WHITE PAPER

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BASE OILS – AN EVOLVING LANDSCAPE

Guest Writers : Alan Outhwaite, John Rosenbaum

Chevron Global Lubricants

Birds of a Feather

... the importance of solubility in the formulation of greases

AXEL

AXEL CHRISTIERNSSON

BASE OILS – AN EVOLVING LANDSCAPE

ALAN OUTHWAITE, Manager, Base Oil Business Development, Chevron Global Base Oils, London, England

Alan has over 27 years experience in the lubricants industry on both the technical and commercial sides of the business. He joined Chevron International Oil Company, based in the UK in 1994 as a product engineer responsible for automotive and industrial lubricants, supporting Chevron's developing business in Russia, CIS and East Europe. Following Chevron's 2001 merger with Texaco, Alan moved to the commercial side of the business. In 2005 he was selected to lead Chevron's base oil expansion in the European market.

Alan graduated with a B.Sc. in Chemistry and Geology and is qualified as a Chartered Chemist with the UK's Royal Society of Chemistry. He has co-authored 2 patents, plus numerous industry papers and presentations.

JOHN ROSENBAUM, Senior Product Development Engineer Chevron Global Base Oils, Richmond, California, USA

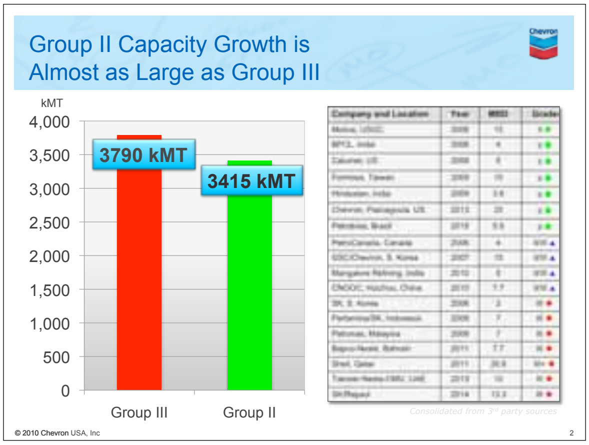
John is in his 29th year at Chevron. He was one of the scientists responsible for the development of Chevron's ISODEWAXING® catalyst system that revolutionized the production of premium base oil. In 1993 he helped launch the world's first ISODEWAXING complex at Chevron's refinery in Richmond, California. He then spent the next seven years supporting Chevron's base oil licensing business at refineries throughout the world. Currently, John is focused on improving the performance of premium base oils to meet the changing needs of the market.

John has a Doctorate in Materials Science and Engineering from the University of California, Berkeley, and is the author or co-author of approximately 40 patents plus numerous publications.

Throughout the world, tightening environmental legislation has lead to stricter performance standards. This is forcing the need for higher performance from lubricants. The introduction of all-hydroprocessed Group II and Group III base oils in the mid 90s made tighter specifications possible. These base oils have exceptional oxidation stability, low volatility for a given viscosity grade and are essentially sulphur-free. In automotive engine oils, by far the largest market for base oils, there is an increasing trend to low and mid SAPS specifications (Sulphated Ash, Phosphorous and Sulphur) and lighter viscosity grades. Due to their high sulphur content, Group I base oils cannot be used in formulations designed to meet these specifications. Formulators must use Group II or Group III base oils. These base oils significantly improve the performance of many industrial oils and greases as well.

The increased demand for all-hydroprocessed Group II and III base oils has lead to significant production expansion globally. In 2008, Group II base oils were introduced in Europe and lubricant manufacturers have been leveraging their benefits since then.

By 2018 Kline and Company estimate that manufacture of Group II and III base oils will account for more than 40% of global base oil capacity. In North America, over 60% of the supply is already Group II quality or higher. Given the increasing demand for Group II and III base oils and the corresponding declining demand for Group I base oils, some high cost Group I manufacturing facilities are vulnerable to closure. During the next 10 years Purvin and Gertz estimate that over one third of the existing European Group I base oil manufacturing facilities could be at risk. As the market evolves, it is important that lubricant manufacturers have a secure and 'future-proof' base oil supply strategy in place.



Growing industrialisation and the need to meet higher-quality motor oil specifications is driving demand. New formulations will emphasize these characteristics: lighter viscosity grades for increased fuel economy; low volatility for reduced oil consumption; improved oxidation and thermal stability for longer drain intervals; and improved high-temperature, high-shear (HTHS) viscosity characteristics for application to modern engine designs.

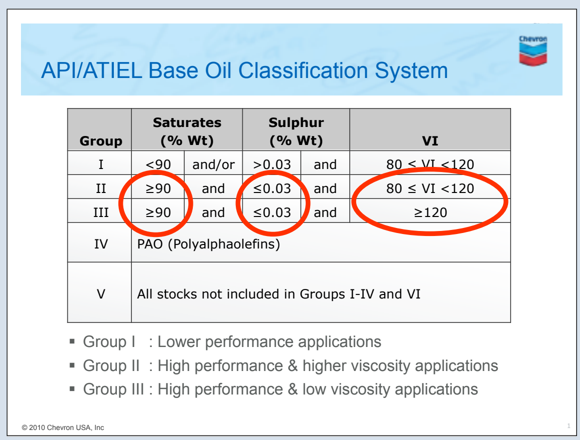
Many of these characteristics are also highly desirable in greases. Producing a low-viscosity and low-volatility lubricant requires a highly paraffinic, high-viscosity index (VI) base stock. High oxidation stability and thermal stability are obtained by using base stocks that contain minimal amounts of unstable aromatics. Base stocks that have these qualities include synthetics such as polyalphaolefins (PAO) and hydroprocessed mineral base oils. Hydroprocessed mineral base oils vary from high quality and high VI (95 to 105 VI) to excellent quality unconventional base oils (UCBO) with VI ranging from 115 to 140 and above.

Because of their ultra low sulphur content, they also offer increased compatibility with emission control devices such as diesel particulate filters.

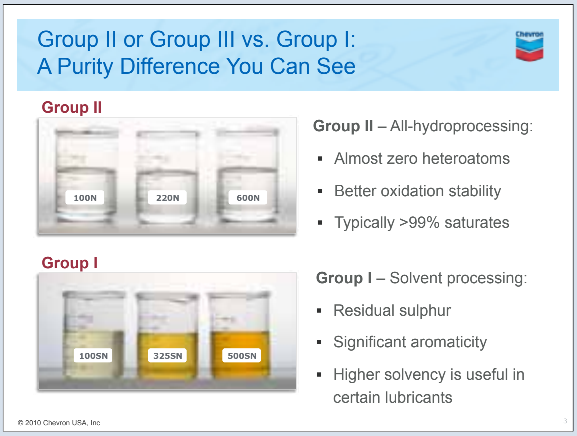
For compounding greases, Group II base stocks offer the right viscosity compared to Group III, much better solubility than Group III or Group IV (PAO), and much better colour and oxidation stability than Group I, or naphthenics. Plus their cost position is more advantageous than Group III or PAO base oils.

Lubricant Base Oil Chemistry

Feedstocks for base oil manufacture may come directly from crude (vacuum gas oil, VGO), from refinery process streams (hydrocrackate or deasphalted oil, DAO), or from process streams in an existing lube facility (slack wax). The performance properties of the base oil will depend on the hydrocarbon structure of the feed. Generally, hydrocarbons can be classified into four categories: 1) normal- and iso-paraffins, 2) naphthenes, 3) aromatics, and 4) heteroatoms.



Group	Saturates (% Wt)		Sulphur (% Wt)		VI
I	<90	and/or	>0.03	and	80 ≤ VI <120
II	≥90	and	≤0.03	and	80 ≤ VI <120
III	≥90	and	≤0.03	and	≥120
IV	PAO (Polyalphaolefins)				
V	All stocks not included in Groups I-IV and VI				



The most desirable hydrocarbons in base oils are C20+ iso-paraffins with high VI, low pour point, and excellent resistance to oxidation. Naphthenic compounds in this molecular weight range with long, branched alkyl side chains are also very desirable molecules. For a given viscosity, these highly paraffinic molecules have low volatility relative to aromatics.

Normal paraffins have high VI and high resistance to oxidation. However, they are undesirable as base oil components due to their high pour points. For the same reason, some iso-paraffins, naphthenic and aromatic compounds with long paraffinic chains are also undesirable. Naphthenic aromatics are typically susceptible to oxidation. Polycyclic naphthenic aromatics have low VI and poor stability. Organic molecules, which contain heteroatoms such as nitrogen, oxygen or sulphur, have very low VI and often have poor thermal and oxidative stability.

To produce high-quality base oil, most of the undesirable compounds need to be either transformed chemically to more desirable molecular structures, or removed physically and/or chemically during base oil manufacturing.

Chevron's ISODEWAXING technology is particularly efficient at producing high-quality base stocks because it isomerizes the molecular structure of wax into predominantly a desirable mix of iso-paraffins and stable naphthenic compounds. The result is high-VI, low-pour point base oils. These base oils are an optimised combination of stabilised naphthenic and isoparaffinic compounds which provide good

BIRDS OF A FEATHER ... THE IMPORTANCE OF SOLUBILITY IN THE FORMULATION OF GREASES

Lubricating grease is a multi-phase system consisting of a "thickening agent in a liquid lubricant". It is therefore a thickened oil, not a thick oil. However, the base fluid, i.e. the liquid lubricant, typically represents some 85% of the final formulation and will consequently exert considerable influence on the behaviour of the finished grease. In order to fulfil its roll in a wide range of applications, the base fluid must offer a combination of appropriate properties. These include solubility, viscosity and viscosity index, oxidation stability, evaporation loss, low temperature rheology etc. In addition, even environmental and health aspects are affected by the base fluid used. Base oils used to formulate lubricating greases are normally of mineral (petroleum) origin but both synthetic and natural oils are sometimes used for special applications. Perhaps the most important factor in the choice of the oil is its solubility characteristics. For both the manufacturing process and the final performance of the grease, it is important that the solubilities of the thickener and the base oil are *properly weighted*. Optimised solubility will result in a better yield (less thickener needed to achieve a given consistency), rapid dispersion during manufacturing, less oil separation, better storage stability and will also contribute to many other properties such as additive response, elastomer compatibility, etc.

solubility for additives plus the high stability required for formulating premium greases and other finished lubricants.

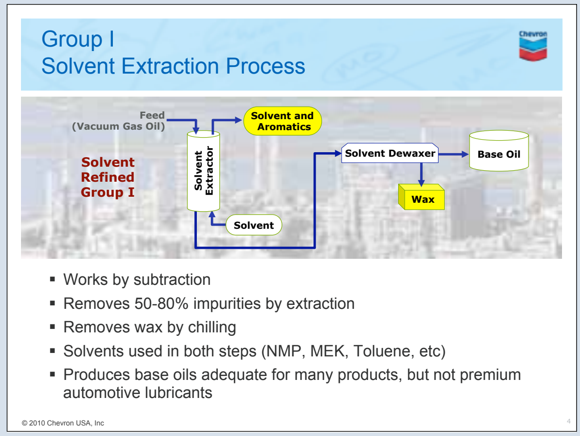
Base Oil Processing Steps

There are typically three main steps in processing base oils from VGO and DAO:
(1) Refining to increase VI,
(2) Dewaxing to reduce pour point, and
(3) Finishing to improve stability and colour.

In addition, distillations are often used before, between, and/or after the refining, dewaxing, and finishing steps to adjust viscosity, flash point and volatility. The goal is to obtain consistent product, that meets target product specifications.

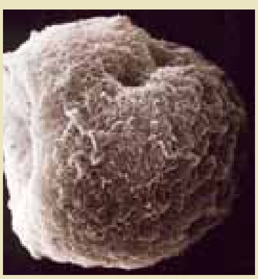
Refining to increase VI

Solvent refining uses solvents such as furfural or n-methyl-2-pyrrolidone (NMP), to extract undesirable components such as the low VI aromatics, naphthenes, and some heteroatoms from the waxy base oil feed stream. The resulting by-product is a high-sulphur extract which has relatively low value. This extract can be blended into fuel oil or further processed in a fluid catalytic cracker (FCC) or a fuels hydrocracker (HCR).



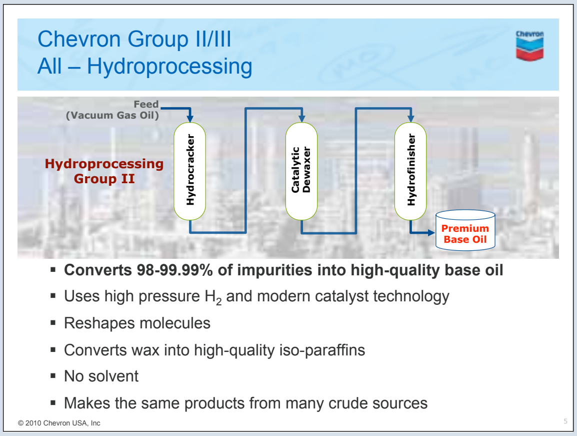
In contrast, the hydrocracking/ hydrotreating (HCR/HDT) process boosts VI by chemically converting low VI components to higher VI base oils. The by-products of hydrocracking include valuable transportation fuels such as gasoline, jet, and diesel.

For a given feed, HCR/HDT creates higher-VI components and preserves more molecules in the lube boiling range than solvent refining.



In practice, the use of solubility parameters can be difficult and confusing since a mineral oil consists of thousands of different components, all with varying solubility characteristics. In addition, depending on what we want to achieve, we might have to consider three solubility parameters to take into account three types of forces between molecules, dispersive forces, polar forces and hydrogen bonding. A rule of thumb previously used to predict solvency in oils was that "an increase in the aromatic content increases solvency power" and, in the past, aromatic oils were commonly used in the grease industry. This is however, not always true and it is not enough to only consider the hydrocarbon type distribution. Other test methods commonly used to measure solubility include the viscosity gravity constant (VGC) and the Aniline Point (AP). The VGC, according to ASTM D 2501, is a dimensionless constant based on a mathematical processing

A "THICKENING AGENT" (LITIHUM SOAP)

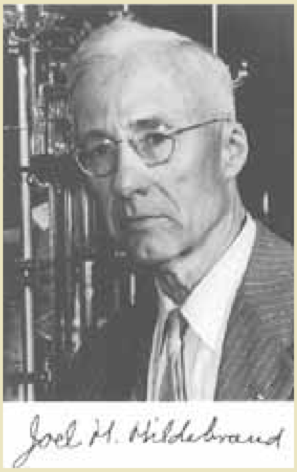


Consequently, HCR/HDT provides higher lube yield for a target VI, or produces higher product VI when processing to an equivalent yield level. HCR/HDT also allows the use of lower-VI crudes as lube feedstocks such as Alaska North Slope. With HCR/HDT, refiners have more feedstock options and greater product flexibility.

Dewaxing reduces pour point of base stocks
There are two basic processes for dewaxing: solvent and catalytic. The solvent dewaxing (SDW) process uses solvents, such as methyl ethyl ketone/toluene, to remove wax (various forms of paraffins) by crystallization and filtration. The products of this process are a dewaxed base oil (SDWO) and slack wax.

Conventional catalytic dewaxing (CDW) lowers base oil pour point by using a zeolite catalyst that selectively cracks wax to naphtha and gases. CDW base oils have VI and yield similar to, or lower than, their SDW counterparts. There are some hybrid, operationally complicated processing schemes where catalytic processes are used with SDW and recycling of unconverted slack wax to produce 140 VI base oils.

Chevron's (all hydroprocessed) catalytic dewaxing process, ISODEWAXING, was commercialized in 1993; it catalytically isomerizes the molecular structure of the wax into high-VI, low-pour point iso-paraffins. Because the ISODEWAXING technology preserves the lube oil's paraffinicity, it can produce higher product VI and/or higher yields than either CDW or SDW. The by-products of the ISODEWAXING technology consist primarily of high-quality diesel and jet fuel.



of the viscosity and density values and the AP is defined in ASTM D 611 as the lowest temperature at which a mineral oil is completely miscible with an equal volume of aniline. From practical experience through the years, we have learned that "like dissolves like" (i.e. birds of a feather flock together) and that substances with similar solubility parameters are generally miscible with each other in much higher ratios.

The concept of a solubility parameter is not new, not even in the grease business, but it is seldom referred to in formal papers and presentations. Already in the August 1970 edition of the NLGI Spokesman an article by G.S. Bright of Texaco explored the relationship of the **"Hildebrand Solubility Parameter"** of various oils to the properties of lithium soap greases made from them.

The Hildebrand solubility parameter (δ) is a measure of the intermolecular forces in a liquid. It gives an estimate of the

When using the ISODEWAXING process, a broader range of feeds can be processed into a broader range of products. The ISODEWAXING technology can process feeds with low wax content up to those with close to 100% wax, such as slack wax, Fischer-Tropsch derived wax, and hard wax. It is only the once-through dewaxing process where 140 VI base oils can be made from slack wax without recycling of unconverted wax. Refiners using the ISODEWAXING technology can produce base oils with VI ranging from 95 to 140 and above. Pour points may range from low (–9 to –15°C) to ultra-low (less than –24°C).

Using very high VI base oils in grease manufacture provides for proper lubrication over an extended temperature range.

Finishing improves oxidation stability and colour

Traditional methods of base oil finishing include adsorbent clay treatment or base metal-catalyzed hydrofinishing. Adsorbent clay removes some of the undesirable molecules in the base oil, including solvents or solvent-decomposed compounds from the preceding processes.

ISODEWAXING TECHNOLOGY WAS INVENTED BY CHEVRON IN 1993. TODAY OVER TWO-THIRDS OF THE WORLD'S GROUP II AND GROUP III BASE OILS ARE PRODUCED USING THIS TECHNOLOGY BECAUSE OF THE HIGH PURITY OF THE BASE OIL.

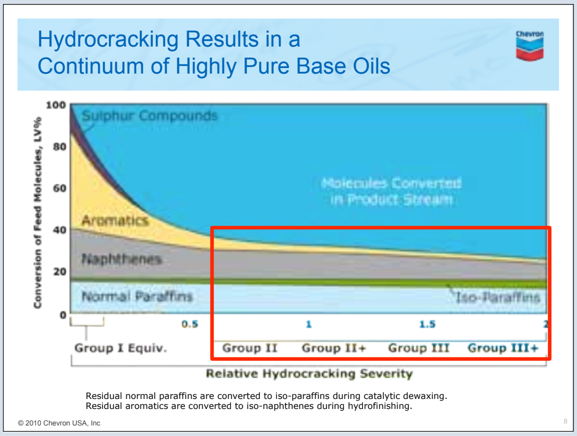
cohesive forces between molecules in a liquid and can be calculated as follows :

$\delta = (-E/V^{l})^{1/2}$

... where –E is the energy of vaporisation to the gas at zero pressure (infinite separation of the molecules) and V^{l} is the molal volume of the liquid.

Bright came to the conclusion that there appears to be a straight line (inverse) relationship between the solubility parameters of the oils and the dropping points of lithium-12-hydroxystearate greases made from them. The higher the Hildebrand parameter, the lower the dropping point. For oil separation, the correlation was also in the (for him) "expected" direction i.e. greases prepared from oils in which the soap is the most soluble show the greatest tendency to separate oil, while greases made with oils in which the soap is less soluble form a tighter soap matrix and exhibit a lesser bleeding tendency.

Subsequent research by AXEL has confirmed most of the *results* reported by Bright some forty years ago but, due to the fact that this new work was conducted over a much wider range of solubilities compared to the original work, somewhat different *conclusions* have been drawn. In the Bright study, which concentrated on mineral oils, the solubilities varied between 7.62 and 8.17 on the Hildebrand scale. In contrast, the AXEL study was not limited to only petroleum products and the scope could therefore be widened, now covering a solubility range between 6.8 and 9.0. As a basis for his work, Bright plotted the critical solution temperatures for zinc and lead stearates against the solubility parameters of the solvents and this gave a curve with a sharp minimum point at a Hildebrand value of approximately 8.9. This was then used as a "read across" for the lithium soap in the different oil "solvents". However, this level of 8.9 is actually higher than the oil



Conventional hydrofinishing uses a base metal catalyst to saturate the remaining aromatics in a hydroprocessing unit. For hydrocracked stocks a high-pressure unit is often necessary.

Over twenty years ago Chevron introduced ISOFINISHING, a hydrofinishing technology that uses noble metal catalysts instead of base metal catalysts. With noble metal catalysts, excellent oxidation stability and colour can be achieved at lower pressures and reactor volumes than those required when using non-noble metal catalysts. With a non-noble metal catalyst, processing temperatures must be higher so colour quality is sacrificed in order to achieve sufficient oxidation stability. When hydrofinishing is performed with a noble metal catalyst, it is possible to get both superior colour (practically water-clear) as well as excellent oxidation and colour stability.

Advantages of hydroprocessing

The growing interest in hydroprocessing and hydroprocessed Group II base stocks is due to:

(1) Enhanced feed flexibility:

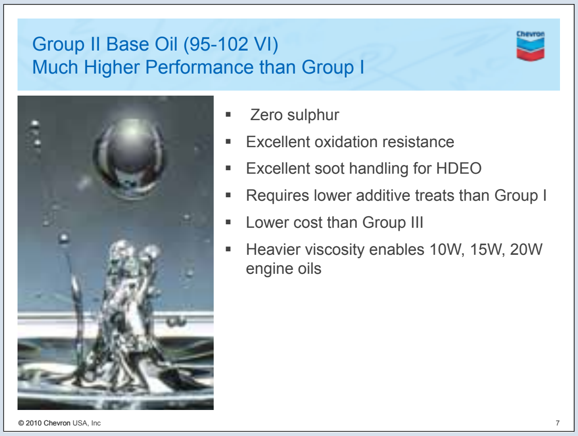
Refineries process crudes from various locations, including the North Sea, the Middle East and the Former Soviet Union. Using a hydrocracker or hydrotreater provides greater VI increase and contaminant removal, thus enabling refiners to produce consistent base oil quality despite inevitable variations in crude supply.

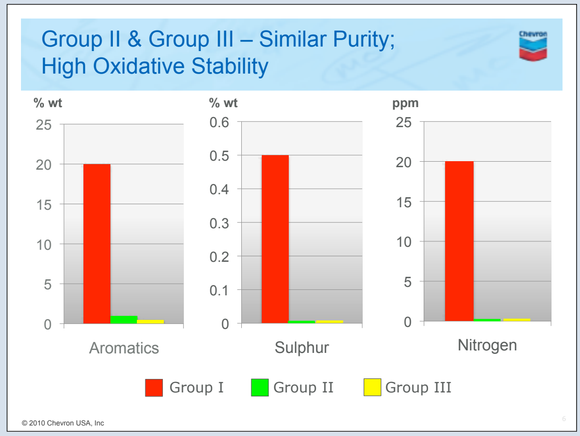
(2) Good grade flexibility:

A carefully designed hydroprocessing complex can produce all viscosity grades of base oils, including bright stocks. When demand changes, operations in both the distillation and the hydroprocessing

with the highest solubility in the Bright study (8.17), and the conclusion of a straight line relationship between dropping point and solubility is therefore perhaps not too strange and to be expected.

In the AXEL study, different types of oils were chosen to cover as wide a range of solubilities as possible, from PAOs to synthetic esters. To keep things as simple as possible, and to facilitate repeatability and reproducibility, a pure lithium-12-hydroxystearate soap with a very slight excess of alkalinity was chosen. Raw material samples were taken from the same package(s) to avoid unnecessary variations. Because of the wide range of solubilities a compromise relationship of 10% soap to 90 % base fluid was chosen. In addition, the viscosity of the base oil was fixed at 100 mm^2/s at 40°C. This was decided within the scope of a separate project concerning the response of different EP additives. The greases were manufactured using the same procedure in the same (open) pilot kettle. In the first basic tests, a sharp minimum point was found, just like in the Bright study using critical solution temperature. In this case, we found a clear minimum value for both worked penetration and dropping point at about the 8.2 level on the Hildebrand scale. If, as in the Bright study, 8.1 had been the highest value investigated, we too would have drawn the conclusion that there was a straight line inverse relationship. In fact, for the range 6.8 to 8.1, the correlation coefficient between solubility and worked penetration is as high as 0.92. However, at higher levels of solubility, the trend is seen to reverse and a direct relationship was observed above 8.2 where both penetration and dropping point increased as solubility increased. When it comes to oil separation, the AXEL results completely contradict the Bright study. The lowest oil separation was found at the same sharp "minimum value" as for both penetration and dropping points. At the





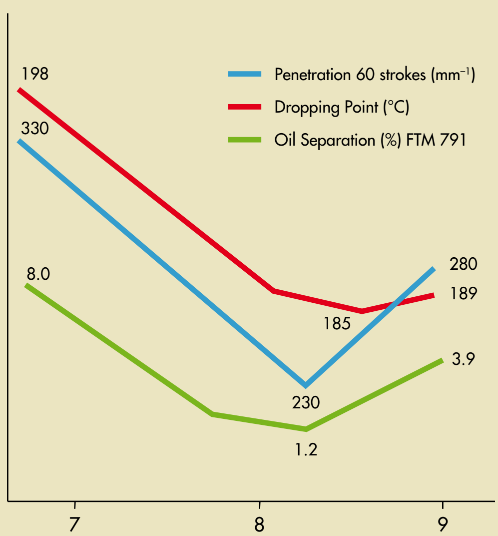
complex can be economically adjusted to achieve the target product specifications.

(3) Superior product quality:
Hydroprocessing produces base oils with better oxidation stability, thermal stability, and cold flow properties than solvent processing. When all-hydroprocessed base oils are subjected to a turbine oil stability test (TOST), there is less viscosity increase in the oil than there is with base oils produced from other process configurations.

Motor oils made with Chevron's commercial Group II base oils have oxidation stabilities comparable to that of motor oils made with PAO.

(4) Good product flexibility:
Using hydrocracking, hydrotreating and ISODE-WAXING processes, a refiner can make either conventional base oil (CBO), UCBO or both, depending on the requirements of the market.
(5) Good balance between lubes and fuels:
With an all-hydroprocessing scheme, non-lube

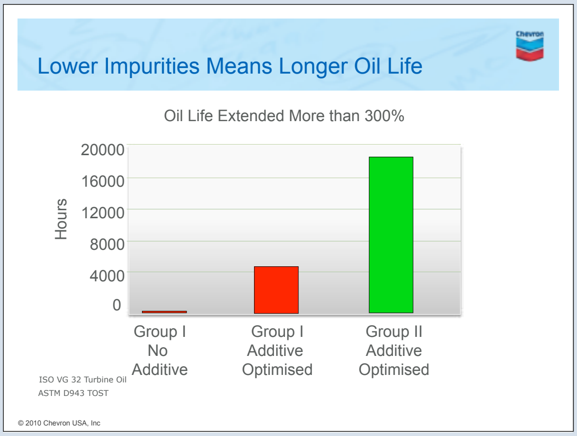
Lithium Grease with Different Base Fluids
(10% lithium-12-hydroxystearate ; 90% base fluid)



extremes of solubility, oil separation was higher. In a simplistic analysis, we see clearly the "like dissolves like" relationship and we have taken the liberty of drawing a highly generalised and albeit rather unscientific conclusion based on inverse logic that the solubility parameter of the lithium soap corresponds to about 8.2 and not 8.9 reported by Bright for both zinc and lead stearate. And, just as a matter of interest, EP additive response was also seen to be dependent on whether or not the solubilities of the base fluid and the thickener were in balance. This was once again an inverse relationship, the closer to the point of balance, the worse the response.

For the grease formulator, it is therefore of the utmost importance to understand the dynamics between the solubilities of the base fluid and the thickener system. The

SOLUBILITY DYNAMICS



by-products consist mainly of high-quality fuels, allowing refiners to economically satisfy both fuels and lube demand.

Group II Lubricants Bring Competitive Advantages to Blender

As the need for improved product quality increases, the impurities in Group I base oils will make them technically untenable for blending high-performance lubricants.

All of the major additive companies have experience in optimizing performance with Group II base oils in both industrial and engine oil applications.

Industrial Oils – Improved Performance; Relatively Low Qualification Hurdles

Historically, industrial oils have been formulated with Group I base oils. The formulations were sufficient to meet performance requirements and were cost-effective to produce and market. The performance of many industrial formulations could be dramatically improved if they were converted to using Group II base stocks.

The standard ASTM D 943-04a TOST test for turbine oils was modified to accommodate the extended performance of the Group II base oils. By decreasing the sample withdrawal volume from the test oxidation cell by half, one can extend the maximum run time from 10,000 to 20,000 hours. Thus, the Group II base oils can significantly extend turbine oil life.

results presented here are, of course, only valid for one particular lithium soap and other thickener systems give somewhat different results. The desired properties of the finished grease can therefore be designed for purpose by choosing whether or not to "balance" the solubility characteristics of the separate components. So, today, instead of trial and error, we can select these different parameters. Know-why instead of know-how.

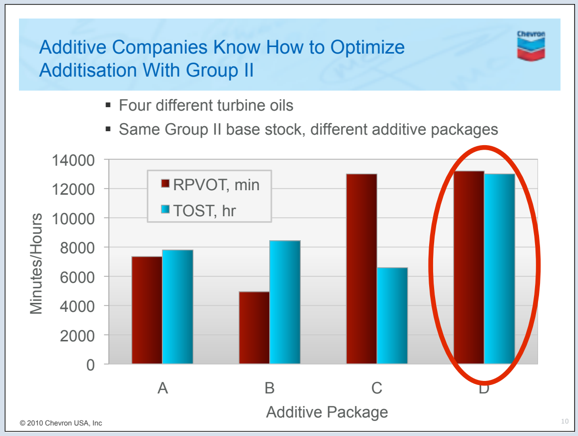
In the white section of this Lubrisense™ White Paper, guest writers Alan Outhwaite and John Rosenbaum of Chevron Global Lubricants provide an excellent overview of the different base oils available at present and a forecast on the future market trends for these types of products. In the grease business, we have gradually moved from highly aromatic oils to severely refined naphthenics and paraffinics.

BALANCING SOLUBILITY …

Summary – Group II and III Base Oils Capacity Will increase Bringing Both Performance and Economic Benefits

Due to tightening specifications for automotive lubricants and increased performance expectations for industrial oils all-hydroprocessed Group II and III base oils will increase in their importance for use in lubricant formulations. The recent introduction of Group II base oils into Europe and their global availability are accelerating this trend, providing lubricant manufacturers with secure and stable supply of high performance base oils.

Alan Outhwaite
John Rosenbaum



And now, the pending transition from Group I oils to Group II (and perhaps even Group III) oils will offer interesting possibilities and create significant challenges for the grease formulator. Group II and Group III oils have, for instance, lower solubility compared to their previous counterparts and, for many applications, this will require adequate compensation, somehow or another. In addition, the relatively low kinematic viscosity of these "new" oils may not be sufficient for many grease applications and they may require "reinforcement" from other types of base fluids. And, if we can "kill two birds with one stone", all the better. So the combination of Group II and Group III oils with high viscous naphthenics, or perhaps even high viscous synthetic esters would, at first sight, seem an interesting way forward.

… AND GETTING IT RIGHT

NEXT ISSUE

The next issue of the Lubrisense™ White Papers will deal with issues involving choosing the "right" lubricating grease for any given application. Nowadays, a variety of multipurpose products may suffice for up to 70 % of the market. However, under more extreme conditions such as higher temperatures, heavier loads and more intense vibration, demands will certainly increase. To be able to choose the most appropriate grease for any particular application, it is of the utmost importance to consider three extremely significant factors, the component itself, the temperatures involved and the surrounding environment. And, of course, not to forget the old saying that "right" lubrication is getting the "right" grease into the "right" place, in the "right" amount, at the "right" time .. and for many many users, even at the "right" price" ! At AXEL, we define "Lubrisense™" as the art of choosing the right grease. General guidelines will be given together with a practical example of how the "right" grease can provide considerable advantages both in terms of technology and economy.

As usual, we encourage reader contribution, feedback and proposals concerning relevant topics for future issues of our White Papers.

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