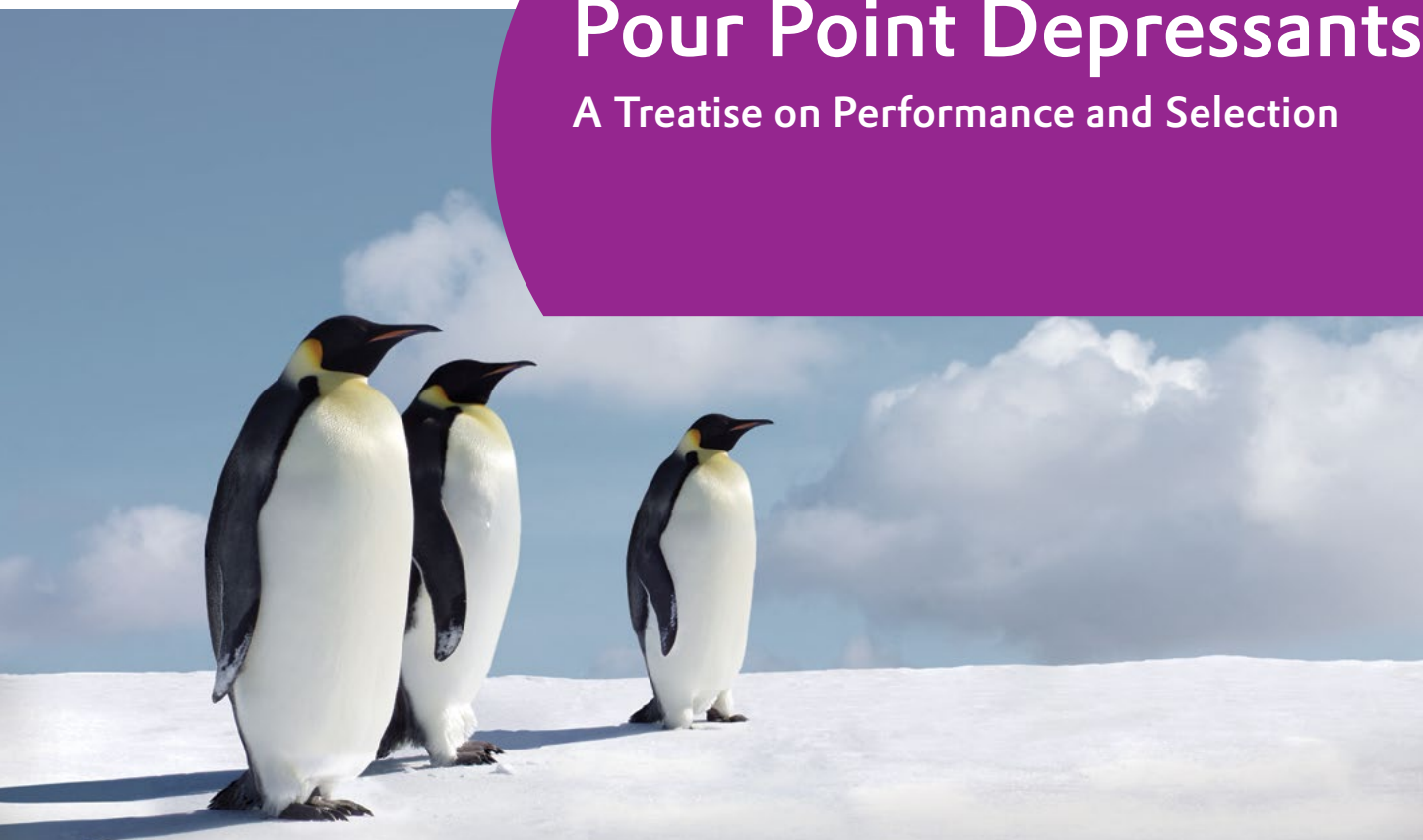


Pour Point Depressants

A Treatise on Performance and Selection





Introduction

The ability of a lubricant to flow under low-temperature, low-shear conditions is crucial to the operation of engines and equipment expected to run in cold climates. Without the proper selection and treat rate of a pour point depressant, a mineral oil lubricant formulation will exhibit poor low-temperature properties, leading, in the worst case, to lubrication “starvation” and equipment failure.

Virtually all paraffinic mineral oil base stocks contain small amounts of waxy materials. As the temperature of the oil is decreased, some of the waxy components come out of solution as tiny crystals, and the solution begins to appear hazy to the naked eye. The temperature at which this occurs is called the **cloud point**. As additional wax precipitates, the crystals grow into plates and, finally, if the temperature is decreased far enough, the plates will grow together to form a three-dimensional network that totally immobilizes the oil. This solidification process is sometimes referred to as gelation. The lowest temperature at which the oil is fluid is called the **pour point**.

Since wax normally makes up only a small percentage of the hydrocarbons in oil, the wax structures contain large amounts of trapped liquid, resulting in a matrix that is quite fragile. Since these networks of wax are easily destroyed by shaking or stirring, wax is not an important factor in low-temperature engine cranking. However, in many applications where the bulk of the oil is in a stagnant environment, such as an oil sump or reservoir, the wax structuring very effectively restricts pumpability, thereby placing a lower temperature limit on the utility of the lubricant.

History of Pour Point Depressants

Prior to the 1930s, the options for dealing with cold flow problems were very limited. Heat was an obvious solution, and as foolish as it may seem today, stories of fires being built under the sumps of vehicles are indeed authentic. A more reasonable alternative, at least in some instances, was to increase the solvency power of the fluid portion of the oil by the addition of kerosene to the lubricant, but this also decreased the viscosity of the oil at high temperature. There was also the alternative of adding one of several naturally occurring materials, such as asphaltenic resins or microcrystalline waxes, which were removed at various stages of the refining process. Unfortunately, while such materials were sometimes reasonably effective, they were not broadly applicable.

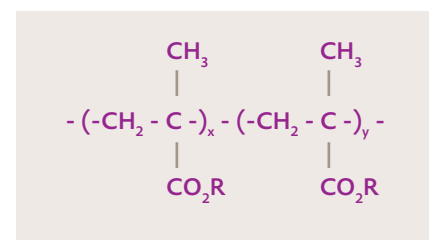
Because these materials depress the pour point of oil, they were designated **pour point depressants**. The existence of these naturally occurring pour point depressants suggested that there could well be synthetic materials that could function at least as well and probably better. The structures of natural

hydrocarbon pour point depressants, all waxy materials themselves, provided clear clues to the early synthetic efforts. In 1931, alkylated naphthalenes, wherein the alkyl groups contained linear waxy paraffinic structures, were introduced. This development encouraged the examination of other waxy materials as candidates, and in 1937, Rohm and Haas patented the first polymeric pour point depressants, **poly alkyl methacrylates (PAMAs)**, again based on waxy alkyl groups.

Over the years, a wide variety of synthetic materials has been introduced commercially as pour point depressants. Chlorinated wax is the most notable example of small-molecule chemistry, but most commercial products are moderate to high molecular weight polymers, such as polymethacrylates, polyacrylates, acrylate-styrene copolymers, esterified olefin- or styrene maleic anhydride copolymers, alkylated polystyrene, and vinyl acetate-fumarate copolymers.

Chemistry of Pour Point Depressants

Even after 75 years, polyalkylmethacrylates, the first of the polymeric pour point depressants, continue to be viewed as the best chemistry available today, with a worldwide market share that far outstrips alternatives. The primary reason for this widespread preference is the molecular structure of the polymers and the tremendous flexibility in chemical structure. The basic structure of a PAMA pour point depressant is as follows:



where the groups R and R' are a mixture of alkyl groups from C1 to C22. The products are free radical solution copolymers.

Pour point depressing activity is only weakly dependent on polymer molecular weight, and the degree of polymerization (x+y) of PPDs may vary from about 200 to 2000. Indeed, the molecular weight of PAMA pour point depressants is not determined by their primary function, but rather by such issues as thickening ability, shear stability, or even handling characteristics. Most blenders prefer to use a single product in a full range of lubricant applications, with shear stability requirements for the most demanding application, gear oils, generally setting the standard. Molecular weights of most of the product line thus tend to be concentrated in the low end of the range.

In order for the PAMA to effectively interact with wax, R groups must be linear and contain at least 14 carbon atoms. Because there is a distribution of wax molecule chain lengths in the oil, the best pour point depressant activity is achieved when there is also a distribution of R groups. In general, the interaction of an alkyl group with wax intensifies as its length increases, and the optimum positive interaction with wax requires a very careful balance of the waxy alkyl groups.

Figure 1 demonstrates a typical response curve for a PAMA pour point depressant as a function of the Wax Interaction Factor (WIF) in a specific base stock. The Wax Interaction Factor takes into account the amount of each alkyl group that can interact with wax and the relative strength of the interaction. WIF refers specifically to the PPD, not the base stock, and is a useful tool to differentiate PPDs. The response shown here is generic; the nature of the response curve is characteristic of what would be found with most low-temperature, low-shear test methods. Note that there is a rather specific WIF for optimum interaction. However, the size of the response window becomes wider and the response becomes stronger as the concentration of pour point depressant increases. There can be too much of a good thing, but that issue will be discussed later in the PPD Selection and Treat-Rate Principles section.

Figure 1: Typical PPD response curve

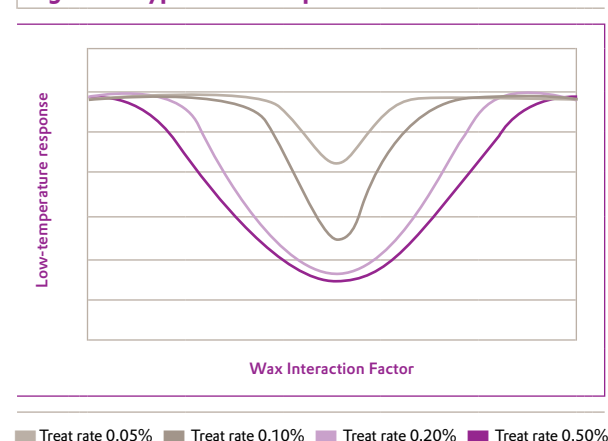


Figure 2: Base stock low-temperature response to PPDs with varying WIFs

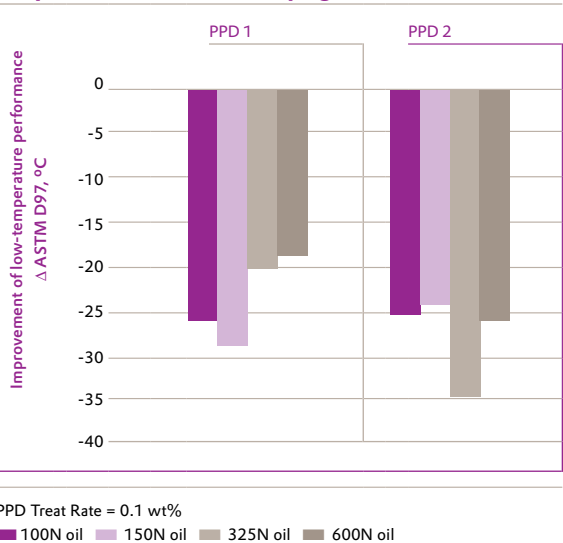


Figure 2 shows the degree of low-temperature performance improvement (Δ) by ASTM D97 testing in four Group I, solvent-refined base stocks from the same refinery. Two PPDs were added to each oil at a 0.1 wt% treat rate, with PPD 2 having twice the amount of waxy side chains as PPD 1. In the lighter, less waxy 100N and 150N, PPD 1 with a lower WIF tends to control pour point better. In the heavier, more waxy 325N and 600N stocks, PPD 2 with more waxy side chains and a greater WIF gives better D97 performance. While PPD 1 and PPD 2 are not necessarily the best PPDs for these oils, their performance demonstrates that the heavier base stocks respond better to waxier PPDs, and the lighter oils respond better to a PPD with lower wax content.

The WIF of the PPD is controlled by the average carbon number of the R groups in the PAMA polymer. Lower carbon number R groups are included to achieve lower WIF PPDs, and also to provide a broad spread of R numbers, which broadens the PPD activity range to more closely match the temperature range over which waxes crystallize in real-world lubricant fluids.

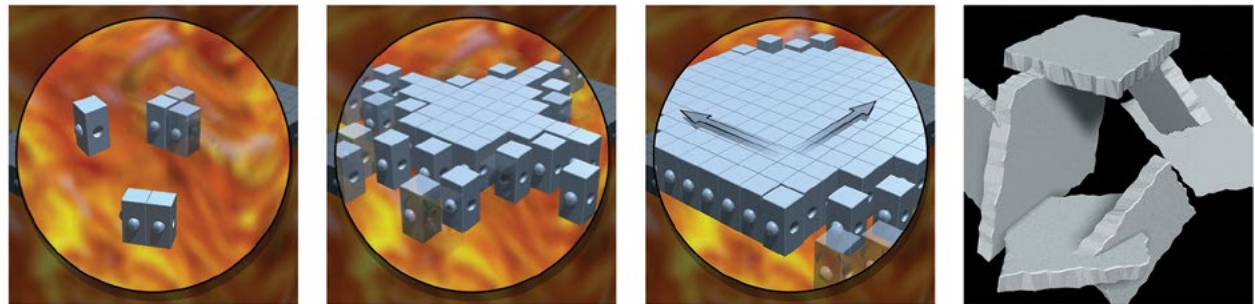
Mechanism of action

Pour point depressants do not in any way affect either the temperature at which wax crystallizes from solution or the amount of wax that precipitates. Rather, when wax crystals form, pour point depressants co-crystallize along with the wax species present in the oil and modify the growing pattern of wax crystal structures. Additionally, the wax crystals are kept apart from each other by the PPD backbone, and as a result of this steric hindrance, the wax crystals are no longer able to form three-dimensional structures that inhibit flow. While prevention of gelation is aimed at ensuring the oil's pumpability (from an overall perspective), the oil can be expected to still exhibit a wide range of behavior, from complete fluidity to borderline gelation. Total fluidity is obviously more desirable, but this can only be achieved if the pour point depressant structure ensures optimum interaction, such that the wax exists only as a stable dispersion of tiny crystals.

An important fact to note is that as temperature is decreased, all fluids will eventually "solidify" or, more accurately, become immobile, regardless of wax issues. This is simply a matter of the viscosity becoming so high that oil will not flow under the influence of gravity. This is normally called the viscous pour point. The viscosity at which the viscous pour point is reached is generally considered to be upwards of 100,000cP. Recognizing this type of behavior is important since pour point depressants are occasionally accused of not being effective in heavy stocks or losing effectiveness at low temperatures. It is important to be aware of the viscosity limitations of pour point in order to know if wax modification can be of any benefit.

How VISCOPLEX® PPDs modify wax crystals at low temperatures

Without VISCOPLEX® PPD (with temperature dropping from 1 to r)



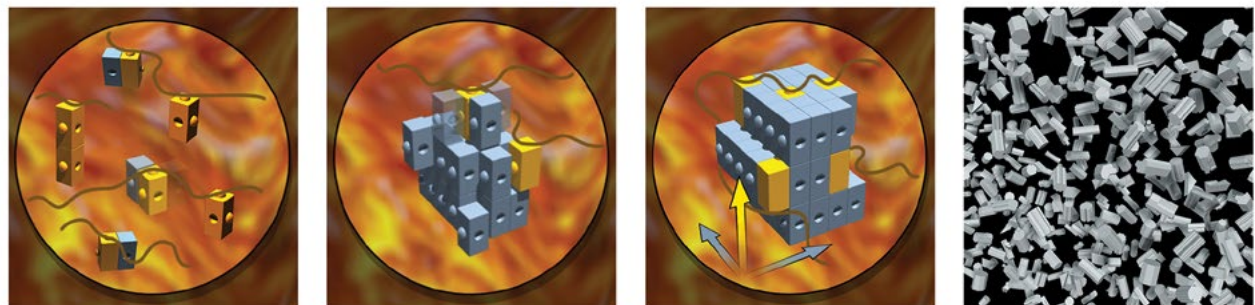
Crystallization of wax molecules below cloud point temperature

Mainly lateral growth forms needles or plates

Wax crystal structure continues to grow

Large, structured 3D crystal network formation, crystal size > 100µm, oil ceases to flow

With VISCOPLEX® PPD (with temperature dropping from 1 to r)



Co-crystallization occurs between wax molecules and VISCOPLEX® PPD crystalline units

VISCOPLEX® PPD modifies wax crystal growth

Interlocking of wax crystals is prevented, leading to smaller and more random structure

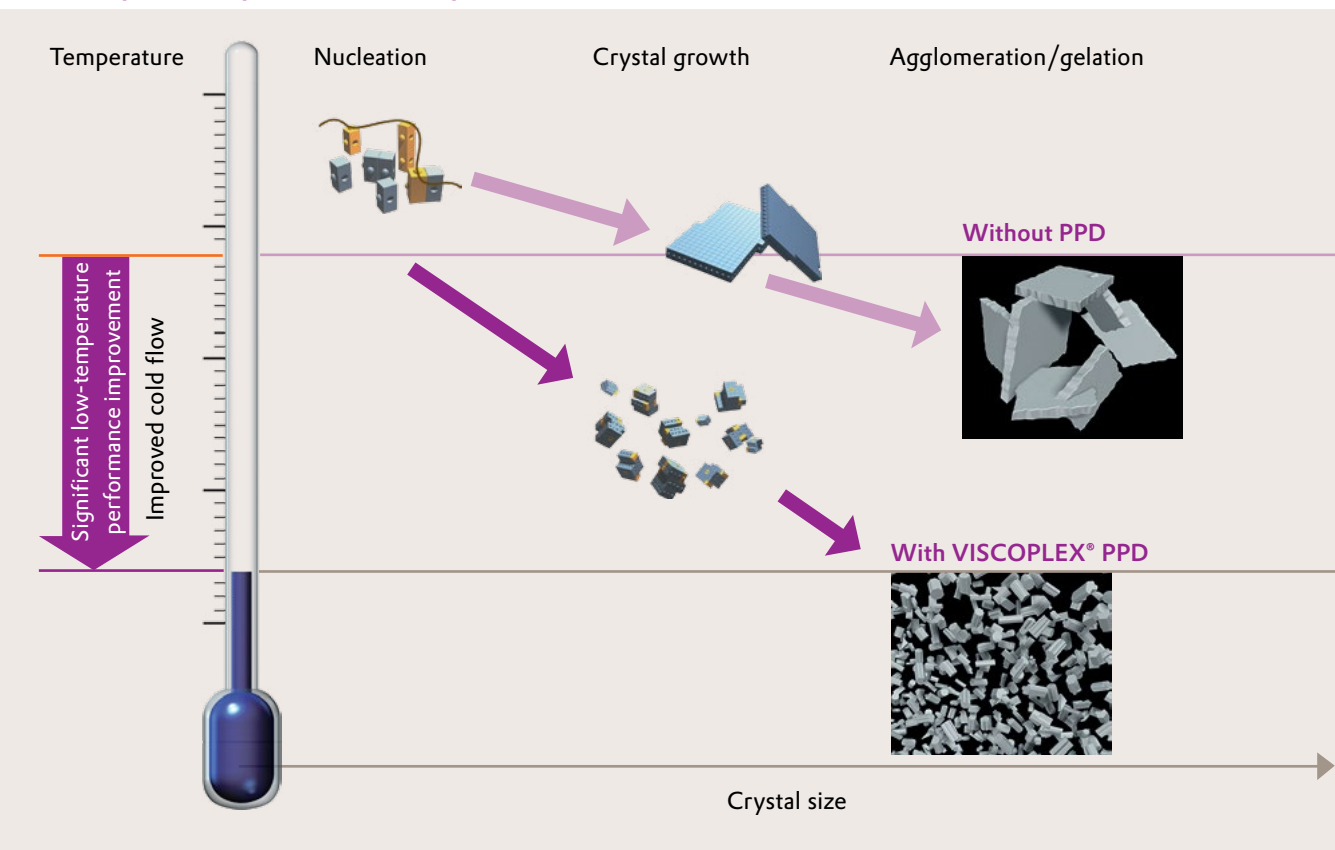
No aggregation of gel-like wax network, oil continues to flow without yield stress

Crystalline unit formed by n-paraffins

Crystalline unit formed by VISCOPLEX® PPD

VISCOPLEX® Polymer backbone

Interaction of VISCOPLEX® PPDs with wax crystals resulting in low-temperature performance improvement



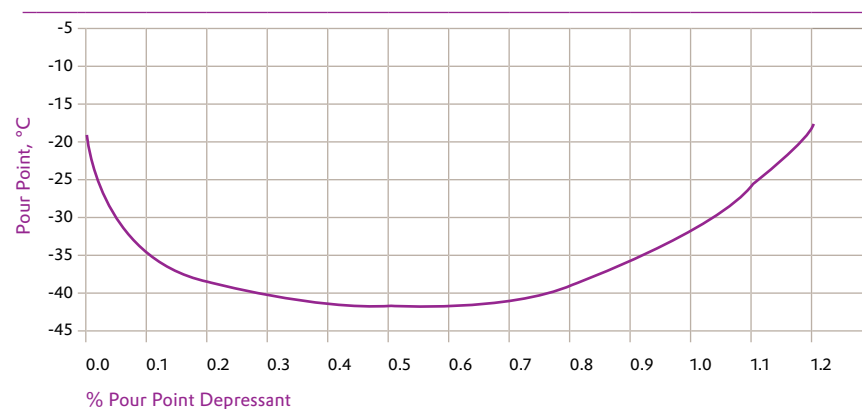
Crystalline unit formed by n-paraffins

Crystalline unit formed by VISCOPLEX® PPD

VISCOPLEX® Polymer backbone



Figure 3: Effect of treat rate on the ASTM D97 Pour Point Test



Note the similarity between the shapes of the curves in Figures 1 and 3. Figure 1 is low-temperature response as a function of the pour point depressant's chemical structure (its WIF), while Figure 3 is low-temperature response as a function of its concentration. In fact, product composition and use concentration are to some degree a trade-off. Inadequate wax interaction can often be overcome by the use of a higher treat rate; conversely, treat rate may sometimes be decreased with an optimization of the wax composition of the PPD.

The reversal of performance response, resulting from over-treatment with a pour point depressant, as shown in Figure 3, is reasonably straightforward. This phenomenon is called pour point reversion. But there is also a more subtle type of reversal. Many wax-related phenomena are a function of time and thermal history. Hence, one sometimes finds acceptable performance in a low-temperature response, only to discover that control of that property is lost during storage. The wax solution behaves like a super-cooled liquid, in which wax crystallization takes place over an extended period of time, thereby converting a fluid system to a gel.

PPD selection and treat rate principles

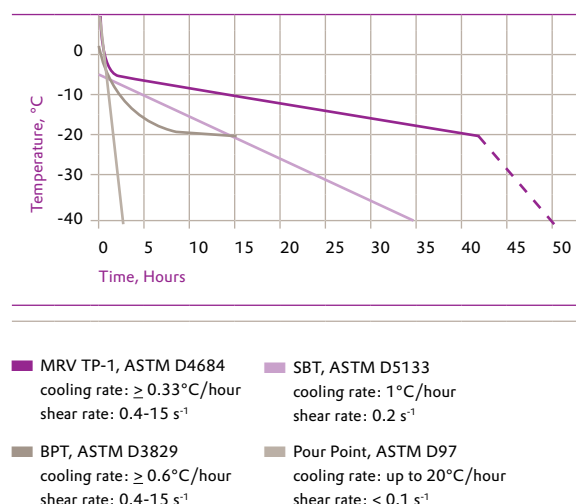
When new pour point depressants are designed or existing ones are used, it is important to recognize that these additives are themselves waxy materials. Therefore, in the process of adding a pour point depressant to a lubricant, one is in fact adding wax to the system. Hence, the dosage must be carefully selected to get an optimum response, and PPD over-treatment should be avoided to prevent reversion of low-temperature properties.

A typical concentration response curve, which can be inferred from a vertical slice of Figure 1, is shown in Figure 3. This particular example happens to be the ASTM D97 Pour Point Test, but the shape of the response curve is again generic. A properly selected pour point depressant will provide a dramatic enhancement of low-temperature performance even at low concentrations. Raising concentration may offer additional, minimal improvement. Once wax issues are completely under control, additional pour point depressant offers no additional benefit and the performance response becomes flat. Further increases in pour point depressant concentration are, in effect, only adding more wax to the system, leading eventually to a reversal of performance gains. In the extreme, an over-treated oil may have poorer low-temperature properties than the untreated oil.

Low-temperature performance requirements

The control of low-temperature properties of lubricants is such a complex effort that no single test can ensure that an oil will remain freely fluid over a wide range of conditions. Most engine oils are extremely non-Newtonian at low temperatures, and the range of shear rates involved in oil flow is quite large. Furthermore, thermal history, temperature cycling, and cooling rates all play a major role in low-temperature rheology. Hence, various test methods have been developed over the years, many in response to a specific issue encountered in the field. Descriptions of tests both current and historical follow below, and a visual depiction comparing the different temperature profiles of several tests is shown in Figure 4.

Figure 4: Cooling rate comparison of various low-temperature tests



Tests with very rapid cooling rates such as pour point are often not good indicators of low-temperature operability. A fast cooling rate does not allow wax content in a formulation enough time to fully crystallize and form three-dimensional structures. More sophisticated methods, such as ASTM D4684 (Viscosity and Yield Stress by MRV TP-1), use slower cooling rates and longer temperature profiles to better predict low-temperature pumpability. The temperature profile for MRV TP-1 is based on real-world temperature conditions that caused engine oil failures in the 1980s. Adopting a low-temperature test regime that reflects realistic cold weather conditions allows for a test that truly assesses a PPD's ability to control wax crystallization in severe conditions that the oil could actually encounter.

The low-temperature properties of most lubricants (for example, automatic transmission fluids, gear oils and hydraulic fluids) are normally specified by the use of pour point and Brookfield viscosity. Evaluation of engine oils is far more complex, with common requirements including pour point, MRV TP-1, Scanning Brookfield, and MRV TP-1 after the oil is conditioned from the Sequence IIIG engine test or ROBO.

Pour Point (ASTM D97)

A sample of oil in a small cylindrical glass container is cooled rapidly (up to 20°C/hour). The cylinder is turned on its side at 3°C intervals in order to determine oil fluidity. The lowest temperature at which perceptible fluid movement is observed is the pour point.

Brookfield Viscosity (ASTM D2983)

A sample of oil is cooled in a glass test tube at the desired test temperature for 16 hours. The viscosity is then measured using a low-shear viscometer called a Brookfield viscometer. A spindle immersed in the test fluid is rotated at a prescribed speed, depending on the viscosity, and the torque determined during spindle rotation is converted to a viscosity.

Stable Pour Point (SAE J300, Appendix B; or FTM 791b, Method 203, Cycle C)

This is also sometimes called the Cycle C Pour Point. A sample of oil in a glass cylinder, per ASTM D97, is stored through a complex, seven-day temperature cycle, which includes three excursions through a temperature range typical of the cloud points of most oils.

MRV Pumping Viscosity, MRV TP-1 (ASTM D4684)

An oil sample is placed in a rotational viscometer called the Mini-rotary Viscometer and subjected to a very slow cooling rate of ~0.33°C per hour down to -20°C, followed by a more rapid cool to the final test temperature as determined by the SAE viscosity grade. Total test time ranges from 45 to 53 hours. At the final test temperature, a measurement of viscosity and yield stress is made.

Borderline Pumping Temperature (ASTM D3829)

This is a predecessor to ASTM D4684. An oil sample is cooled rapidly in the Mini-rotary Viscometer to the desired test temperature over a 10-hour period and held at the test temperature for the remainder of one 16-hour period. Viscosity is measured, and the procedure is repeated at a minimum of at least three temperatures. The Borderline Pumping Temperature is interpolated as the temperature at which the viscosity is 30,000 cP. A yield stress is also determined.

Scanning Brookfield Viscosity (ASTM D5133)

Viscosity is measured continuously by a Brookfield viscometer as the temperature is decreased at a rate of 1°C/hour, from -5°C to -40°C, or the temperature at which the viscosity reaches 40,000 cP, whichever comes first. In this way, continuous tracking of viscosity versus temperature is obtained. The viscosity data is plotted using the Walther-MacCoull-Wright relationship; the Gelation Index is the first derivative of this curve. The most commonly reported result from this data treatment is the maximum value of the Gelation Index and the temperature at which it occurs.

Low-Temperature Fluidity of Hydraulic Fluids (ASTM D6351)

An oil sample is held at a selected temperature appropriate for the fluid application for a period of 7 days, after which the test jar is tilted horizontally to observe if the oil still flows. This method is particularly useful for vegetable oil based lubricants that have the tendency to solidify in extended cold temperature storage.

ROBO (ASTM D7528)

The Romaszewski Oil Bench Oxidation (ROBO) test is a laboratory procedure that mimics the oxidation and volatilization conditions of the Sequence IIIG engine. The oil sample is conditioned at 170°C in the presence of catalysts for 40 hours, during which time constant mixing, oxidation, nitration, and volatilization occur. The aged oil generated from the ROBO procedure is measured using MRV TP-1 (ASTM D4684) to evaluate the low-temperature performance of the aged oil after oxidation. The test also measures oil volatility and viscosity increase. Starting with ILSAC GF-5, ROBO is a bench test alternative to running the Sequence IIIGA, saving both time and money. Evonik’s Oil Additives Team developed the test as the low-temperature performance of aged oil became increasingly important for engine oil specifications.

Base stock trends

The growing range of base stocks in the market today is adding complexity to the wax-related issues confronting the formulation chemist. Since the dewaxing process is one of the most capital-intensive processes in a refinery, change has come slowly, and older, classic solvent-dewaxed stocks are still used. Variability in crudes is also an issue. Economic pressures encourage the use of multiple sources or spot purchases on the open market, leading to a constantly changing slate of crudes going through a refinery. This crude variability will result in different base oil wax character and appetite for PPDs.

Even more profound issues are being encountered as hydrocracked stocks become more common in markets worldwide. API Group III and Group IV oils have dramatically different solvency from that of solvent-refined stocks, thereby introducing their own unique set of formulation considerations. Gas-to-liquid (GTL) stocks represent the latest advancement in base oil technology, where the Fischer-Tropsch process converts natural gas to base oil. These GTLs as well as highly refined Group III base stocks still contain wax that needs to be treated with PPDs, but require a PPD technology different from the products used to treat solvent-refined stocks.

Other low-temperature tests are often misinterpreted as being related to PPD performance. The Cold Cranking Simulator (CCS, ASTM D5293) is a low-temperature test designed to test engine oils to ensure low temperature engine cranking at start-up. PPDs are relevant only in low-temperature, low-shear environments. However, CCS is run at low temperatures but at a high shear rate. The high shear aspect of the CCS breaks any wax structure and makes the test irrelevant to wax crystallization phenomenon and thus PPD selection.

The recent emulsion test according to ASTM D7563 is another example of a method often confused as a PPD-related issue. While a dispersant PPD can have a strong impact on the emulsifying properties of oil, such functionality is outside the realm of low-temperature control. While multi-functional additives are usually desirable, a PPD should only be expected to provide cold flow improvement. For instance, if a blender was not aware of a PPD’s dispersant property, use of such a dispersant product could easily harm a hydraulic formulation, where it is desirable for oil and water to separate.

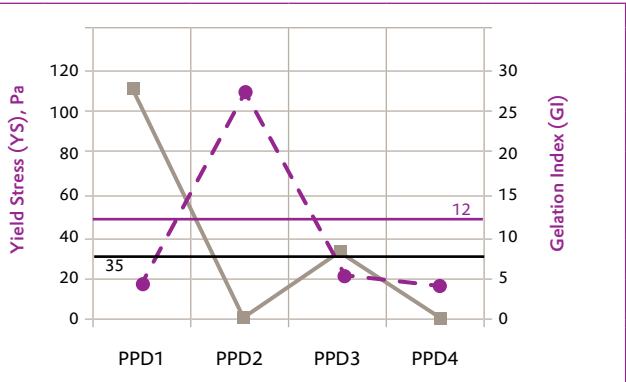
Finally, there is a small but growing use of biodegradable base stocks (vegetable oils) in some applications. These vegetable oils contain triglycerides instead of paraffinic wax, but the structure of these molecules is wax like. Hence, the effective concentration of wax is extremely high, and control of low-temperature fluidity is a major challenge. Overall, then, the number and complexity of wax-related issues has never been greater. All indications are that this trend will continue.

PPD selection guide

The screening of pour point depressants is best conducted on lubricants that are fully formulated but lacking pour point depressants. The base oil for a lubricant is normally a combination of two or more base stocks. A pour point depressant with one level of WIF is optimum for one base stock component, while a different level of WIF is preferred for the other base stock. The situation can become considerably more complex if a third component is used, such as a heavy stock or a bright stock.

Another critical factor in pour point depressant selection is the role of other additive components. Any additive containing a hydrocarbon structure, which is wax like, can have a dramatic effect on low-temperature performance. This is because waxy structures forming in a lubricant at low temperature need not be exclusively base-oil derived. These other “wax-like” additives can contribute to the wax structure formation to a greater or lesser extent. By far the most dramatic example of this is the high-ethylene-content OCP viscosity modifier (VM). It contains long sequences of ethylene, which can exert a profound influence on pour point depressant selection. Due to the impact of the other performance additives that comprise a formulation, it is important that PPDs are evaluated in fully-formulated oil instead of the base stock alone. Figure 5 demonstrates the consequences of selecting a PPD based on the response in straight oil. In the 150N oil, PPD 1 provides passing MRV TP-1 Yield Stress results while PPD 2 fails that test. However, when the same 150N is used to make an SAE 10W-40 engine oil containing VM and detergent inhibitor (DI) package components, PPD 1 now fails MRV TP-1 in the fully formulated engine oil, while PPD 2 controls Yield Stress. The VM and performance package contribute waxy components to the oil, and the proper PPD must be able to accommodate their influence on the formulation’s low-temperature performance.

Figure 6: ASTM D4684 YS, ASTM D5133 GI

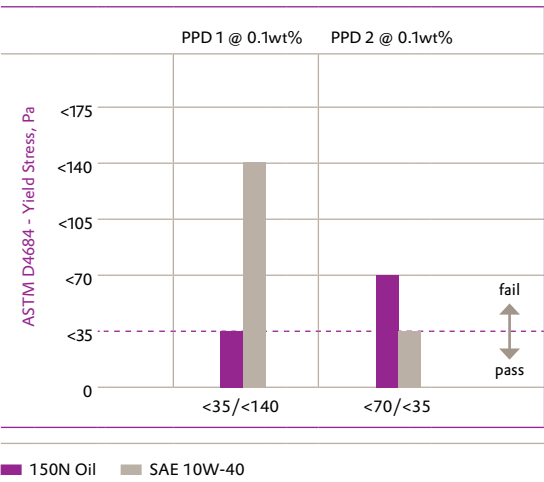


PPD 4 passes both Yield Stress & GI
35 line represents the maximum limits for the Yield Stress test
12 line represents the maximum limits for the Gel Index test
--- ASTM D4684 YS ——— ASTM D5133 GI

The biggest single issue in pour point depressant selection is the sometimes conflicting requirements of low-temperature tests. A pour point depressant simply cannot be selected based on any single test. For instance, Figure 6 shows Scanning Brookfield Gelation Index and MRV TP-1 viscosity run on the same SAE 5W-30 engine oil. The black line shows the MRV TP-1 Yield Stress, and the purple line shows the Scanning Brookfield Gelation Index (GI). The horizontal lines show the maximum limits for each test, so the ideal PPD would provide appropriate wax control to keep both results below these lines. Due to differences in cooling profile, shear rate, and time, each PPD demonstrates a specific response to the two tests. PPD 1 has very good GI performance but fails MRV TP-1 due to the presence of high Yield Stress. On the other hand, PPD 2 passes MRV TP-1 with no Yield Stress but fails to provide adequate low-temperature control in Scanning Brookfield, where the oil registers a high GI. Only PPD 4 is properly balanced to control the wax crystallization phenomenon in the low-temperature, low-shear environments that both tests represent. Therefore, it is crucial to consider all of the cold-temperature requirements of a lubricant, as a passing result in one low-temperature test does not guarantee success in another.

In addition to trade-offs between tests within a specific application, there must also be consideration of the requirements within the viscosity grades of a product line, as well as the requirements across product lines. While it would be possible to define an optimum pour point depressant for every product, this is obviously not practical. It is unusual that a single, “universal” pour point depressant would be optimized for all of the products in a blending plant. However, one pour point depressant will sometimes meet all of a plant’s needs with an up-treat in dosage in certain products. The blender must weigh this option against the logistical issues of handling a second pour point depressant for part of the product mix.

Figure 5: PPD performance in base oils and fully formulated oils



Another essential PPD consideration that has evolved considerably over the past decade is the low-temperature performance of engine oils after oxidation, either from the Sequence IIIG engine test or the ROBO bench test. Starting with GF-4, ILSAC-graded engine oils have been required to pass MRV TP-1 after undergoing oxidative thickening. Thus, the PPD not only has to provide adequate control of wax crystallization in the fresh oil, but has to properly control low-temperature properties in the aged oil. Since the oxidized oil contains polar molecules that can

structure at cold temperatures, the PPD must be able to handle both the crystallization of wax species and the agglomeration of polar molecules. Similar to the scenario outlined in Figure 5, a PPD that works well in the fresh oil does not always guarantee success in the aged oil. For instance, Figure 7 shows the response of three PPDs treated at 0.3 wt% in fresh and oxidized versions of the same SAE 5W-30 engine oil. All three PPDs provide passing MRV TP-1 results in the fresh oil, so as long as those PPDs also passed the other required low-temperature tests,

then either PPD 1, 2, or 3 would be a suitable additive for the formulation. However, the PPDs vary greatly in their ability to provide low-temperature control in the aged oil environment. The oxidized oil using PPD 1 is completely frozen in MRV TP-1, and the use of PPD 2 exhibits high viscosity. Only PPD 3 has the properly balanced composition to pass both fresh oil and aged oil low-temperature testing.

Evonik’s VISCOPLEX® Pour Point Depressants

The Oil Additives specialists at Evonik offers several lines of pour point depressants, all based on PAMA chemistry. Most members of these series have excellent shear stability, thereby ensuring their applicability to all lubricant applications. Some, with a higher molecular weight, also provide some contribution to the viscosity of the lubricant.

VISCOPLEX® series 1 products are PPDs that have a long history of broad applicability in all lubricant applications. They remain an excellent, cost-effective choice in most cases:

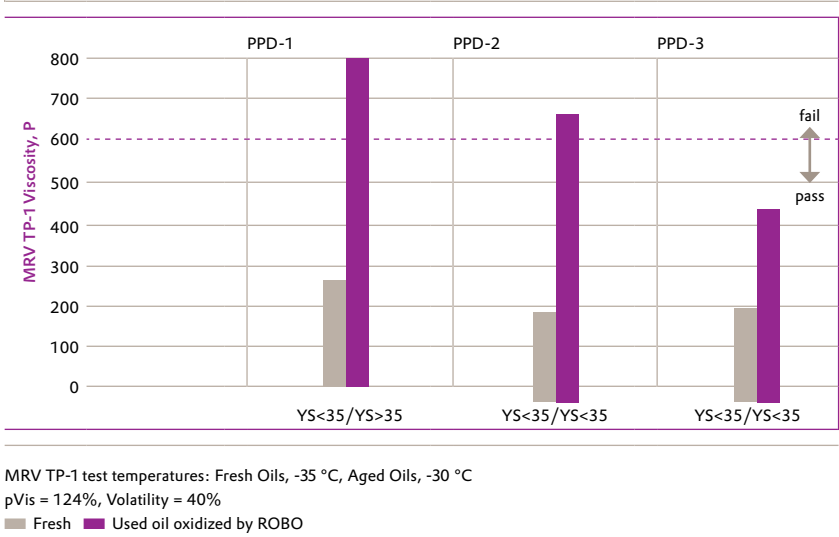
VISCOPLEX® 1-100 and 1-200 series

VISCOPLEX® 1-100 and 1-200 series PPDs are conventional pour point depressants particularly effective in lubricants formulated with solvent-refined base stocks and for industrial or gear oil applications requiring basic pour point or Brookfield performance.

Figure 8: VISCOPLEX® biodegradable PPDs keep vegetable-based lubricants flowing at extreme cold temperatures



Figure 7: PPD selection: fresh and aged oil



VISCOPLEX® 1-300 series

VISCOPLEX® 1-300 series PPDs are tailored to provide robust, customer-specific, low-temperature solutions. They are particularly effective in controlling MRV TP-1 yield stress and Scanning Brookfield Gelation Index. In general, the applicability of the VISCOPLEX® 1-300 series is broader than that of the 1-100 and 1-200 series.

VISCOPLEX® 1-400, 1-600, and 1-700 series

VISCOPLEX® 1-400, 1-600, and 1-700 series PPDs are customized PPDs designed for advanced engine oil performance, including the aged oil requirements for ILSAC GF-category PCMO. These PPDs are especially effective in PCMO and HDMO formulations using modern base stocks and higher ethylene content OCP viscosity index improvers.

VISCOPLEX® 1-800 series

VISCOPLEX® 1-800 series PPDs consist of higher molecular weight pour point depressants, which provide cold-temperature performance and simultaneously increase the viscosity index of the treated oil.

VISCOPLEX® 10 series

VISCOPLEX® 10 series PPDs are designed for use in environmentally friendly lubricants, providing better pour point performance and cold-temperature storage stability improvement in biodegradable lubricants made from a variety of vegetable oil or other bio-derived sources. This series of PPDs use mineral oil, vegetable oil, or ester as carrier fluids and are effective in applications ranging from chain saw oils to transformer oils. One of the main advantages of 10 series PPDs is their ability to prolong the lubricant’s ability to remain fluid over extended periods of time at low temperature. An example is shown in Figure 8, where use of a PPD keeps a vegetable oil-based lubricant formulation fluid for over 15 days, while the untreated sample is frozen after just 24 hours.

Case study

As ILSAC- and API-graded engine oils have adopted aged oil low-temperature requirements, PPD selection programs have become increasingly more complex. The following data shows the low-temperature response of a fully formulated ILSAC GF-5 quality SAE 5W-30 PCMO using North American Group II base oils and high ethylene-content OCP VM. MRV TP-1, pour point, Scanning Brookfield technique, and ROBO performance were evaluated on three versions of the formulation: untreated, and with 0.4wt% of two different PPD products. The data is presented below as the result of fresh oil low-temperature tests (PP, MRV, SBT) or aged oil tests (ROBO).

Figure 9: PPD selection study for ILSAC GF-5 oil

Fresh oil			
SAE 5W-30 using GF-5 package, HE-OCP VM and NAR Group II base oils			
PPD	—	A	B
PPD treat rate, %	untreated	0.4	0.4
ASTM D97			
Pour Point, °C	-18	-33	-30
ASTM D4684			
MRV TP-1, -35°C			
Viscosity, cP	17,600	16,900	16,700
Yield stress, Pa	<35	<35	<35
MRV TP-1, -40°C			
Viscosity, cP	134,000	60,000	59,000
Yield stress, Pa	<105	<35	<35
ASTM D5133			
Scanning Brookfield			
Gelation index	5.2, -11.2°C	5.1, -37.7°C	5.6, -37.7°C
Aged oil			
ASTM D7528			
ROBO			
Volatiles, %	47		
Viscosity increase, 40°C, %	113		
PPD	—	A	B
PPD treat rate, %	untreated	0.4	0.4
MRV TP-1, -30°C			
Viscosity, cP	solid	127,900	43,600
Yield stress, Pa	—	<105	<35

*5W-30 sample was post-treated with PPD A and PPD B after ROBO.

Notice the good low-temperature performance of the untreated 5W-30 sample in MRV TP-1 testing. Without any PPD, the oil has no yield stress and a viscosity below 20,000cP at -35°C. The passing result here is due to the high quality Group II base oil and the influence of the GF-5 package. As discussed earlier, DI chemistry may impact low-temperature control and often contains species very similar to the active components contained in a PPD. Balancing this DI impact becomes crucial for selecting the appropriate PPD and treat rate.

When treating the 5W-30 with 0.4 wt% of either PPD A or PPD B, the fresh oil low-temperature response is identical. MRV TP-1, pour point, and Scanning Brookfield all demonstrate that both PPDs provide excellent low temperature control. Even at the -40°C MRV TP-1 test temperature normally used for 0W-XX oils, these 5W-30 samples have no Yield Stress and continue to maintain good pumping viscosity.

On the other hand, after conditioning the oils with ROBO, PPD A shows drastically different performance from PPD B. After ROBO, the 5W-30 oil with the 0.4% PPD A treat rate has high viscosity and Yield Stress in MRV TP-1 testing at -30°C. PPD B, though, continues to control the wax and polar species present in the oxidized, aged oil environment. Although both PPDs provide excellent results in the fresh oil, PPD B is clearly a better fit for the aged oil. These results emphasize the importance of balancing all of the required low-temperature tests and not making decisions on PPD choice on fresh oil performance alone.

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