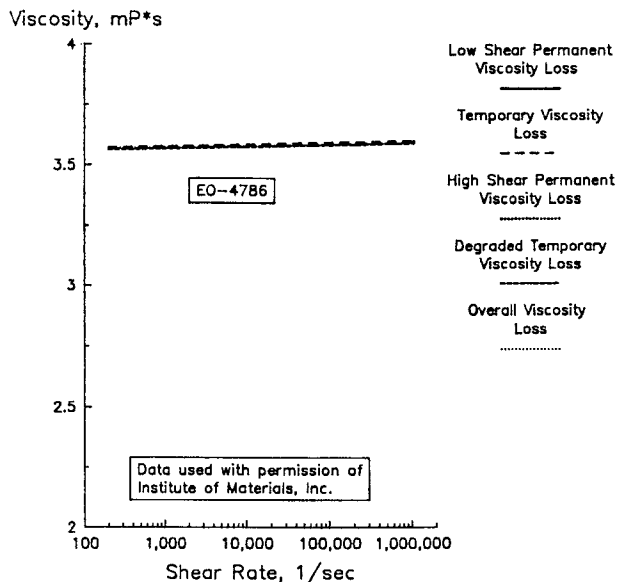
The Viscosity Loss Trapezoid, or VLT, is collapsed into a straight virtually horizontal line as would be expected with a straight-graded oil having little or no shear susceptibility.

However, some straight-graded oils do have limited shear susceptibility and this reflects the influence of some of the additives or higher molecular weight base stocks. **Figure 6** shows two SAE 30 grade oils from the IOM North American database which are representative of straight-graded oils with some shear susceptibility. The VLT indicates that EO-4853 shows some degradation of one of the additives but essentially no orientation effects. The conclusion is that there was no orientable molecules in the oil. Thus, the degradation could have affected macromolecules whose viscous contribution was degradable but not orientation prone.

In contrast, the SAE 30 represented by EO-4912 shows both effects -- degradation and slight orientation. However, as with EO-4853 the degradation of viscosity is about the same at low and high shear rates. This suggests that the molecules which were degraded are not the molecules showing orientation effects.

So, three SAE 30 grade oils yield some interesting basic VLT interpretations.

NON-NEWTONIAN ENGINE OILS AT 150°C

Examples of North American SAE 10W-30 Oils - One of the grades of engine oils growing in popularity on the North American continent is the SAE 10W-30. Two of these oils are shown in **Figure 7**.

Figure 7
North American SAE 10W-30 Engine Oils
Trapezoids Determined at 150 C
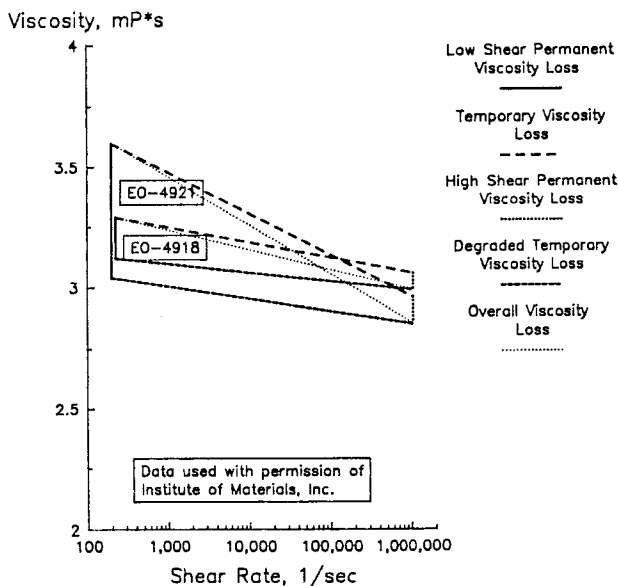
They have quite different VLTs. In fact, the VLT of EO-4918 almost fits within the larger VLT of EO-4921. (Note that the line representing LSPVL for EO-4918 is slightly offset to a shear rate of 225 1/sec. to aid in quickly understanding the graph.) While both oils show both degradation and polymer orientation effects, EO-4918 has much fewer molecules available for degradation as shown by the differences in both LSPVL and HSPVL between the two oils.

The two 10W-30 oils show obviously different strategies in making an acceptable engine oil. From other information in the IOM database, the strategy for EO-4921 results in a Viscosity Index (VI) of 149 and a Cold-Cranking Simulator (CCS) value of 3570 mPa*s. In contrast, EO-4918 results in a VI of 135 and a CCS of 3200 mPa*s, a more acceptable value. This, coupled with a higher final DHSV of 2.99 versus 2.85 mPa*s for EO-4918 and EO-4921, respectively, shows the superiority of the former strategy of blending and the ease with which Viscosity Loss Trapezoid (VLT) analysis reveals the differences.

Example of German SAE 10W-30 Oil - While 10W-30 oils are not as popular in Europe, IOM data on a German-manufactured oil of this SAE grade, identified as GO-203 in the IOM Database, is shown in **Figure 8**.

Figure 8
German SAE 10W-30 Engine Oil
Trapezoid Determined at 150 C
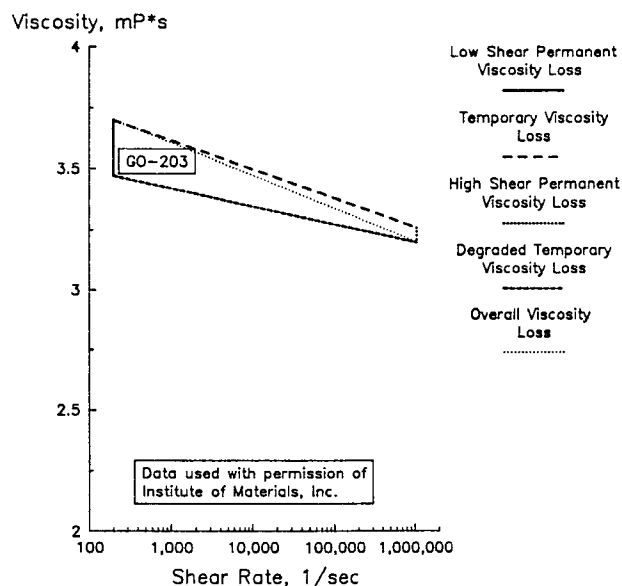
Immediate differences with the two North American oils are apparent. The trapezoid is displaced to higher viscosity values and the amount of degradation is more like that of EO-4918, although the residual orientation is greater.

The associated VI and CCS values are 141 and 3610 mPa*s respectively.

Examples of Japanese SAE 10W-30 Oils -

The IOM Engine Oil Database for Japan provided several examples of the application of the VLT procedure as shown in **Figure 9**.

Figure 9
Japanese SAE 10W-30 Engine Oil
Trapezoid Determined at 150 C
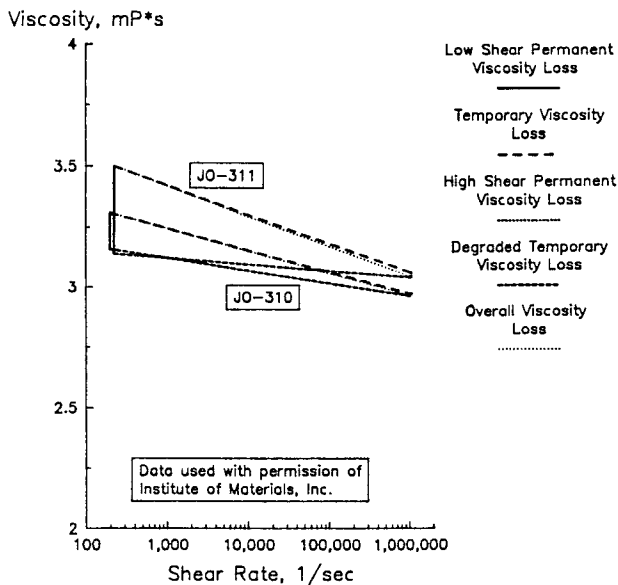
These trapezoids for JO-310 and JO-311 are interesting in that both oils show little or no change in TVL with shear degradation. In fact, the oil identified as JO-311 shows little residual orientation response after shear degradation -- the DTVL is only 2.9%. The fact that both oils show little TVL change suggests interesting VI Improver properties.

The VI and CCS values for Japanese oils JO-310 AND JO-311 are 140 and 147, and 3340 and 2910 mPa*s, respectively. The latter value is impressively low for the other viscometric values shown at high temperature.

Examples of North American SAE 5W-30 Oils - A grade of oil which has only recently gained general favor in North America is the SAE 5W-30 favored by American automobile manufacturers. However, this grade also pushes against the lower

level of viscosity tolerated by today's engines. Consequently, it is necessary to assure that the various forms of viscosity loss do not emasculate the ability of the oil to produce a sufficiently thick hydrodynamic film to avoid high wear levels. In this respect, the Viscosity Loss Trapezoid provides a very informative view of blending strategies (and their deficiencies). This is particularly true when it comes to the value of DHSV and how it is produced by the response of the oil to both high shear and degradation.

Two SAE 5W-30 oils are shown in **Figure 10** and are interesting to compare.

Figure 10
North American SAE 5W-30 Engine Oils
Trapezoids Determined at 150 C
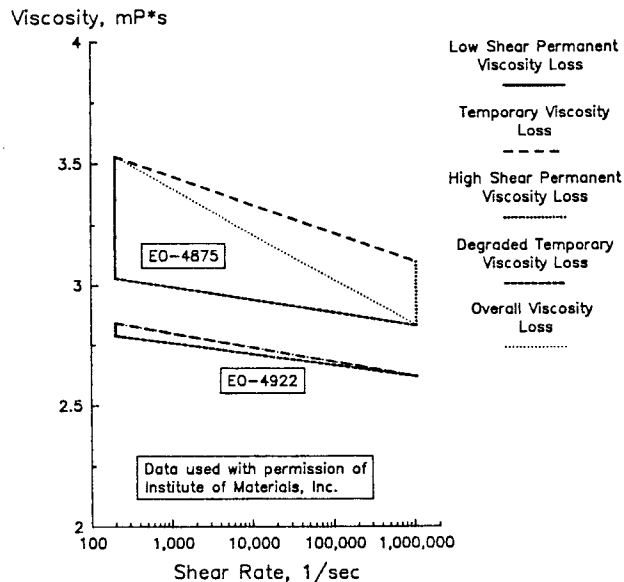
It is quite clear that they represent very different blending approaches with very different consequences in regard to the important DHSV. Oil EO-4875 starts with a ULSV of 3.53 mPa*s and ends with a DHSV of 2.83 mPa*s -- an Overall Viscosity Loss (OVL) of 19.8%. In contrast Oil EO-4922 starts with a ULSV of 2.84 mPa*s and ends with a DHSV of 2.62 mPa*s -- an OVL of 7.7%. Some American automobile manufacturers have, in the

past, been willing to accept a minimum viscosity of 2.60 mPa*s or higher. However, the new SAE J300 requires a minimum of 2.9 mPa*s for SAE 5W and higher W-grades.

The VI and CCS values for these two North American oils EO-4875 and EO-4922 are 155 and 167, and 3310 mPa*s and 2740 mPa*s, respectively.
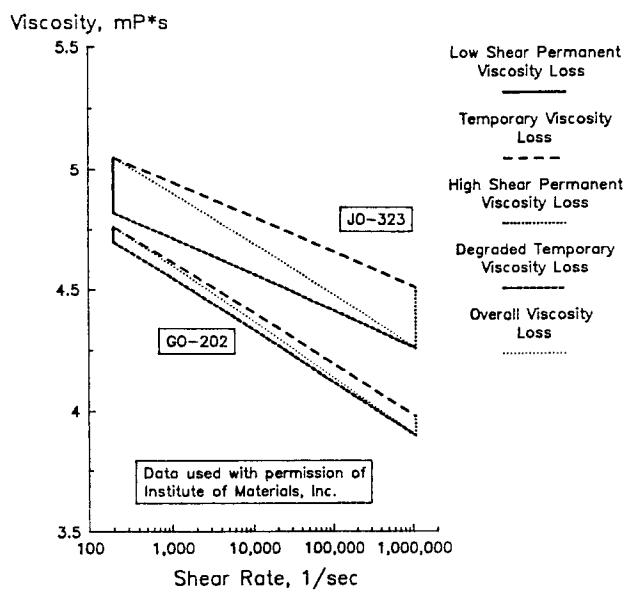
Contrast of SAE 10W-40 Oils from Germany and Japan - SAE 10W-40 engine oils remain highly popular around the world. However, each country's oil manufacturers very often use considerably different basestocks, blending techniques, and additive technologies. This is clearly shown by the VLTs of **Figure 11**.

Figure 11
German and Japanese SAE 10W-40 Engine Oils
Trapezoids Determined at 150 C

Interestingly, in both cases the TVL and the DTVL are constant within each oil. The TVL/DTVL ratio of JO-323 is 0.96 and the TVL/DTVL ratio of GO-202 is 0.98. Thus, although both oils show some shear degradation susceptibility, particularly JO-323, the orientation effects do not change which provides an interesting conundrum

which the author believes to be associated with the average molecular weight and molecular weight distribution before and after shear degradation. (A future paper will discuss the possible interpretations of the VLT in its many manifestations.)

Considering the related VI and CCS values for JO-323 and GO-202, these values are 152 and 156, and 4740 mPa*s and 3330 mPa*s, respectively. It is obvious that the CCS value for the JO-323 is well above SAE J300 requirements and the oil should be characterized as an SAE 15W-40.

The VLT and Wide-Grade Ranges - Many engine oil blenders like to offer wide grade-range engine oils for racing and other services. The VLTs of these oils often offer interesting patterns and insights.
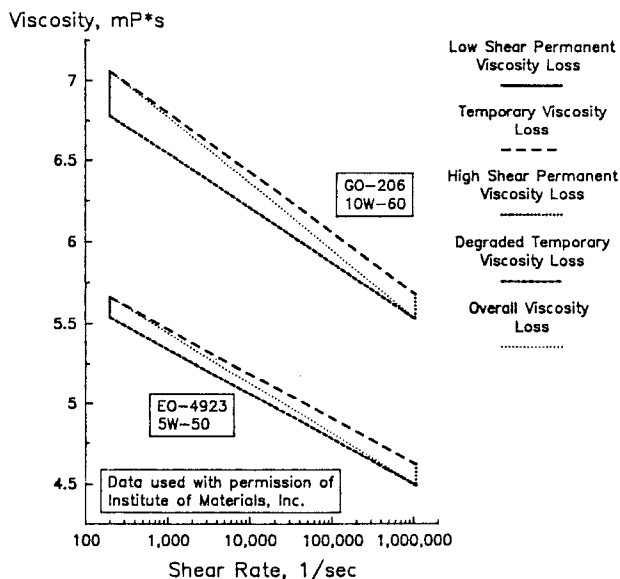
Figure 12 shows two wide-grade oils, a North American SAE 5W-50 and a German SAE 10W-60. Both are said to be synthetically based and both are made under similar brand names by separate and relatively autonomous companies in a larger corporation.

Figure 12
N. American and German SAE Wide-Grade Oils
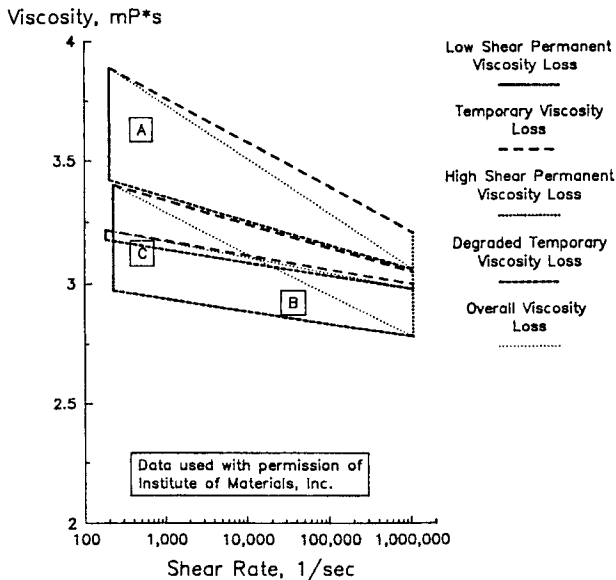Trapezoids Determined at 150 C

The forms of the VLTs are reminiscent of some previously presented and provide insights into these kind of VLTs. Primarily, the two VLTs show relatively low levels of PVL at either high or low shear rates coupled with high TVL values. In addition, the TVL/DTVL ratio is relatively near a value of 1.0 (GO-206 is 1.10; EO-4923 is 0.99 This, then, might be the hallmarks of oils made with synthetic base oils. Judged from this view, the 10W-40 from Germany shown in **Figure 11** as GO-202 might be synthetic-based and the Japanese oil in the same **Figure 11** (JO-323) might be part synthetic.

The VI and CCS values shown by the IOM Database associated with these two oils are 183 and 178, and 3270 mPa*s and 2970 mPa*s respectively for EO-4923 (5W-50) and GO-206 (10W-60).

TEMPERATURE EFFECTS ON THE VLT

Earlier in the paper it was mentioned that a study of the VLT of an oil at two or more temperatures gives added insights. Three North American 5W-30 engine oils containing different VI Improver approaches were analyzed at both 100° and 150°C. The results are given in **Tables 1 and 2** and in **Figures 13 and 14**.

Figure 13
North American SAE 5W-30 Engine Oils
Trapezoids Determined at 150 C

Figure 14
North American SAE 5W-30 Engine Oils
Trapezoids Determined at 100 C

Selby-11
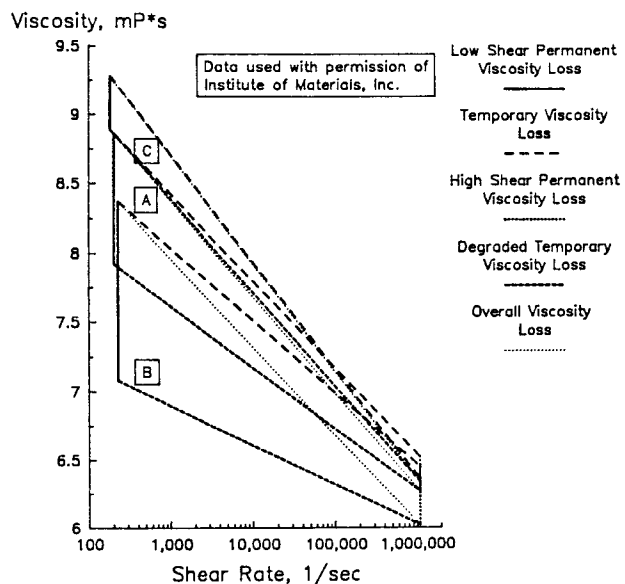
Table 1
North American 5W-30 Engine Oils
150 C

	Low Shear Fresh (ULSV)	Low Shear 20 cycles* (DLSV)	High Shear Fresh (UHSV)	High Shear 20 cycles* (DHSV)
	All values in units of mPa*s (cP)			
OIL A	3.89	3.42	3.21	3.06
OIL B	3.40	2.97	3.05	2.78
OIL C	3.22	3.18	3.00	2.98

Table 2
North American 5W-30 Engine Oils
100 C

	Low Shear Fresh (ULSV)	Low Shear 20 cycles* (DLSV)	High Shear Fresh (UHSV)	High Shear 20 cycles* (DHSV)
	All values in units of mPa*s (cP)			
OIL A	8.86	7.92	6.52	6.27
OIL B	8.37	7.08	6.45	6.02
OIL C	9.28	8.89	6.36	6.34

Two of the VI Improvers (used in Oil A and B) were olefin copolymers (OCPs). One of these was a dispersant variety (Oil A). Both were presheared before making the lubricant but Oil A was more drastically treated than Oil B. Oil C was a hydrogenated styrene-isoprene (HSI) known to have high tolerance to degrading forces.

From both **Figure 13** and **Figure 14**, it is evident that there are basic similarities between the VLTs of Oil A and Oil B but that both of these are considerably different from the VLT of Oil C. Both Oils A and B have ULSVs (initial viscosities at low shear) that are considerably higher than Oil C. At 150°C, Oil C shows the least response to shear conditions either of degradation or of orientation.

However, at 100°C, Oil C is **more** subject to orientation effects than either Oil A or Oil B. In addition, both its ULSV and DLSV (initial and degraded low shear viscosity) are higher than any of the low shear values of Oils A and B. It is reasonably well known that lower temperatures of the baseoil increases its "viscous grip" on the extended polymer coils of a completely dissolved VI Improver causing greater orientation at these lower temperatures.

However, as shown in **Tables 3 and 4**, when increases in orientation effects on TVL and DTVL are compared among the three 5W-30s, Oil C increases by more than a factor of 4 compared to an increase of somewhat more than a factor of two

Table 3
North American 5W-30 Engine Oils
150 C

	LSPVL	TVL	HSPVL	DTVL	OVL
OIL A	12.08%	17.48%	3.86%	9.25%	21.34%
OIL B	12.65%	10.29%	7.94%	5.59%	18.24%
OIL C	1.24%	6.83%	0.62%	6.21%	7.45%

Table 4
North American 5W-30 Engine Oils
100 C

	LSPVL	TVL	HSPVL	DTVL	OVL
OIL A	10.61%	26.41%	2.82%	18.62%	29.23%
OIL B	15.41%	22.94%	5.14%	12.66%	28.08%
OIL C	4.20%	31.47%	0.22%	27.48%	31.68%

for the two OCP containing 5W-30 oils. This behavior strongly supports other reports that the HSI VI Improver changes its molecular configuration somewhere between 100° and 150°C whereas the other two polymers are simply distorted or oriented more in the clutches of the more viscous base oil at the lower temperature of 100°C.

Without going further into interpretation of the responses of these North American 5W-30 oils, it is evident that the VLT provides incisive information on their similarities and differences -- information which can be extended to other lubricants and formulations.

CONCLUSIONS

In this paper the author has shown a new technique for studying the effect of VI Improvers on viscosity loss. The method seems to clearly differentiate among several different approaches to the manufacture of automotive engine oils. In particular, the method shows clear distinctions among a number of blending strategies.

Since shear stability is growing as a concern in the manufacture of engine oils, particularly in the manufacture of the less viscous grades such as the 5W-30, the Viscosity Loss Trapezoid is a relatively rapid visual appraisal of both efficiency and overall effectiveness in meeting the needs of the motorist.

Coupling this technique with use of two or more temperatures of analysis opens up avenues of greater understanding. Even more information can be generated by knowing or determining the base oil viscosity contribution.

Thus, the Viscosity Loss Trapezoid is thought to have wide application in the appraisal of the comparative viscous effects of polymers and synthetic fluids.

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