Viscometric and Low Temperature Behavior of Lubricants with Blended VI Improvers

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Abstract

Polymeric viscosity index improvers (VII) are routinely used to modify oils to the proper viscosity and VI for an application. There are many commercially available polymer chemistries (PMA, PB, OCP etc.) to choose from when selecting a VII product for formulation. Improper selection of a polymer in a formulated oil can reduce pour point, raise Brookfield viscosity, and inhibit the pumpability of the product in cold climate conditions. Oils formulated with shear stable polymers are more prone to this issue due to the higher treat level required.

This study investigates the appropriateness of different polymer chemistries in Group II, Group III and PAO fluids and the polymers' effect in low temperature pour point testing. Technical discussion will cover viscosity and gelation of polymers in oil. Based on these fundamental principles, several strategies for synergistic combinations of VII for maximum VI improvement and minimal effect on low temperature viscosity are proposed.

1. Introduction

1.1 Viscosity Index and Lubrication

The viscosity of oil decreases temporarily as temperature increases. This occurs due to the increased thermal (kinetic) energy allowing the individual oil molecules to move faster and overcome the internal attraction or 'cohesion' between molecules. Variation in viscosity with temperature during start-up, operation, or wear of a lubricant can cause a lubricant's viscosity to fall out of grade for a particular application. The desired viscosity is dependent on intended operating temperature, load, and speed.[1] The rate at which viscosity declines with temperature, from 40˚C to 100˚C, is expressed as the viscosity index (VI). Most base oils have a VI of 90 – 110. An oil with VI 100 has a KV100 roughly 1/10th the KV40. An oil with VI 200 has a KV100 about 1/5th the KV40.

Commercial lubricant VI varies widely. ANSI AGMA 9005 specifies four distinct ranges of VI for industrial applications: 90, 120, 160, and 240.[1] A review of 200 commercial motor/gear oils demonstrates that VI is critical for multi-grade oils. Roughly, a VI of 120 - 140 can be expected for 20W-X and 15W-X oils, 140 – 160 for 10W-X and 5W-X oils, and 160 – 180 for 0W-X oils. Exceptions apply depending on conventional, synthetic, or blended formulas.

In many cases, a low VI (50 – 90) or mono-grade (90 – 110) lubricant is sufficient for a simple application where there is no fluctuation in temperature from weather, operation, or wear. However, vehicles, mobile equipment, and areas that experience wide seasonal temperature swings benefit from multi-grade ("all-season") oils. Low VI products operating in varying temperature environments require replacement to meet changing lubrication requirements. Every 15-20˚C variation in operation temperature necessitates roughly one ISO grade up or down in a mono-grade VI 100 oil.[1] This shortens oil drain intervals, increases downtime, and poses the risk of cross-contaminating old and new lubricants.

Higher VI fluids also benefit from requiring lower viscosity grades to achieve the same lubrication. For example: the lubrication guidelines in AGMA 9005 (Table B.1-3) for spur/helical/bevel gears operating at 65˚C with a pitch line velocity of 10 m/s specify a VI 90 ISO 220, VI 120-160 ISO 150, or VI 240 ISO 100 oil. Lower viscosity, high VI products require lower treat of thickener since higher ISO VG is avoided.

1.2 VI and Grease

It is important to remember that oil is an integral part of grease lubrication. While the basis of this work - simple formulations of VI improvers in various fluids - applies directly to oil-based lubricants these concepts apply to the mobile oil phase of greases. The majority of grease is produced using an ISO 220 base oil for both general use and EP applications.[2] Higher or lower viscosity grades are advisable depending on the application speed with high viscosity base oils being favorable in low speed applications and vice versa. This work produced a range of oils with varying VI and low temperature performance as quantified by ASTM D97 pour point. High VI fluids would be excellent for greases intended to operate at elevated temperatures – aluminum complex, clay, and polyurea greases – which may benefit from the lower change in oil viscosity with temperature. Low pour point formulations present here would be best in cold weather greases – lithium complex and calcium sulfonate – where pumpability is a key concern.

1.3 VI Improvement

Viscosity index improvers (VII) are low to high molecular weight (1,000 – 250,000 g/mol) polymers which are added to oil to counteract the effect of oil thinning as temperature increases.[3] Polymers are large molecules prepared from connecting many individual repeat units, called 'monomers', into single structure.[4] This structure may be very linear like a chain or highly branched like a tree. The structure and choice of monomers determines the behavior of a polymer.[5]

Polymethacrylates (PMA) were one of the first VI improver polymers in the early 1900's.[3] [6] Motor oils benefited from higher VI products which allowed a single oil to operate across many different seasons and climates. Polyisobutylene (PIB) gained favor due to greater cost effectiveness which in turn was later replaced by polyolefin copolymers (OCP). Each chemistry continues to be used to this day for applications that best fit each polymer's advantage. The use of polymers has expanded from motor oil to hydraulic fluids, gear oils, and other lubricants.

The mechanism for polymer-based VI improvement is due to the thermally responsive behavior of polymers when dissolved in solution or a lubricant.[7] Polymers exist in solution or lubricant as very large coiled chains and occupy large spaces in the oil.[8] According to Stokes-Einstein theory, large molecules like polymers experience drag while they drift through oil due to continuous collisions with many smaller oil molecules.[9] These collisions slow the overall motion of the oil and raise the viscosity. The increase in viscosity increases with the cross-section of the polymer coil.

Conveniently, the size of a polymer coil increases with temperature.[8] Increasing temperature causes the polymer to uncoil into a larger sphere with larger cross-sectional area. **Figure 1.1** demonstrates this principle. The larger coils undergo more collisions across the larger cross-sectional area and produce greater enhancement of viscosity. A suitable VI improver polymer will overcompensate for the loss in oil viscosity at high temperature (KV100) relative to lower temperature (KV40). This temperature-sensitive effect produces a net increase in the viscosity index (VI).

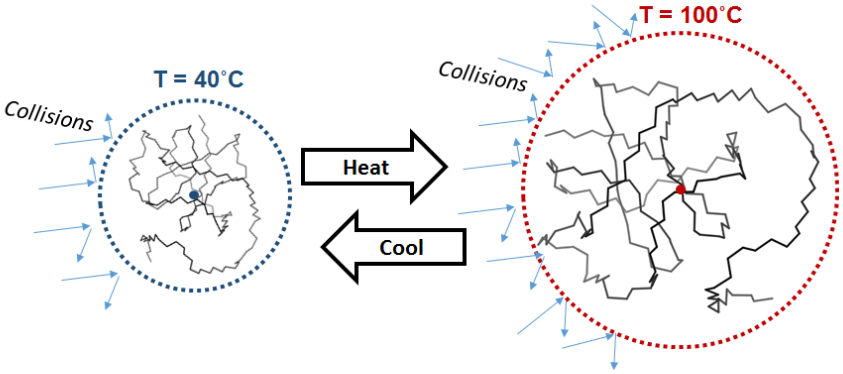


Figure 1.1: The classic depiction of a VI improver in oil by expansion of a polymer coil is shown above. At high T, polymer coils will absorb more oil and expand in solution to counter-act the effects of decreasing base oil viscosity. The depiction is very simplistic and evidence shows it is not always true.[10] This study will focus on when and why VI improvers deviate from this behavior.

1.4 Low Temperature Behavior and Pour Point

The behavior of oil at low temperature (below room temperature to -70˚C (-94˚F) or colder) is far less predictable than behavior at 40˚C and 100˚C due to the gradual solidification of the oil. As oil cools, wax (linear alkanes) form a network of fine crystals which traps the remaining oil in a rigid gel.[11] Upon heating the solid reverts to the original liquid lubricant. This process is highly complex and risks extensive damage to equipment if the lubricant is not carefully selected for anticipated cold conditions.[12] Extensive testing of lubricants under various circumstances at low temperature is required to circumvent this risk.

ASTM D97 pour point is one of the most well-known low temperature tests routinely performed on lubricants. Pour point (p.p.) is defined as the temperature at which an oil will not flow under its own weight while cooling quickly (~1˚C/minute). The manual test (D97) is performed by progressively cooling a tube of oil via a series of baths or environmental chambers until the oil does not flow when the tube is tilted. Several automatic methods (ASTM D5949, D5950, D5985, D6749) have been devised with varying degrees of automating temperature and tilt of the sample.[13] Oil at temperatures below the pour point becomes a semi-solid which will not pour from drums, cannot be pumped or risk damage to pumps, and will starve lubrication systems by remaining in the sump.[12]

Pour point for a given lubricant is roughly set by the pour point of the base oil which comprises the majority of the formulation. Higher refinement of oil (Gr. II or III) or synthesis from alpha-olefins (polyalphaolefin, PAO) produces high amounts of isomerized or branched alkanes which resist the tendency to gel. The wax that facilitates the pour point effect is attributed to long, linear alkanes (C18 to C30) that result from processing of crude oil into lubricant oil. Any additive used in the oil to produce a fully formulated lubricant can contribute additional wax from the diluent oil or the active ingredient may act inherently as a wax.

Pour point depressants (PPDs) are additives designed to reduce the pour point of an oil to allow it operate at lower temperatures.[14] This is achieved by modifying the shape and size of the wax crystals that develop in the oil under low temperatures. For this reason PPDs are also called ‘wax crystal modifiers’.

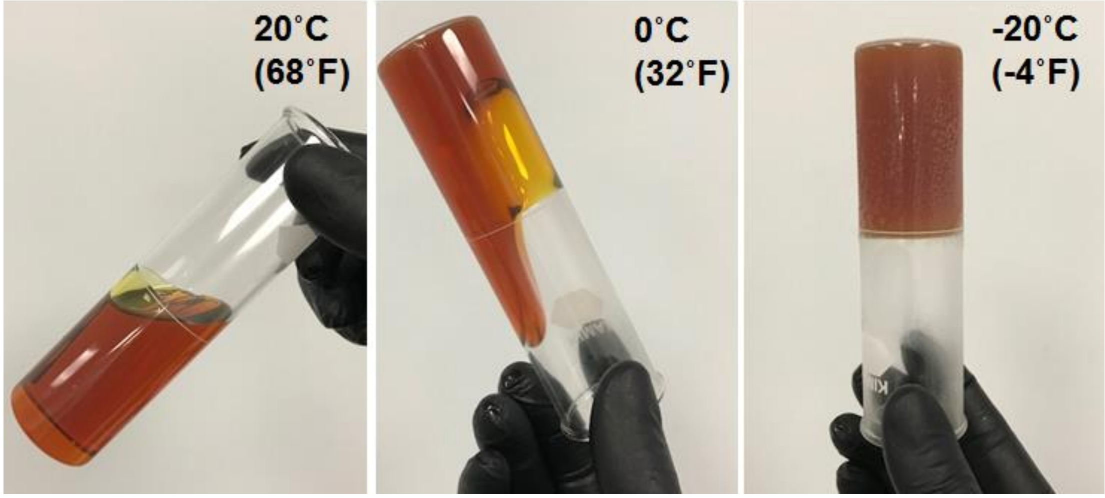


Figure 1.2: A single oil sample (p.p.=-15 ˚C) is shown at multiple temperatures above and below the pour point to demonstrate the significance of pour point on the flow of oil. The vial shown is a standard ASTM D97 pour point tube for performing the manual tilt test method (tilting of the oil sample is exaggerated to show viscous behavior).

2. Experimental

2.1 Materials

Three VI improvers (VII) were chosen to represent major commercial VI improver chemistries. Typical properties of the three products used in this study are listed below in Table 2.1. PB, PMA, and OCP products were selected with the same thickening efficiency (10% in Group I ISO 32 = 9.0 – 9.5 cSt @ 100˚C).

Table 2.1: Typical properties of the three VI improvers (VII) studied in this work

VII	Chemistry	%Polymer wt%	MW (g/mol)	PSSI ASTM D6278	KV100 cSt	Application
“PB”	Polybutene	100%	2,000 – 3,000	0%	4000	Gear
“PMA”	Polymethacrylate	50 - 80%	10,000 – 30,000	1%	1100	Hydraulic
“OCP”	Olefin Copolymer	5 – 20%	50,000 – 100,000	22%	3500	Crankcase

Polybutene (PB) is pure low molecular weight (< 3000 g/mol) polymer in the form of a viscous liquid. PB is prepared from the low temperature polymerization of butene isomers including isobutylene and 1-butene. Various grades of PB are assigned by molecular weight and correspond to handling viscosity, thickening efficiency, and shear stability. The advantage of PB is excellent shear stability and low cost. The disadvantage is that the high treat required to improve viscosity and VI can often lead to worse low temperature properties and lowering of base oil solvency (i.e. haze).

Polymethacrylates (PMA) are highly branched copolymers of short (C1 – C5), medium (C6 – C11), and long ($\geq$C12) methacrylate esters.[6] Uniquely, PMA includes the polar ester functional group. The advantage is very high VI improvement and excellent improvement of low temperature properties by pour point depression. The disadvantage is cost and moderate thickening efficiency. PMA was prepared in highly refined mineral oil with monomers and MW optimized for high thickening and VI improvement relative to its high shear stability.

Olefin copolymer (OCP) is a copolymer of ethylene and one of more olefins including propylene, butylene, or octene. OCP polymers are very long molecules with low branching and high molecular weight. The advantages are high thickening efficiency and low cost. The disadvantages are poor shear stability and some OCPs can behave like wax if ethylene content is too high (>50%). Solutions of OCP were prepared in paraffinic Group II oil.

Table 2.2 lists typical properties of three different base oils used to test the PB/PMA/OCP blends. Each base oil possessed substantially different wax characteristics. Viscosity grades were limited to lighter grades from ISO VG 22 to ISO VG 32. PAO was based on C10/polydecene chemistry. Each paraffinic oil was treated with 0.2wt% PPD.

Table 2.2: Typical properties of the three base oils tested

Oil	**API Group**	**KV40** cSt	**KV100** cSt	**Viscosity Index**	**Pour Point, ˚C** No PPD	**Pour Point, ˚C** 0.2wt% PPD
"Group II"	II	31.9	5	113	-18	-39
"Group III"	III	19.6	4	122	-15	-42
"PAO"	IV	30.2	6	137	-61	N/A

2.2 Methods

2.2.1 Sample Preparation

Varying combinations of two VI improvers in one of three base oils produced 81 unique formulations. Blended VI improver formulations were prepared for PB-OCP, OCP-PMA, and PB-PMA combinations using 5/10/20% of each product (10 – 40% total) in each base oil. Samples were prepared at 100 gram scale. Nine formulations were prepared for each pair of VII (5%+5%, 5%+10%, 5%+20%, 10%+5%, etc.). Treat level of each VII was labeled as "low" (5wt%), "medium" (10wt%), and "high" (20wt%). Appendix A lists each formulation and the measured data.

Group II formulations were treated with 0.2wt% of Group I/II-specific PPD while Group III formulations were treated with 0.2wt% of Group III-specific PPD. Both PPD were based on polymethacrylate chemistry with the blend of monomers designed to treat the different species of saturated waxes in Group II and III oils.[6,15] No PPD was added to PAO formulations to emphasis the wax contribution of each VII.

No additive packages were included. This study focuses on the viscometrics and low temperature properties of VII in oil as baseline for further formulation. Formulations presented in this work are starting points for low temperature industrial and/or automotive lubricants. Commercial additive packages are available to easily produce a finish product.

2.2.2 Visual Inspection

Visual inspection of sample clarity occurred after storage at room temperature (20˚C) for one week. Multiple formulations produced haze upon cooling to room temperature or after 24-48 hours. These formulations were marked as "Haze" in appearance in Appendix A. High PB or PMA content in PAO separated into two separate liquids after standing at room temperature. These samples received a rating of "Separation" in appearance.

Samples marked for "Haze" were included in the discussion of results. However, these formulations must be further treated by replacing 5% of the base oil with a synthetic ester or alkylated naphthalene for improved solvency. Saturated dibasic esters (adipate), trimethylol propane (TMP), or pentaerythritol esters are suggested. Samples marked for "Separation" are not considered as formulations in the following results and discussion sections.

2.2.3 Viscometrics

Kinematic viscosity at 40˚C (KV40) and 100˚C (KV100) were measured using a Cannon capillary viscometer in a Koehler liquid mineral oil bath per ASTM D445. Viscosity index was calculated from KV40 and KV100 data according to ASTM D2270. Pour point for each blended oil formulation was measured by ASTM D97 (Group II and III) or ASTM D6749 (PAO) method. Haze and separation in each oil was evaluated by visual inspection.

2.2.4 Viscosity Grade Assignment

ISO VG (ISO 3448, ASTM D2422) and AGMA (ANSI AGMA 9005) viscosity grades were assigned on the basis of KV40. SAE J300 Crankcase and SAE J306 Gear viscosity grades were assigned on the basis of KV100. Many formulations were observed with both an ISO/AGMA viscosity grade (KV40 specification) and SAE crankcase/gear grade (KV100 specification).

3. Results

3.1 Viscosity and grades

Appendix A (attached) contains the formulas and experimental data for all 81 samples prepared for this work.

Table 3.1 summarizes the range of viscometric and pour point data for the various formulations by base oil. Formulations were observed with KV40 from 37 to 764 cSt and KV100 from 7.3 to 75.1 cSt. This covered the majority of ISO/AGMA and SAE Crankcase/Gear viscosity grades as shown in Table 3.2. ~41% of samples conformed to an ISO 3448 or AGMA 9005 viscosity grade. ~54% conformed to SAE J300 Crankcase and ~78% to J306 Gear. All formulations conformed to at least one grade. These assessments were made by simple comparison to KV40 or KV100 requirements. In many cases, a single formulation met an ISO/AGMA grade, an SAE Crankcase grade, and an SAE Gear grade. For example, Formulation 5 in Appendix A (10% PB / 10% PMA in Gr. II) met the required KV40 and KV100 for ISO 100 / AGMA 3 / SAE 40 / SAE 90 viscosity grades.

Table 3.1: Statistics on KV 40, KV100, VI, and p.p. of the 81 samples prepared in this study, arranged by base oil, to demonstrate trends in viscometrics and VI due to the choice of base oil

		Group II	**Group III**	**PAO**
KV40	Min	62.8	36.9	61.2
	Max	763.7	557.4	423.9
	Average	192.0	137.5	193.8
KV100	Min	10.0	7.3	10.8
	Max	75.1	61.2	47.1
	Average	24.3	19.9	25.4
VI	Min	130.3	145.0	153.6
	Max	179.4	211.4	194.0
	Average	161.2	178.1	170.2
p.p.	Min	-45.0	-45.0	-52.0
	Max	-24.0	-24.0	-38.0
	Average	-35.5	-37.2	-47.1

Table 3.2: Statistics on ISO/AGMA/SAE viscosity grades obtained from the 81 blended VII samples prepared in this study. Multiple formulations qualified for several viscosity grades based on KV40 and/or KV100.

Visc. Grade	#	Visc. Grade	#	Visc. Grade	#
ISO 46 / AGMA 1	2	**SAE 20**	2	**SAE 80**	5
ISO 68 / AGMA 2	8	**SAE 30**	13	**SAE 85**	11
ISO 100 / AGMA 3	7	**SAE 40**	13	**SAE 90**	12
ISO 150 / AGMA 4	2	**SAE 50**	12	**SAE 110**	13
ISO 220 / AGMA 5	6	**SAE 60**	4	**SAE 140**	10
ISO 320 / AGMA 6	6			**SAE 190**	9
ISO 460 / AGMA 7	2			**SAE 250**	2
ISO 680 / AGMA 8	0				
Total:	32		44		63
% of Samples:	40.7%		54.3%		77.8%

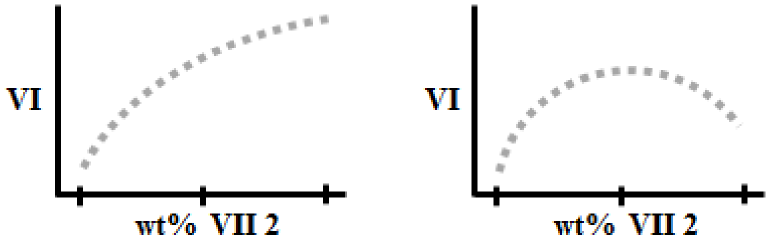
3.2 Viscosity index trends

Viscosity index (VI) in the formulations ranged from 130 to 211. Average VI of tested formulations in Table 3.1 increased from Group II (base VI =113) to Group III (base VI =124) base oil. VIs in PAO (base VI = 137) were lower than expected due to separation in several high PB/PMA samples which would have otherwise increased the average VI. These samples produced high VI in Group II/III but were not included as PAO formulation due to drop-out.

Formulations were compared in groups of three with low/medium/high (5%/10%/20%) treat of one VII varied to demonstrate trends in viscosity and VI with the combination of a second VII. Blending different classes of VI improver (PB, PMA, OCP) produced complex trends in VI with treat level. **Figure 3.1** demonstrates the four observed cases for change in VI with increasing wt% VI improver. KV40 and KV100 increased in all cases when blending PB, PMA, and/or OCP. However, KV40 and KV100 increased at different relative rates with increasing treat. A large different in the relative change of KV40 and/or KV100 produced a changed in VI.

Case 1
VI increases continuously

Case 2
VI increases, then decreases
or remains constant



Case 3
VI remains same

Case 4
VI decreases continuously

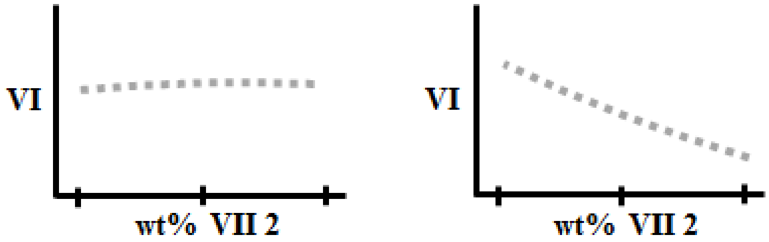


Figure 3.1: The VI of a formulation with increasing treat of VII responded in one of four qualitative cases (1 – 4). Generic plots above demonstrate the response in VI to VII relative to the initial VI. Absolute VI is not compared and, for example, a formulation with Case 4 behavior may have a higher VI than a Case 1 formulation.

3.3 Pour point trends

Pour point (p.p.) showed strong contrast between mineral oil and PAO-based formulations. In Group II and III, pour point was limited from -24 to -45˚C. PAO produced pour points from -38 to -52˚C. Pour point was generally independent of VI with several instances where VI increases with treat of VII and pour point decreased and vice versa. In commercial products, pour point varies over a range of 20-30˚C for a given VI. However, p.p. generally improves (decreases) with VI.

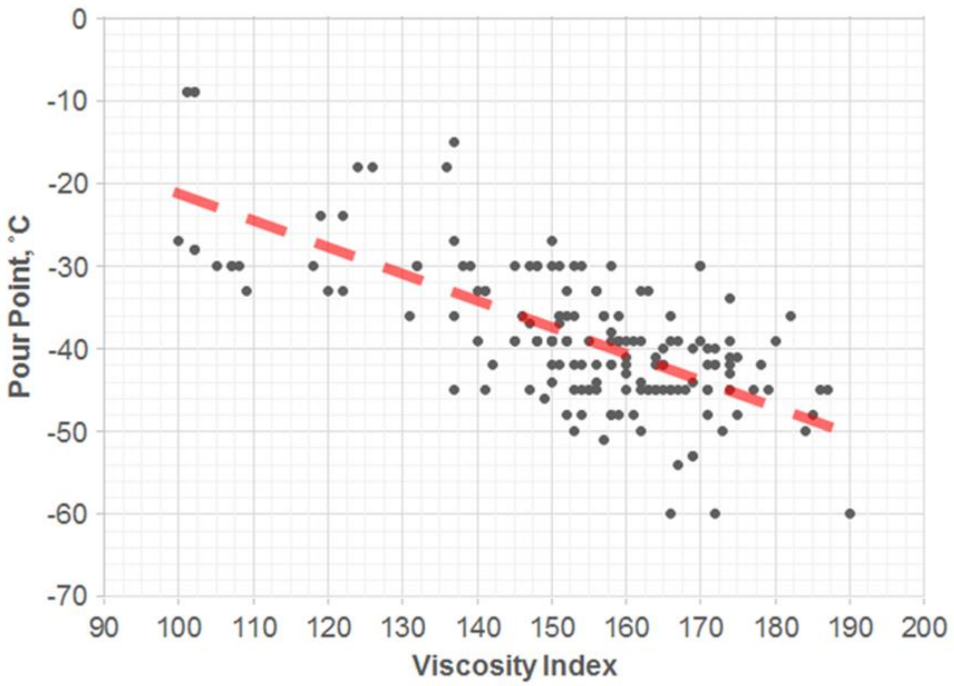


Figure 3.2: Pour point of commercial motor oils plotted against the corresponding viscosity index. This demonstrates the variability in required pour point to achieve commercial low temperature specifications. However, higher VI products tend to yield better p.p.

The pour point is a separate phenomenon from the measurement of VI at 40˚C and 100˚C. Oil undergoes complex and chaotic physical processes during the pour point test. The simple exponential curve of viscosity versus temperature, which can be obtained from VI and KV40 or KV100, simply does not anticipate the viscosity increase and change in flow at low temperature.

The change in pour point with varying treat of a second VII in a formulation was straightforward and followed one of three cases (A, B, C) as shown in **Figure 3.3**. ASTM D97 pour point was reported with a precision of +/- 3˚C. Any variation of 3˚C or less between two samples was regarded as negligible.

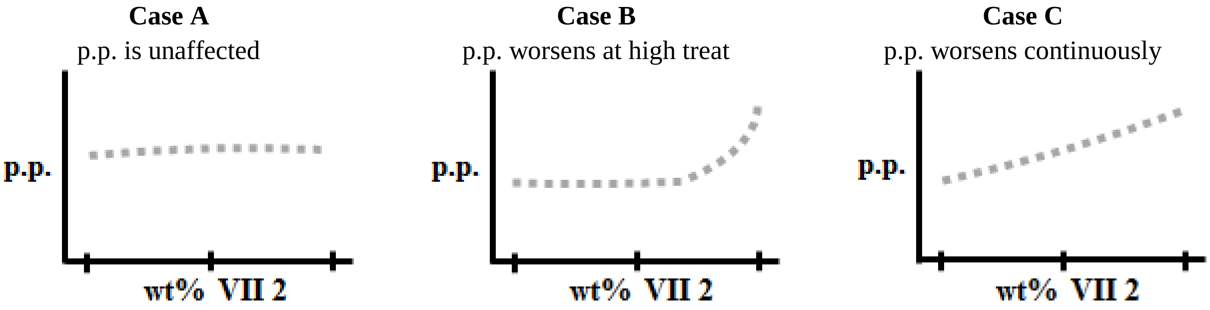


Figure 3.3: The relative change in pour point with varying amount of VII was assigned to one of three qualitative cases (A, B, or C) to simplify the analysis of a complex phenomenon. Generic plots for Case A/B/C are shown above that demonstrate the relative change in p.p. with VII. Absolute p.p. was not compared (i.e. a Case C formulation may have better p.p. than a Case A formulation however the Case A formulation pour point is more stable with VII)

4. Discussion

4.1 Trend in VI with blending VII

Due to limitations in cost or demanding specifications like shear stability it is often attractive to blend multiple types of VI improver to achieve the desired properties in a lubricant. The goal of this work was to blend VII with separation advantages and disadvantages to investigate opportunities for synergy.

Synergy occurs where two or more formulated components provide better performance (higher VI and/or lower pour point) than either product individually. The opportunity for synergy occurs because each VI improver chemistry tested (PB, PMA, OCP) contributes to the VI differently due to different molecular weights and chemical structure. Blending multiple polymers in solution can produce non-intuitive effects on the expected viscosity or VI since polymers in solution interact.[16] These effects can be positive or negative. Section 3.2 identified four different cases for the change in VI with blending two VII improver chemistries (**Figure 3.1**).

Case 1 – continuous increase in VI with treat – is the most desirable situation for a formulator since using more product to achieve high viscosity will also provide improved VI. Case 1 is the ideal situation for polymer-based VI improvement as described previously. The basic explanation of VI improvement requires the individual polymer coils in oil to expand with increasing temperature to counteract the thinning of oil under heat.[7] Higher treat of the polymer increases the number of coils in oil and multiplies the effect of thermal expansion in the coils. Case 1 behavior for VII is the generally accepted understanding for how polymers behave in oil. However, this picture is often not true.[10] [17] The exact performance of VII polymers is highly variable and three other responses to VII blending were observed: Case 2, 3, and 4.

Case 2 – initial increase in VI at low/medium treat with a decreasing or constant VI at high treat – tended to occur exclusively with adding PMA or OCP at 5-20wt% to another VII. Bell-shaped or parabolic responses of performance versus wt% of an additive is common when formulating lubrications and this over-treat effect is often called 'reversion'. The difference between the ideal Case 1 (continuous improvement with added VII) versus the reversion seen in Case 2 can be explained by considering effects not shown in the simple VI improvement explanation (**Figure 1.1**). Reversion (Case 2) occurs most often for higher MW polymers, PMA and OCP, which have MW on the order of 10,000 and 100,000 g/mol respectively. The lower MW polymer PB (roughly 1,000 g/mol) generally expressed Case 3 or Case 4 change in VI (**Figure 3.1**). This suggested the Case 2 behavior related to polymer size in solution. Polymer behavior in solution is known to be dependent on concentration and size.[8]

Polymer solution theory, the understanding of how polymers behave in solution, is divided into three regimes: dilute, semi-dilute, and concentrated.[8] Dilute polymer solutions is defined as the concentration range where polymer coils are sufficiently diluted to avoid contact with other polymer coils in solution. This is the ideal condition assumed in Case 1. Semi-dilute polymer solutions occur when the concentrate of polymer coils achieves a critical concentration where polymer coils regularly contact one another in solution. Concentrated polymer solutions occur when the concentration of polymer coils causes polymer coils to overlap extensively in solution and form entangled networks. These conditions are directly dependent on the molecular weight of the polymer which defines the size of the polymer coil. Very small, low MW polymers require higher concentrations to reach the semi-dilute range while very large, ultra-high MW polymers can exhibit semi-dilute behavior at fractions of a percent by weight.

The three VI improvers use polymers of different MW at different wt% to deliver roughly the same thickening efficiency in paraffinic oil as previously summarized in Table 2.1. Polymer MW and concentration are important and proprietary information for an VI improver formulator. Knowing both pieces of information would allow the transition between dilute and semi-dilute polymer behavior for the polymers at treat to be calculated. However, the wt% at which this transition occurs can be identified for a given polymeric VI improver by plotting the log of specific viscosity (KV of oil+VII / KV of oil – 1) and log of wt% VII.[8] A change of slope in the log-log plot indicates a transition from dilute to semi-dilute. **Figure 4.1** below demonstrates a qualitative plot for the PB, PMA, and OCP products tested.

From **Figure 4.1**, it is apparent that the high MW OCP (~100,000 g/mol) creates a semi-dilute condition at 4-5wt% in oil. Most examples of Case 2 VI behavior with increasing treat occurred with OCP VII. The explanation is that increasing contact between the large polymer coils inhibits coil expansion at high temperature. Coils cannot expand through another coil. The loss of expansion reduced the VI improvement in the thinning base oil and lowered VI with high treat. PMA (on the order of 10,000 g/mol) also exhibited Case 2 behavior and **Figure 4.1** shows that the dilute/semi-dilute transition occurred within the 5-20wt% treat tested in this study.

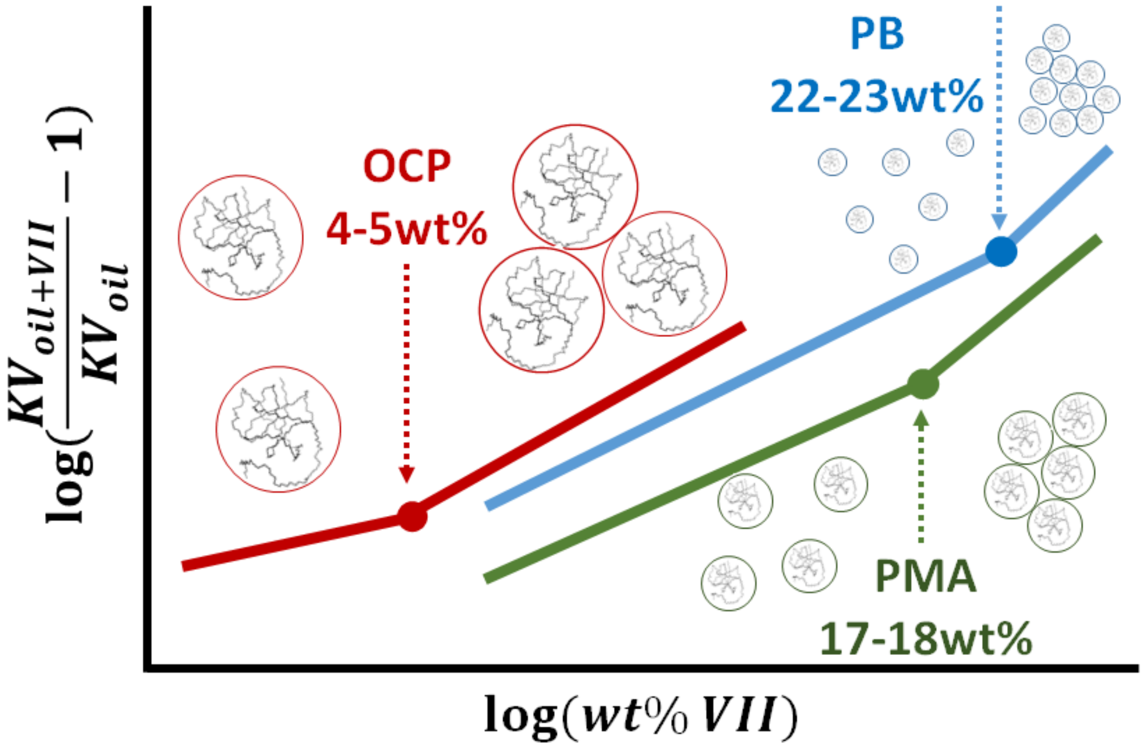


Figure 4.1: Plotting specific viscosity ($KV_{oil+VII}/KV_{oil}$-1) versus wt% VII on a log-log plot reveals a critical concentration where the slope of the line suddenly increases. This inflection point indicates that polymer coils sufficient large and/or concentrated enough for polymer coils to contact in solution. 'Dilute' solution theory handles polymer solutions below this critical concentration while 'semi-dilute' solution theory treats concentrations above this transition. Individual polymer coils are shown before (dilute, isolated) and after (semi-dilute, in contact) the critical concentration.

Case 3 – VI remains same with varying wt% – is useful for high VI base fluids whose VI is already appropriate for an application. A formulator may wish to further increase the viscosity within affecting the VI. Case 3 occurred most often in cases of varying PB in the formulation (Table A-2 in Appendix A). PB is unique among the three VII improver chemistries due to its very small molecular weight and high shear stability. The fundamental explanation for Case 3 is based the different ability of small or large polymers to coil or uncoil with temperature.

Liquid PB additives are typically found up to 2,800 g/mol or less which consists of a mere 50 butylene units or less. As demonstrated in **Figure 4.2**, it is intuitive that longer polymers have a greater potential to coil and uncoil: where N is the number of repeat units, an average polymer coil is proportional to $N^{1/2}$ in size and a fully stretched chain's length is proportional to N.[5] The size ratio between the fully extended polymer chain and its coil size is therefore depending on MW and is proportional to $N^{1/2}$ (or, $N / N^{1/2}$). Real polymer chains do not fully extend to the straight 'zig-zag' alignment shown in **Figure 4.2** but the visual aid is intended to demonstrate the potential for long polymer chains provide the VII effect. For low MW PB, N is typically <50 units while ethylene-based OCP may have N from 1k to 10k units. Case 3 likely occurs where low MW polymers approach the size of the base oil and the size of the expanded (KV100) and contracted (KV40) coil are not sufficiently to overcompensate for the thinning of base oil with temperature. In this case, low PB acted more as a thickener or high viscosity base oil than a VII.

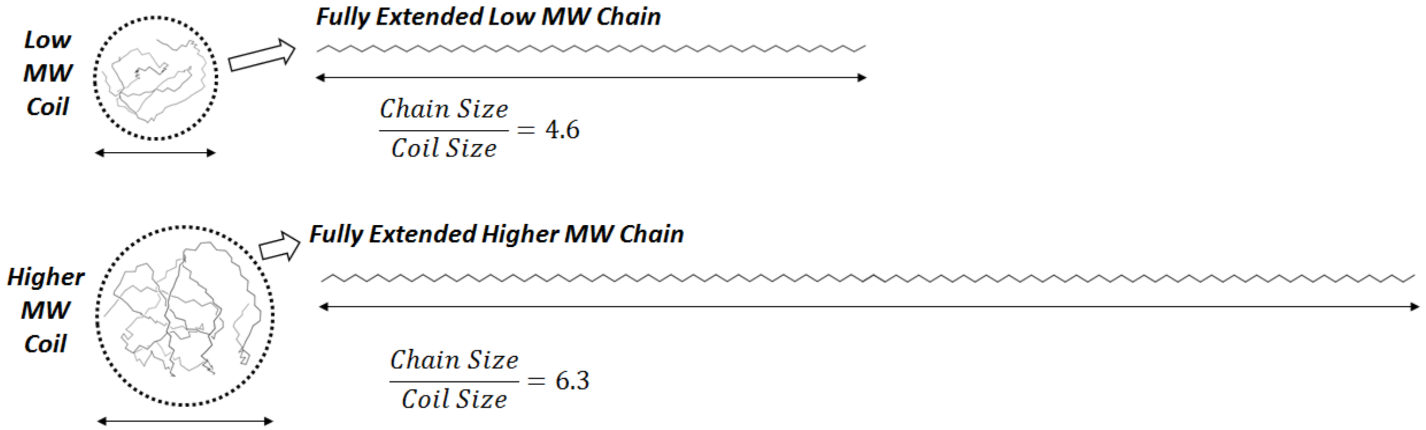


Figure 4.2: Higher MW polymers contract into a coil in solution to a greater degree than lower MW polymers as demonstrated by the ratio of end-to-end chain length versus coil diameter. This ratio scales by $N^{1/2}$ where N = number of monomers. If ideal VII behavior is dependent on coil expansion then more contracted, high MW polymers will provide better VI improvement. Case 3 behavior occurs when polymers are low MW and cannot provide sufficient expansion to compensate for base oil thinning.

Case 4 – continuous decrease in VI with added VI improver – was not an expected outcome of adding VII may be acceptable in the case of a high VI base oil like PAO. The Case 4 trend suggested that the addition of polymers could directly reduce VI unlike all other Cases. This case occurred most often in low solvency (Group III, PAO) base oils and with varying PB VII. The origin of VI decrease may be attributed to the overall solubility of polymers in solution.

Polymer-oil compatibility is a critical issue in high performance oils. The formulation for these products generally uses high treat of shear stable VII and a highly refined or synthetic base oil with poor solvency. The strain on compatibility produced by this strategy is two-fold: 1) higher wt% polymer means lower wt% base oil; 2) polymer which has replaced the oil is a poor solvent for other polymers or additives and reduces solvency of the oil.

A robust framework for approaching polymer-solvent compatibility was developed by Hansen in the 1960's to aid in the formulation of solvent-based products like paint, cleaners, and halogen replacements.[18] This mathematical model considers the balance of different molecular interactions (non-polar, polar, and hydrogen bonding) and the molar volume of each component in the oil or solvent.[19] Molar volume defines the molecular weight of a component divided by its density (MW/ρ) and is a rough estimation of the size of a molecule in solution. Hansen solubility calculation takes parameters from a given polymer and each component of the solvent or oil and returns a 'relative energy difference' ("RED") value for that combination of materials. RED ranges from < 1.0 (very good solvent) to 2.0 – 3.0 (borderline) or higher. **Figure 4.3** shows the calculated RED (from 1.0 – 1.5) for an arbitrary VII polymer of 100,000 MW in an example oil containing 0-30% polybutene of varying molecular weight. As MW of PB increases, the RED increased (compatibility decreased) with treat of PB at an accelerating rate.

The key parameter in the **Figure 4.3** plot was the increasing molar volume of higher MW PB. It is known that most petroleum-based oils range from 300-700 MW and that increasing viscosity (and MW) reduces the solubility of polymers.[20] [21] The corresponding molar volume is 400 – 900 cm^3/mol. The substitution of base oil for concentrated VII like polybutene rapidly increased overall oil molecular volume (cm^3/mol > 1,000).

Figure 4.4 demonstrates the effect of increasing solvent or oil size on polymer compatibility. Ideally, a 'proper' solvent for a polymer is only 50 – 200 cm^3/mol or no bigger than the molar volume of the polymer's monomer.[19] This requirement occurs because oil and solvent must diffuse into the polymer coil to dissolve it or expand with temperature.[5] As concentrated VII like PB or PMA was added to oil, the molar volume of the oil increased and reduced the solvency. Polymers and other large solvent components in the formulated oil are too large to fill the space inside the polymer coil.

Some instances of Case 3 behavior with non-PB VII, especially PMA, may also be due to Case 4 effects. Shear stable PMA VII must include higher amounts of polymer and less diluent oil to achieve acceptable thickening efficiencies comparable to OCP and other competing technologies. The lower solubility of the polymer causes the polymer coils to become smaller in solution and expand less at high temperature which may induce Case 3 (no change in VI) behavior.

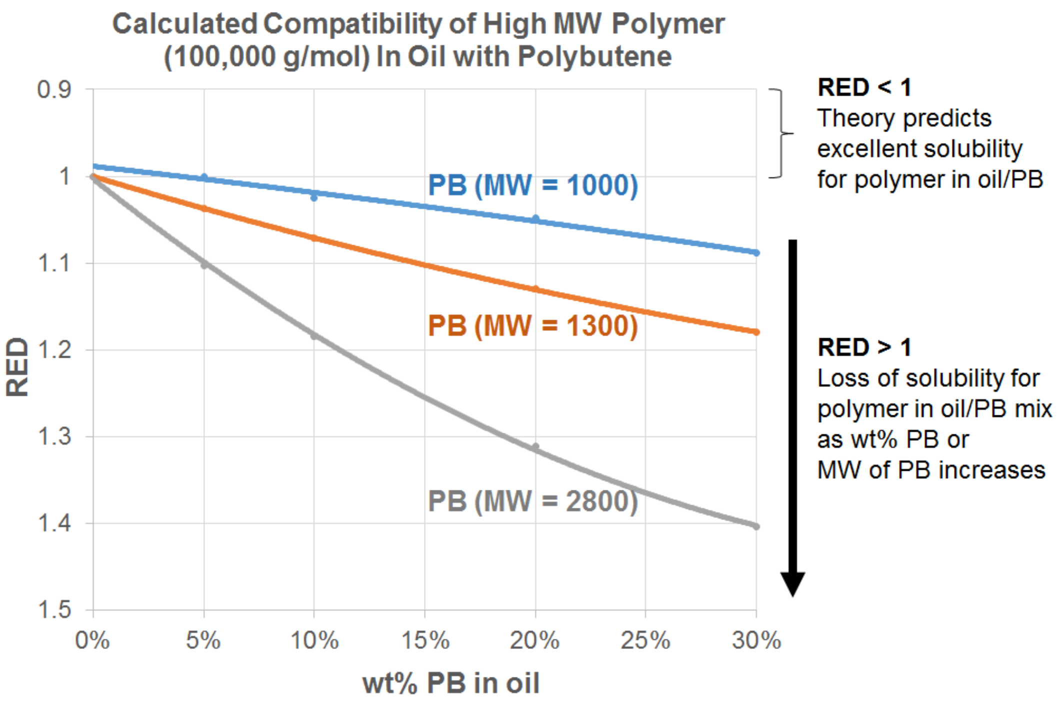


Figure 4.3: Hansen solubility theory calculates the compatibility of oil and polymer as an RED (relative energy difference) value: <1.0 predicts excellent solubility of the polymer while values above 1.0 indicate increasing solubility problems.[19] Calculated RED between a high MW OCP polymer and a mixture of oil with PB shows that increasing MW and/or wt% of the polybutene negatively affects the polymer's solubility. This is attributed to poor solvency of PB and the reduced solvency of the oil/PB mix.

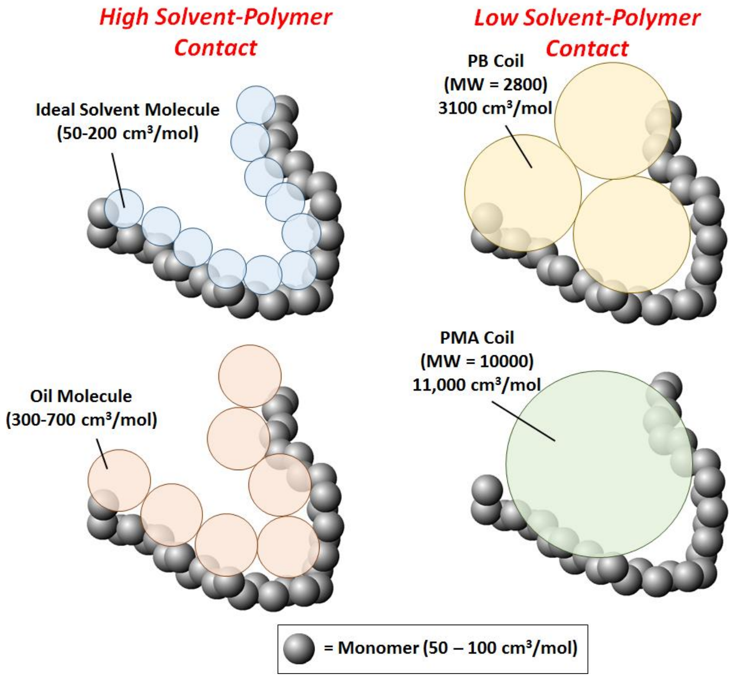


Figure 4.4: An example segment of a polymer coil is shown above with gray spheres representing individual monomers. The colored circles represent different components of an oil – solvent molecules or polymers – of increasing molar volume (MW/ρ). As the individual components of an oil become larger, the components cannot fit inside the polymer coil and exhibit very low polymer-solvent contact. Low contact and interaction between polymer and solvent causes the polymer to become less soluble in the oil molecule and the coil size collapses. Low thickening or haze/drop-out occurs.

4.2 Trend in pour point with blending VII

Pour point of unmodified oil has been found to be a function of viscosity, density, and molecular weight.[22] The exact process of how oil forms a temporary gel at this temperature varies by oil. Paraffinic oil gel due to separation of long, waxy linear alkanes at low temperature to form a semi-solid gel. Highly branched synthetic fluids (PAO, ester) will crystallize.[23] The addition of extra components – VI improver, pour point depressants, friction modifiers, and other packages – will influence the pour point of a fully formulated lubricant by contributing waxy species and affecting both viscosity and molecular weight of the total mixture.

The mixed VII formulations in Group II, III, and PAO exhibited three separate cases (A to C, **Figure 3.3**) in pour point behavior with increasing treat of VII. All Group II and III oil formulations were treated with 0.2wt% of a base oil-specific PPD to inhibit oil-based wax. PPD level was not increased after adding VII to observe the effect of VII on p.p.

Figure 4.5 summarizes occurrence of cases A-C by oil and by VII for all data from Tables A-1 and A-2.

Figure 4.6 demonstrates the co-occurrence of Cases 1-4 (VI trends) and Cases A-C (p.p. trends). 50% of formulations with Case A pour point behavior (no change in p.p. with VII) exhibited Case 4 (VI continuously worsens with treat). 62% of formulations with Case C pour point behavior (p.p. continuously worsens with VII) exhibited Case 2 VI behavior (temporary increase in VI at low/medium treat with decrease in VI at high treat). Since Case A and Case 4 occurred together it can be assumed that their origin is related to collapse of the polymer coils as previously discussed. Case C occurred with Case 2 which was explained by the behavior of polymers at the semi-dilute concentration.

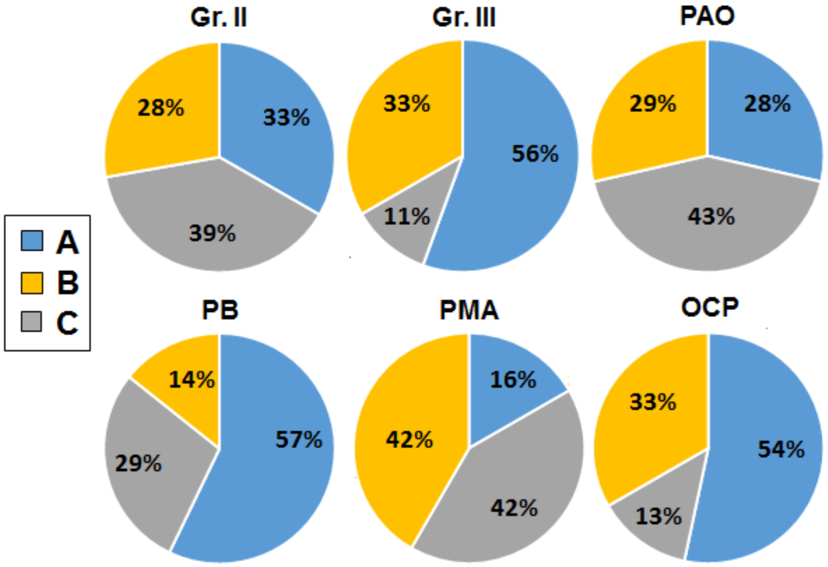
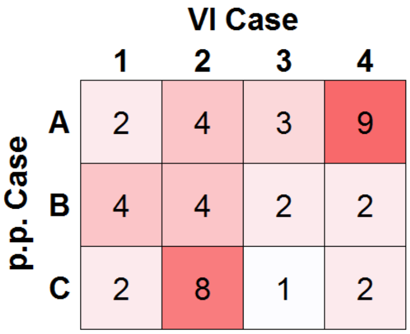


Figure 4.5: Comparison of p.p. trend cases (A-C) by base oil and varying VII to determine if specific base oils or polymers are responsible for different trends



p.p. Case \ VI Case	1	2	3	4
A	2	4	3	9
B	4	4	2	2
C	2	8	1	2

Figure 4.6: Grid comparing the occurrence of specific VI trends (Case 1-4) with specific p.p. trends (Case A-C) to determine if mechanisms for either behavior may be related. Case A occurred in 50% of formulations with Case 4 VI behavior and Case C occurred in 62% of formulations with Case 2 VI behavior. High co-occurrence of Case A+4 and C+2 suggest the trends occur under the same conditions and from the same causes.

Case A – pour point unaffected by VII – occurred most often for two types of formulations: a) Group III with varying treat of PB or OCP; and b) blends containing PMA and PB VII. PB is common to most Case A formulations. Polybutenes are highly branched or ‘isomerized’ structures unlike the linear C20 to C30+ alkanes attributed to wax in oil.[24] [11] Linear alkanes gel oil due to crystallization of long -CH_2- repeat units which coordinate into orderly structures at low temperature. The short and random branching of methyl, ethyl, and propyl side groups from the polybutene chain prevent orderly packing of –CH_2- groups and improves low temperature flow of polybutenes.[25] Polybutenes up to 100,000 g/mol will flow spontaneously, albeit slowly, at room temperature while polyethylene and polypropylene form rigid waxes at very low MW (< 1,000 g/mol) due to crystallinity. Highly isomerized and wax-free polybutene at high treat will dilute the wax content of oil and help prevent a critical mass of wax crystals from forming.[11]

The relation between Case A p.p. behavior (no change in p.p. with VII) and Case 4 VI behavior (VI worsens continually with VII) was demonstrated in **Figure 4.6** and occurred in PMA and PB blends. Calculated polymer solubility versus PB content in oil in **Figure 4.3** suggests that PB reduces the solubility of PMA. This caused collapse of the PMA polymer coil and poor VI (Case 4 behavior) but also prevented the worsening of p.p. with VII (Case A). Smaller polymer coils appeared to be related to better low temperature properties while the connection between Case C p.p. behavior (p.p. worsens continuously with VII) and Case 2 (VI improves at low/medium treat, worsens at high treat; semi-dilute effect). Comparing the two situations suggests that the network-like interaction between coils in the semi-dilute concentration range (**Figure 4.1**) accelerates wax formation at low temperature while collapsing the coils with solvent effects will prevent the polymers from aiding wax formation.

Case B – pour point worsens at high treat – also occurred frequently with PMA and OCP blends. Most instances of Case C in PAO occurred from blending OCP. No VI improver case (1 – 4) was observed greatly favoring Case B p.p. behavior in **Figure 4.6**. However, Case B occurred 67% as either Case 1 or Case 2. Case B was also significantly less common in PB formulations as shown in **Figure 4.5**. These findings suggest that Case B behavior is related to Case A but is due to an effect that is lacking in PB. One key difference is that PB is used in pure form (100wt% polymer) while PMA and OCP VII were diluted in a Group II paraffinic oil (see **Table 2.1**). It is reasonable to conclude that the loss of low temperature performance at high treat in Case B is due to the accumulation of wax from the diluent oil.

Case C – pour point worsens continuously – was common in blends of PMA with OCP. Case C likely originates from the same cause as Case 2 VI behavior since both Case C and Case 2 trends occurred together frequently (**Figure 4.6**). This behavior is due to a high concentration of large polymer coils in oil which begin to overlap in solution and form a network. PMA and OCP both achieve semi-dilute concentration at < 20wt% in oil as demonstrated in **Figure 4.1** with a change in slope of the log-log plot. Wax formation similarly relies on the formation of a network throughout the oil.[11] The pour point data suggests that contact between polymers (semi-dilute condition) tend to help the formation of the wax crystal network and worsen the pour point temperature.

No pour point improvement was observed using the PMA VII among the tested formulations. Low temperature properties of the tested PMA were less than expected for polymethacrylates. Polymethacrylates are commonly used as pour point depressants and their effectiveness is highly dependent on the selection of monomers.[26] PMA did improve pour point behavior relative to OCP. Formulations with Case B or C p.p. behavior with OCP often improved to Case A or B, respectively. However, PPDs for mineral oil are limited in effectiveness to very low (0.1 – 0.5wt%) treat with less effect at higher treat. The 5 – 20wt% treat of PMA used in this study exceeds the useful range for observing PPD behavior with polymethacrylate chemistry.

4.3. Recommendations for starting point formulations

Several general recommendations for formulators can be summarized from Sections 4.1 (VI behavior) and 4.2 (p.p. behavior) for designing low temperature, high VI products.

Negative VI and p.p. performance occurred with at the semi-dilute polymer concentration where polymer coils were of sufficient number and size to contact in solution. This prevented the expansion of the coils at high temperature to offset the thinning of the oil (bad VI improvement) and reinforced the formation of a wax network (pour point greatly reduced). The dilute/semi-dilute transition may be easily measured with simple viscosity equipment following the plot in **Figure 4.1** for a given VII product. The treat rate of the VII for high VI and low p.p. lubricants should not exceed the critical concentration. High MW polymers should be avoided and may only be allowed at a few wt% but can provide substantial thickening to meet target viscosities.

Formulations with the highest rated VI and p.p. behavior (Case 1 + Case A, Case 1 + Case B, or Case 2 + Case A) were found with low treat (5wt%) of PB with PMA or OCP. Case 1 + Case A was only found with Group III oil. Due to solubility issues few useful PAO formulations were found in this study due to the need for esters to improve solubility. **Table 3.1** is a useful resource to observe which viscosity, VI, and p.p. ranges were possible in each base oil. **Table A-1** and **Table A-2** in Appendix A show the components, viscometrics, VI, p.p., and viscosity grade (based on KV40 or KV100) data for each formulation prepared.

Table 4.1 and **Table 4.2**, below, summarize the four VI and three p.p. behavior cases. By understanding the cause of each observed trend with VII it is possible to recommend several actions to improve VI and p.p.

Table 4.1: Summary of the four observed cases in VI behavior with blended VII

	Trend	Explanation	Suggested Improvements	Figure
Case 1	VI increases continuously from low to high treat	Polymer coils expand at high temperature to increase KV100; higher KV100 per KV40 means VI improves	N/A	Fig. 1.1
Case 2	VI increases at low/medium treat; VI decreases or remains constant at high treat	Polymer coil concentration is sufficient for coil-coil interference (semi-dilute behavior)	Replace some wt% of VII with higher viscosity base oil	Fig. 4.1
Case 3	VI unaffected by additive wt%	Polymer expansion is too small to compensate for base oil thinning at high temperature	Use higher MW VII and/or increase initial base oil VI	Fig. 4.2
Case 4	VI decreases continuously	Polymer coils collapse due to high polymer content and/or low oil solvency	Replace some wt% of VII with higher viscosity base oil Increase base oil solvency with low viscosity ester/AN	Fig. 4.4

Table 4.3: Summary of the three observed trends in pour point with suggested improvements

	Trend	Explanation	Suggested Improvement
Case A	Pour point unaffected by VII treat level	PB + OCP - Dilution of waxes by PB and polymer wt% is in dilute concentration PB + PMA – collapse of polymer chains prevents polymer coils from accelerating wax formation	N/A
Case B	Pour point worsens at high treat	Similar to Case A; wax from diluent oil in VII at high treat increases total wax content of oil	Use VII with higher wt% polymer or more refined oil Reduce VII use by increasing base oil viscosity
Case C	Pour point continuously worsens from low to high treat	High MW polymer coils begin to form a network in oil (semi-dilute condition) which helps the wax network form at low temperature	Reduce wt% or MW of VII to avoid semi-dilute condition Replace some VII with high viscosity base oil

5. Conclusions

Polymeric VII products have complex effects on viscosity, VI, and pour point when blended at high concentration necessary for high shear stability lubricants using lower MW polymers. VI improvement is generally understood to involve the simple thermal expansion and contraction of the polymer coil in oil to counteract the effects of base oil thinning at high temperature. In practice, several non-ideal behaviors are observed. These non-ideal cases in the VI or p.p. with the blending low to high treat of VIIs in oil can be explained by fundamental principles in polymer science and polymer solution theory. This work provides a framework for rationalizing non-intuitive behavior of VI and p.p. and suggested several recommendations to correct for the fundamental concepts at work.

Future work is required to further develop the ideas presented in this study. The dilute/semi-dilute transition appears to be critical in determining if high treat of a polymer will cause loss of VI improvement or sudden loss of low temperature flow. Base oil solvency with the addition of components like PB or ester appear to be able to shift the dilute/semi-dilute transition by collapsing the polymer coils slightly. This would allow more polymer in solution before coil-coil contact (the semi-dilute condition) is reached.

Several recommendations for improving the low temperature or VI characteristics of a formulation involved the partial substitution of VII for a higher viscosity base oil. It was also stated that increasing viscosity or MW of base oil can further reduce solvency for high MW polymers in oil. The balance of reducing polymer treat by increasing oil viscosity versus the lower solvency of higher viscosity oil warrants further investigation.

In summary, the activity of polymeric VII in shear stable and low temperature lubricants requires anticipating the behavior of polymers in solution through established fundamental concepts. This study has provided an outline for troubleshooting non-intuitive results from formulating various VII combinations in multiple oils.

Appendix A – Formulation Data Table

Table A-1 shows all 81 samples prepared including formulation, viscometric, low temperature, and viscosity grade information.

There are six ways to present the results for blending the single VII at constant wt% with a second VII at varying wt%. **Table A-1** shows three combinations. **Table A-2** shows the remaining three combinations by rearranging data from Table A-1. This allows each combination to be viewed together in one place by using two tables.

To determine which chart to reference for a given pair of VII, consult the following chart:

		Varying VII		
		PB	**PMA**	**OCP**
Constant VII	**PB**	---	Table A-1	Table A-1
	PMA	Table A-2	---	Table A-1
	OCP	Table A-2	Table A-2	---

The "Cases" column in each table refers to the four cases of VI and p.p. behavior described in Results sections 3.2-3.

Table A-1. Formulations, Constant PB or PMA with Varying OCP or PMA

	Formula					Viscometrics			Low T	Cases		Appearance			Viscosity Grade			
#	Base Oil	PPD wt%	PB wt%	PMA wt%	OCP wt%	KV 40	KV 100	VI	p.p.	VI	p.p.	Haze	Separation	Overall	ISO VG	AGMA VG	SAE	SAE Gear
1	Gr. II	.2	5	5		64.0	10.0	141	-42	1	B	No	No	Good	68	2	30	80
2		.2	5	10		74.3	12.1	160	-45			No	No	Good	68	2	30	85
3		.2	5	20		127.5	19.6	176	-30			No	No	Good			50	110
4	Gr. II	.2	10	5		81.6	12.5	151	-42	3	B	No	No	Good			30	85
5		.2	10	10		101.6	14.7	150	-33			No	No	Good	100	3	40	90
6		.2	10	20		132.9	18.7	159	-30			No	No	Good			50	110
7	Gr. II	.2	20	5		176.4	21.5	145	-33	4	A	No	No	Good			50	110
8		.2	20	10		221.0	25.2	144	-33			No	No	Good	220	5	60	140
9		.2	20	20		262.3	26.3	130	-33			No	No	Good				140
10	Gr. II	.2	5		5	77.8	11.6	142	-36	2	A	No	No	Good			30	85
11		.2	5		10	176.4	21.5	174	-33			No	No	Good			50	110
12		.2	5		20	324.0	38.7	170	-36			No	No	Good	320	6		190
13	Gr. II	.2	10		5	110.6	15.3	145	-36	1	C	No	No	Good			40	90
14		.2	10		10	174.1	30.9	152	-33			No	No	Good				140
15		.2	10		20	436.9	50.1	177	-30			No	No	Good	460	7		250
16	Gr. II	.2	20		5	232.2	28.0	157	-33	1	C	No	No	Good	220	5		140
17		.2	20		10	325.6	38.0	167	-27			No	No	Good	320	6		190
18		.2	20		20	763.7	75.1	177	-24			No	No	Good				
19	Gr. II	.2		5	5	62.8	10.6	159	-45	2	A	No	No	Good	68	2	30	85
20		.2		5	10	92.6	15.0	171	-42			No	No	Good	100	3	40	90
21		.2		5	20	104.0	16.2	168	-42			No	No	Good	100	3	40	90
22	Gr. II	.2		10	5	66.5	11.7	173	-45	1	D	No	No	Good	68	2	30	85
23		.2		10	10	127.7	19.7	176	-42			No	No	Good			50	110
24		.2		10	20	317.3	39.9	179	-33			No	No	Good	320	6		190
25	Gr. II	.2		20	5	133.7	20.2	174	-30	3	A	No	No	Good			50	110
26		.2		20	10	223.5	29.8	174	-27			Yes	No	Poor	220	5		140
27		.2		20	20	525.4	54.8	169	-27			Yes	Yes	Bad				
28	Gr. III	.2	5	5		36.9	7.3	167	-36	2	A	No	No	Good			20	
29		.2	5	10		46.2	9.3	189	-36			No	No	Good	46	1	30	80
30		.2	5	20		89.4	15.2	180	-33			No	No	Good			40	90
31	Gr. III	.2	10	5		56.6	9.8	160	-39	2	C	No	No	Good			30	80
32		.2	10	10		72.3	12.4	171	-33			No	No	Good	68	2	30	85
33		.2	10	20		167.5	23.3	168	-24			No	No	Good			60	110

34	Gr. III	.2	20	5		124.7	16.7	145	-36	1	B	No	No	Good			50	90
35		.2	20	10		138.5	18.3	148	-36			No	No	Good	150	4	50	110
36		.2	20	20		193.4	24.9	160	-27			No	No	Good			60	140
37	Gr. III	.2	5		5	51.5	9.5	171	-39	1	A	No	No	Good			30	80
38		.2	5		10	92.8	15.7	181	-42			No	No	Good	100	3	40	90
39		.2	5		20	213.5	30.4	185	-39			No	No	Good	220	5		140
40	Gr. III	.2	10		5	74.5	12.8	173	-39	2	A	No	No	Good	68	2	40	85
41		.2	10		10	132.8	19.7	170	-39			No	No	Good			50	110
42		.2	10		20	302.2	38.8	180	-42			No	No	Good	320	6		190
43	Gr. III	.2	20		5	153.1	21.0	161	-36	1	A	No	No	Good	150	4	50	110
44		.2	20		10	236.4	29.9	167	-36			No	No	Good	220	5		140
45		.2	20		20	557.4	61.2	181	-39			No	No	Good				250
46	Gr. III	.2		5	5	40.6	8.3	186	-42	2	B	No	No	Good			20	80
47		.2		5	10	66.9	12.8	195	-42			No	No	Good	68	2	40	85
48		.2		5	20	182.7	28.4	195	-42			No	No	Good				140
49	Gr. III	.2		10	5	50.0	10.7	211	-39	4	A	No	No	Good	46	1	30	85
50		.2		10	10	80.0	15.4	205	-39			No	No	Good			40	90
51		.2		10	20	194.3	29.8	195	-39			No	No	Good				140
52	Gr. III	.2		20	5	82.0	15.8	206	-33	4	A	No	No	Good			40	90
53		.2		20	10	120.6	18.6	173	-33			Yes	Yes	Bad				
54		.2		20	20	216.2	28.8	172	-33			Yes	Yes	Bad				
55	PAO		5	5		51.9	9.0	155	N/A	--	--	Yes	Yes	Bad				
56			5	10		59.2	10.9	178	N/A			Yes	Yes	Bad				
57			5	20		N/A	18.6	N/A	N/A			Yes	Yes	Bad				
58	PAO		10	5		75.7	11.2	139	N/A	--	--	Yes	Yes	Bad				
59			10	10		82.0	12.7	154	N/A			Yes	Yes	Bad				
60			10	20		N/A	26.2	N/A	N/A			Yes	Yes	Bad				
61	PAO		20	5		154.8	20.2	151	N/A	--	--	Yes	Yes	Bad				
62			20	10		205.5	24.6	149	N/A			Yes	Yes	Bad				
63			20	20		224.7	26.7	153	N/A			Yes	Yes	Bad				
64	PAO		5		5	73.3	12.0	160	-51	1	C	No	No	Good	68	2	30	85
65			5		10	114.4	17.4	168	-50			No	No	Good			50	110
66			5		20	309.7	42.4	194	-38			No	No	Good	320	6		190
67	PAO		10		5	105.3	15.5	156	-50	1	C	No	No	Good	100	3	40	90
68			10		10	165.2	22.3	162	-46			No	No	Good			60	110
69			10		20	395.2	47.1	179	-42			No	No	Good				190
70	PAO		20		5	217.4	26.2	154	-46	2	B	No	No	Good	220	5		140
71			20		10	327.2	37.8	165	-48			No	No	Good	320	6		190
72			20		20	423.9	44.8	162	-40			No	No	Good	460	7		190
73	PAO			5	5	61.2	10.8	169	-52	1	B	Yes	No	Poor			30	85
74				5	10	91.5	15.1	174	-52			Yes	No	Poor	100	3	40	90
75				5	20	246.2	33.5	182	-44			Yes	No	Poor				190
76	PAO			10	5	77.1	13.3	176	-51	1	--	Yes	No	Poor			40	90
77				10	10	105.1	17.5	184	-50			Yes	No	Poor	100	3	50	110
78				10	20	N/A	33.9	N/A	N/A			Yes	Yes	Bad				
79	PAO			20	5	N/A	19.9	N/A	N/A	--	--	Yes	Yes	Bad				
80				20	10	412.7	29.8	101	N/A			Yes	Yes	Bad				
81				20	20	786.6	47.3	106	N/A			Yes	Yes	Bad				

Table A-2: Reorganized Table A-1 to show ‘constant PMA or OCP/varying PB’ and ‘constant OCP/varying PMA’ trends

	Formula					Viscometrics			Low T	Cases		Appearance			Viscosity Grade			
#	Base Oil	PPD wt%	PB wt%	PMA wt%	OCP wt%	KV 40	KV 100	VI	p.p.	VI	p.p.	Haze	Separation	Overall	ISO VG	AGMA VG	SAE	SAE Gear
1	Gr. II	.2	5	5		64.0	10.0	141	-42	2	B	No	No	Good	68	2	30	80
4		.2	10	5		81.6	12.5	151	-42			No	No	Good			30	85
7		.2	20	5		176.4	21.5	145	-33			No	No	Good			50	110
2	Gr. II	.2	5	10		74.3	12.1	160	-45	4	A	No	No	Good	68	2	30	85
5		.2	10	10		101.6	14.7	150	-33			No	No	Good	100	3	40	90
8		.2	20	10		221.0	25.2	144	-33			No	No	Good	220	5	60	140
3	Gr. II	.2	5	20		127.5	19.6	176	-30	4	A	No	No	Good			50	110
6		.2	10	20		132.9	18.7	159	-30			No	No	Good			50	110
9		.2	20	20		262.3	26.3	130	-33			No	No	Good				140
28	Gr. III	.2	5	5		36.9	7.3	167	-36	4	A	No	No	Good			20	
31		.2	10	5		56.6	9.8	160	-39			No	No	Good			30	80
34		.2	20	5		124.7	16.7	145	-36			No	No	Good			50	90
29	Gr. III	.2	5	10		46.2	9.3	189	-36	4	A	No	No	Good	46	1	30	80
32		.2	10	10		72.3	12.4	171	-33			No	No	Good	68	2	30	85
35		.2	20	10		138.5	18.3	148	-36			No	No	Good	150	4	50	110
30	Gr. III	.2	5	20		89.4	15.2	180	-33	4	C	No	No	Good			40	90
33		.2	10	20		167.5	23.3	168	-24			No	No	Good			60	110
36		.2	20	20		193.4	24.9	160	-27			No	No	Good			60	140
55	PAO		5	5		51.9	9.0	155	N/A	--	--	Yes	Yes	Bad				
58			10	5		75.7	11.2	139	N/A			Yes	Yes	Bad				
61			20	5		154.8	20.2	151	N/A			Yes	Yes	Bad				
56	PAO		5	10		59.2	10.9	178	N/A	--	--	Yes	Yes	Bad				
59			10	10		82.0	12.7	154	N/A			Yes	Yes	Bad				
62			20	10		205.5	24.6	149	N/A			Yes	Yes	Bad				
57	PAO		5	20		N/A	18.6	N/A	N/A	--	--	Yes	Yes	Bad				
60			10	20		N/A	26.2	N/A	N/A			Yes	Yes	Bad				
63			20	20		224.7	26.7	153	N/A			Yes	Yes	Bad				
10	Gr. II	.2	5		5	77.8	11.6	142	-36	1	B	No	No	Good			30	85
13		.2	10		5	110.6	15.3	145	-36			No	No	Good			40	90
16		.2	20		5	232.2	28.0	157	-33			No	No	Good	220	5		140
11	Gr. II	.2	5		10	176.4	21.5	174	-33	4	B	No	No	Good			50	110
14		.2	10		10	174.1	30.9	152	-33			No	No	Good				140
17		.2	20		10	325.6	38.0	167	-27			No	No	Good	320	6		190
12	Gr. II	.2	5		20	324.0	38.7	170	-36	2	C	No	No	Good	320	6		190
15		.2	10		20	436.9	50.1	177	-30			No	No	Good	460	7		250
18		.2	20		20	763.7	75.1	177	-24			No	No	Good				
37	Gr. III	.2	5		5	51.5	9.5	171	-39	4	A	No	No	Good			30	80
40		.2	10		5	74.5	12.8	173	-39			No	No	Good	68	2	40	85
43		.2	20		5	153.1	21.0	161	-36			No	No	Good	150	4	50	110
38	Gr. III	.2	5		10	92.8	15.7	181	-42	4	C	No	No	Good	100	3	40	90
41		.2	10		10	132.8	19.7	170	-39			No	No	Good			50	110
44		.2	20		10	236.4	29.9	167	-36			No	No	Good	220	5		140
39	Gr. III	.2	5		20	213.5	30.4	185	-39	3	A	No	No	Good	220	5		140
42		.2	10		20	302.2	38.8	180	-42			No	No	Good	320	6		190
45		.2	20		20	557.4	61.2	181	-39			No	No	Good				250
64	PAO		5		5	73.3	12.0	160	-51	4	B	No	No	Good	68	2	30	85
67			10		5	105.3	15.5	156	-50			No	No	Good	100	3	40	90
70			20		5	217.4	26.2	154	-46			No	No	Good	220	5		140
65	PAO		5		10	114.4	17.4	168	-50	3	A	No	No	Good			50	110
68			10		10	165.2	22.3	162	-46			No	No	Good			60	110
71			20		10	327.2	37.8	165	-48			No	No	Good	320	6		190
66	PAO		5		20	309.7	42.4	194	-38	4	A	No	No	Good	320	6		190
69			10		20	395.2	47.1	179	-42			No	No	Good				190
72			20		20	423.9	44.8	162	-40			No	No	Good	460	7		190
19	Gr. II	.2		5	5	62.8	10.6	159	-45	2	B	No	No	Good	68	2	30	85
22		.2		10	5	66.5	11.7	173	-45			No	No	Good	68	2	30	85

25		.2	20	5	133.7	20.2	174	-30			No	No	Good			50	110
20	Gr. II	.2	5	10	92.6	15.0	171	-42	3	B	No	No	Good	100	3	40	90
23		.2	10	10	127.7	19.7	176	-42			No	No	Good			50	110
26		.2	20	10	223.5	29.8	174	-27			Yes	No	Poor	220	5		140
21	Gr. II	.2	5	20	104.0	16.2	168	-42	2	C	No	No	Good	100	3	40	90
24		.2	10	20	317.3	39.9	179	-33			No	No	Good	320	6		190
27		.2	20	20	525.4	54.8	169	-27			Yes	Yes	Bad				
46	Gr. III	.2	5	5	40.6	8.3	186	-42	2	C	No	No	Good			20	80
49		.2	10	5	50.0	10.7	211	-39			No	No	Good	46	1	30	85
52		.2	20	5	82.0	15.8	206	-33			No	No	Good			40	90
47	Gr. III	.2	5	10	66.9	12.8	195	-42	2	C	No	No	Good	68	2	40	85
50		.2	10	10	80.0	15.4	205	-39			No	No	Good			40	90
53		.2	20	10	120.6	18.6	173	-33			Yes	Yes	Bad				
48	Gr. III	.2	5	20	182.7	28.4	195	-42	3	C	No	No	Good				140
51		.2	10	20	194.3	29.8	195	-39			No	No	Good				140
54		.2	20	20	216.2	28.8	172	-33			Yes	Yes	Bad				
73	PAO		5	5	61.2	10.8	169	-52	--	--	Yes	No	Poor			30	85
76			10	5	77.1	13.3	176	-51			Yes	No	Poor			40	90
79			20	5	N/A	19.9	N/A	N/A			Yes	Yes	Bad				
74	PAO		5	10	91.5	15.1	174	-52	--	--	Yes	No	Poor	100	3	40	90
77			10	10	105.1	17.5	184	-50			Yes	No	Poor	100	3	50	110
80			20	10	412.7	29.8	101	N/A			Yes	Yes	Bad				
75	PAO		5	20	246.2	33.5	182	-44	--	--	Yes	No	Poor				190
78			10	20	N/A	33.9	N/A	N/A			Yes	Yes	Bad				
81			20	20	786.6	47.3	106	N/A			Yes	Yes	Bad				

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