The Viscosity Loss Trapezoid -
Application of the Viscosity Loss Trapezoid in Determining Overall Features of VI Improver Molecular Weight Distribution

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Information from Lubrication Savants

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ABSTRACT

Building on his previously presented paper concerning the development of the concept of the Viscosity Loss Trapezoid (VLT), the author shows how closely related dynamic viscosities and viscosity loss parameters produced by measuring the high and low shear rate viscosities of a VI Improver-containing oil before and after degradation of the Viscosity Index Improver can produce a view of the latter's molecular weight distribution. The information gained was enhanced by determining the VLT at two different temperatures of 100° and 150°C

The method is relatively simple and straightforward and requires no knowledge of the components of the lubricant examined in order to be quite informative.

BACKGROUND

In earlier papers and oral presentations as well as one of more recent vintage (1,2,3,4), the author defined the concept of the Viscosity Loss Trapezoid (VLT). In those presentations it was shown that four different measures of the viscous characteristics of a blend would define a geometrical figure -- a trapezoid -- which reflected the viscous contributions and responses of the VI Improver in the blend. In doing so, it was apparent that, to the degree that these several viscous contributions were collectively unique, the trapezoid would be similarly unique. It was also evident that VI Improvers of the same chemical 'family' should show a 'family' resemblance in the shape of the resulting trapezoid.

The four viscous measures of the oil's response to stress used by the author in his work over the years were:

State 1: The low shear rate ($\sim$200 s^{-1}) viscosity of the fresh oil,

State 2: The very high shear rate viscosity ($\sim$10^6 s^{-1}) of the fresh oil,

State 3: The low shear rate viscosity after the oil has gone through some repeatable, highly energetic form of mechanical polymer degradation, and

State 4: The very high shear rate viscosity of the degraded oil.

These measures of viscosity also corresponded to both familiar and unfamiliar measures of viscosity loss. For example, the familiar 'temporary viscosity loss' (TVL) is given by the difference in viscosity between State 1 and State 2 while the familiar 'permanent viscosity loss' (PVL) caused by VI Improver degradation under extraordinary shearing forces, is given by the difference in viscosity between State 1 and State 3.

In the previous presentations and publications, the author also introduced three relatively unfamiliar measures of viscosity loss. One of these was termed 'high shear permanent viscosity loss' (HSPVL) and is given by the viscosity difference between State 2 and State 4. Another was termed 'degraded temporary viscosity loss' (DTVL) and is given by the viscosity difference between State 3 and State 4. Lastly, as a measure of the combination of PVL and TVL the author defined the 'overall viscosity loss' (OVL) as the difference in viscosity between State 1 and State 4.

An example of a Viscosity Loss Trapezoid reflecting these values and definitions is shown in **Figure 1**.
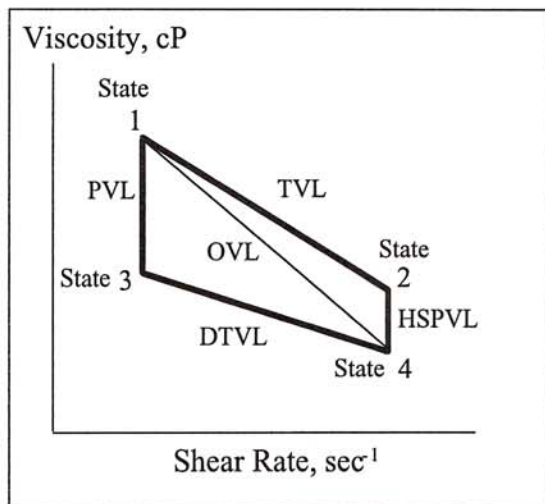
Figure 1 - Sample Viscosity Loss Trapezoid showing four viscosity values and five viscosity loss functions.

As the development of the Viscosity Loss Trapezoid continued, it became evident that, in addition to its use in helping identify polymer type, the VLT might be able to be used in further applications. One of these applications related to the possibility of obtaining information about molecular weight and molecular weight distribution of the VI Improver used in the lubricant.

This paper is a presentation of that concept as well as its underlying rationale and use of the VLT in obtaining insights into the molecular weight distributions of several VI Improvers in a common base oil.

RATIONALE
General

'VI Improver' is a term used in lubricant circles to describe a polymer solvated by an oil which is added to the lubricant to improve its Viscosity Index (an empirical technique from the 1930's to compare the viscosity-temperature characteristics of lubricants).

Over the last 60 years much information has been presented by many authors concerning both the theory of polymer dynamics in solution as well as the results of many experimental studies of such systems in simple solvents and in mineral oil. Part of the reasoning used in applying the Viscosity Loss Trapezoid technique to the determination of MW distribution comes from these studies.

Polymer-in-oil solutions are a particularly interesting subset of the more general area of polymer solutions because

1) such systems are widely encountered in lubrication

2) oil viscosity is high enough to have a considerably stronger influence on polymer solution behavior than most simple, low molecular weight solvents.

Shear Stress Effects on VI Improver Contribution to Viscosity

The strength of the VLT technique comes from the use of the viscometric measurements made of an oil when in each of the four previously mentioned 'States' or conditions. These four conditions actually represent the four 'States' or viscometric aspects of the particular oil/VI Improver blend behavior when subjected to three levels of shear stress

a. relatively low,

b. moderate to high, and

c. extraordinarily high.

From four aspects of one polymer-in-oil system or blend, it is reasonable to consider that this should be capable of giving insight into the characteristics of the VI Improver producing such rheology. Moreover, multiplying the rheological information on the system by obtaining another four views at a considerably different temperature should markedly increase the information leading to conclusions about the nature of the VI Improver used in the blend.

Relationship between Orientation and Degradation Phenomena

An important consideration in this rationale for application of the VLT to the estimation of initial and degraded MW distribution is the fact that the forces leading to orientation phenomena (the distortion of a VI Improver's polymer molecules in laminar flow producing States 2 and 4) must be less than the forces producing permanent degradation of the molecules (which results in the degraded viscosity values evident in States 3 and 4). In other words, it is a reasonable presumption that the forces required to orient a polymer molecule without degrading it are less than those forces degrading the polymer molecule. A corollary of this severity ranking of shearing effects is that there will be molecular weights within the molecular weight distribution of the VI Improver which are susceptible to orientation but not to degradation -- at least within the range of degradation energies familiar to automotive mechanisms such as the engine, automatic transmission, power-steering pump, and differential.

One way of thinking of this orientation/ degradation relationship is to view the oil molecules solvating the VI Improver macromolecules as

having a 'viscous grip' on the macromolecules during flow. As the flowing forces increase, the 'viscous grip' of the oil layers flowing at dissimilar rates distend and stretch out the domain of the macromolecules -- first by orienting the macromolecule in the direction of flow and then, at extraordinarily high shear stresses, snapping (degrading) the polymers chain backbone if level of shear stress can be raised high enough by the 'viscous grip'.

It has also been frequently observed that the MW threshold required for degradation in each different mechanical device may differ considerably. For example, the degradation in automotive engines is considerably less than that in differentials. Similarly, difference in orientation and degradation susceptibility would be expected for different polymer chemistries, molecular weights, MW distributions, spatial configurations, concentrations, and solubilities in the oil.

Another reasonable assumption -- and one helpful for the sake of simplifying subsequent interpretations -- is that orientation and shear degradation responses of each VI Improver be considered to have a certain threshold MW weight above which they become evident. Both responses are dependent on four factors:

    1. molecular weight,

    2. molecular weight distribution,

    3. molecular configuration, and

    4. the proportion of molecules in the oil susceptible to either or both orientation and degradation.

Figure 2 shows three conceptualizations of different molecular weight distributions for three soluble polymers in a base oil whose MW distribution is also shown. On the basis of the foregoing assumption regarding the corresponding effects of orientation and degradation and their respective
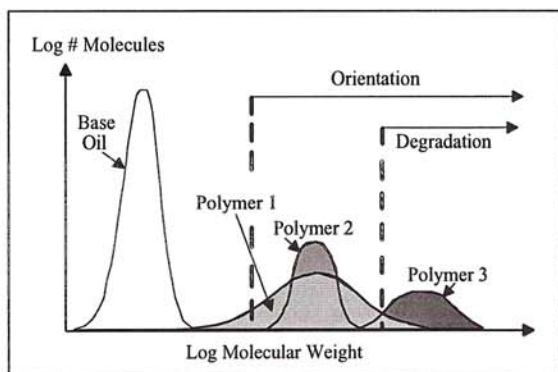
Figure 2 - Sketch of MW distributions of three illustrative forms of polymers in a base oil

thresholds, it would be expected that these three polymer systems would show the following responses:

Polymer 1: The oil solution of this polymer would show considerable TVL and *some* PVL.

Polymer 2: The oil solution of this polymer would show considerable TVL but *no* PVL.

Polymer 3: The oil solution of this polymer would show considerable TVL *and* PVL.

The critical point is: since this appraisal of shear susceptibility can be made on the basis of the MW distributions shown, then it might also be expected that the converse information would be applicable -- *that sufficient information on the shear susceptibility of a VI Improver would give a reasonable, although somewhat relative and limited, interpretation of the MW distribution responsible for such response to the dual shearing forces.*

Effect of Degradation on the Molecular Weight of Linear Polymers

A further aspect of shear degradation influencing the interpretation of the Viscosity Loss Trapezoid data is the manner in which a linear polymer molecule is torn apart by extreme shearing forces. It has been reasoned that the statistical probability of the location of breakage of the polymer 'backbone' is at the center of the coil where tension caused by oppositively moving sections of the polymer coil reaches a maximum. Thus, any linear polymer coil degraded by shearing forces is more likely to be broken into relatively equal segments of about half the molecular weight of the initial polymer molecule. Another important but easily overlooked relationship: all studies of polymer-in-oil degradation known to the author have shown that the degradation of a polymer always produces remnants having less viscous influence than the original polymer. That is, degradation always produces a loss in viscosity.

Applying this information, the MW distributions shown in **Figure 2** would be expected to become like those in **Figure 3** after shear degradation. Polymer 1 shows some loss of its highest molecular weight components and a related increase in lower molecular weight components. In contrast Polymer 2 does not change since none of its distribution is over the threshold of those molecular weights above which degradation occurs. Finally, Polymer 3 undergoes a massive change in molecular weight distribution as a consequence of most of its initial distribution being above the degradation threshold. The DTVL and HSPVL of the Viscosity Loss Trapezoid will reflect these changes and their
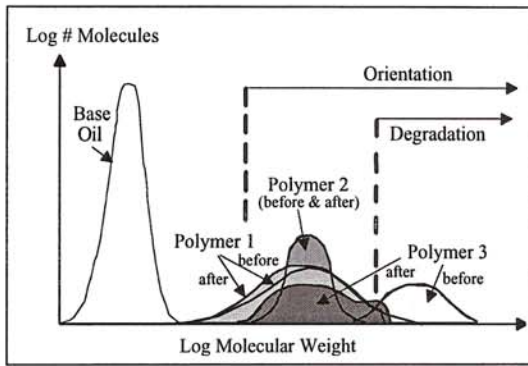
Figure 3 - Sketch of degradation effects on MW distributions of the three polymers shown in Figure 2.

relationship with the TVL and PVL. Such information is the basis of the concept of applying the VLT to gaining information about the MW distribution of VI Improvers.

It should be understood that these three examples of both initial and final molecular weight distributions are only three of many possible forms of molecular weight distribution. Moreover, not all VI Improvers are linear polymers -- some are highly branched, some are fibril bundles, still others are mixtures of two polymers with mixed MW distributions. Then, too, there are highly homogeneous synthetic base oils composed of smaller polymeric molecules from which modern lubricants are formulated in part or in whole.

Orientation Tendency

From the point of view of the polymer molecule particularly but any molecule in general, orientation tendencies are determined by the aspect ratio of the molecule which, in turn, is affected by the molecule's degree of deformability in flow. Deformability, in turn, is affected by the stiffness of the polymer backbone relative to its length and the degree to which the polymer molecule may unfold into the oil matrix (i.e. the solubility of the polymer). In short, the degree of orientation is determined by the degree of departure from a spherical domain or aspect during exposure to the forces causing flow.

From the point of view of the oil matrix within which the polymer molecule finds itself embedded, the viscosity or 'viscous grip' of this matrix on the polymer molecule may be said to be the underlying cause of all polymer response since, as previously noted, it is through this matrix that the forces of shear are brought to bear upon the polymer molecule. Thus, higher viscosities will always be expected to bring about more distortion/orientation of the polymer molecule unless for any reason the

polymer molecule contracts and, thus, limits its exposure to the oil matrix.

The degree to which such molecular orientation will reduce the viscosity at higher shear forces is dependent on what viscous contribution the molecule has at lower shearing stresses, how much of this contribution is subject to shearing forces, and how many of the flowing molecules will experience some degree of orientation at the shearing force level applied. Thus, even smaller polymer molecules may demonstrate a small orientation phenomena if their shape, stiffness, and number are appropriate. This relationship between numbers of molecules and their collective degree of susceptibility to orientation is important to the appraisal of orientation response in, for example, synthetic fluids.

Rules of the Viscosity Loss Trapezoid

Within the knowledge of polymer-in-oil dynamics, there are many possible trapezoids that can be formed. There are also a number that are not rational and these can be defined by certain 'rules of the VLT'. From **Figure 1**, the most evident rules are:

1. The value of State 2 must be equal to or less than State 1.

2. The value of State 4 must be equal to or less than either States 1, 2, or 3.

3. The value of HSPVL must be equal to or less than PVL.

4. The value of DTVL must be equal to or less than TVL.

All of these relationships are, of course, limited by the precision of the viscometers used.

EXPERIMENTAL INFORMATION
Base Oil and Blends

Several commercial VI Improvers of different chemistries were obtained and blended into a common 150 Neutral base oil at a level sufficient to obtain a Kinematic viscosity of approximately 16 cSt at 100°C -- a value reflecting the high SAE 40 classification range for engine oils. Blend information is given in **Table 1**.

TABLE 1 - Component and Blend Information			
Base Oil and VI Improvers	Characteristics	Percent Added to Base Oil	Kin. Viscosity at 100°C, cSt
Base oil	150 N	neat	5.16
Polymer O	Olefin Co-polymer	1.85*	16.29
Polymer A1	Polymethacrylate (MW$_{high}$)	10.7	16.28
Polymer A2	Polymethacrylate (MW$_{mod}$)	11.5	16.04
Polymer A3	Polymethacrylate (MW$_{low}$)	12.0	15.83
Polymer S1	Styrene-Isoprene (linear)	14.5	16.01
Polymer S2	Styrene-Isoprene ('Star')	12.9	15.82
* Provided as a solid			

Viscometric Equipment Used

Low shear rate data was obtained using the rotational viscometer shown in **Figure 4**.
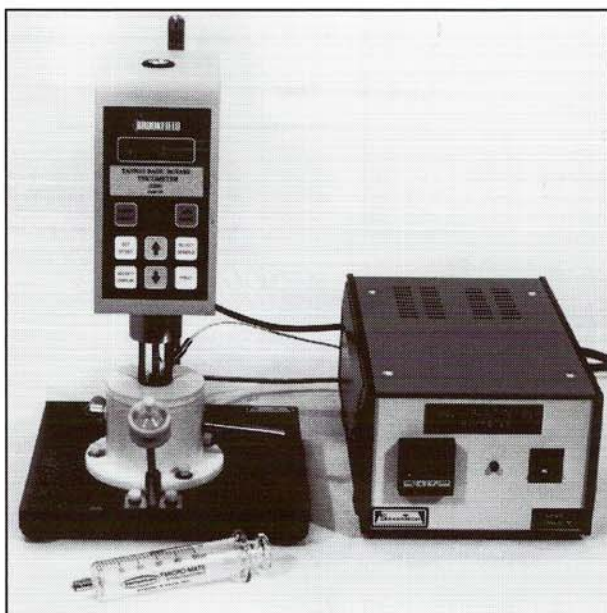
Figure 4 - Tannas Model TBR low shear rate rotational viscometer

Rotational viscometry at low shear rates was chosen in preference to the more common and more precise Kinematic (capillary) viscometry. There were two reasons for this choice:

1. Since Kinematic viscosity is a function of viscosity and density, it was preferable to avoid density effects among oils by measuring the viscosity value directly.

2. Rather than have the broad shear rate range imposed by both low and high shear rate capillary viscometry, it was very important to VLT interpretation to work with only one shear rate across the shearing gap.

A further advantage of the particular rotational viscometer used was the fact that it did not require a liquid bath for acceptable temperature control and, thus, operating temperatures could be changed in 10 minutes or less. Equally important, the calibration values determined at one temperature were valid for all temperatures **(1,5)**. All of these factors were of advantage in Viscosity Loss Trapezoid analysis.

Of the various levels of lower shear rate available with the instrument, a shear rate of 200 sec^{-1} has chosen for all of the VLT work to date.

Very high shear rate data was obtained on a Model 400 synchronous-motor-equipped Tapered Bearing Simulator-Viscometer (TBS) shown in **Figure 5** at 150°C and on a Model 600[1] whose larger, synchronous motor is shown in **Figure 6** for work at 100°C where blend viscosities above 12 cP may be encountered with commensurably higher torque requirements. At high shear rates, particularly with shear stress dependent orientation effects, having a known, constant, and singular shear rate across the gap is an important element of VLT analyses. This is particularly true when attempting to operate at different temperatures.

For this latter need in establishing an accurate shear rate at any temperature, the Tapered Bearing Simulator's absolute viscometry allows this to be done while the instrument is operating **(6)**.

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[1] The Model 600 TBS is used from 12 to ~100 cP.

Figure 5 - Model 400 Tapered Bearing Simulator-Viscometer for very high shear rate rotational viscometry.


Figure 6 - Motor of Model 600 Tapered Bearing Simulator-Viscometer for high shear rate viscometry above 12 cP.

Shear degradation of the polymer-containing oils was obtained using the Fuel Injection Shear Stability Tester (FISST) developed a number of years ago by Texaco and in 1980 developed as an ASTM Standard Method D 3945b-86 **(7)**. For use of the VLT method, however, any shear degradation technique or device may be used as long as the method is reasonably consistent from test to test. Engine or automatic transmission tests are perhaps more acceptable than bench tests (if consistent) since the shear degradation occurring in such devices would give ultimate value in applying the VLT. However,

each mechanical device will give its own view of the VI Improver's influence and the final molecular weight distribution will be conditioned by the shear degradation level of the device.

In the present work, as in the past studies by the author, 20 cycles through the FISST were applied to obtain the level of degraded oil for VLT analysis. As in all tests using the FISST, the reference shear stability standard called for in ASTM D 3945B was used each day to establish the severity level. One of the strengths of the FISST in comparison to other Diesel injector tests is the durability of its nozzle and the long-term repeatability of the device. This is shown in **Figure 7** covering several months of operation in the Savant Laboratories.
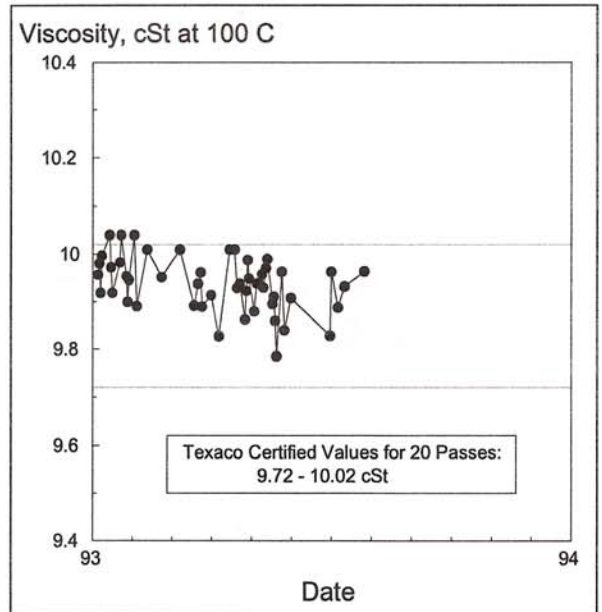
Figure 7 - Repeatability of FISST over several months

RESULTS OF VISCOMETRIC STUDIES

The base oil and each of the blends were analyzed viscometrically at both high and low shear rates. Results are shown in **Table 2**. From these data the various values of viscosity loss were determined and given in **Table 3** while their percent viscosity loss values are shown in **Table 4** for a more direct comparison.

Table 4 clearly shows how much variation there is in the various viscosity loss parameters among the various VI Improvers studied. This table also shows clearly how these parameters varied from 100° to 150°C.

Blends	KV	Low Shear Rate, 200 sec⁻¹				Very High Shear Rate, 10⁶sec⁻¹			
	100°C	100°C, cP		150°C, cP		100°C, cP		150°C, cP	
	cSt	fresh	FISST	fresh	FISST	fresh	FISST	fresh	FISST
150 Neutral Base oil	5.16	4.28	4.28	1.82	1.86	4.26	4.26	1.91	1.91
Polymer O	16.29	13.37	11.31	5.27	4.49	8.76	8.74	3.94	3.89
Polymer A1	16.28	13.40	9.21	5.95	4.02	8.00	7.49	3.60	3.26
Polymer A2	16.04	13.26	10.64	5.83	4.59	8.54	8.08	4.06	3.80
Polymer A3	15.83	13.10	11.51	5.76	5.04	9.68	9.30	4.31	4.13
Polymer S1	16.01	13.16	9.35	5.30	3.81	8.24	7.42	3.77	3.32
Polymer S2	15.82	12.88	11.98	5.24	4.86	7.43	7.40	3.54	3.45

TABLE 2 - Viscometric Information at Low and High Shear Rates and 100° and 150°C

Blends	100°C, cP				150°C, cP			
	PVL	TVL	HSPVL	DTVL	PVL	TVL	HSPVL	DTVL
150 Neutral Base Oil	0.00	0.02	0.00	0.02	-0.04	-0.09	0.00	-0.05
Polymer O	2.06	4.61	0.02	2.57	0.78	1.33	0.05	0.60
Polymer A1	4.19	5.40	0.51	1.72	1.93	2.35	0.34	0.76
Polymer A2	2.62	4.72	0.46	2.56	1.24	1.77	0.26	0.79
Polymer A3	1.59	3.42	0.38	2.21	0.72	1.45	0.18	0.91
Polymer S1	3.81	4.92	0.82	1.93	1.49	1.53	0.45	0.49
Polymer S2	0.90	5.45	0.03	4.58	0.38	1.70	0.09	1.41

TABLE 3 - Viscometric Information on the Various Loss Parameters at 100° and 150°C

Blends	100°C, cP				150°C, cP			
	%PVL	%TVL	%HSPVL	%DTVL	%PVL	%TVL	%HSPVL	%DTVL
Polymer O	15.4	34.5	0.2	19.2	14.8	25.2	0.9	11.4
Polymer A1	31.3	40.3	3.8	12.8	32.4	39.5	5.7	12.8
Polymer A2	19.8	35.6	3.5	19.3	21.3	30.4	4.5	13.6
Polymer A3	12.1	26.1	2.9	16.9	12.5	25.2	3.1	15.8
Polymer S1	29.0	37.4	6.2	14.7	28.1	28.9	8.5	9.2
Polymer S2	7.0	42.3	0.2	35.6	7.3	32.4	1.7	26.9

TABLE 4 - Viscometric Information on the Various Loss Parameters at 100° and 150°C in Percent

VISCOSITY LOSS TRAPEZOIDS

From the data of **Table 2**, the associated Viscosity Loss Trapezoids can be formed. **Figures 8** through **13** show these VLTs. In these plots, the x-axis (abscissa) is logarithmic to convey the range of shear rate covered by the data even though only two very widely spaced shear rate values are used. The straight line connecting the viscosity values over this shear rate range is a construct to assist the understanding of the VLT rather than an indication of the mid-range values of non-Newtonian viscosity over this entire range of shear rates. (However, this construct has some technical validity since, using the Tapered Bearing Simulator-Viscometer over the shear rate range of 10^5 to $2 \cdot 10^6$ sec^{-1}, it has been shown that an exponential relationship closely approximates the data gathered on various oils containing different VI Improvers **(8,9,10)** and it is likely that this relationship extends down to still lower shear rates than 10^5 sec^{-1}.)

Base Oil VLT

VLT results on the 150 N base oil is helpful in understanding the degree of precision of the technique when using modern rotational viscometry and also shows the basic behavior of a blend having no orientable or degradable components. **Figures 8a** and **8b** at 100° and 150°C, respectively, show essentially horizontal straight lines -- a collapsed trapezoid -- since there is, and should be, no component of the oil which can be oriented or degraded. Further, the data show that the base oil is truly Newtonian over this shear rate range and that the
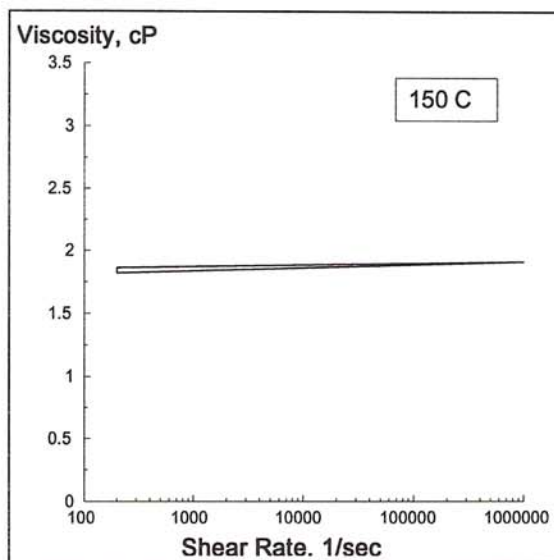
Figure 8b - VLT of base oil at 150°C

values at high and low shear rates agree within, at most, 0.1 cP from low shear rate to high shear rate. It is of interest to keep this simple behavior of the 150 N base oil in mind when studying the VLTs of the VI Improved blends.

Olefin Copolymer VLTs

The olefin copolymer VLT is shown in **Figure 9a** at 100°C and in **Figure 9b** at 150°C. It is evident from these figures that, while the blend shows considerable TVL and PVL at both temperatures, interestingly and significantly, the HSPVL is essentially nil at either. This is also shown in **Table 4**. Such behavior in HSPVL can be simply
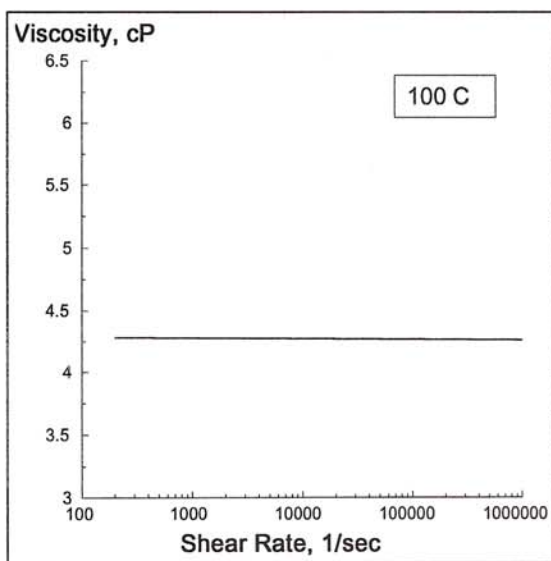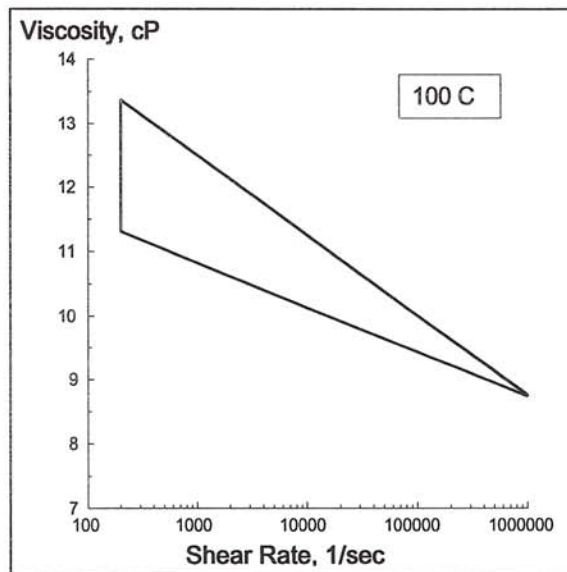

Figure 8a - VLT of base oil at 100°C

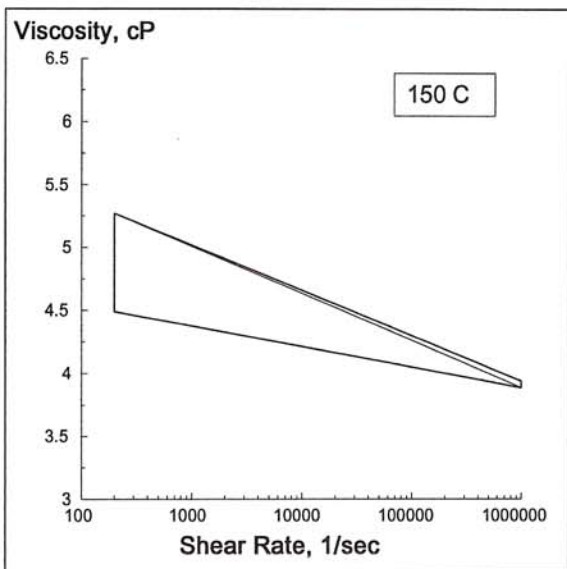Figure 9a - VLT of olefin copolymer at 100°C

Figure 9b - VLT of olefin copolymer at 150°C

indicative that the orientation susceptibility is unaffected at high shear rates by any PVL. It would be difficult to defend such a point of view since loss of the viscosity contribution of those orientable and degradable macromolecules would certainly affect the value of both parameters. Rather, further thought suggests that PVL with polymers of certain MW_{avg} and MW distribution may generate half-MW shards which contribute more viscosity in the degraded state than in the oriented state -- although the overall viscosity contribution of the degraded polymer at high shear stress is never greater than the undegraded polymer. Such considerations are given more attention in the **Discussion** section of this paper.

From **Tables 2,3** and **4** it is evident that there has been a considerable change in the orientation loss of viscosity with degradation. It is of interest and relevance to use the relationship

% Orientation Loss = %(1-[TVL-DTVL]/TVL) to calculate such change in orientation effects. It is found that the process of degrading the VI Improver in the blend results in a DTVL having about 56% of the TVL at 100°C and 45% at 150°C (where the viscous grip is weaker in producing both TVL and DTVL). This can be viewed as a loss of 44% in orientation susceptibility at 100°C and 55% at 150°C by those larger macromolecules affected by degradation. The decrease in %TVL values in **Table 4** also show that the viscous grip of the oil weakens with increasing temperature.

Polymethacrylate VLTs

The next set of **Figures 10a** through **12b** show the VLTs of a series of three members of a 'family' of polymethacrylate-based VI Improvers having relatively different molecular weights as previously noted in **Table 1**. Again, the VLTs were obtained at both 100° and 150°C to enhance the information generated by the VLT technique.

VLTs of higher MW polymethacrylate VI Improver, Polymer A1, are shown in **Figures 10a** and **10b**. This VI Improver is shown to contribute
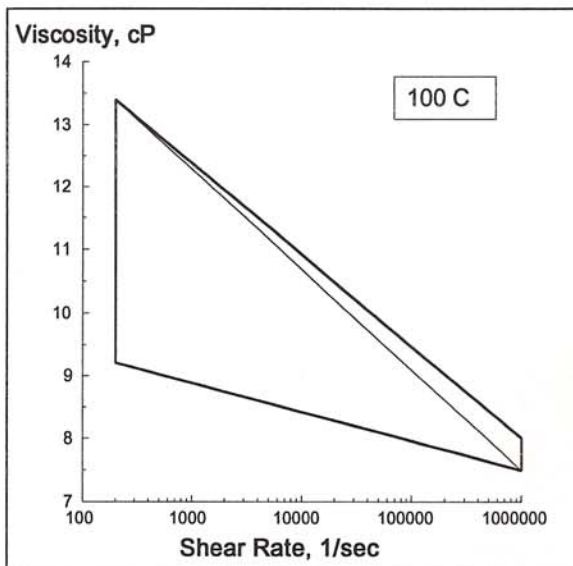

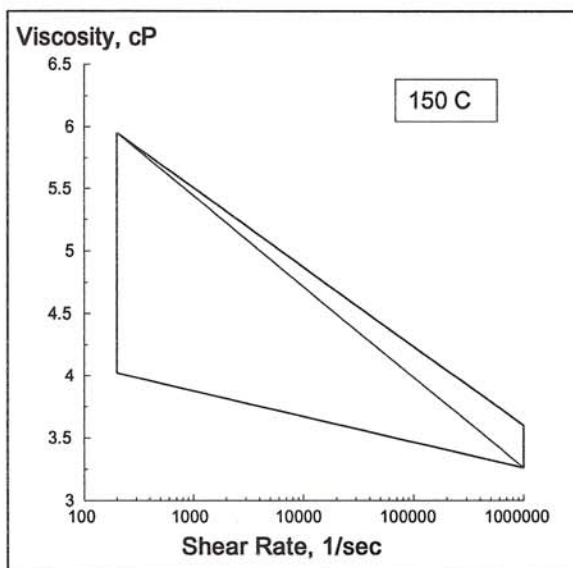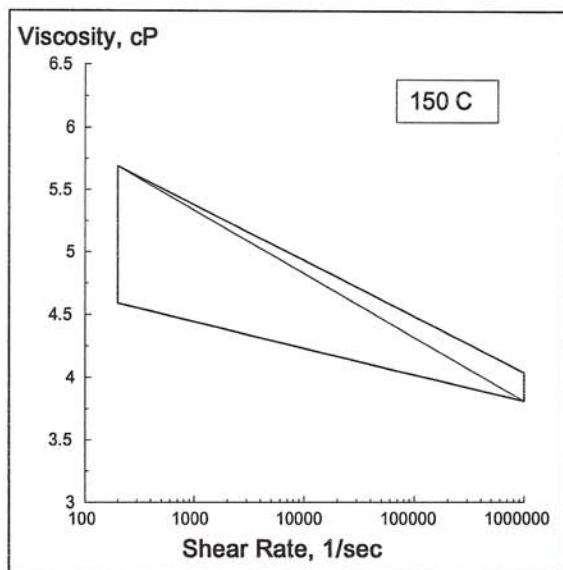Figure 10a - VLT of high MW polymethacrylate at 100°C.

Figure 10b - VLT of high MW polymethacrylate at 150°C

Page 9

considerable viscosity to the base oil at relatively low concentrations and to be fairly vulnerable to both forms of shearing forces -- orientation and degradation. Both the PVL and the TVL are markedly higher than the respective values for the other two polymethacrylate VI Improvers -- a consequence easily associated with the expected behavior of a higher MW polymer. In contrast to Polymer O, it will be noted in **Table 4** that the %TVL (which is a measure of distention of the polymer coil) remains essentially constant -- 40.3% vs. 39.5% from 100° to 150°C. Polymethacrylates have long been known **(11)** to find mineral oils a fair, but not excellent, solvent at low temperatures. Since viscous grip is expected to diminish with the greater mobility and intermolecular distances of higher temperatures, the fact that the %TVL remains nearly constant suggests that the polymethacrylate coils of Polymer A1 has retained this level of orientation by becoming more extended -- balancing the effects of the reduced viscous grip of the oil.

The values of TVL and DTVL in **Table 3** again can be used to show that Polymer A1 experienced a marked loss of 78% of its orientation susceptibility at 100°C and the same amount at 150°C.

VLTs of the intermediate MW polymethacrylate VI Improver, Polymer A2, are shown in **Figures 11a** and **11b**. In comparison to the size of the higher molecular weight polymethacrylate trapezoids shown in **Figures 10a** and **b**, the VLTs of the
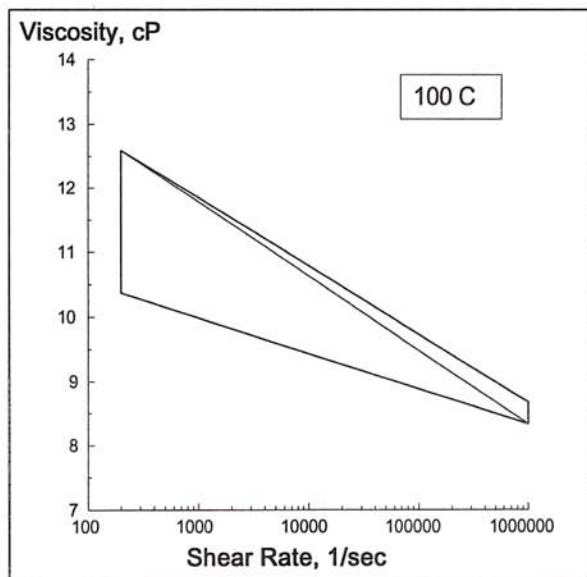

Figure 11b - VLT of moderate MW polymethacrylate at 150°C

intermediate MW polymethacrylate polymer are smaller in area as would be expected with less TVL and PVL. (In general, less trapezoid area is associated with greater resistance to PVL and a more horizontal configuration of the trapezoid is necessarily associated with fewer macromolecules subject to orientation whether this be by concentration or lower MW effects; the minimal trapezoid is, of course, the horizontal, straight line associated with simple oils as has been shown in **Figures 8a** and **8b**).

From **Table 4**, Polymer A2, in comparison to Polymer A1, shows both a reduction in the value of %TVL -- in agreement with its lower MW -- and a somewhat lower %TVL with increasing temperature -- 35.6% at 100°C and 30.4% at 150°C. It would appear that this member of the polymethacrylate VI Improver family is somewhat more soluble in mineral oil.

The values shown by the TVL and DTVL in **Table 3** indicate that with Polymer A2 the loss in orientation susceptibility is 48% at 100°C and 53% at 150°C -- suggesting a considerable reduction in the number of degradable macromolecules even though the total number of macromolecules present would be expected to increase because of the lower MW_{avg} of this VI Improver and, thus, the need to add more macromolecules to the base oil in order to have the same low shear rate blend viscosity.

Figure 11a - VLT of moderate MW polymethacrylate at 100°C.

VLTs of the lower MW polymethacrylate VI Improver, Polymer A3, are shown in **Figures 12a** and **12b**. Again it is evident that both the area and horizontal configuration of the VLTs for Polymer A3 are reduced in comparison to the VLTs of Polymers A1 and A2 in **Figures 10a** through **11b**.
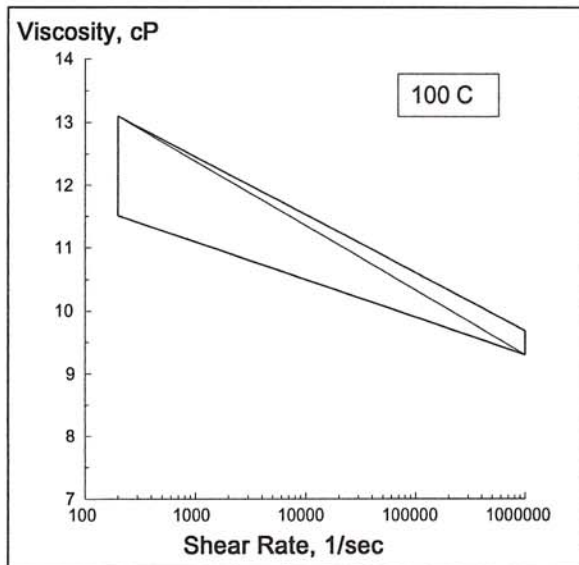
Styrene Isoprene VI Improvers

The styrene isoprene VI Improvers in this study are said by the manufacturer to exist in two forms -- Polymer S1 is said to have a linear configuration while Polymer S2 is said to have a so-called 'star-shaped' configurations -- a central core with a number of long radial 'arms'.

VLTs of the Linear Styrene Isoprene, Polymer S1, are given in **Figures 13a** and **13b**. At 100°C the configuration appears somewhat similar to the higher MW polymethacrylate, Polymer A1.

Figure 12a - VLT of low MW polymethacrylate at 100°C.
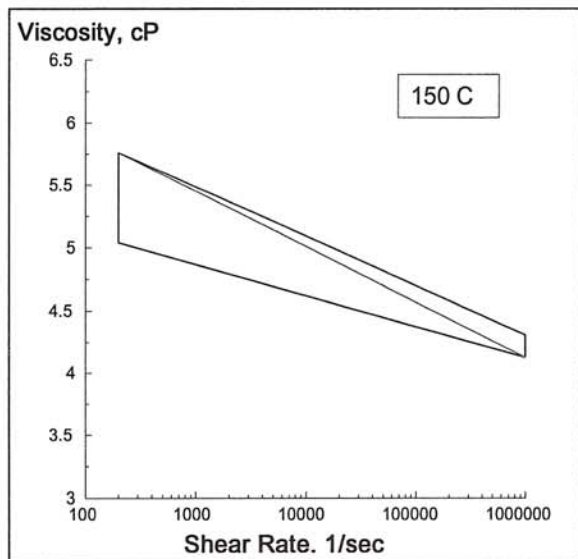
Figure 12b - VLT of low MW polymethacrylate at 150°C

Values of TVL and DTVL in **Table 3** show that 35% of the orientation susceptibility is lost at 100°C and 37% at 150°C, confirming the trend to lower loss of orientable polymer coils as the lower MW reduces the number of these coils in the degradation region. Again, the values of %TVL remain essentially constant with increasing temperature.
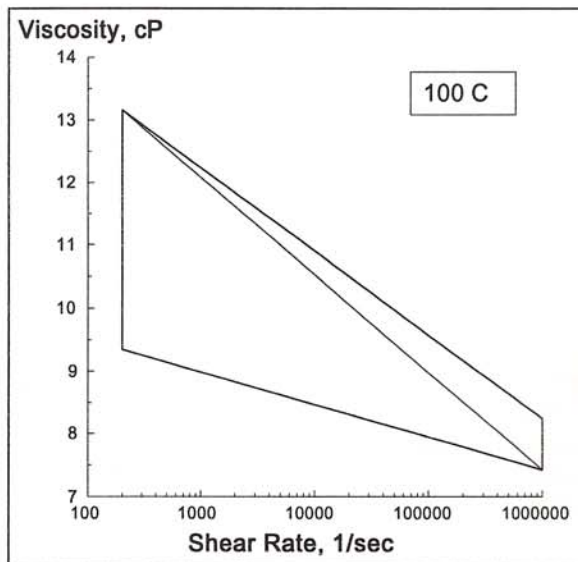
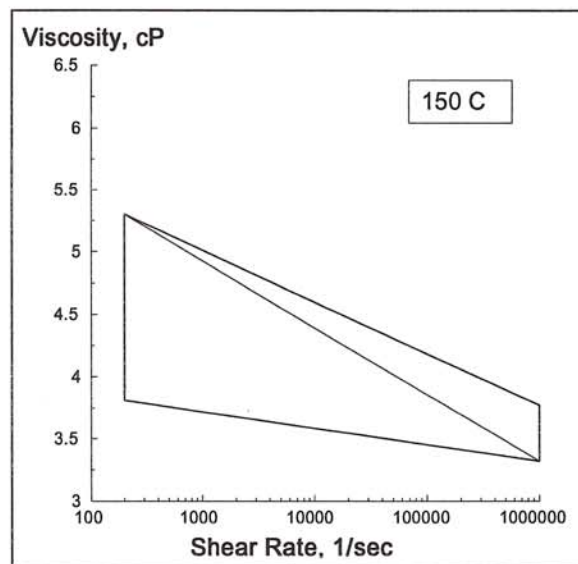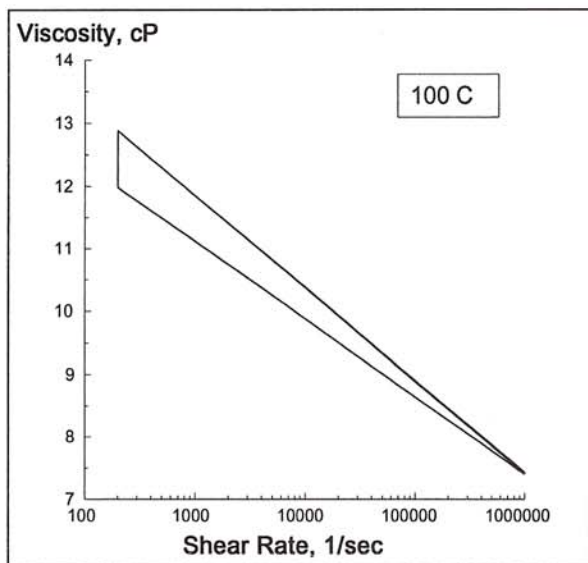**Figure 13a** - VLT of linear styrene-isoprene VI Improver

Figure 13b - VLT of linear styrene-isoprene VI Improver at 150°C

Analyzing the %TVL values of **Table 4**, it is evident that these values fall off with increasing temperature -- from 37.4% to 28.9% with increase of temperature from 100° to 150°C. Apparently, this VI Improver finds the oil a good solvent at 100°C.

Determination of the orientation loss values for Polymer S1 from the TVL and DTVL data of **Table 3** shows a 61% orientation loss at 100°C and a 68% loss at 150°C -- less severe but in the same general range of severity as Polymer A1
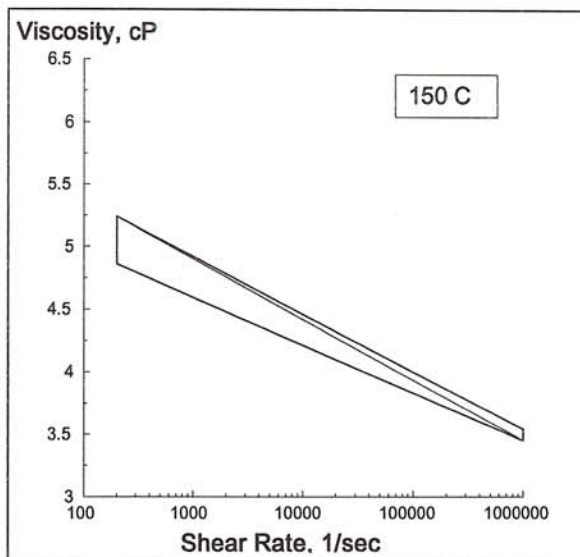
VLTs of the Styrene-isoprene 'star' VI Improver, Polymer S2, are shown in **Figures 14a** and **14b**. It would be expected that results from this different configuration would be somewhat unusual compared with the linear polymers comprising the bulk of the study.

Figure 14b - VLT of 'star' styrene-isoprene VI Improver at 150°C

of only 16% at 100°C and essentially the same amount, 17%, at 150°C. Further, while it is evident from the VLTs that PVL is much lower than the linear VI Improvers, conversely, TVL is the highest of the VI Improvers studied particularly after degradation. Evidently, degradation affects very few of the orientation-prone macromolecules comprising the 'star' VI Improver. Thus, it is evident that the 'star' configuration shows high susceptibility to orientation but low susceptibility to degradation.

Figure 14a - VLT of 'star' styrene-isoprene VI Improver at 100°C

The VLTs are significantly different than the other VI Improvers studied as shown by the relatively highly sloped, narrow, configurations. While %PVL is very low at both temperatures, %TVL is essentially as high or higher than any of the other VI Improvers, depending on the temperature of study. From comments made earlier regarding the other VI Improvers, %TVL changes in a manner with increasing temperature indicating that Polymer S2 -- as Polymer S1 -- finds the oil a good solvent. s

Orientation loss data obtained from the TVL and DTVL values of **Table 3** show that this polymer is considerably different with orientation losses

DISCUSSION

General Comments

As mentioned earlier in this paper, the four measures of the responses of the VI Improvers to low, very high, and extremely high shear stress can be used to identify the VI Improver. However, it was the primary purpose of this paper to show how such viscometric measures can be used to produce understanding of the polymer VI Improver components contributing to the blend viscosity.

Earlier in this paper (**Rationale** section), **Figures 2** and **3** were interpreted to predict what viscosity loss characteristics would result from the molecular weight changes shown. It was noted that the relationship between MW and viscosity losses should be reciprocal. That is, if the change in molecular weight distribution can indicate the expected degree of change in the viscosity loss parameters, then the viscosity loss parameters values should be capable of roughly anticipating the MW distribution before and after polymer degradation.

In this **Discussion** section it will be shown how the four viscosity loss parameters of PVL, TVL, HSPVL, and DTVL by themselves and in certain relationships lead to certain expectations in regard to the molecular weight distribution of several different VI Improvers.

Starting from simple identities of the viscosity loss parameters, the concepts used to define the MW distributions will be developed and shown in application.

The Meaning, Effects and Interrelationship of PVL, TVL, and DTVL

Degradation of a polymer in oil solution by the application of extremely high shear stresses always produces a loss in the viscosity of the blend if the macromolecules fall into the degradation region of **Figures 2** and **3**. Thus, PVL is identified with a reduction in the length or complexity of a macromolecule in oil solution. The effect is usually viewed as the breaking of the linear polymer backbone or the shearing off of long side-chains in the case of non-linear VI Improvers.

Since greater length of a macromolecule also affects its vulnerability to the milder forces of orientation, the reduction of that length by the occurrence of PVL is accompanied by a decrease in TVL as evidenced by the smaller value of the DTVL. As a consequence, it is expected that any blend experiencing PVL to any measurable extent will have a larger number of smaller VI Improver molecules with less orientability. It is possible, and in fact is shown by some of the data in this study,

that the effect of loss of TVL can result in a polymer/oil blend which shows low shear stress PVL but no accompanying HSPVL. This is attributed to the degradation of macromolecules showing considerable TVL which produce degraded macromolecules of twice the concentration of the original degraded macromolecules. With the right circumstances and molecular weights of both the original macromolecules and their shards, a total viscosity contribution after degradation (State 4) at high shear stress could be as high as the original blend (State 2).

The Relationship between PVL and HSPVL

PVL and HSPVL are both measures of the viscosity lost permanently by the VI Improver macromolecules after exposure to extraordinarily high stresses. However, contrary to casual consideration, these two parameters are affected quite differently by degradation. Degradation removes some of the viscosity contribution of the originally larger macromolecules when measured at low shear stresses/rates.

In contrast, at high shear stresses/rates, degradation removes some of the viscosity *lost by orientation effects* as well. This reflects the most common observation in VLT plots (as in this paper) that the PVL>HSPVL. Moreover, depending on the molecular weight and distribution involved, it is quite within reason that, in **Figure 1**, State 2 = State 4. This can occur when the high shear loss of viscosity by orientation (State 2) is completely offset by the combination of remnant orientation of the smaller original polymer coils (which were not subject to degradation) plus the additional viscosity contribution of the increased number of half-MW shards of the degraded coils (which are relatively invulnerable to orientation at that smaller size). Such behavior is, in fact, shown in this study by Polymer O. (Polymer S2 also shows this effect but for a different reasons to be immediately discussed.)

HSPVL Values under Limited Degradation

The second, comparatively simple mechanism by which HSPVL may fall to lower levels (State 4≅State 2) is when the polymer coils are not vulnerable to degradation because the molecular weight distribution curve does not extend much over the threshold of degradation. In this case PVL will also be relatively low.

This is believed to be the explanation for the low HSPVL values for Polymer S2 and for all VI Improvers whose values for PVL are low.

Comments on the DTVL

In all cases in which there is degradation of the VI Improver, the DTVL will take a value reflecting the level of undegraded, orientable macromolecules left in the blend -- the higher the value of DTVL, the greater the number of such molecules and/or the greater the response of those macromolecules capable of responding to orientation forces. That is, there are two forms of contribution to the DTVL -- either a large number of molecules each capable of smaller orientation effects or relatively few, highly viscosity-contributing, macromolecules capable of large orientation effects. Obviously the latter, larger molecules would also be more likely to enter the degradation zone. A third form of behavior affecting the DTVL is the case in which a small amount of highly orientable polymer is added to a large number of slightly orientable molecules.

When, on the other hand, the value of DTVL is low, this is taken as an indication that essentially all of the orientable macromolecules were also degradable and that the shards were of low enough MW to be resistant to orientation. Instances have been observed in which the value of DTVL was essentially zero.

In concert with the TVL and within a family of VI Improver polymers, the DTVL reflects the MW_{avg} of the individual VI Improvers from the viewpoint of how much of the initial TVL is lost in the process of degradation. As has been shown earlier, the two values show how much of the polymeric distribution is in the degradation zone.

Interpreting the VLT to Obtain Information on the MW Distribution

In the ensuing discussion, it is not the author's intent or capability to present a precise analysis of either MW or its distribution. What is intended is to show that with relatively simple and straightforward viscometry of a formulated blend, an interesting and informative view may be obtained concerning the MW properties of the VI Improver. That is to say, the viscosity loss parameters can provide fairly unambiguous information on the general characteristics of the relationship among MW, MW distribution and the thresholds of orientation and degradation for a given mechanical device such as the FISST. The following discussion will present the results and reasoning behind the interpretation of the VLTs of the polymers studied for this paper including a preliminary consideration of the VLT of the base oil used in the blends.

Consideration of the VLT of the Base Oil

As mentioned earlier, the VLT of the base oil used in blending is valuable in giving perspective to the use of the VLT concept in appraising the relative molecular weight and its distribution. **Figures 8a** and **b** show that without polymeric components, the VLT of **Figure 1** collapses to a horizontal straight line within the precision of the instruments used to determine viscosity at comparatively high and low shear rates and temperatures. From this information it is apparent that the MW distribution of the system would be approximated by **Figure 15**.
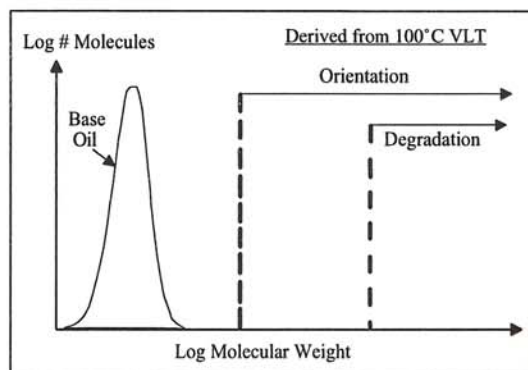
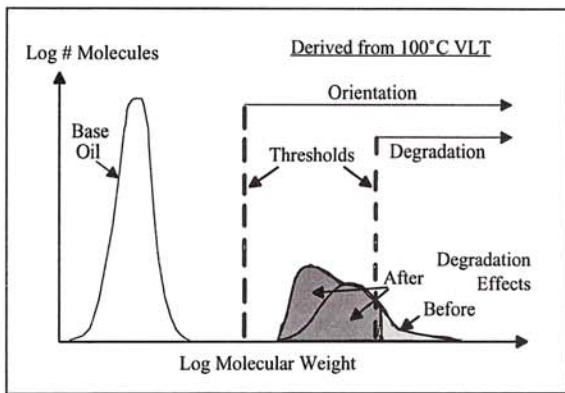Figure 15 - Sketch of likely MW distribution of the base oil used in blending.

As is evident in **Figure 15** and expected from the foregoing data and discussion , none of the base oil MW distribution enters the thresholds of either orientation or degradation and this rough plot satisfies the information contained in the VLT of the base oil.

Polymer O (Olefin Copolymer) MW Characterization

Considering the VLT of Polymer O at 100°C given in **Figure 9a**, a few characteristics stand out. One of these is evident PVL while another is the low value of HSPVL. A third characteristic is the evident TVL and DTVL as well as their differences in the form of a value of the OLR indicating that the TVL is 79% greater than the DTVL.

In the light of previous discussion, the suggested MW distribution before and after degradation is shown in **Figure 16**.

The sketch in **Figure 16** reflects the 100°C VLT by showing that the olefin copolymer used in this study exhibits a fairly high TVL which, in turn, indicates a considerable number of macromolecules in the orientation range. Of these, a fair number were also vulnerable to degradation as shown by the evident PVL and the loss of orientation effects -- more than 44% of the orientation-contributing

Figure 16 - Sketch of likely MW distribution of Polymer O in a base oil before and after degradation.

macromolecules were degradable as well . Even so, about half of the orientation-prone macromolecules were available after degradation including those half-MW shards of the degraded macromolecules.

The latter molecules are shown in **Figure 16** as considerably less susceptible to orientation forces (note their appearance in the sketch as the heavier gray area resting on the left flank of the original distribution curve). Thus, it would be expected that the viscosity contribution of these shards would be higher and the orientation tendency lower -- both of which would decrease the HSPVL as the viscometric values of State 4 trend toward State 2. This would account for the VLT's indication that there was little, if any, overall loss of high shear rate viscosity after degradation.

In this manner the VLT is interpreted by the author in **Figure 16** as suggesting the two MW distribution curves (before and after degradation) for the olefin copolymer VI Improver, Polymer O.

VLT data obtained at 150°C should normally support and amplify the 100°C data. This is so for Polymer O -- that is, the 150°C VLT does not alter the analysis given in **Figure 16**. The loss of orientation susceptibility at 150°C is 55% -- up from 45% at 100°C -- which may again suggest the weakening of the oil's 'viscous grip' at this higher temperature.
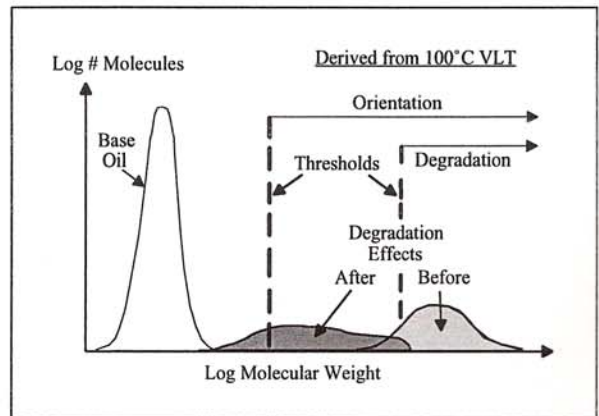
Polymer A1 (High MW Polymethacrylate) MW Characterization

The VLTs of Polymer A1 in **Figures 10a** and **10b** show comparatively large susceptibility to orientation and degradation shearing forces. This is not surprising when considering that Polymer A1 is identified as a high MW polymer. Both the PVL and the TVL were the highest of the group of VI Improvers analyzed at both 100° and 150°C. It was shown earlier that the orientation loss after

degradation was high at 78% indicating that most of the polymer coils of this VI Improver were degraded in the shearing device.

It was also noted earlier that the orientation loss shown by data at 150°C were about the same as at 100°C which interestingly suggested that the coils of this VI Improver were further distending at the higher temperature as the solvency of the oil increased. This further distention could have compensated for the reduced viscous grip of the oil at this higher temperature.

From this data, it would appear that the MW distribution before and after shear degradation may appear as in **Figure 17**.

Figure 17 - Sketch of likely MW distribution of Polymer A1 in a base oil before and after degradation.

Polymer A2 (Moderate MW Polymethacrylate) MW Characterization

Viscosity Loss Trapezoids for Polymer A2, the intermediate MW VI Improver of the polymethacrylate type, previously presented in **Figures 11a** and **b**, gave the suggested MW distribution shown in **Figure 18**. This distribution was drawn to reflect the fact that this VI Improver had lower
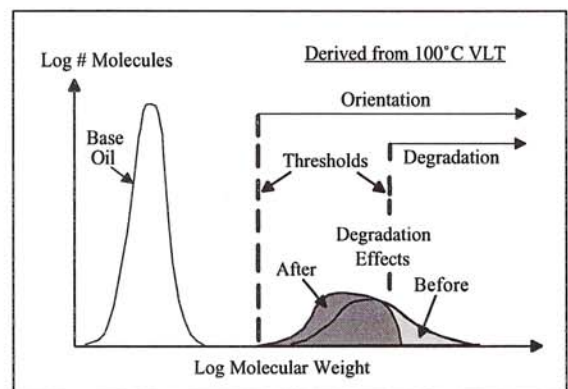
Figure 18 - Sketch of likely MW distributions of Polymer A2 in a base oil before and after degradation.

susceptibility to shearing forces of both orientation and degradation than either Polymer O or Polymer A1.

In comparison to Polymer A1, Polymer A2 showed a reduction in PVL of about 40% at 100°C and about 36% at 150°C. This view of reduced degradation was supported by the fact that the orientation loss shown by TVL and DTVL was much less with Polymer A2 -- 48% at 100°C and 53% at 150°C in comparison to 78% at both temperatures with Polymer A1.

Polymer A3 (Lower MW Polymethacrylate) MW Characterization

The VLTs of **Figures 12a** and **12b** indicate that as expected, Polymer A3, the lower molecular weight version of Polymers A1 and A2, shows less degradation effects than either of the other two. The PVL at 100°C is 62% less than Polymer A1 and 39% less than Polymer A2. Similarly, the orientation loss shown by the values of TVL and DTVL at 100°C is only 35% in comparison to 78% and 48% for Polymers A1 and A2, respectively.

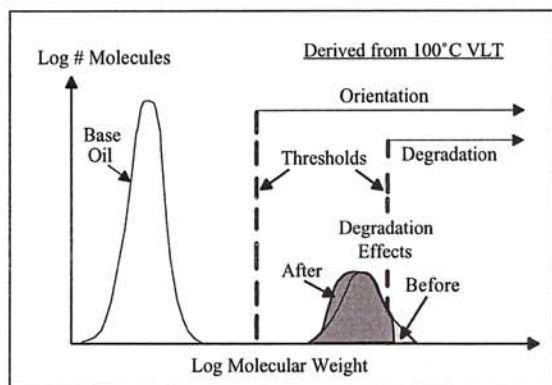From the VLT at 100°C, **Figure 19** shows suggested molecular weight distributions for both

Figure 19 - Sketch of likely MW distributions of Polymer A3 in a base oil before and after degradation.

the fresh and degraded blends.

Polymer S1 (Linear Styrene-Isoprene) MW Characterization

The VLTs of Polymer S1 are somewhat similar to those of Polymer A1, the higher MW polymethacrylate VI Improver. Values of PVL were somewhat lower for Polymer S1 but were nonetheless the second highest of the VI Improvers studied. These values, as previously discussed, indicate that a considerable number of the macromolecules comprising the makeup of the VI Improver are over the degradation threshold and in the degradation region. Orientation losses, too, were indicative. TVL and DTVL values from **Table 3** showed that the

orientation loss was 61% at 100°C and 68% at 150°C, again the second highest of the group of VI Improvers studied.

On the basis of this information, **Figure 20** was sketched to indicate the suggested MW distri-
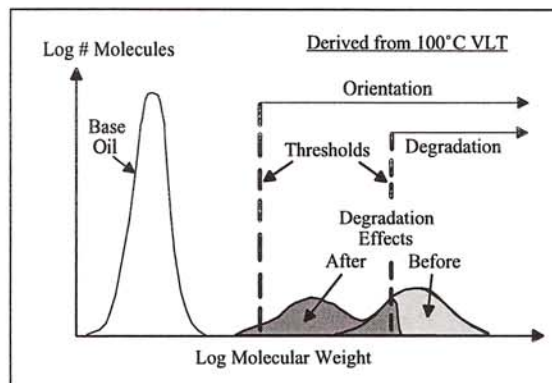

Figure 20 - Sketch of likely distributions of Polymer S1 in a base oil before and after degradation.

butions of both the fresh and degraded blends.

## Polymer S2 ('Star' Styrene-Isoprene) MW Characterization

Of all of the VI Improvers in this study, the results with the so-called 'star' styrene-isoprene polymer was the most unusual. This is evident in the distinctive VLTs shown at 100° and 150°C. Particularly noticeable is the low level of degradation response accompanied by average-to-high levels of orientation response.

The fact that this VI Improver was stated to be different in spatial configuration than the linear forms constituting the other VI Improvers in the study, is reason enough to expect different behavior in oil solution. Some specific observation of the VLTs of **Figures 14a** and **b** were that the PVL was the lowest of any of the VI Improvers in this study while the TVL was as high as the degradation-prone Polymer A1 at 100°C although considerably lower than Polymer A1 at 150°C. The HSPVL was essentially as low as the very low results of Polymer O. Contrasted, however, to Polymer O, in the case of Polymer S2, the simultaneously low value of PVL suggested that whatever macromolecules extended into the degradation region were relatively few in number

Interestingly, the above observation of the low level of degradation response accompanied by high levels of orientation response suggested a very narrow MW distribution just below the critical threshold of degradation. Moreover, with very low

orientation losses in the order of 16-17%, this could be taken as further evidence that few macromolecules were affected by degradation. Considering the spatial implications of a 'star' configuration, it is evident that while the molecular weight could vary considerably with different numbers and lengths of 'arms' on the core segment, the presentation of the molecule to the surrounding oil molecules during flow would not be greatly influenced by such MW differences. Moreover, such configurations of macromolecules would be expected to have a strong orienting tendency, particularly with relatively highly flexible 'arms'.

On the basis of this information, the VLTs of **Figures 14a** and **b** would suggest the molecular weight distributions for fresh and degraded blends
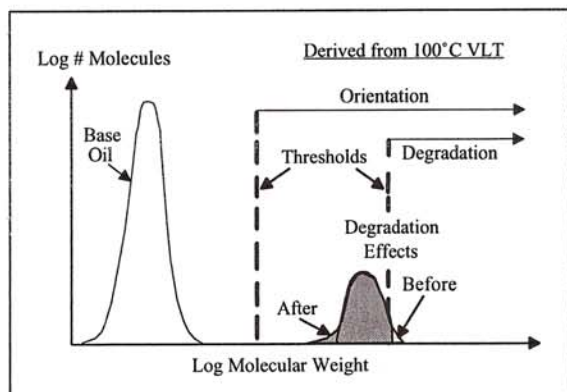
Figure 21 - Sketch of likely MW distributions of Polymer S2 in a base oil before and after degradation.

of Polymer S2 shown in **Figure 21**.

SUMMARY

The foregoing information applies the VLT technique to the interpretation of the effective molecular weight distributions of VI Improvers in oil solution both before and after experiencing the degradation of the higher molecular weight components of the VI Improvers under extreme shearing forces. It is shown that by applying certain rules of behavior typical of such polymer solutions, reasonably unambiguous configurations of the polymeric MW distribution can be generated which, of course, must conform to the VLT used to generate them. This is not to say that other interpretations cannot be made but that if such other interpretations can be generated they too must meet all of the criteria of the VLTs.

From this early beginning in applying the VLT to interpretation of MW distribution of VI Improvers, the next step is to learn more about the MW distributions present by information from gel permeation chromatography. This would have the dual benefit of refining the interpretation of the VLT values and confirming their application.

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